CATALYTIC CONVERTERS AND OTHER EMISSION CONTROL DEVICES

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Keywords: Alternative fuels, Catalytic Converters, Diesel Engines, Environmental Pollution, Exhaust Emissions, Fuels, Internal Combustion Engines, Lubricants, Three Way Catalysis, Vehicle catalysts, Vehicles.

Contents

Summary

The control of pollution from internal combustion engines (ICE) can be achieved through the design of the engine combustion system, by designing the composition of the fuel, and through post combustion treatment of exhaust gases. Considerable attention is also devoted to the maintenance of the performance of the new vehicles, since the emission controls can deteriorate during the service life of the vehicle.

The present chapter describes devices used for post combustion treatment of exhaust emissions, for the control of crankcase and evaporative emissions, and for other engine applications. Particular attention is devoted to the main catalytic reactions. The typical approaches to the in-use control of the deterioration of emission controls through inspection and maintenance and on-board diagnostics are also outlined.

1. Introduction

The control of pollution from internal combustion engines (ICE) can be achieved by engine design, fuel design, and devices for treatment of exhaust gases.

The need to control engine emissions was recognized as early as 1909. The first engine exhaust gas treatment devices were introduced in 1975. As a point of reference, the upper limits of the US legislation at that time were: carbon monoxide (CO) – 9.3 g km^{-1}, total hydrocarbons – 0.93 g km^{-1} and total nitrogen oxides (NO$_x$) – 1.93 g km^{-1}. In 1991, the US car regulations permitted 2.1g km^{-1} for CO, 0.25 g km^{-1} non-methane organic compounds (NMOC) and 0.62 g km^{-1} NO$_x$.

The implementation of the more stringent future Tier 2 US standards has to start after 2003. They impose even stricter controls for new vehicles. For instance, light duty vehicles and trucks should emit less than 2.1 g km^{-1} CO, 0.047 g km^{-1} NMOC, 0.04 g km^{-1} NO$_x$ and 0.005 g km^{-1} aldehydes (HCHO). Greater reductions are envisaged for vehicles sold in California.
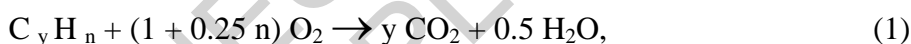
These examples illustrate the steep road towards the sustainable development of one of the privileges of modern civilization – fast and in comfort physical mobility. Neither previous successes nor the ambitious future environmental goals can be achieved without adequate investments and efforts for the development of advanced technologies for pollution control.

Catalytic devices, devices to control evaporative emissions, etc. and the optimized application of all available emission control options, discussed below, play an essential role in all these achievements.

2. Devices for Post Combustion Control of Engine Emissions

The main purpose of the post combustion treatment of exhaust emissions is to perform the following major reactions in the gases leaving the combustion chamber:

Oxidation of hydrocarbons and CO:

$$C_yH_n + (1 + 0.25\ n)\ O_2 \rightarrow y\ CO_2 + 0.5\ H_2O, \tag{1}$$

$$CO + 0.5\ O_2 \rightarrow CO_2, \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \tag{3}$$

and

Reduction of NO or NO$_2$ to N$_2$:

$$NO\ (or\ NO_2) + CO \rightarrow 0.5\ N_2 + CO_2, \tag{4}$$

$$NO\ (or\ NO_2) + C_yH_n \rightarrow (1 + 0.25)\ N_2 + 0.5\ n\ H_2O, \tag{5}$$

$$(2 + 0.5\ n)\ NO\ (or\ NO_2) + H_2 \rightarrow 0.5\ N_2 + H_2O, \tag{6}$$
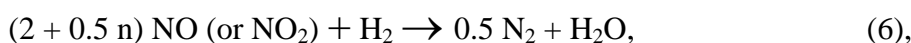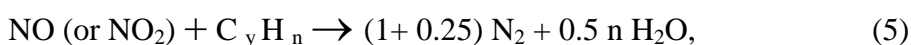
where y is the number of carbon atoms, n – the number of hydrogen atoms, O is the chemical symbol of oxygen, NO, NO_2, CO, CO_2, H_2O are the corresponding formulas of nitrogen oxide, nitrogen dioxide, carbon monoxide, carbon dioxide and water. The general formula of the hydrocarbons further implies that they may have different structures and molecular masses.

The analysis of the above scheme from a chemical point of view leads to important conclusions, some of which are summarized below:

- The oxidation and reduction reactions are very sensitive to the oxygen (air) – fuel ratio. The stoichiometric ratio of a combustion reaction is the ratio between the exact amount of oxidizer (i. e., oxygen, air) and reducing agent (the oxidized compound, i. e., CO, C_yH_n). It is calculated from the moles participating in the reactions. If the quantity of the oxidizer is higher than the stoichiometric, the combustion system is called "lean", if it is lower - "rich".
- The efficiency of the oxidation of CO and hydrocarbons will be high in lean conditions, and low – in rich conditions. The efficiency of reduction of nitrogen oxides will be high in rich conditions, and low – in lean.
- Relatively high temperatures, or medium temperatures and suitable catalysts are required to perform the above reactions. There will be a minimal "light-off" temperature for whatever system, above which the reactions will effectively start. As described in the previous article, CO and hydrocarbons are oxidized in the combustion process mostly by hydroxyl radicals (OH). So, the above oxidation reactions actually summarize a set of intermediate reactions, involving atomic oxygen, atomic hydrogen and hydroxyl radicals, generated in combustion. The more of these active species are present in the exhaust, the better will be the oxidation of the pollutants.
- Carbon monoxide, hydrocarbons and NO_x, but also all intermediate species in the exhaust emissions, will be influenced in the processes postulated by the above reactions. This may lead to positive (i.e., reducing the amount of toxic compounds) and/or negative (i. e., generation of new pollutants) effects.

2.1. Devices for Post Combustion Control of Spark Ignition Engines

As discussed in the previous article, the most important pollutants from *four-stroke spark ignition (SI) engines* are hydrocarbons, CO and nitrogen oxides.

The first post combustion control devices attempted to perform only the oxidation reactions in the above scheme. They did not use catalysts and relied on existing heat and active oxidation species produced in the combustion chamber. The most important device was the adiabatical thermal reactor in which the oxidation was completed, eventually with some additional supply of air providing more of the oxidizer.

The thermal reactors were very quickly superseded by catalytic systems. The first obvious reason for that was the lack of influence on NO_x. Moreover, temperatures above 900 K for hydrocarbons and above 1000 K – for CO and residence time of the order of 50 milliseconds are required for effective conversion in a thermal reactor. Temperatures of the exhaust gases of SI engines can vary between 600 K at idle and

1200 K during high power operation. Typically, the temperature of the exhaust is most of the time between 700 K and 900 K.

The first generation (1976 – 1979) catalytic converters provided only oxidation since the requirements for NO_x abatement then could be achieved without after treatment (i.e., only with exhaust gas re-circulation). Typically at that time, the engine was operated just rich of stoichiometric to further reduce NO_x, and additional air was pumped into the exhaust gas to provide sufficient amount of air for the oxidation catalyst.

Following relevant experience in industrial catalysis, the first catalytic converters were in the form of beads of γ-Al_2O_3 (aluminum trioxide), impregnated with platinum (Pt) and palladium (Pd). The γ-Al_2O_3 was providing the huge surface, needed for adsorption, while the precious metals were complementing each other in oxidation.

Later the monolith, honey comb ceramic structure for the support was developed. This is the structure, which is still preferred in modern catalysts because of its low pressure drop. Lower pressure drop can be achieved with metal supports developed by some companies, but they are used only in specific applications, which allow for higher cost and strict temperature limitations.

The precious metals Pt and Pd continue to be the most widely used metals in engine catalysts. Cheaper combinations based on copper, chromium, nickel, manganese, etc. have been tested, but could not achieve comparative cost-efficiency. Research continues on the most promising copper-based systems.

During 1976 – 1979 most present problems and possible solutions of the catalytic conversion of exhaust engine emissions were outlined. These include poisoning and sintering of the aluminum oxide and the precious metals at high temperatures.

Typical catalytic poisons in engine exhaust emissions are the lead from tetra ethyl lead used as octane booster, sulfur oxides from gasoline, and sulfur, phosphorus (P), zinc (Zn), and silicon from lubricant oil additives. Zinc comes mainly from Zn dithiophosphates, widely used as antioxidation, and antiwear additive in motor oils. Silicon oil in very small amounts is contained in lubricating oils as antifoaming additive. Lead forms low-active alloys with precious metals. With banning of lead, this problem will be avoided.

As discovered later, SO_2 adsorbs onto the precious metal cites below 300 ^{o}C preventing the conversion. At higher temperatures it is oxidized to sulfur trioxide (SO_3), which either leaves, or in lean conditions, reacts with some aluminum oxide, forming aluminum sulfate, which does not have the surface area of the oxide. In rich conditions, the sulfate compounds are reduced to foul smelling hydrogen sulfide (H_2S).

Phosphorus deposits on catalytic cites as a P_2O_5 polymeric film or a glass like mass which causes blockage and masking of pores. Solutions to these problems are being sought through the reduction of sulfur in gasoline, reducing oil flux into the combustion chamber and replacing Zn dithiophosphates, optimization of catalyst composition, and capturing or scavenging H_2S.

Sintering is due to the high temperatures, involved in engine modifications trying to achieve higher fuel efficiency. It results in transforming the aluminum oxide into a crystalline phase with a lower surface area, and in crystallization of the precious metals reducing the amount of active cites.

Research has lead to the use of small amounts of lanthanum oxide (La_2O_3) and barium oxide (BaO), which effectively control the problem with the aluminum oxide surface. It was discovered also that Pd is more stable to sintering than Pt.

The second-generation catalysts (1979 – 1986) were targeted at converting not only CO and hydrocarbons, but also NO_x. The first such converter was the dual bed catalyst. The reduction of NO_x by CO and hydrocarbon species (which are in the same time oxidized) is performed in the first bed in sufficiently rich conditions.

The oxidation of the remaining, not oxidized pollutants takes place in the second bed after injecting some additional amount of air to provide the lean conditions.

The first reduction catalyst was ruthenium. It was changed later to rhodium (Rh), which produced less ammonia and was overall more effective than Pd and Pt (also tried in the first combinations).
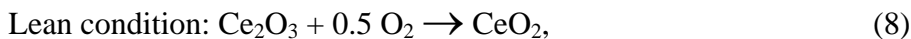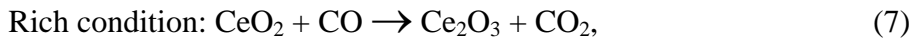
After the development of the exhaust gas oxygen sensor, which can control the air-fuel ratio close to the stoichiometric, the first three way catalysis (TWC) in a single bed was introduced. In a typical TWC technology, both the oxidation and the reduction can be performed.

High conversion of all three pollutants (CO, hydrocarbons and NO_x) can be achieved only if, as discussed above, the stoichiometric conditions are very strictly controlled. The stoichiometric ratio for gasoline is approximately 14.7 grams air per gram of fuel. It has to be noted that this ratio is calculated from a rather simplified average formula of gasoline (C_7H_{16}). If the composition or density of the gasoline is significantly changed, negative impact on the TWC might be expected.

The oxygen sensor is in the center of the TWC technology. Typically, it is composed of anionic conductive solid electrolyte of stabilized zirconia and electrodes of high surface Pt and measures the oxygen content of the exhaust. It acts also as a catalyst converting CO and hydrocarbons if enough oxygen is available.

The total TWC system is a sophisticated electronically controlled scheme. It includes besides the sensor and the catalyst, a microprocessor and an electronic carburetor or a fuel injection system. Whenever the stoichiometric balance is tilted outside the prescribed limits, the sensor, situated before the catalytic unit, sends a signal and the electronic carburetor or the fuel injection system restores the balance.

Because the system is based on feedback control, there is some time lag, associated with the adjustment of the air-fuel ratio. This effect was proved significant, so a new component – cerium oxide (CeO_2) was added to the Rh/ Pd/ Pt combination. The cerium oxide acts through the chemical reactions, shown below:

Rich condition: $CeO_2 + CO \rightarrow Ce_2O_3 + CO_2$,   (7)

Lean condition: $Ce_2O_3 + 0.5\ O_2 \rightarrow CeO_2$,   (8)

The very small amount of oxygen exchanged in these reactions is sufficient to significantly compensate the lag time of the sensor. Additionally, CeO_2 participates as a catalyst in both the oxidation and reduction reactions. Cheaper combinations for replacement of CeO_2 are being experimented but have not been introduced widely yet.

The modern three way catalysts typically contain 0.1 to 0.15 per cent precious metals, 10 to 20 per cent CeO2, the rest being aluminum oxide, stabilized with 1 to 2 per cent La_2O_3 and/or BaO.

Further improvements of the TWC were introduced with the third generation catalysts (1986 – 1992). The development of the system was dictated by the high temperatures related with the engine modifications introduced at the time, and especially the fuel-shut off technology.

Major improvements include the partial overcoming of the poisoning and sintering problems, the identification of the reaction at high temperatures and rich conditions between Rh and the aluminum oxide and/or the CeO_2, which deactivates all participants. The first solutions to the behavior of Rh were also outlined.

Positive effects were sought in separating CeO_2 and Rh in different layers, addition of oxides of barium, zirconium and lanthanum to CeO_2, deposition of Rh on the less reactive zirconium oxide instead of the Al_2O_3, etc.

The last years of the 20th century mark further major advances of the TWC technology. These concern solutions for the cold start problems, universal oxygen sensor and a dual sensor system, attempts for lean burn catalysts and the first commercial installation of the fourth generation all Pd system.

In cold start, both the catalyst and the oxygen sensor have to reach particular light-off temperatures to start functioning. Since the air-fuel mixture is rich, at cold start up to 60 to 80 per cent of the total amount of the not oxidized CO and hydrocarbons are emitted. One possible solution of this problem is the heating of both sensor and catalyst with an in-built metal coil in the monolith.

Two other possible solutions are the introduction of a dual catalytic system with one bed placed in the manifold to reach fast the light-off temperature, and a trap to adsorb hydrocarbons released in cold start. The former option needs new materials able to work at 1100 ^{o} C, when the engine is heated up. The major problems for cold start control remain the additional costs, and the ability of the new systems to endure the future requirements of 160 000 km without changing. Research into this area continues.

Experts are pessimistic about the prospects for any cold start emissions adsorption trap, but electrically heated catalyst may be used in a limited number of engine types, in

which cold start emissions are difficult to control. The latter is considered an interim solution, which will be replaced by a variable insulation catalyst. A recently reported design of this system uses insulation in vacuum provided from a metal salt with changing thermal conductivity.

At cold start, the converter is quickly heated to the light-off temperature. When a critically high temperature is reached, hydrogen is released from a metal hydride, the specific metal salt insulation becomes highly conductive and the heat is dissipated. At cooling, the hydride absorbs back the hydrogen and the insulation is restored.

The traditional oxygen sensor reacts only to the departure of the air-fuel mixture from a pre-set ratio. In order to decrease time lag, new universal oxygen sensors are developed. A universal sensor has a smaller response time.

It registers not only the occurrence of a change in the air-fuel ratio, but also the direction and amount of the change. In a dual sensor system, the second sensor controls the first one and the performance of the catalyst. It is also a back up when the first sensor diminishes efficiency because of its higher working temperatures.

The reduction of NO_x in lean environment is another important direction of the current TWC studies. It is connected with the possibility to use TWC with the very efficient lean-burn engines (see *Control of Exhaust Emissions from Internal Combustion Engined Vehicles*). The catalyst (eventually based on copper on zeolites – Cu/ZSM-5) has to be integrated with the engine. It has to use the available hydrocarbon species to reduce NO_x according to the reaction, given below.

$$C_y H_n + NO_x + O_2 \rightarrow N_2 + CO_2 + H_2O \qquad\qquad (9)$$

Since lean burn engines emit a relatively small absolute amount of pollutants, conversion efficiency of about 50 per cent may be enough. This reaction depends also on the reactivity of the particular hydrocarbons. Ethylene, for instance, can reduce NO_x even below 200 ^{o} C, while propane needs at least 500 ^{o} C. A further concern is the durability of the catalyst.

New Pd-only catalysts are now capable of withstanding exposure to temperatures as high as 1050 ^{o} C and, as a result, can be moved very close to the exhaust manifold to enhance catalyst light-off performance.

Post combustion treatment of exhaust emissions has been demonstrated *for two stroke spark ignition engines* as well. Motorcycles and mopeds with catalytic converters have been used for several years in Austria and Switzerland and other countries have experimented with off board and other engines.

Emissions of CO, hydrocarbons and NO_x have been reduced significantly. Most vehicles were using retrofitted four stroke catalytic systems. The major problem seems to be the overheating of the catalyst housing, which might damage the passenger and/or create explosion and fire.

Lasting solutions can be achieved, when professionally manufactured catalytic systems are synchronized with the engine and fuel options, so that the concentrations of the pollutants in the exhaust leaving the engine are conditioned for the typical catalytic systems.

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Biographical Sketch

Georgi St. Cholakov is Associate Professor at the University of Chemical Technology and Metallurgy in Sofia. He received his first hands-on experience of ecological problems during compulsory his military service as the Head of the Fuels and Lubricants Unit of an airbase. His PhD dissertation was on development of replacements for lubricant additives synthesized from the sperm oil, obtained from blue whales. He did a post doctoral specialization in tribology at the University of Birmingham, U.K. Later he specialized in effective and ecological processing and use of petroleum derivatives at Imperial College, London, the French Institute of Petroleum, and other leading universities. The scientific and research interests of G. St. Cholakov are centered around petroleum processing and petroleum derivatives – environmentally compatible processes and products, process and product design for the petroleum industry, chemistry of combustion and ecology, etc. He is teaching advanced courses in related academic disciplines – alternative fuels and lubricants, air pollution management, chemistry of combustion and ecology, additives for fuels and lubricants, technological computation in petroleum processing, etc. He has contributed more than 50 papers in refereed international journals and co-edited the Bulgarian edition of Miall's Dictionary of Chemistry. He is member and has served in elective positions in different Bulgarian and Balkan professional organizations. He has been member of the editiorial boards of two journals, published in Bulgaria in the English language.