



A review paper on NO_x reduction catalytic convertors in lean based engines

Shivan patel¹

¹Department of Mechanical Engineering, LDRP-ITR, India.

ABSTRACT : The awareness regarding the air pollution and its effects on our environment has inspired many researchers. Tail-end emission of pollutant gases such as NO_x, CO, unburnt hydrocarbons (HC), etc. from the engines are the biggest contributors in air pollution. Engines with a lean air-fuel ratio have better fuel efficiency and a low operating cost. However the NO_x emission from a lean engine is difficult to control. These economical engines produce exhaust fumes that are particularly rich in oxygen and therefore the conventional three-way catalytic converter is not suitable for converting the generated NO_x into nitrogen. This review paper discusses the usage of the NO_x storage catalytic convertor as a measure to reduce NO_x emissions from such oxygen rich (higher a/f ratio) engines.

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1. Introduction

The emission control technologies have faced many problems. Atypical exhaust gas composition at the normal engine operating conditions are: carbon monoxide (CO, 0.5 vol.%), unburned hydrocarbons (HC, 350 ppm), nitrogen oxides (NO_x, 900ppm) hydrogen (H₂, 0.17 vol.%), water (H₂O, 10 vol.%), carbon dioxide (CO₂, 10 vol.%), oxygen (O₂, 0.5vol.%).^[3] The NO_x is formed at higher temperatures (~1500 °C) of the combustion process due to thermal disintegration of nitrogen molecule. The reduction of such hazardous emissions can be achieved by two measures: Primary (i.e. inside engine) and Secondary (i.e. outside engine). The primary measures include combustion of lean air fuel mixture, multistage injection fuel, loading of additional water into cylinder volume, etc. While secondary measures for engine exhaust includes a range of advanced technologies based on oxidation-reduction, 3-way catalyst adsorption storage and filtration process. As a result of researcher's efforts to produce more efficient and low-emission engines, lean burn petrol and diesel engines have come to the market. Lean-burn engines effectively improve the fuel efficiency, but produces oxygen rich exhaust gases. Removal of NO_x from such oxygen rich exhaust is extremely difficult by a conventional 3-way catalyst. The 3-way catalytic converter technology is successful for stoichiometric internal combustion engines, however it will not function at O₂ levels in the emission exceeding 1.0%^[5]. Because of the increasing need to limit NO_x emission, technologies such as Exhaust Gas Recirculation (EGR) and selective catalytic reduction (SCR) have been used. However both the systems have their persistent limitations in their effectiveness. Hence NO_x storage catalysts were developed.

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2. Emission characteristics of a lean burn engine:

In a lean petrol or diesel engine the exhaust consists of a complex mixture, the composition depends on a variety of factors such as engine type (2- or 4- stroke, petrol or diesel), applications (stationary or mobile), speed, acceleration/deceleration, etc. Figure: 1 shows the effect of A/F ratio on composition of engine emissions and power:

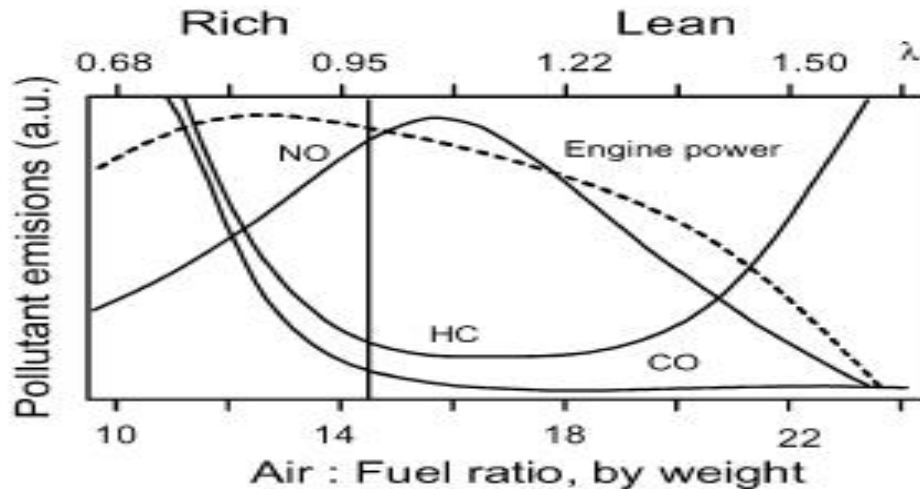


Fig. 1 Effect of A/F ratio on engine emissions and engine power

In general, the exhaust emissions depend on the Air-to-fuel (A/F) ratio as describes in fig.1. Tuning of the engine to rich feed gives the highest power output, which, however, occurs at expenses of high fuel consumption. However under lean conditions the NO_x emission increases upto certain level and then substantially decreases due to misfire which occurs at higher A/F ratios.

Table 1: comparison of exhaust conditions for four stroke stoichiometric burn spark ignited (SI) engine and a four stroke lean burn SI engine ^[7].

Exhaust components	Four stroke stoichiometric burn SI engine	Four stroke lean burn SI engine
NO _x	100-4000 ppm	1200ppm
HC	500-5000 ppm C	1300 ppm C
CO	0.1-6%	1300 ppm
O ₂	0.2-2%	4-12%
H ₂ O	10-12%	12%
CO ₂	10-13.5%	11%
SO _x	15-60 ppm	20 ppm
A/F ratio	14.7	17

There are several advantages in removing NO_x from the exhaust under the lean conditions (i.e. A/F > 14.5) compared to stoichiometric condition (A/F = 14.5) of a petrol engine where emissions are controlled by a conventional Three Way Catalytic converter (TWC). Another important aspect is the fuel economy which is higher in lean engines. In 1990's due to introduction of the TWC's in vehicles by the enforcement of strict environmental laws, an increase in fuel consumption of vehicles occurred. This was due to the fact that TWC's require a stoichiometric A/F ratio to achieve best performance. Apart from this, several other reasons such as the increase

in vehicle weight due to air conditioning, security features, etc. significantly contributed to increased fuel consumption.

Another advantage of a lean burn engine is that the highest exhaust temperatures are lower ($\sim 800-850^{\circ}\text{C}$)^[6] compared to stoichiometric engines where highest temperature of the exhaust reaches to 1100°C . Such a high temperature may result into catalyst failure in terms of durability.

3. Catalysts for NO_x reduction in Lean Engines

In the modern times, there is a race among the automobile giants to reduce the fuel consumption in vehicles along with lowering the end emissions. The reason behind this is mainly the rising prices in fossil fuels and strengthening of the laws and legislations pertaining to environment. Hence this has prompted the necessity to develop more effective and advanced catalysts to reduce NO_x emissions. As we discussed earlier that lean burned engines have considerable fuel savings due to a higher A/F ratio, however under these conditions the conventional catalytic converters (TWC's) are inefficient. This is primarily due to excess O₂ which competes for a reducing agent, especially CO.

Thus the studies on NO_x reduction under lean conditions have been the interests of many. After it was discovered that hydrocarbons (HC's) could act as selective reducing agents under excess O₂ in the early 90's, a feverish activity in the field of lean NO_x reduction was followed. And more than 50 catalysts were reported in 1991-92^[6]. As mentioned in a report issued by MECA (Manufacturers of Emissions Controls Association)^[6] there are two main strategies to control NO_x emissions under lean conditions:

- Lean DeNO_x catalysts
- NO_x adsorbers

Lean DeNO_x catalysts are based on direct reduction of NO_x, usually by Pt/Al₂O₃ catalyst (for low temperatures) and metal loaded zeolite (for high temperatures). Such types of adsorption catalysts are also called NO_x reduction and storage (NSR) catalysts. Let us examine some of the systems briefly:

3.1. Pt/Al₂O₃ catalytic system:

The use of noble metals in catalytic converters is well known. Hence we will summarize the typical reaction profile for NO_x reduction over Pt/Al₂O₃ catalyst. It is evident that maximum number of NO conversions occurs at lower temperatures^[7]. Such catalysts use unburnt HC's as a reducing agent, and hence there is a significant NO₂ formation at high temperatures because at higher temperatures all the HC is completely burnt. The nature of reducing agent also effects the conversion of NO due to its higher sensitivity. At low temperatures there is a significant formation of N₂O (di-nitrogen oxide), and Pt catalyst has poor selectivity towards N₂O^[8]. Thus, selection of Pt catalysts is highly dependent on the nature of the reducing agents.

3.2. Other DeNO_x catalytic systems:

Other DeNO_x catalysts mainly include Cu-ZSM5 and other metal oxide catalysts. Even though Cu-ZSM5 catalysts face problems such as poor hydrothermal stability due to presence of Cu ions in the zeolite frame and poor NO_x affinity at high exhausts velocities^[8], the Cu-zeolite systems show appreciable activity at high temperatures. Hence such catalysts are more favourable for lean based engines, where such high temperatures are easily met.

At higher temperatures, to improve the thermal stability of zeolite structure, a variety of metal oxides have been tried with Cu. Such metal oxides include oxides of Chromium (Cr), Silver (Ag), Manganese (Mn) and Cerium (Ce). Such additives improve the activity as well as the temperature range of the catalyst.

3.3.NO_x Adsorbers:

The base of such NO_x traps was laid by the Toyota Group after the discovery of so-called NSR catalysts. In such NO_x adsorbers, NO_x gases are stored under oxidising conditions at the surface of Barium (Ba)- based catalyst in form of nitrides or nitrates. After certain period of time the engine is made to run at a lower A/F ratio and the stored NO_x is reduced over Pt catalyst in presence of unburnt HC. However this is a complex process due to the complex nature of the species.

Conclusions

There has been a significant development in the field of catalytic converters in the last few years due to more and more demanding government regulations on pollution control. The requirement of more efficient engines must be alongside with the developments in the field of catalytic converters. Moreover the problem of NO_x removal under oxidising conditions requires huge efforts. Even though, many efforts have been made in developments of DeNO_x catalysts, their performance is still insufficient. Also the durability of such converters should be same as that of the car. Technology for control of pollution will find an increasing demand in the next years. In particular, technology pertaining to the use of "Nano-technology" can transform the conventional strategies of pollution control. This is further necessary in order to obtain a miniaturisation of the system without compensating its effectiveness, and therefore application in automobiles.

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