
Air Pollution from Mobile Sources: Formation and Effects and Abatement Strategies

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Abstract

An overview of the issue of air pollution from mobile sources is presented in the present chapter. The chapter is divided into three sections. The first section contains a general introduction on specific aspects of air pollution from internal combustion engines. The topics covered include a description of the primary and secondary pollutants formed and their adverse effects on health and the environment; the mechanisms of pollutant formation and, consequently, the factors which affect their formation; and a historical perspective of the legislative measures progressively introduced over the years. Finally, a brief description of the abatement strategies which may be generally adopted will be given (primary methods vs. secondary methods). The second section describes the state-of-the-art pollution abatement technologies for gasoline, lean-burn and diesel engines. The third section describes aspects related to pollution abatement in the marine sector. Air pollution abatement from ships is of high current interest due to the recent and ongoing introduction of legislation in the area. The specific problems associated with the marine sector are described, along with the strategies/technologies adopted to affront these problems. Historically, thanks in part to the success achieved, there has been a shift in emphasis of the focus of the problem, which has evolved from gasoline-fuelled engines, to diesel and lean-burn gasoline engines, to, more recently, off-road vehicles and marine engines. The present contribution will centre on the development of emission abatement from road vehicles, which have been largely responsible for the technological advances made in the field, and marine engines, which have recently become the subject of attention and can be considered to represent the challenge for the future. The situation regarding off-road vehicles will not be specifically considered as related solutions are derived from the above quoted areas. The contribution is based on a seminar held at the summer school of the International PhD in Environmental Science and Engineering, Cagliari, September 2008.

Keywords

Air pollution • Mobile sources • Air quality strategies • Kyoto Protocol • Selective catalytic reduction (SCR)

1 Air Pollution: Formation and Effects

1.1 Introduction

Air pollution has been defined as “the presence in the earth’s atmosphere of one or more contaminants in sufficient quantity to cause short- or long-term deleterious effects to human,

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animal or plant life, or to the environment” (Painter 1974). These contaminants are divided into (1) primary pollutants, which are emitted directly into the atmosphere, and (2) secondary pollutants, which are formed in the atmosphere by subsequent reaction of primary pollutants or between primary pollutants and other gaseous species of the atmosphere.

The issue of air pollution and air quality is vast: A multitude of substances may be considered as pollutants and there are many sources which can result in the presence of polluting substances in the atmosphere. However, a limited number of anthropogenic activities are particularly problematic, and therefore, the substances related to these activities are of particular concern. For example, signatories to the United Nations Economic Commission for Europe (UNECE) Convention on Long-Range Transboundary Air Pollution (LRTAP) are required to provide inventories on a range of substances subdivided according to various categories (Adams et al. 2012):

Main pollutants: nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOC), sulphur oxides (SO_x), ammonia (NH_3), carbon monoxide (CO)

Particulate matter (PM): subdivided as primary PM (fine particulate matter (PM_{2.5}) and coarse particulate matter (PM₁₀)) and total suspended particulates (TSP)

Heavy metals (HMs): subdivided as priority heavy metals – lead (Pb), cadmium (Cd) and mercury (Hg) – and additional HMs: arsenic (As), chromium (Cr), copper (Cu), nickel (Ni), selenium (Se) and zinc (Zn)

Persistent organic pollutants (POPs): polychlorinated dibenzodioxins/dibenzofurans (PCDD/Fs), polycyclic aromatic hydrocarbons (PAHs), hexachlorobenzene (HCB), hexachlorocyclohexane (HCH) and polychlorinated biphenyls (PCBs)

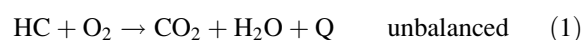
In addition, reporting of a number of individual PAHs is required: benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene and indeno(1,2,3-cd)pyrene. The US EPA controls 187 substances classified as toxic air pollutants (US EPA 2013b).

Activities or potential sources which lead to the formation of polluting substances in the atmosphere include biogenic sources, solvent use, agriculture, treatment and disposal of waste, extraction and distribution of fuels, combustion plants, electricity generation and transport. Combustion processes contribute enormously to the problem and the emergence of petroleum products added a new dimension to the problem of combustion-related pollution. More specifically, the massive increase in the use of internal combustion engines (ICE) in various forms of transport contributed to greatly increased problems of pollution, with the biggest concerns surrounding the problem of community pollution. Once the problem was identified, intense efforts have been devoted, since the second half of the twentieth century, to reduce the contribution associated with automotive sources. These efforts have met with significant success and, for

example, have led to the introduction of catalytic control of exhaust gas emissions as a standard feature of modern automobiles. Indeed, thanks in part to the success achieved, there has been a shift in emphasis of the focus of the problem, which has evolved from gasoline-fuelled engines, to diesel and lean-burn gasoline engines, to, more recently, marine engines.

1.2 Pollutant Formation in the Internal Combustion Engine (ICE) (Hickey et al. 2006)

The ideal chemical reaction for a combustion process, and therefore also in an ICE, may be represented as in Eq. 1:



where HC represents the fuel and Q the energy liberated in the form of heat from this highly exothermic process. However, a number of factors may interfere with this ideal process, with the result that substances (pollutants) other than carbon dioxide and water are present after the combustion process. Both physical (e.g., incomplete combustion) and chemical (e.g., fuel impurities and secondary reactions) factors are involved. In the following sections, the main pollutants found in engine exhaust and the variables or mechanisms which lead to their formation will be considered.

1.2.1 Carbon Monoxide (CO)

CO is produced when there is insufficient oxygen (O_2) for the complete oxidation of hydrocarbons, either on a global or on a local basis. Thus, on a global basis, CO emissions are high when the engine is operated under conditions in which there is an excess of fuel with respect to the oxygen necessary for its combustion. This can occur, for example, during acceleration. These are known as rich conditions. However, for local mixing reasons (local basis), CO formation does not reduce to zero under the so-called lean conditions, when there is an excess of O_2 (Fig. 1). Furthermore, the formation of CO is favoured by low combustion temperature, such as those encountered immediately after engine start-up, or by temperature inhomogeneity in the combustion chamber.

Although CO is considered as an ozone precursor (see sect. 1.2.3), the effects of CO alone on the environment are limited and the main concern surrounding this pollutant is its very high toxicity, which acts by limiting O_2 transport in the body. The affinity of CO for haemoglobin (carboxyhaemoglobin), which carries O_2 from the lungs to the tissues in the form of oxyhaemoglobin, is approximately 210 times greater than that of O_2 (Prockop and Chichkova 2007). Other known mechanisms of the detrimental effects of carbon monoxide on body processes include its ability to bind to myoglobin and mitochondrial cytochrome oxidase.

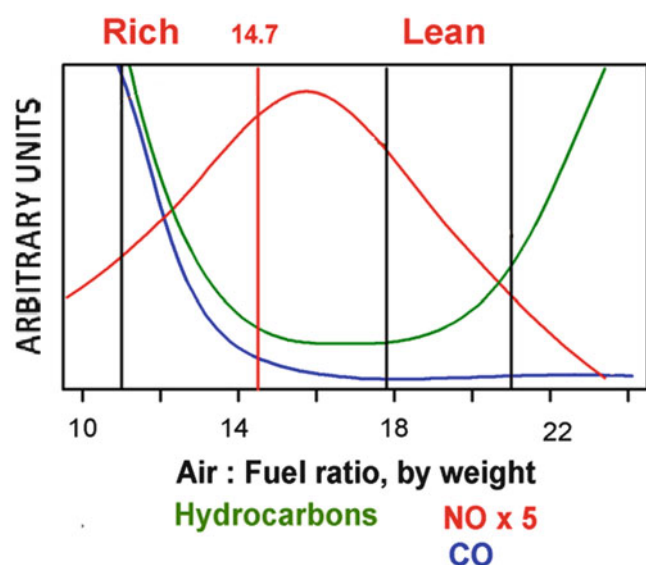


Fig. 1 Effect of air-to-fuel (A/F) ratio (w/w) on emissions of hydrocarbons, CO and NO_x . An A/F ratio of 14.7 corresponds to a stoichiometric mixture (Adapted from Kaspar et al. (2003))

1.2.2 Hydrocarbons (HCs)

Fuels for mobile sources contribute to the presence of hydrocarbons in the atmosphere at all stages of their use (from refining to refuelling) through evaporation losses. However, the emissions strictly associated with the combustion process itself are due to unburned or partially combusted fuel. In reality, the collective designation of HCs covers a multitude of specific compounds. The US EPA has listed more than 1,000 different compounds present in exhaust or evaporative emissions from on-road and non-road equipment, using conventional (gasoline, diesel) and various alternative fuels (e.g., ethanol, biodiesel, compressed natural gas) (US EPA 2013a). The nature of the HCs emitted depends on the characteristics of the fuel. For example, for light fuels, such as gasoline, the HCs emitted are not necessarily those present in the fuel. In fact, HCs with 1–3 carbon atoms ($\text{C}_1\text{--C}_3$) are common. For heavier fuels, such as diesel, they can also be the fuel itself.

The HCs emitted can also result from various reaction processes which take place during combustion, such as cracking, hydrogenation and dehydrogenation.

Various factors lead to the appearance of the unburned HCs, which is often linked with that of CO formation (Fig. 1): low temperature, lack of homogeneity during combustion (temperature or mixing) or physical factors which impedes combustion process. The temperature of the air/fuel mixture as it enters the combustion chamber can be a factor, as too low a temperature can result in poor mixing and consequently partial misfire. In general, engine misfire due to ignition, fuel delivery or air induction problems leads to the emission of HCs. For example, both inadequate spark

(mixture too rich) and a non-combustible mixture (too lean) lead to HC emissions. Another potential reason for HC emissions is the phenomenon of wall quenching, in which the relatively cool temperature of the chamber walls causes the flame to extinguish prematurely and some of the fuel remains unburned. In addition, there are physical phenomena in the engine which contribute to HC emissions. During engine operation, porous coke chamber deposits are formed. Adsorption and trapping of the fuel in these deposits allow fuel to escape combustion, and this uncombusted fuel is subsequently expelled.

There are various health issues associated with the presence of HC in the atmosphere. From this point of view, unsaturated and aromatic HCs are considered to be the most problematic. HC emissions were initially thought to present a relatively low toxicity threat, and, as will be seen in the next section, the main concern was their determining role as precursors to the secondary pollutant ozone (O_3) and its build-up at a tropospheric level along with other hazardous secondary pollutants. In fact, both NO_x and HCs are often referred to as ozone precursors. However, the potential health hazards of specific HCs or categories of HC have, over time, become evident. Many are carcinogens or mutagens and the effects of long-term exposure to many of the individual substances have not been fully established. In the case of automotive emissions, benzene, buta-1,3-diene, formaldehyde, acetaldehyde and polynuclear aromatic hydrocarbons (PAHs) are of particular concern. Furthermore, when they react with the other components of the atmosphere or the exhausts, they can generate more dangerous secondary pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and benzene derivatives. These secondary HC pollutants can reach the bloodstream when inhaled, so their abatement is therefore of the highest importance. From an environmental point of view, another potential problem is that of water pollution.

It should be noted that, given the large number of possible HC compounds, they are usually considered together and their concentrations are often reported as ppm of carbon equivalent (*ppm C*) (Kaspar et al. 2003).

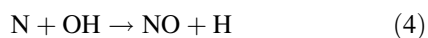
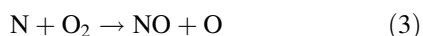
1.2.3 Nitrogen Oxides (NO_x)

The designation “nitrogen oxides (NO_x)” is used to refer to any combination of NO and NO_2 .

There are three recognised routes to NO_x formation during fuel combustion:

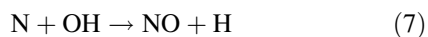
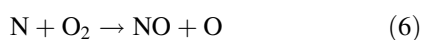
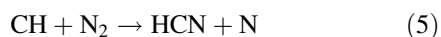
1. Thermal NO_x species are formed by the Zeldovich mechanism, in which atmospheric nitrogen and oxygen react together to form NO_x . This process is summarised as follows:





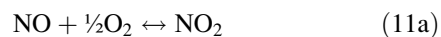
The mechanism is favoured by high oxygen radical concentration and, above all, by high temperature.

2. Prompt NO_x species are formed in hydrocarbon-rich flames via the interactions of hydrocarbon radicals with nitrogen to produce various nitrogen-containing species (nitriles, amines, amides, cyanides, etc.). These are then oxidised to produce NO_x . Prompt NO_x forms by the Fenimore mechanism (Fenimore 1975, 1976), which can be represented as follows:



3. Fuel NO_x is formed by the oxidation of fuel-bound nitrogen, i.e., nitrogen-containing species in the fuel itself. Consequently, its contribution depends only on the quantity of nitrogen present in the fuel and is independent of the oxygen content and the temperature. During combustion, fuel compounds such as amines, amides, pyridines, etc., generate other volatile compounds of nitrogen, such as ammonia and cyanides, which are then oxidised to NO and CO_2 .

In relation to the formation of NO_x in gasoline-fuelled ICE, there are two important features, i.e., thermal NO_x is favoured under most engine conditions and therefore combustion temperature is the most important control factor, and NO is effectively the only NO_x species present. This is because at the temperature of fuel combustion, the equilibrium between NO and NO_2 (Eq. 11a) is shifted far to the left.



With regard to its environment effects, primary NO_x emissions contribute to the process of eutrophication of aquatic systems and, to a limited extent, to the formation of acid rain. From the point of view of health effects, NO presents a very low toxicological threat. NO_2 on the other hand is a highly toxic brown-red gas. Its presence in the atmosphere is therefore highly undesirable. As indicated earlier, a significant cause for concern surrounding the

presence of NO in the atmosphere is its presence in combination with HCs and CO and their further reaction to form secondary pollutants during photochemical smog episodes. On cooling, atmospheric NO can be slowly converted into NO_2 via Eq. 11a, as the equilibrium lies to the right at low temperature. The NO_2 formed can undergo a photochemical dissociation to NO and atomic oxygen. The atomic oxygen produced reacts with O_2 to form ozone. A circular reaction process is completed when the NO reacts with O_3 to form NO_2 and O_2 . The levels of O_3 (and NO_2) are regulated by this cycle. In the presence of hydrocarbons and CO, however, this cycle is broken, resulting in increased NO oxidation to NO_2 , build-up of tropospheric ozone and the formation of hazardous secondary pollutants such as peroxy acyl nitrates (PANs and formaldehyde). This type of air pollution episode is known as photochemical smog and was first unequivocally identified in Los Angeles in the mid-1940s. The European Environment Agency monitors levels of NO_x , CO, CH_4 and non-methane volatile organic compounds (NMVOCs) as ozone precursors (EEA 2013a).

1.2.4 Particulate Matter (PM)

Particulate matter is a collective term for an often highly complex mixture of solids and liquids (Matti Maricq 2007; Twigg and Phillips 2009). The issue of airborne PM and its relationship with transport is highly complex. A large number of interrelated factors are involved in the formation and development of airborne PM, for which the situation is probably more complex than for any other pollutant. In the following paragraphs, a number of relevant features with regard to PM will be discussed.

1.2.4.1 PM Composition

As indicated above, PM is a collective term for a mixture of substances. This mixture can include oxides, sulphates, sulphites, carbonates, chlorides, metal compounds, fuel and soot carbon. The composition of PM derived from combustion is related to the fuel type and purity. For road transport, diesel applications are the worst offenders, while PM emissions from gasoline engines are significantly smaller.

Diesel PM is divided into three main categories: soluble organic fraction (SOF), sulphates and soot. The SOF is composed of heavy HCs from the fuel and lubricating oil or is formed during combustion. This is often condensed on existing solid particles. Sulphates arise from the presence of sulphur in the fuel, which is converted into SO_2 during combustion and then into SO_3 . These gases can also react with water in the exhaust gases to form hydrated sulphuric acid. More generally, sulphates form part of the so-called inorganic fraction of PM. Other potential contributors to this inorganic fraction are inorganic compounds added to lubrication oil (and sometimes to the fuel itself) for various reasons (as viscosity modifiers, as antioxidants, as anticorrosives, to keep solid matter, especially soot, in suspension).

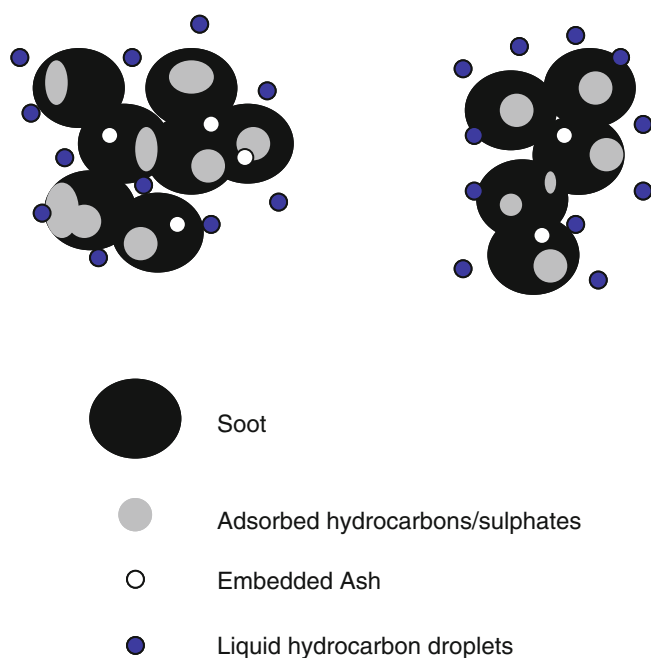


Fig. 2 Schematic representation of PM composition (Adapted from Matti Maricq 2007; Twigg and Phillips 2009)

Finally, soot is formed from incomplete combustion of the fuel. The complex nature of PM composition is illustrated schematically in Fig. 2.

As will be discussed later, the issue of marine fuel sulphur content is of fundamental importance in the formation/prevention of PM from marine engines.

1.2.4.2 PM Classification

PM is classified in a number of related ways. The most common classification of particulates is according to particle size, or fractions, which can range across four orders of magnitude. As particles are unlikely to be spherical, a generally accepted method of measurement and comparison must be adopted. The most widely used definition is the aerodynamic diameter: A particle with an aerodynamic diameter of 10 μm behaves in a gas like a sphere of unit density with a diameter of 10 μm . The notation PM10 is used to describe particles of 10 μm or less, whereas PM2.5 indicates particles with an aerodynamic diameter of less than 2.5 μm . Similarly, PM1 is another commonly used indication.

On this general basis, PM is often defined as coarse PM (2.5–10 μm), fine PM (particles from 0.1 to 2.5 μm) and ultra-fine PM (particles smaller than 0.1 μm). Another classification, related to their potential health effects, is based on their capacity to penetrate into the respiratory system.

1.2.4.3 PM Sources: Primary and Secondary PM

While there are usually multiple sources for any pollutant, in the case of PM there are a considerable number of

natural sources. These include sea spray (sea salt), soil and sand moved by the wind, biogenic aerosols (e.g., pollen) and volcanic emissions. Furthermore, in the case of automotive transport, there are a number of sources of PM generally related to vehicle use, but not directly related to the combustion process. These include primary PM from attrition processes – wear of brakes and tyres, wear of the road surface and PM derived from suspension of deposited matter by passing vehicles. Finally, there is the PM derived from the combustion process itself. However, even this is further subdivided into primary PM from the combustion process (usually less than 1–2.5 μm) and secondary PM which form in the atmosphere through chemical and physical processes starting from the primary precursors. All of these possibilities, along with the above-discussed variable composition of PM, give rise to a very complex situation in which the various sources are not easily apportioned.

The issue of secondary PM formation is of fundamental importance because the PM present in the atmosphere does not necessarily correspond with that emitted from the engine during the combustion process. In fact, PM emissions are commonly studied with dilution tunnels in attempts to mimic the chemical and physical processes which lead to the growth and/or formation of secondary PM in the atmosphere. The process of transformation is illustrated in Fig. 3. Chemical reactions may also come into play. For example, the above-discussed hydrated sulphuric acid formed during combustion can in turn interact with other gases and particles in the air to form sulphates and other products.

The concerns surrounding PM have grown significantly in recent years, along with the observation that PM concentrations in urban areas are unacceptably high. As may be inferred from the above discussion, certain PM can reach the deepest recesses of the lungs, and many studies have linked PM with a series of respiratory related. In fact, the European Environmental Agency (EEA) report that “Two pollutants, fine particulate matter and ground-level ozone, are now generally recognised as the most significant in terms of health impacts” (EEA 2013b), while the US Environmental Protection Agency (US EPA) state that “Of the six (criteria) pollutants, particle pollution and ground-level ozone are the most widespread health threats” (US EPA 2013b).

1.2.5 Sulphur Oxides (SO_x)

The designation “sulphur oxides (SO_x)” is used to indicate any mixture of SO_2 and SO_3 . In combustion processes, the SO_x formed originate from the sulphur present in the fuel. Both are toxic, colourless gases, with a pungent odour and a high solubility in water. This property is responsible for one of the main concerns surrounding SO_x emissions, i.e., their

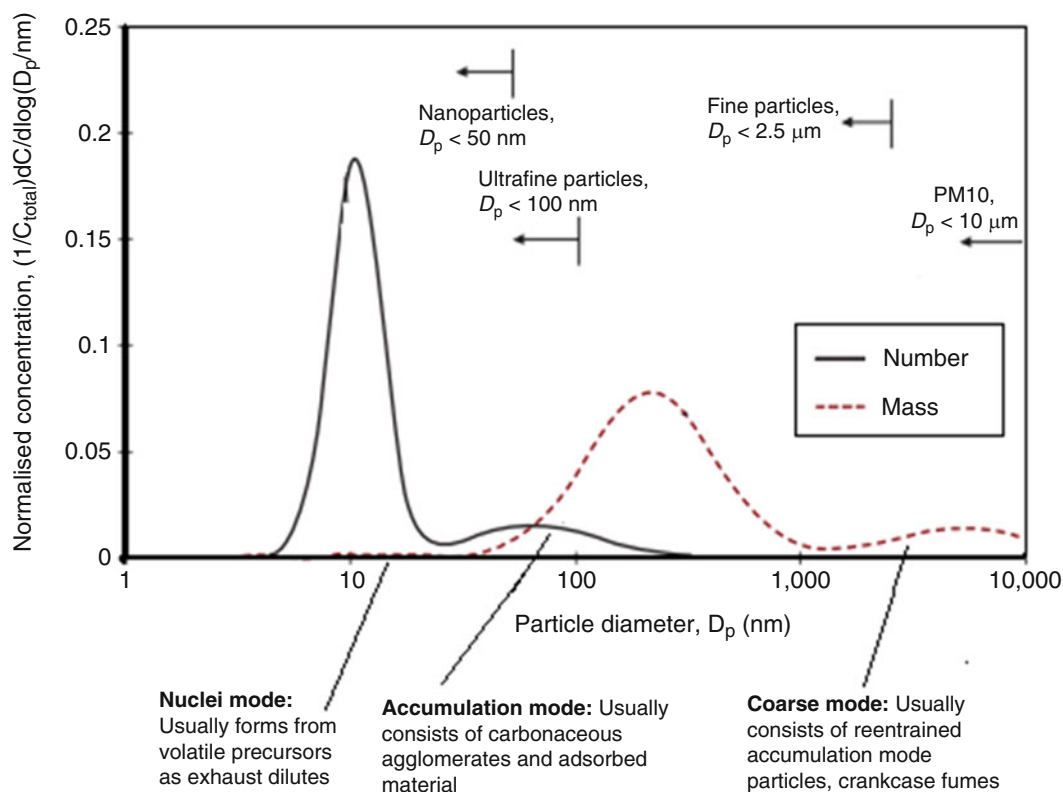


Fig. 3 Evolution of particulate matter (PM) (Adapted from Dieselnets 2013; Twigg 2011a)

acid nature. Dissolved in rainfall (acid rain), they can cause significant damage both to the environment and to buildings. In comparison, the acid-forming potential NO_x is much lower. As indicated above, the high solubility in water means that hydrated sulphuric acid can form during the combustion process itself. In the presence of high fuel sulphur concentrations, as in the case of marine fuels, the formation of the so-called acid mists gives rise to another potential problem relevant to the present discussion. These acid mists can cause severe corrosion damage to the post-treatment abatement systems. In addition, sulphur is a poison for many catalysts and its presence can determine catalyst choice in catalytic posttreatment systems.

As may be inferred from the discussion of PM, the issue of SO_x cannot be completely separated from that of PM. In the case of automotive fuels, as a pollution prevention measure, the level of the sulphur in the fuel has been progressively reduced to 10 ppm in Europe. This concentration leads to the formation of very low levels of SO_x and sulphate PM in the exhaust. For this reason, land-based transport makes a relatively small contribution to atmospheric SO_x levels. However, as will be outlined in Sect. 3, while similar measures are only now being adopted in the marine transport sector, the amount of sulphur in marine fuel is still high. This situation represents one of the biggest challenges for pollution abatement in the marine sector.

1.2.6 Carbon Dioxide (CO_2)

Combustion of fossil-based fuels necessarily leads to CO_2 formation. CO_2 is a direct greenhouse gas, and there is much debate centred on CO_2 because its atmospheric concentration is increasing, with transport in general making a significant contribution. The Kyoto Protocol, in which many countries committed to reduce CO_2 levels (UNFCCC 2013), is a direct consequence of the concerns surrounding the role of CO_2 in global warming. Furthermore, in 1998, the European Commission reached an agreement with the European Automobile Manufacturers' Association (ACEA), the Japanese Automobile Manufacturers Association (JAMA) and the Korean Automobile Manufacturers Association (KAMA) to comply with voluntary limits (140 g/km by 2008). After an initial period which saw significant CO_2 reductions, non-compliance resulted in the introduction of mandatory limits (vide infra).

1.3 Factors Which Affect Pollutant Formation

From the preceding paragraphs it emerges that the factors which affect pollution formation may be broadly divided into three main related categories. It is useful to summarise these below:

1.3.1 Engine Type (NO_x , CO, HCs)

For the purposes of pollution abatement, for simplicity, the discussion can be divided into two large categories, i.e., stoichiometric and lean engines. As will become evident, this distinction is useful for the discussion of the types of post-combustion depollution systems possible. The difference is related to air-to-fuel (A/F) ratio, usually denoted by λ (Fig. 1). A value of $\lambda = 1$ indicates the point where the amount of oxygen present is exactly that required for full stoichiometric combustion of all of the fuel present. This corresponds to an A/F ratio of 14.7 (w/w) for an oxygen-free gasoline. This discussion is also linked to the type of fuel used. Gasoline engines are typically run stoichiometric, while engines using heavier fuels (light-duty diesel, heavy-duty diesel, marine engines) are all operated under lean conditions, in which there is an excess of air ($\lambda > 1$). Here the discussion will be limited to the commonly engine types/fuels used. The situation for alternative fuels, e.g., methane, gpl and hydrogen, will not be specifically considered.

1.3.2 Engine Operating Conditions (NO_x , CO, HCs)

Within the framework of the engine and fuel type used, the engine operating conditions (or driving conditions) also come into play as this influences the A/F ratio and temperature. The exact composition at any given time thus strongly depends on these two factors.

1.3.3 Fuel Quality (SO_x , PM)

As discussed above, the fuel type and fuel quality are the determining factors in the formation of PM and SO_x species.

Figure 1 shows the variation in the production of NO_x , CO and HCs as the A/F ratio varies. In fuel-rich combustion mixtures ($\lambda < 1$, net reducing), the highest amounts of CO and HC are formed. Their levels of production decrease as the ratio approaches the stoichiometric point ($\lambda = 1$). Initially, in the fuel-lean situation ($\lambda > 1$, net oxidising), most of the fuel is consumed by the available O_2 , which results in low production of CO and HCs. However, as λ increases, HCs output begins to increase because combustion becomes inefficient (or misfire occurs). This picture represents a general scheme since the region of misfire depends on the type of engine (lean or stoichiometric).

In the case of NO_x , its formation is low in fuel-rich conditions due to a scarcity of O_2 . NO_x production increases to a maximum as the A/F ratio passes through stoichiometry ($\lambda = 1$) into fuel-rich stoichiometries ($\lambda > 1$). The amount formed then starts to decrease as the temperature of combustion falls, due to the presence of an increasing amount of air. This decrease in temperature results in a decrease in NO_x production. Another temperature-related feature is the situation immediately after start-up, when the engine temperature has not reached its normal operating level. In this period

the lowest concentrations of NO are formed while CO and HCs levels are high.

All of this means that the amount and types of pollutants vary (Kaspar et al. 2003). It is important to note that, although related, reducing pollution from each engine type represents a different problem and, as will be seen later, for this reason the abatement solutions also vary. In fact, the dependency of the nature of the emission of the engine type has been recognised not only as composition but also in terms of their impact: In a recent meeting the International Agency for Research on Cancer (IARC; Lyon, France) classified diesel engine exhaust as “carcinogenic to humans” (Group 1), whereas gasoline engine exhaust was considered as “possibly carcinogenic to humans” (Benbrahim-Tallaa et al. 2012). Interestingly, this carcinogenic classification of diesel exhaust has been questioned (Pallapies et al. 2013) since it does not take into account the significant evolution of diesel engines, e.g., the introduction of common rail technology (Hesterberg et al. 2011; McClellan et al. 2012). Furthermore, it should be remembered that the nature of the fuel can affect the amount and nature of emissions, as indeed was observed when blends of regular and biodiesel were employed on the same engine (Magara-Gomez et al. 2012).

1.4 Pollution Legislation

Legislative measures progressively introduced over the years have been largely responsible for stimulating progress in the abatement technologies adopted in the automotive sector. The progressive introduction of increasingly stringent measures led first to the adoption of pollution prevention measures and then to the introduction and subsequent development of the so-called end-of-pipe technologies. In the following sections, an overview of legislative measure in the automotive sector will be considered.

Urban air pollution problems have existed for centuries and legislative measures to control the problem are underway for well over a century. Two particular types of urban air pollution came to the fore during the twentieth century: London-type smog and photochemical smog (Jacobson 2002). Initially, the focus was on London-type smog. This was caused by the burning of fossil fuels in the presence of fog (SMoke + fOG) and became a serious public health and safety issue with the Industrial Revolution. Episodes of this type of pollution were very frequent in London but the phenomenon was common in many industrial areas. The increasing frequency and seriousness of these episodes in the nineteenth and first half of the twentieth century lead to a greater attention to the problem. However, it was only after the Second World War that determined efforts were devoted to air pollution management, in particular after the so-called Great Smog of 1952 in London. In 1956, the UK passed its first Clean Air Act. The first federal “Pollution Control Act”

was passed in the USA in 1955, in which the Public Health Service was financed to study the sources and problems related to air pollution. For a variety of reasons, initial measures generally met with limited success. For example, compliance control measures were inadequate. Similarly, rather than on pollution prevention or control, the focus was on measures to reduce the presence of harmful gases in urban areas, for example, through the use of taller chimney stacks, thereby moving the pollution sources away from the cities. However, these laws represented the first steps towards a serious legislative effort to affront the problem of urban pollution.

With regard to photochemical smog, the problem is directly linked with the widespread diffusion of automobiles. By the late 1930s/early 1940s, the problem of reduced urban visibility became evident in Los Angeles, and by the mid-1940s, it was realised that the pollution was not only from smokestacks but from a wider variety of sources, including automobiles. In fact, the first legislative measures which identified automobiles as sources of pollution were introduced in California in 1947. However, no specific countermeasures were adopted. The first US Federal standards which specifically required control of automotive emissions were introduced by the Clean Air Act of 1970, while in 1970, Europe, with directive 70/220/CEE, fixed its first standards to control pollutants generated in internal combustion engines. Both have been frequently amended and updated in the intervening years. Californian legislation limits have been independently set since 1977 by the Californian Air Resources Board (CARB). Legislation in California represents the most severe emission standard in the world.

Initial US Federal legislation required a 90 % reduction of CO and HC emissions from 1970 model years by 1975 and a 90 % reduction of NO emissions from 1971 model years by 1976. Initial strategies to meet the targets were based on prevention: Engine modification allowed CO and HCs emissions to be reduced. However, the more demanding

limits introduced for the 1975 model year meant that catalytic control had to be introduced. Significant reductions of CO and HC emissions were required, which led to the introduction of conventional oxidation catalysts (COCs – Pd, Pt/Al₂O₃), together with engine modifications and the use of unleaded gasoline. Engines were operated in lean conditions to provide the O₂ necessary for the oxidation catalyst to function. Some degree of NO_x control was achieved by non-catalytic methods, especially exhaust gas recirculation (EGR). As NO_x limits became stricter, COCs were superseded by a combination of COC and three-way catalysts (TWCs), to specifically tackle NO_x emissions, and, finally, by TWCs only. TWCs will be discussed in more detail in Sect. 2.

1.5 Automotive Emission Standards

The initial EU legislation closely reflected the legislation which had been recently introduced in the USA. However, in the successive development of its legislation, the EU began to introduce EU-specific standards. A very important consideration, for example, is the significantly higher incidence of diesel engines in the Europe. Consequently, from the early 1990s, there has been a gradual phasing-in of the modern European emission standards, known as Euro 1 to Euro 6 standards. Standards set before this are generally referred to as Euro 0. In the automotive sector, emission standards are set for various pollutants on the basis of vehicle/engine types and are divided into two main categories: (1) passenger cars and light-duty (LD) vehicles (<3.5 t) and (2) heavy-duty (HD) vehicles and buses. Other engine types, such as motorcycles and non-road diesel engines, are also legislated, but these will not be considered here. The situation in relation to marine engines will, however, be discussed in Sect. 3.

To exemplify the temporal development of legislation, Table 1 outlines European emission standards since 1993

Table 1 Selected EU emission standards for passenger cars

Standard	Year	CO (g/km)	HC	NMHC	NO _x	HC + NO _x	PM
<i>Diesel</i>							
Euro 1 ^a	1992	2.72 (3.16)	–	–	–	0.97 (1.13)	0.14 (0.18)
Euro 2	1996	1.0	–	–	–	0.7	0.08
Euro 3	2000	0.64	–	–	0.5	0.56	0.05
Euro 4	2005	0.50	–	–	0.25	0.30	0.025
Euro 5	2009	0.50	–	–	0.18	0.23	0.005
Euro 6	2014	0.50	–	–	0.08	0.17	0.005
<i>Gasoline</i>							
Euro 1 ^a	1992	2.72 (3.16)	–	–	–	0.97 (1.13)	–
Euro 2	1996	2.2	–	–	–	0.5	–
Euro 3	2000	2.3	0.20	–	0.15	–	–
Euro 4	2005	1.0	0.10	–	0.08	–	–
Euro 5	2009	1.0	0.10	0.068	0.06	–	0.005
Euro 6	2014	1.0	0.10	0.068	0.06	–	0.005

^aVaues in parenthesis are conformity of production (COP) limits

Table 2 European Union sulphur limits in automotive fuel

Date	Maximum sulphur content
1993	0.2 % w/w
2000	350 ppm
2005	50 ppm
2010	10 ppm

for selected pollutants. Similarly, in the USA, Tier I standards were phased in between 1994 and 1997, while Tier II standards were phased in between 2004 and 2009. Even more stringent Tier III standards have been agreed, to be phased in between 2017 and 2025. It should be noted that a fundamental aspect in the application of emission legislation is the procedure used to test engine compliance. Compliance tests are performed on a chassis dynamometer and involve prescribed cycles, which, however, will not be further discussed here.

An important distinction exists between the emission measurement units for HD diesel vehicles and other categories. For HD diesel vehicles, the limits are expressed as a function of power output (g/kWh), while they are expressed as a function of the driving distance for the other categories (g/km). As will be discussed in Sect. 3, the recent introduction of emission limits in the marine sector treats such engines in the same way as land-based HD engines from this point of view.

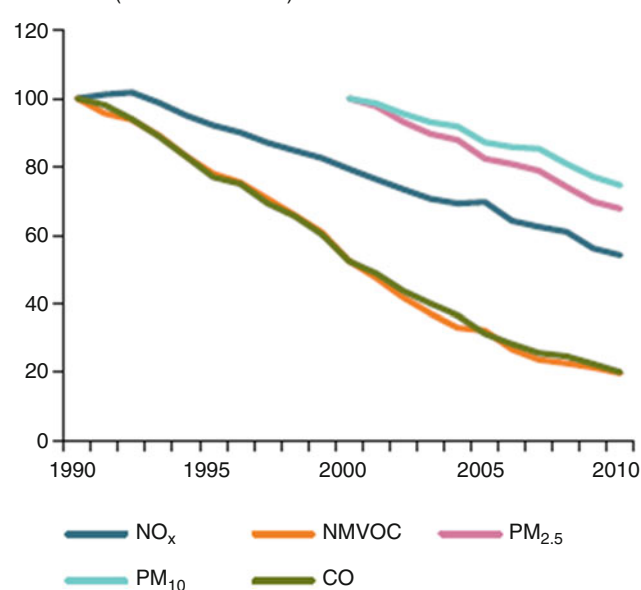
The EU has recently adopted two regulations which address CO₂ emissions from passenger cars and light commercial vehicles. CO₂ emission targets for new passenger cars were adopted in April 2009. The regulation established a fleet-average CO₂ emission target of 130 g/km to be reached by 2015, with a target of 95 g CO₂/km to be reached from 2020 also defined. CO₂ emission targets for light commercial vehicles were proposed in October 2009. The regulation establishes a fleet-average CO₂ emission target of 175 g/km, fully phased-in from 2016, and a target of 135 g CO₂/km from 2020.

With regard to the emission of SO_x, EU legislation has implemented a progressive reduction of the sulphur content in automotive fuel since the beginning of the 1990s (Table 2). Currently, automotive fuel contains a maximum of 10 ppm of sulphur. In the USA, ultra low-sulphur diesel (ULSD) contains a maximum of 15 ppm S.

1.6 The Progress Made in Pollution Abatement

The efforts which have been made to reduce emissions of pollutants in recent years have been quite successful. This is illustrated in Fig. 4, which shows the decrease in emissions of airborne pollutants from road transport in the EU-27

Emissions (Index 1990 = 100)

**Fig. 4** EU-27 road transport emissions trends 1990–2010 for the main airborne pollutants (Adapted from Adams et al. 2012)

countries between 1990 and 2010. Road transport represents one of the main pollution categories, and the regulation measures introduced have contributed significantly to specific and overall reductions. However, whereas this chapter is focussed essentially on automotive and marine emissions, it must be evidenced that off-road engines also significantly contribute to overall emissions and, accordingly, regulation limits have also been set for these engines. It is estimated that in 1996, before any standards had become effective, emissions from land-based off-road engines, locomotive engines and marine diesel engines accounted for about 40 % of the mobile source emissions of PM and 25 % of NO_x. Of this, land-based off-road diesel engines contributed about 47 % (Van Rensselaar 2011).

1.7 Pollution Abatement Strategies

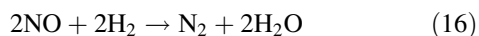
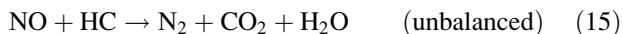
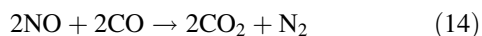
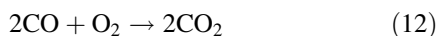
Pollution abatement strategies may be divided into two categories: measures to prevent pollution (primary methods) and measures to reduce emission of the pollutants once formed (secondary methods). As may be inferred from the above discussion, both approaches have been extensively employed for pollution control from transport. Preventative measures include engine modification; the use of reformulated, Pb-free and low-sulphur fuels; and the use of alternative fuels such as liquefied petroleum gas (LPG) and natural gas (NG) which are intrinsically cleaner than diesel or gasoline. However, the very high limits imposed by legislation made it necessary to introduce post-combustion technologies, and preventative

measures must be used in combination with these, not as alternatives. In the following sections, the state of the art in automotive catalytic technologies will be discussed.

2 State of the Art in Automotive Pollution Technology

2.1 Three-Way Catalysts (TWCs)

Three-way catalysts (TWCs) are the current state-of-the-art technology for emission control for gasoline automobiles, and they are without doubt the most successful post-combustion catalytic technology introduced in the automotive sector. A schematic representation of a TWC is shown in Fig. 5. The name TWC derives from the ability to simultaneously convert the three primary pollutants CO, NO_x and HCs (Kaspar et al. 2003):



TWC formulations have evolved and improved remarkably in terms of performance since they were first introduced. However, the improvements observed are not the result of changes in formulation only. A large number of factors – materials advances, improved engine characteristics, improved engine control, improved fuel characteristics, etc., – have been responsible for their success.

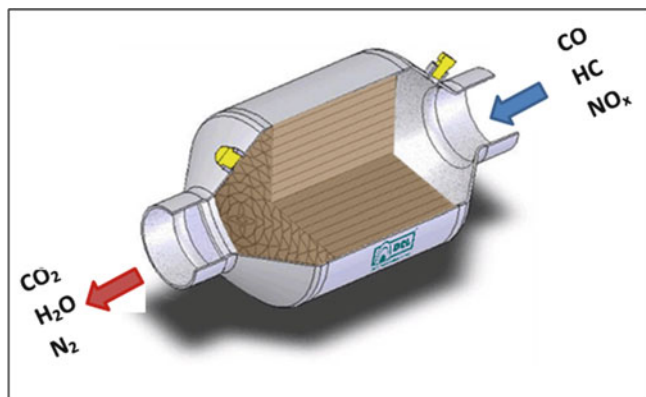


Fig. 5 Schematic arrangement of a three-way catalyst (TWC) (Adapted from Govconsys 2013)

The catalyst is formed by three main components:

- A *honeycomb* monolith substrate
- A *washcoat* support for the active phase
- An *active phase*

2.1.1 The Substrate

The substrate is a honeycomb monolith made of cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) or metal. This is mounted in a steel container with a resilient matting material to ensure vibration resistance. This arrangement protects the catalyst and facilitates installation. Traditionally, cordierite monoliths have been extensively employed, primarily due to their lower production cost. Metallic substrates have a number of advantages however, such as a high thermal conductivity and low heat capacity, which allow very fast heating. In addition, they can be fabricated with very thin foil, which gives low back pressure and high geometric surface area, combined with good mechanical strength. These characteristics make metal monoliths suitable for specific applications such as close-coupled catalysts (CCCs), which are installed as close as possible to the engine in order to reduce the light-off time (vide infra).

A wide variety of substrate sizes with different cell densities and wall thicknesses are available. In fact, the cell density can range from 10 to more than 1,000 cells per square inch (cpsi), and various cross-channel sections are possible (triangular, hexagonal, trapezoidal and round). Very high cell densities (>1,000 cpsi) are common for TWCs, while densities in the range near 400 cpsi are more common for diesel applications (vide infra) (Dieselnet 2013).

2.1.2 The Catalyst: Washcoat + Active Phase

The active catalyst is supported (washcoated) onto the monolith by dipping it into a slurry which contains the catalyst precursors. After removal of the excess mixture, the honeycomb is calcined to obtain the finished catalyst.

The washcoat plays a number of key roles in the catalysis:

- It increases the surface area to maximise the contact between gas and active species. Consequently, it must have a high surface area which is stable at elevated temperatures.
- It ensures a high dispersion of the active phase. By interaction with the active phase, it should also maintain this high dispersion at elevated temperatures.
- In some cases, it acts as a co-catalyst.

Sintering of the either washcoat support or active phase results in dramatic loss of activity.

The exact composition of a TWC is a matter of confidentiality. Different formulations exist for different manufacturers, and indeed formulations have varied significantly over the years, depending on a variety of factors, including economic considerations based on the price of the metals used in the active phase. However, modern

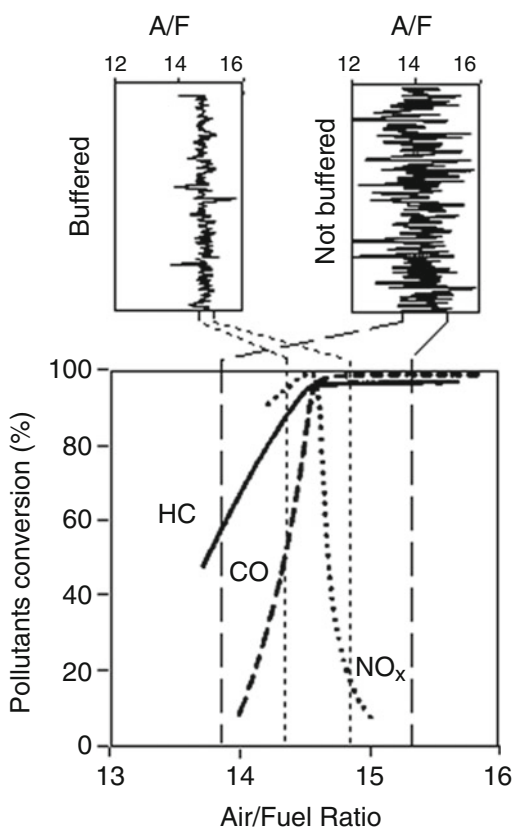


Fig. 6 Effect of air-to-fuel (A/F) ratio on the conversion efficiency of a three-way catalyst (TWC) (Adapted from Kaspar et al. 2003)

TWC all contain a number of main components in their formulations:

- Alumina, which is employed as a high surface area support (washcoat)
- $\text{CeO}_2\text{-ZrO}_2$ mixed oxides
- Precious Group Metals (PGMs) as active phases (Rh, Pt and Pd)
- Various oxides as stabilisers of alumina surface area, activity promoters and selectivity promoters

With regard to the last point, there are many possibilities: Iron, manganese, calcium, strontium, barium, lanthanum, neodymium, praseodymium and zirconium may all be used (Twigg 2011a). Formulations normally contain more than one of these additives.

2.1.3 TWC Operation

Before discussing the role of each component, a number of technological aspects regarding catalysis functionality will be outlined. These aspects may be useful to fully understand the role of each component.

In order to function correctly, TWCs require that stoichiometric conditions are maintained over the catalyst. The dependence on conversion efficiency A/F ratio is indicated in Fig. 6. Very high conversion is observed only if the A/F is

maintained within a narrow operating window. Achieving this narrow window is achieved by the integrated engine on-board diagnostics (EOBD) system. The system is composed of two oxygen sensors, known as λ sensors, located at the inlet and outlet of the converter. The signal from the first sensor is used as a feedback for the fuel and air injection control loop. Ceria-based oxides are included in the catalyst formulations to further buffer the A/F fluctuations over the catalyst, through the redox properties of this element (vide infra). By comparing the oxygen concentration before and after the catalyst, A/F fluctuations are detected. Excessive fluctuations of A/F at the outlet signal system failure.

A further important feature which should be considered is the position of the catalyst. TWCs are capable of converting close to 100 % of the three pollutants once they reach their operating temperature and efficient A/F control is maintained. Heating of the catalyst is achieved by the exhaust gases themselves. However, in the time take to reach this temperature, conversion is low and a significant proportion of the overall emissions occur in this warm-up period after engine start-up (cold start). This may result in non-compliance during test procedures, especially for the more demanding legislation. The solution to this problem is to use a close-coupled catalyst (CCC). Basically, the catalyst is positioned closer to the engine, which significantly reduces the time it takes to reach operating temperature and dramatically affects vehicle emissions immediately after the start-up of the engine. As temperatures up to 1,100 °C are routinely met as a consequence of this location of the catalyst, an extremely efficient and robust catalyst is required.

2.1.4 The Role of PGMs

The PGMs represent the key component of the TWC, as the catalytic activity occurs at the metal centre. Rh, Pd and Pt have long been employed in TWCs. There is general agreement on the specificity of Rh to promote NO removal, while Pt and Pd are used mainly to perform the oxidation reactions, even though the oxidation activity of Rh is also good. In the early COCs, Pt was used, along with smaller amounts of either Pd or Rh to provide durability under lean conditions. However, once catalytic NO_x reduction became necessary, Rh/Pt was used. With improvements in catalyst performance, lower cost Pd/Rh TWCs were developed. The choice of Pt/Rh or Pd/Rh strongly depended on the balance of HC/CO/ NO_x from a particular engine and application (Twigg 2011a). Pd was extensively added to TWC formulations starting from the mid-1990s being, at that time, cheaper than other PGMs. Formulations with Pd as the only PGM were in fact developed and commercialised for a period. Better A/F control and modification of the support provided adequate NO_x conversion even in the absence of Rh. Economic factors did to some extent come into play in this choice. However, the increased use of Pd in the TWC

technology also resulted in strong increases in Pd market price. In the past, a strongly disadvantage of the use of Pd was sensitive to poisoning by sulphur or lead. However, lead levels are now close to zero and fuel sulphur levels have been markedly reduced so these considerations are less important than previously. Consequently, most modern TWCs are based on Pd/Rh formulations.

2.1.5 The Role of Al_2O_3

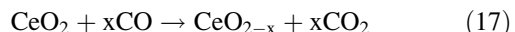
The main role of Al_2O_3 is as a high surface area support to promote PGM dispersion and stability. In most cases $\gamma\text{-Al}_2\text{O}_3$ is employed due to its high surface area and good thermal stability under the hydrothermal conditions of the exhausts. However, other aluminas such as $\delta\text{-}$ and $\theta\text{-Al}_2\text{O}_3$, which exhibit even higher thermal stability, can also be employed for specific applications such as in the CCCs (Kaspar et al. 2003), for which the issue of thermal stability is particularly important. Alumina stabilisation is necessary to prevent its transformation to the low surface area $\alpha\text{-Al}_2\text{O}_3$ (surface areas typically below $10 \text{ m}^2 \text{ g}^{-1}$). A number of stabilising agents have been reported in the literature: Lanthanum, barium, strontium, cerium and zirconium oxides or salts have been widely investigated. Efforts to produce highly stabilised alumina-based oxides, along with efforts to understand the stabilisation mechanisms, remain an ongoing area of research (Hernandez-Garrido et al. 2013).

2.1.6 The Role of CeO_2

A number of beneficial effects have been attributed to CeO_2 (Kaspar et al. 2003; Trovarelli 1996):

- It promotes the PGM metal dispersion.
- It increases the thermal stability of the Al_2O_3 .
- It promotes the water-gas shift (WGS) reaction
- It favours catalytic activity at the interfacial metal-support sites.
- It promotes CO removal through oxidation by lattice oxygen.
- It stores and releases oxygen under respectively lean and rich conditions

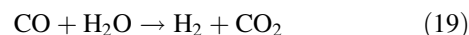
Of particular importance is the ability of ceria to store and release oxygen under lean and rich conditions, respectively. In reducing conditions, the excess reductant reacts with the ceria, which is reoxidised in oxidising conditions:



This redox ability is known as the oxygen storage capacity (OSC) and the net effect is that the OSC buffers oscillations in the A/F ratio. It is an important control factor in maintaining the stoichiometric conditions necessary for efficient conversion. Maintaining the OSC is highly

important for both catalytic and technological reasons. From the catalytic point of view, the TWC activity is directly related to the OSC performance, while from a technological point of view, as above-discussed, the OBD technology is based on monitoring OSC efficiency.

Clearly, the OSC also contributes to removal of CO (and HC) in lean conditions. Another important means of CO removal is the WGS reaction, which is catalysed by ceria:



From the mid-1990s, $\text{CeO}_2\text{-ZrO}_2$ mixed oxides have gradually replaced pure CeO_2 as the OSC materials in TWCs. The replacement of CeO_2 with $\text{CeO}_2\text{-ZrO}_2$ mixed oxides in TWC formulations has significantly increased their performance due to the high thermal stability of these materials (Hernandez-Garrido et al. 2013).

2.2 Diesel and Lean-Burn Gasoline Engines

As outlined in Sect. 1, diesel and lean-burn gasoline engines operate at A/F ratios higher than stoichiometric (>14.7). These engines, due to the high A/F used in the combustion process, can achieve significant fuel savings. This reduction in fuel consumption translates to reduced emissions of CO_2 . However, as these engines present a different composition with respect to gasoline engines, the problem of pollution abatement must be resolved by different methods. The TWC in fact does not work efficiently for NO_x reduction as the excess of O_2 competes for the reducing agent, in particular CO. The issue of diesel engines is particularly relevant in Europe, where there is a very high incidence of automotive diesel engines.

It is worth recalling that such engines operate at lower temperatures with respect to gasoline engines, which results in the production of lower amounts of NO_x . However, it is in fact the problem of NO_x reduction under oxidising condition which represents the biggest difficulty. The second “peculiarity” is the formation of significant amounts of PM in the case of diesel engines, although some PM is also formed in lean-gasoline engines which use direct fuel injection (DI). Importantly, nowadays many modern gasoline engines use DI technology and accordingly mostly run under lean conditions (Wang-Hansen et al. 2013).

In order to comply with the stringent legislation introduced for these engines, a number of specific post-combustion technologies have been successfully introduced and developed for the individual pollutants from these engines. The following discussion will be organised according to the solutions proposed for individual pollutants. For the sake of completeness, some discussion will also be

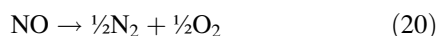
devoted to potential solutions which have been tested at the development/research stage, but which, for various reasons, have not been commercialised.

2.2.1 NO_x Technologies

There are two major strategies to control NO_x emissions under oxidising conditions:

- deNO_x (lean-deNO_x) catalysts
- NO_x adsorbers (NO_x traps)

It should be noted that a significant amount of research was in the past devoted to a third option, that of direct catalytic decomposition of NO_x (Imanaka and Masui 2012; Roy and Baiker 2009).

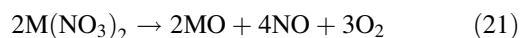


This reaction is in fact thermodynamically very favourable. However, despite the significant amount of early research, a catalyst which shows suitable activity and, above all, stability under the severe conditions of automobile exhaust has not been found and the focus has shifted to the other options.

2.2.1.1 NO_x Storage-Reduction (NSR) Catalysts

The NO_x storage-reduction (NSR) catalyst (concept), sometimes called lean NO_x trap (LNT) or NO_x adsorber catalyst (NAC), was developed and commercialised by Toyota (Matsumoto 1997; Miyoshi et al. 1995; Takahashia et al. 1996) for lean-burn engines. The operating principle is illustrated in Fig. 7. Under oxidising conditions, NO is oxidised to NO₂, which is stored at the surface of an alkaline storage component. The storage component is usually barium, but strontium may also be used. Periodic switching to a fuel-rich exhaust, achieved by fuel injection, results in release of the stored NO_x species, which are reduced to N₂ over a TWC-type catalyst.

The mechanism of NO_x adsorption and desorption/reduction has been extensively investigated. Although the storage/reduction is rather complex process, there is general consensus that the majority of NO_x is stored as nitrate species. The process of nitrate release has been represented as the reverse of adsorption, due to instability of the stored species in conditions of low O₂ partial pressure (Twigg 2011a).



A major drawback of the NSR catalyst is its sensitivity to SO_x, as surface sulphates are invariably more thermally stable than nitrates. Poisoning of the NO_x storage function is directly related to the amount of SO₂ passed over the catalyst. Although the sulphur content of automotive fuels has now reached very low levels, even trace amounts

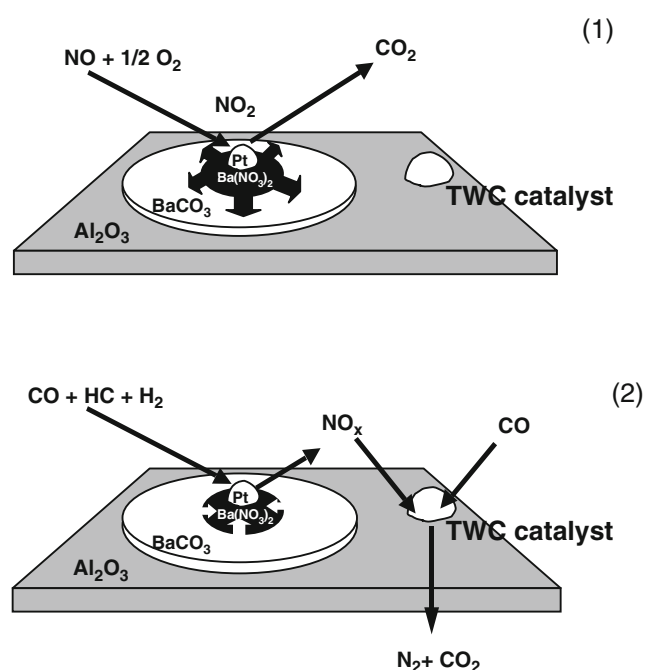


Fig. 7 Principle of operation of a NSR catalyst: NO_x are stored under oxidising conditions (1) and then reduced on a TWC when the A/F is temporarily switched to rich conditions (2) (Adapted from Twigg 2011b)

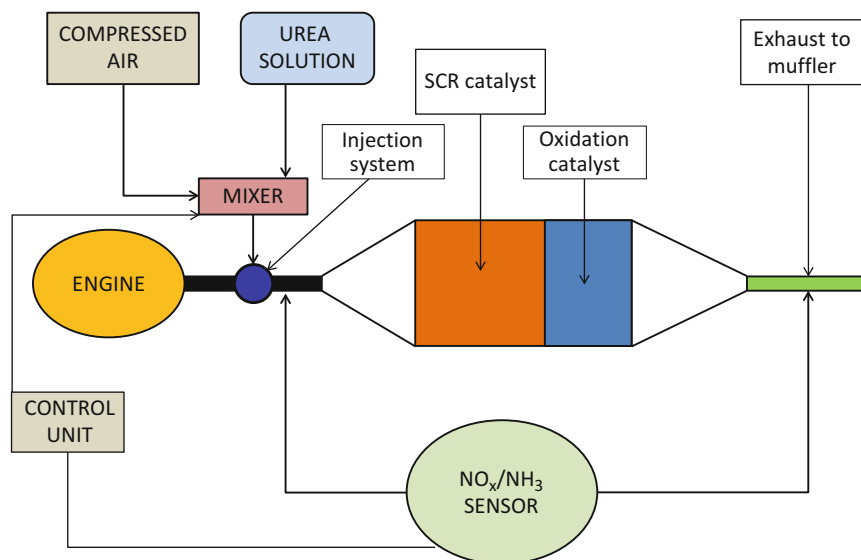
cumulatively reduce capacity. It is therefore necessary to periodically apply high temperature regeneration treatments to restore the full storage capacity to the catalyst. For this reason, thermal deactivation due to sintering of the barium species and formation of barium aluminates is an issue in terms of durability of the catalyst. Accordingly, thermally stable Ba-containing materials are desirable as NO_x adsorbers. Alternative strategies to protect the storage capacity include:

1. Adoption of a SO_x adsorber to the NO_x trap. This is then periodically regenerated.
2. Modification of the catalyst composition to promote of the removal efficiency of the adsorbed SO_x.

2.2.1.2 Selective Catalytic Reduction (SCR)

SCR refers to the selective reduction of NO_x in the presence of excess O₂. Reduction of NO_x under lean conditions using a NO_x reduction catalyst may be achieved by either utilising the unburnt HCs present in the exhaust or injecting a reducing agent after the combustion to achieve this goal. Of these, the most advanced technology, which is in fact used in diesel applications, is SCR using NH₃ as the reducing agent. In fact, SCR originally referred to this process. However, SCR is normally used to indicate the process for any reducing agent, although SCR-HC and SCR-NH₃ are often used to distinguish the two.

Fig. 8 A typical arrangement for abatement of NO_x from a heavy-duty diesel engine using urea as reducing agent (Adapted from Kaspar et al. 2003)



SCR-HC has been the subject of intensive investigations for over 20 years and represents an important area in ongoing automotive catalytic research. Studies on NO_x removal under oxidising conditions were triggered by the discovery in 1991 that hydrocarbons could act as selective reducing agents in an excess of O_2 (Iwamoto and Hamada 1991). This topic has been regularly reviewed in the intervening years. A large number of catalysts have been investigated, which can be generally divided into three categories (Brandenberger et al. 2008; Burch et al. 2002; He et al. 2008; Liu and Woo 2006):

- Metal-loaded zeolites
- $\text{Pt}/\text{Al}_2\text{O}_3$ and derived systems
- Ag-cased catalysts (e.g., $\text{Ag}/\text{Al}_2\text{O}_3$ and Ag/ZrO_2)

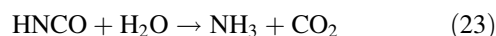
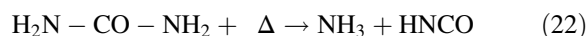
Despite the large research effort which has been devoted to this process (Burch 2004), no catalyst has been found which shows an overall adequate conversion, although the last-mentioned systems, which are the most recent to receive attention, do show some very interesting results, e.g., the promotion of low temperature deNO_x activity of H_2 promoted $\text{Ag}/\text{Al}_2\text{O}_3$ (Breen and Burch 2006) or by using ZrO_2 -based supports (Hickey et al. 2010).

SCR- NH_3 is a well-established technology for NO_x abatement from stationary sources (Forzatti 2001). Typically, vanadia supported on TiO_2 , with different promoters (WO_3 and MoO_3), are employed in monolith-type catalysts (Forzatti 2001; Sagar et al. 2011), but use of metal-loaded zeolites has also received great attention (Brandenberger et al. 2008). The use of WO_3 and MoO_3 is dictated by the need to increase both the sulphur tolerance and acid properties of the surface. SCR- NH_3 has significant disadvantages when applied to passenger cars or trucks, particularly space and weight requirements. The fact that an engine normally operates in nonstationary conditions is a further difficulty. Nevertheless,

SCR using NH_3 has been successfully transferred to the automotive sector, especially for heavy-duty applications.

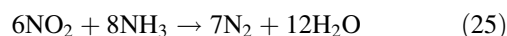
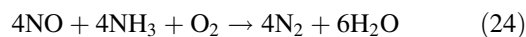
As ammonia is highly toxic, with consequent storage and transport problems, ammonia or ammonium solutions are not used. Urea solutions are instead used as an alternative in-situ ammonia source for NO_x reduction from heavy-duty diesel vehicles.

A urea-based SCR system is schematically illustrated in Fig. 8. The urea solution is vaporised and injected into a preheated zone where hydrolysis occurs in two steps according to Eqs. 22 and 23:



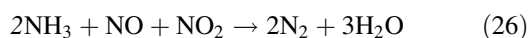
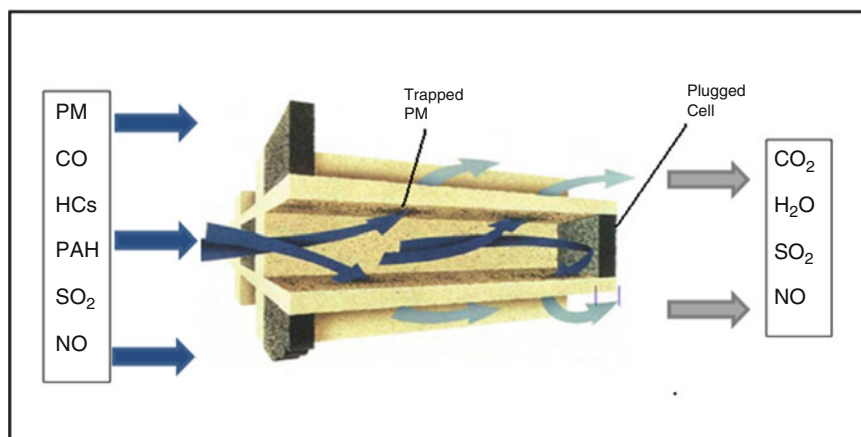
The second step is crucial (Koebel and Strutz 2003), in that, if inappropriate conditions are used, the isocyanic acid (HNCO) may polymerise. The products formed are thermally more stable than urea and they may be deposited on the catalyst. This results not only in ammonia loss but may also cause catalyst deactivation. This can be avoided by correct engineering of the injection system. In fact, if the injection nozzle is too close to curves in the exhaust conduit, the formation of solid deposits is possible.

Ammonia then reacts with NO and NO_2 over the catalyst:



The reaction of NO_2 with NH_3 is much slower. However, when equal amounts of NO and NO_2 are present, another reaction mechanism can be involved, the so-called fast SCR.

Fig. 9 Schematic representation of a diesel particle filter (DPF) (Adapted from Twigg 2011a; Twigg and Phillips 2009)



As it is fast, this reaction is desirable and it is promoted by placing an oxidation catalyst placed before the SCR catalyst, to oxidise the required amount of NO in the exhaust.

This approach has proved to be quite successful and has been commercially applied in HD diesel engines. High NO_x (up to 80 %) can be achieved on HD engines under driving conditions (Koebel et al. 2004). A major challenge of such system is that an extreme care must be used to develop a suitable urea injection strategy that avoids overloading of the system, leading to ammonia slip. To avoid odour and pollution problems, ammonia slip should not exceed 10 ppm. Nevertheless, this solution is the most reliable for the high NO_x abatement required by incoming EU and US regulations.

2.2.2 CO and HC Emissions

2.2.2.1 Diesel Oxidation Catalyst (DOC)

Abatement of CO and HC is generally achieved by monolithic Pt-based oxidation catalysts. These were first introduced by Volkswagen in 1989, before legislation made their use necessary. However, the introduction of the severe legislation in 1993 made them necessary in all new European diesel cars. Although the excess of oxygen in the exhaust might suggest that oxidation of HC and CO under such conditions is a facile process, the situation is complicated by the fact that the temperatures reached by diesel exhaust and therefore by the diesel oxidation catalysts are low (150–250 °C), especially in urban driving conditions, in addition to other factors, e.g., PM interference/deactivation, which makes the technology quite complex (Russell and Epling 2011).

On engine start-up, the catalyst is unheated and is therefore not active, which results in significant cold-start emissions. In addition, the HCs present can adsorb and block the catalytic sites. At higher temperatures, conversion occurs. Incorporation of thermally stable zeolite adsorbers,

which trap the HCs at low temperature and subsequently release them for oxidation at high temperature, significantly improves this situation and reduces cold-start emissions. More serious problems may be encountered in the presence of SO₂ as the temperature is insufficiently high for its subsequent removal. However, the low-sulphur levels now present in automotive fuel means that this is now less problematic. In fact, it has allowed incorporation of Pd into catalyst formulations, which, although less costly, is very susceptible to sulphur poisoning. In such systems, Pd/Pt alloys form, which show higher stability against sintering and higher activity after ageing (Twigg 2011a).

2.2.3 PM Emissions

Diesel particle filters (DPFs) are used to reduce PM emissions from diesel engines. The name is in fact somewhat misleading as such systems are in fact much more complicated than simple filter systems and normally incorporate catalytic functions, using Pt- or Pt/Pd-based catalysts. The most commonly used are porous ceramic wall-flow filters. This is illustrated in Fig. 9. Alternate channels are blocked, which forces the flow through the filter walls, where PM is retained. Accumulation of PM results in gradual build-up of backpressure across the filter which interferes with engine performance and will, if left unchecked, cause the engine to stop. Periodic removal of accumulated PM is therefore necessary. Modern technologies use NO₂ to promote low temperature soot oxidation for diesel particulate filter regeneration, in view of the high oxidation ability of the NO₂ with respect to O₂. However, the efficiency of the process is strongly linked to the exhaust temperature and therefore to driving conditions. It should also be recalled that engine-out NO₂ is usually negligible, so it must be generated in situ with a catalyst.

The reactions involved take place in two separate sections of the device. In the first section, a platinum-based catalyst oxidises the NO to NO₂ according to Eq. 11b.

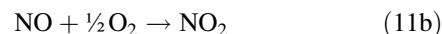
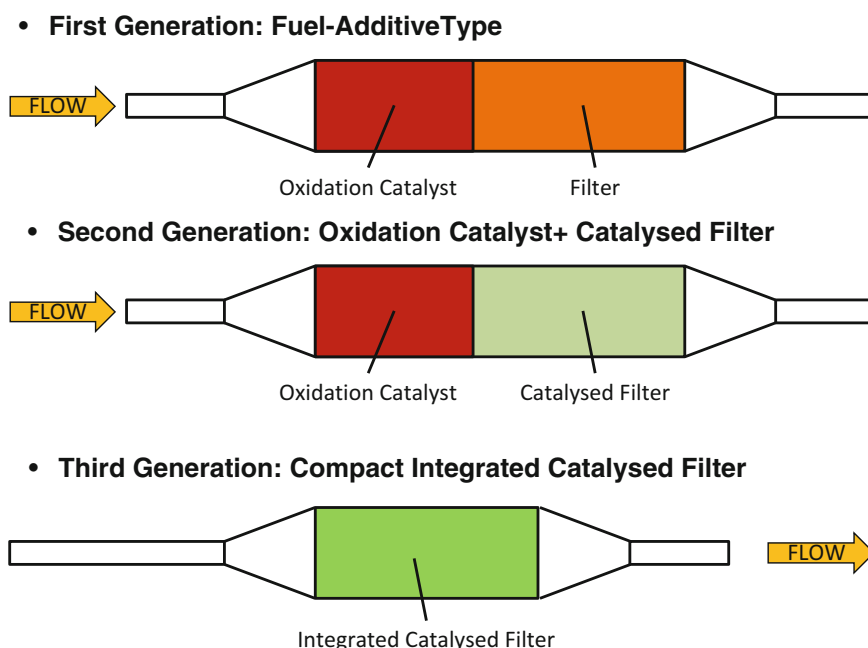
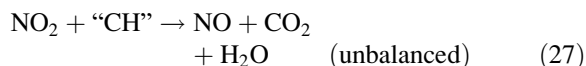


Fig. 10 Diesel particle filter system arrangements (Adapted from Twigg 2011a)



The NO_2 thus produced is then used to oxidise the particulate and uncombusted hydrocarbons, which may be represented by as follows:



In urban driving conditions, the temperature usually is too low for this form of regeneration to take place. However, in extra-urban or motorway driving conditions, the exhaust temperature can reach sufficiently high temperatures to promote NO oxidation to NO_2 over the upstream oxidation catalyst and subsequent oxidation of PM by NO_2 on the downstream filter. This is known as passive regeneration and the concept, developed by Johnson Matthey, is called the Continuously Regenerating Trap (CRT®). It should be noted that NO is produced in the soot oxidation process. In this case, therefore, NO_x abatement is not achieved. When the temperature is too low, as it is under most driving conditions, a form of active regeneration must be used. Additional fuel may be injected and oxidised over the oxidation catalyst. The heat liberated is utilised to initiate PM combustion. Alternatively, the catalyst may be heated electrically.

As outlined by Twigg, three oxidation catalyst/filter arrangements have been developed and commercialised to reduce HC, CO and PM from diesel engines (Fig. 10). The first system employs an oxidation catalyst (or more than one) upstream of a filter. The oxidation catalyst(s) convert(s) NO to NO_2 for passive PM combustion when conditions permit this to take place. CO and HCs are also removed. The catalyst(s) also oxidise(s) extra fuel during active PM combustion. A fuel additive, often ceria based, is used with this system. This is converted to an oxide during the combustion, which, on retention by the filter, catalyses

PM combustion. The main disadvantages of these systems are the high cost and partial blocking of the filter by the retained oxide, leading to increased backpressure. Larger filters may be employed to overcome this problem.

The second type is similar to the first in that it contains two separate functions placed in series: oxidation catalyst(s) upstream of a filter. However, in this case the filter is also catalysed. PGMs (Pt or Pt/Pd) are dispersed in the filter channels to promote PM combustion. This is a commonly used configuration. Fuel additives are not used in this system and thus they do not have their associated disadvantages.

The third system, introduced by Johnson Matthey in 2005, combines the oxidation and filter functions in a single design. This system, in addition to HC and CO oxidation, allows both active and passive filter regeneration. This compact design results in a higher thermal efficiency with respect to the other systems.

To summarise, the present and future developments in the field of automotive pollution abatement are strongly linked to market situation. As far as LD vehicles are concerned, Fig. 11 reports the market share of the diesel-powered new LD vehicles sold in Italy. Introduction of the common-rail diesel engine on the market clearly boosted sales of diesel-powered cars peaking at 60 % of market share in year 2006. In the short term, this clearly influenced global emissions and the global warming effect (Tanaka et al. 2012).

Generally speaking, as low CO_2 emissions are pursued in Europe, the recent trend has been towards downsizing of engines (Johnson 2011, 2013), particularly in the A (minicars) and B (small cars) car segments. This favours adoption of the new lean-gasoline engine technology which allows significant fuel saving. Due to the lower emission rates, catalysts containing lean NO_x trap components can

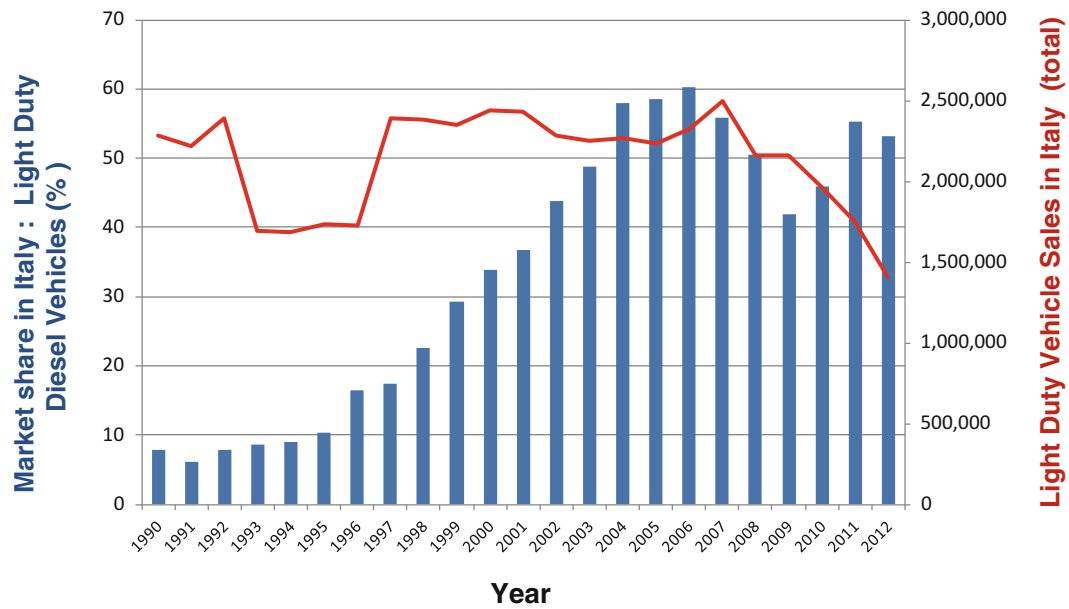


Fig. 11 Market share of diesel-powered new LD vehicles sold in Italy



Fig. 12 Implementation of urea-SCR for LD vehicles would require the installation of a urea distribution network

cope with the issue of NO_x abatement for this type of vehicle. On the other hand, lean-gasoline engines also emit particulates, which requires inclusion of filtering capability to the three-way/lean NO_x catalyst (Twigg 2013).

C- (medium cars) and higher segment light-duty vehicles are mostly equipped with diesel engines. Due to the high

emission rates, efficient NO_x control can be achieved only using urea-SCR technology as already used on HD vehicles (Jayat et al. 2011). This will require an extended network of refilling stations (Fig. 12), as the consumption of the urea solution (Ad-blue) accounts for 3–5 % of the diesel fuel consumption. Refilling of urea may also be problematic

since high purity of Ad-blue must be ensured at the refuelling station: Even slight oil contamination can lead to urea-SCR system failure, accordingly research is aimed at finding alternative ammonia sources (Fulks et al. 2009). DOC and catalysed particulate filters represent the state-of-art technology for PM and HC abatement. Combination of DOC, PM filter and SCR and/or NO oxidation functionality catalyst into a single catalyst/filter body represents today's challenge aimed at simplifying the pollution control system.

3 Pollution Abatement for Marine Diesel Engines

3.1 Introduction

Sea transportation, which represents the most economic method of transportation of goods, has increased steadily over the last 30 years or so. In 2007, it was reported that ocean-going vessels transport ca. 90 % of all trade by volume to and from the 25 EU member states and 80 % by weight of all trade in and out of the USA (Friedrich et al. 2007). An obvious consequence of this increase in the world's ocean-going fleet is that it has given rise to a significant increase in airborne emissions from shipping sources. Thus, there is growing awareness that sea traffic has become a major contributor to airborne pollutants (Eyring et al. 2010; Lack et al. 2009; Winebrake et al. 2009). For example, ship numbers and cargo movements indicate that international shipping in 2001 was responsible for ca. 30 % of global NO_x emissions, 9 % of SO_x emissions and 3 % of CO_2 emissions (Eyring et al. 2005; Friedrich et al. 2007).

The problem is especially acute in relation to often more environmentally sensitive coastal areas. Estimates indicate that at any given time, 80 % of the world fleet is either harboured (55 % of the time) or near a coast (25 % of the time), with the result that 70–80 % of all ship emissions occur within 400 km of land (Friedrich et al. 2007; Corbett et al. 1999), although such estimates do vary significantly (Ritchie et al. 2005a). In any case, port areas are often highly populated, and, clearly, the potential health concerns are appreciable. Pollution abatement from seagoing vessels has therefore become a topic of high current interest (Corbett et al. 1999, 2007).

Historically, the absence of specific legislation governing emissions in the marine sector has meant that the development of specific pollution abatement solutions has somewhat lagged behind the automotive and stationary sectors. Thus, while there has been in a sharp decrease in emissions from road transport (Sect. 1.6) and land-based sources in general, those from international shipping sources continue to grow. It was estimated that, in the absence of countermeasures, total NO_x and SO_x emissions from international shipping sources will surpass those from land-based sources in the 25 EU member states by 2020, as illustrated in Fig. 13. However, the recent introduction of legislation and the proposed legislation in the coming years has prompted an upsurge in research interest in methods or technologies to control pollution from ships. Consequently, it is possible to envisage an analogous development to that observed in the automotive and stationary sectors. Indeed, there appears to be considerable overlap between the areas and the same or similar solutions may be transferred from the automotive and stationary sectors to the marine sector. However, as seen from the experience gained in the automotive sector, the specific problems to be resolved and the potential

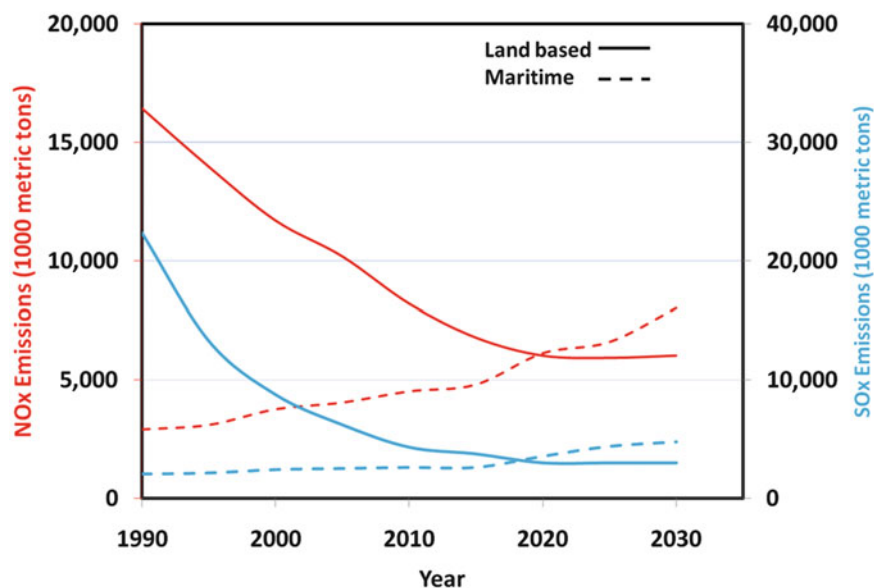


Fig. 13 Inventories and projections of NO_x and SO_x emissions in Europe from land-based and international shipping sources (Adapted from Friedrich et al. 2007)

methods which can be adopted strongly depend on the exact nature of the exhaust gas composition, in addition to a range of other considerations, such as space requirements.

3.2 Emission Legislation in the Marine Sector

The increase in interest in pollution abatement in the marine sector has seen the introduction of a number of general strategic responses. These include legislative measures; voluntary programmes, such as the US Environmental Protection Agency's (EPA) voluntary Blue Sky emission standards; and market-based incentive programmes, such as Sweden's Environmentally Differentiated Fairway Dues Program. The last-mentioned programme has been responsible for an increase in the use of low-sulphur fuel in Sweden's ports through the lowering of the fairway dues to be paid in that case. However, the most significant development regards the legislative measures which are coming into force, essentially through the MARPOL 73/78 convention of the International Maritime Organization (IMO) (IMO 2013). Given the international nature of marine transport, it is important to stress the unique position occupied by the IMO, which represents more than 98 % of the global fleet, to introduce a coordinated global response to the problem. MARPOL (Marine Pollution) 73/78 is in fact a voluntary programme, but it is the basis of most proposed legislation for airborne emissions from ocean-going vessels. Born in the aftermath of the Torrey Canyon oil spill, MARPOL 73/78 is an international convention to prevent marine pollution by ships which was adopted in 1973 by the IMO and revised and expanded in 1978. Since then it has been expanded by Annexes specifically addressing various aspects of marine pollution. The issue of environmental problems associated with the marine sector is the responsibility of the IMO's Marine Environment Protection Committee (MEPC), which can propose modification to MARPOL 73/78.

The MARPOL protocol is composed of six annexes, each of which deals with specific aspects related to marine pollution (adoption date indicated in parenthesis):

- Annex I: Regulations for the Prevention of Pollution by Oil (2 October 1983)
- Annex II: Regulations for the Control of Pollution by Noxious Liquid Substances in Bulk (2 October 1983)
- Annex III: Prevention of Pollution by Harmful Substances Carried by Sea in Packaged Form (1 July 1992)
- Annex IV: Prevention of Pollution by Sewage from Ships (27 September 2003)
- Annex V: Prevention of Pollution by Garbage from Ships (31 December 1988)
- Annex VI: Prevention of Air Pollution from Ships (19 May 2005)

Initially, problems related to airborne emissions were not a priority. The first specific air pollution measures, adopted in 1985, were concerned only with SO_x , while in 1988, NO_x limits were incorporated, along with limits for chlorofluorocarbons (CFCs) used as refrigerants. However, the lenient limits for engine emissions did not result in significant advancements towards air pollution reduction and they were replaced by Annex VI. This protocol was ratified by 15 signatory states to MARPOL on the 18th of May 2004 and entered into force on the 19th of May 2005. Since its ratification, the number of signatories to the protocol has grown from 15 (representing 50 % of world tonnage) to the actual value of 170 states, representing more than 97 % of world tonnage (IMO 2013).

The limits fixed by the MEPC in Annex VI for NO_x and SO_x are specified in regulation 13 and regulation 14, respectively. It is important to underline that the two sets of emission and fuel quality requirements are defined by Annex VI: (1) global requirements and (2) more stringent requirements applicable to ships in special Emission Control Areas (ECAs).

3.2.1 MARPOL 73/78 Annex VI, Regulation 14: Sulphur Oxides (SO_x)

In regulation 14, the recommended strategy for decreasing SO_x emissions is based on a significant reduction of the sulphur content in the fuel. This is due to the high sulphur content of currently used marine fuel. It should be recalled that the sulphur content of the fuel is the sole source of SO_x emissions from any internal combustion engine (ICE). The proposed reductions in maximum fuel sulphur content are indicated in Fig. 14. A number of different fuels are available for marine engines. For example, marine heavy fuel oil (HFO) has an average sulphur content of 2.7 % or 27,000 ppm, in comparison to a maximum European sulphur content of 0.001 % or 10 ppm in the automotive sector. The adoption of low-sulphur content fuels is the one of the main reasons for the sharp decrease of SO_x emissions from land-based sources illustrated in Fig. 13. It should be noted that the 4.5 % maximum on the sulphur content of marine fuels is significantly higher than the present average of HFO.

Reduction in the sulphur will also result in a decrease in PM emissions. A US EPA study has estimated that a decrease in fuel sulphur content from 2.7 to 1.5 % would result in PM reductions of 18 %, while a decrease to 0.5 % sulphur would decrease PM emissions by about 63 % (Ritchie et al. 2005b; US EPA 2003). The effect of the quality of the fuel used on PM composition is illustrated in Table 3, which compares the composition and quantity of the PM produced from low- and high-sulphur diesel fuels. With HFO, more PM is produced and it is composed of approximately 65 % sulphates and metal oxides, compared with 15 % with truck diesel. It is clear that the two systems

Fig. 14 Development of maximum allowed marine fuel sulphur content proposed by the International Maritime Organization (IMO). SECA = Sulphur Emission Control Area

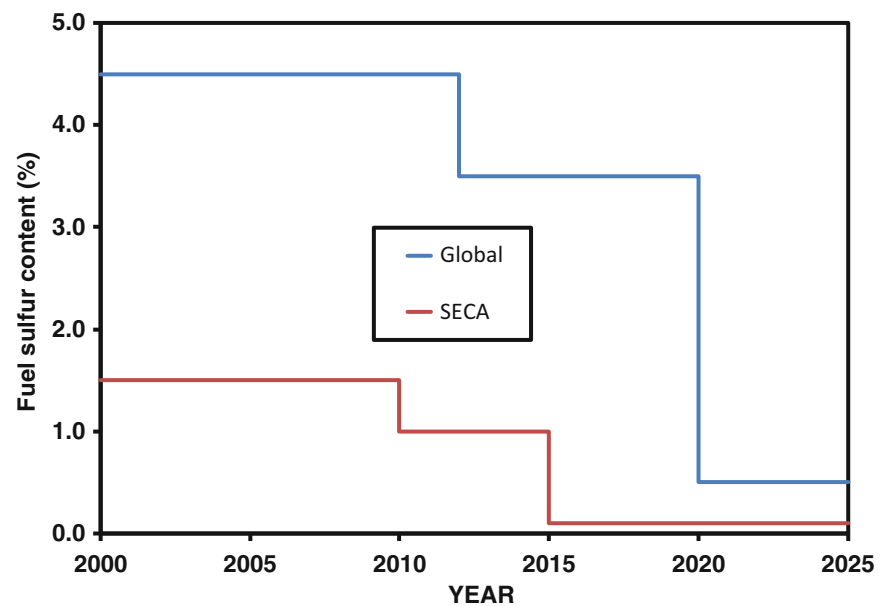


Table 3 Comparison of particulate emission composition

Parameter	Truck diesel engine operating on diesel oil ^a	Medium-speed diesel engine operating on heavy fuel oil ^a
Carbon soot	35 %	25 %
Hydrocarbons (fuel oil, lubrication oil)	50 %	10 %
Ash metal (oxides, sulphates)	15 %	65 %
Typical value	0.15 g/kWh	0.4 g/kWh
Measurement method	ISO 8178	ISO 9096

Data reproduced from US EPA (2003)

^aValues are approximate

present rather different challenges in attempts to reduce emissions. This is especially true from the point of view of any catalytic solution. This interrelationship between SO_x and PM emissions illustrates a very important point in the complex process of pollution abatement: Any measure designed to reduce the emissions of one pollutant can also have a strong effect on the emission of others.

3.2.2 MARPOL 73/78 Annex VI, Regulation 13: Nitrogen Oxides (NO_x)

Regulation 13 defines three emission Tiers. Tiers I and II are global requirements, while Tier III is to be applied in any proposed NO_x ECA (NECA). The standards are applied to any marine diesel engine with a power output of more than 130 kW installed after 2000, and any marine diesel engine with a power output of more than 130 kW which has undergone a major conversion after the 1st of January 2000. The emission limits for the three Tiers are reported in Table 4. The emissions are defined in terms of the engine's operating speed, or rpm values, at any given time. Figure 15 illustrates the NO_x limit variations as a function of the engine speed. Comparison of Fig. 15 with

Table 4 NO_x emission limits for the marine sector

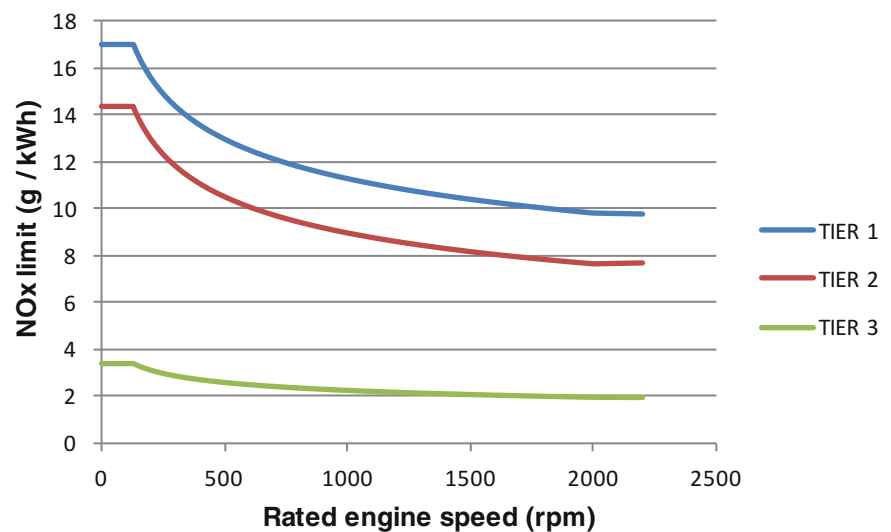
NO _x limit (g/kWh)				
Tier	Date	$n < 130$	$130 < n < 2,000$	$n > 2,000$
Tier I	2000	17.0	$45. n^{-0.2}$	9.08
Tier II	2011	14.4	$44. n^{-0.23}$	7.07
Tier III	2016 ^a	3.4	$9. n^{-0.2}$	1.96

^aIn NO_x emission control areas (tier II standards apply outside ECAs)
 n = rotations per minute (rpm)

the EURO limits for trucks is instructive. For example, the Euro 5 and 6 limits, imposes maximum NO_x emission values of 2 and 0.4 g/kWh. It is evident that only the Tier III NECA NO_x limits have comparable values, but they are still up to five times higher than the automotive HD limits (Lovblad and Fridell 2006).

In an analogously manner to the automotive sector, regulation 13 establishes that the marine engine must have a compliance certificate. To evaluate this compliance, the MPEC has adopted various engine test cycles. Moreover, the compliance of the engine must be certified on a yearly basis.

Fig. 15 Evolution of the International Maritime Organization (IMO) NO_x limits on the basis of the engine speed



Finally, it is worth noting that Annex VI leaves to the individual states the responsibility to impose limits for the other pollutants, such as CO, HC and PM.

3.2.3 Emission Control Areas

An important provision of Annex VI is that of the possibility to designate ECAs. Two Sulphur Emission Control Areas (SECAs) were established immediately. The Baltic Sea, which came into force on 19 May 2006, was the first SECA, while the second SECA is composed of the North Sea and the English Channel and came into force on 22 July 2007. More recently, in 2012, North American Emission Control Areas (SECA and NECA) were established. This includes all of the North American coastline and the Caribbean Sea. France was a co-proposer of this ECA on behalf of its island territories of Saint Pierre and Miquelon. On a worldwide level, further ECAs are planned, including the Mediterranean Sea.

In 2002, the European Commission adopted a strategy to reduce atmospheric emissions from seagoing ships. The current EU position, which is a modification and extension of Annex VI of MARPOL, is outlined in EU Directive 2005/33 on the sulphur content of marine fuel.

The provisions adopted include:

- Implementation of the SO_x Emission Control Areas defined in the IMO's MARPOL Annex VI convention.
- The use of <1.5 % sulphur after 2007 by all passenger vessels on regular services to or from any port within the EU.
- The use of <0.2 % sulphur fuel (0.1 % by 2008) by all ships at berth in all EU ports. Ships which use shoreside electricity are exempt from this requirement.
- The use of 0.1 % sulphur fuel from 2010 by ships travelling on inland waterways.

In addition, ratification of MARPOL Annex VI, including the NO_x emission standard, was encouraged.

In 2003 the USA adopted the Annex VI NO_x standards for international marine diesel engines built after 2004. In addition, the voluntary US EPA Blue Sky standards set much more stringent limits than the rather lenient MARPOL initial standards.

It should be apparent from the above discussion that there is a clear movement towards the introduction of worldwide mandatory limits on emissions from ocean-going vessels. In regulation 14, the strategy of switching to low-sulphur fuels is emphasised. However, alternative approaches are possible. Regulation 4 of Annex VI, *Equivalents*, establishes that any alternative method of reducing emissions is permitted if the method can be shown to be "at least as effective in terms of emissions reductions as that required by this Annex". Alternative methods comprise "any fitting, material, appliance or apparatus to be fitted in a ship or other procedures, alternative fuel oils or compliance methods". Broadly speaking, this means that any pollution abatement measure which meets the emission standards for SO_x or NO_x may be employed. This, of course, opens the possibility of the introduction of post-combustion pollution abatement technologies.

In the case of SO_x emissions, the high costs associated with a switching from high-sulphur content residual oils (ROs) to low-sulphur content marine distillates (MDs) make such measures unattractive mainly from an economic point of view. Thus, "low"-sulphur-containing fuels employed in international shipping are often made of blends, leading to a low environmental advantage (Mestl et al. 2013). Consequently, post-combustion treatment of the flue gas is an approach which has attracted strong interest. Moreover, the possibility to use abatement systems eliminates the problem of switching between different fuels while entering or leaving an ECA (see sect. 3.3.2), which is necessary under the MARPOL

convention. In the case of NO_x emissions, the introduction of post-combustion emission control technologies will almost certainly be necessary. In fact, according to the US EPA, Tier I standards were already respected by the engines and engine modifications were needed to respect Tier II standards, while Tier III standards can only be met by pollution abatement systems.

3.3 Strategies to Reduce Pollutant Emissions in the Marine Sector

As in the automotive sector, both *primary methods* and *secondary methods* are strategies which are actively pursued to reduce emissions from ships, as both offer the possibility to achieve significant reductions. In the following sections, the possible solutions adopted in both cases will be outlined and analysed. It should be noted that the abatement performance data cited in the present section have been taken from references de Jong et al. (2005) and Wahlström et al. (2006) and references therein.

One of the proposed strategies to reduced emissions from ships is the use of shoreside electricity by ships at berth. This is a measure which would considerable reduce *local* emission given the amount of time that ships spend at berth. However, with this measure the problem of pollution abatement is merely shifted to the source of the electricity used and, clearly, the emissions inventory depends on the method of electricity generation. This option will not be further discussed here. Similarly, emissions trading and other market-based solutions will not be considered.

The nature of the problem of abatement of airborne emissions from marine sources is on one level similar to that of diesel engines for road vehicles, especially in relation to NO_x and particulates PM, for which the same problems have been addressed. It is therefore unsurprising that inspiration has been sought from the wealth of experience gained in this area. However, as already indicated, marine diesel and other heavy fuel oils have the added complication of very high sulphur content relative to that found in fuels for road vehicles. In the following, the technical options in relation to NO_x abatement will first be discussed, before addressing the problem of SO_x emissions. As will become clear, the two subjects are not completely independent.

3.3.1 NO_x Reduction Methods

A considerable number of technological options are available for reduction of NO_x from marine vessels (de Jong et al. 2005). These include:

- Internal engine modifications (IEM)
- Technologies which introduce water in the combustion process
- Exhaust gas recirculation (EGR)
- Selective catalytic reduction

The first three options are preventative measures whose aim is to reduce NO_x formation during the combustion process by optimising the combustion conditions or controlling the combustion temperature. Such changes include addition of water to the combustion chamber to decrease the combustion temperature, improved air charge characteristics or altered fuel injection systems (Lovblad and Fridell 2006).

3.3.1.1 NO_x Reduction Through Internal Engine Modification

A large number of parameters influence the combustion process in the reaction chamber: the compression ratio, injection and valve timing, the size and dimension of the fuel spray, etc. Engine modifications which influence these parameters have therefore been adopted to reduce emissions.

Internal engine modifications (IEM) are divided into two categories: basic IEM and more advanced IEM. Basic IEM essentially involves installation of slide valves, which offer the possibility of better fuel spray characteristics. This type of injector optimises the combustion temperature with a better atomisation of the fuel, thus avoiding the characteristic temperature spike on fuel injection. In this way, a 20 % decrease in NO_x emission is possible. Moreover, fuel combustion is improved, minimising the emissions of HC and PM. The main drawback of this solution is that it is applicable only to the slow two-stroke engines. However, the costs are limited and the modifications can be realised during a routine maintenance work.

Advanced IEM include:

- Retarded injection/Miller cycle valve timing
- Higher compression ratio/adjustable compression
- Increased turbo efficiency/two-stage turbocharger
- Common-rail injection/flexible injection system/two-stage injection
- Higher cylinder pressure
- Low intake air temperature

Retarded fuel injection optimises combustion efficiency. The premixing burning phase is reduced, thereby reducing the temperature and pressure in the cylinder, which leads to NO_x reductions of up to 30 %. This solution can be adopted using both mechanical and electronic control devices. The former system implies that the efficiency is achieved only in a limited range of engine regimes, while the second allows high efficiency to be obtained across a wide range of regimes but is applicable only to engines using light fuels.

The main drawbacks of this measure are increased PM emission and a reduction in specific power output, together with higher consumption of fuel. Moreover, significant engine modifications are necessary to efficiently apply this technology.

In the multiple injection solution, the fuel is injected in a calibrated sequence instead of a single injection. A first injection is made to create a homogeneous flame front and this is followed by another injection containing the rest of the fuel. This limits the pressure and temperature peaks typical of the single injection systems, which in turn leads to a maximum decrease in NO_x of ca. 20 %, while avoiding an increase in PM emission. The main disadvantages of the system are related to the costs of installation and maintenance.

In the common-rail fuel injection system, the injection temperature and pressure are controlled electronically, and the fuel injection pressure, which reaches values 2 or 3 times higher than that reached by systems utilising the traditional fuel pump, is maximised. The resulting accurate control in the flame characteristics leads to a decrease in both NO_x formation and fuel consumption. As with retarded fuel injection, this system is not easy to apply to heavy fuel oil (HFO) and is more suitable to engines running on marine distillates (MD).

Cooling of the inlet air decreases the maximum temperature reached in the combustion chamber, which reduces NO_x emissions by about 10–14 %. As the air used is already cold before entering the combustion chamber jet for the medium-speed and low-speed engine, the solution is applicable only to the fast diesel engine. Moreover the solution implies an investment cost to install the air treatment system.

Sometimes a combination of these primary techniques is adopted. In general, the main combinations involve an increase in the injection pressure and optimisation of fuel atomisation, to achieve a more homogeneous combustion.

3.3.1.2 NO_x Reduction by Decreasing the Combustion Temperature

Another general strategy to reduce NO_x emissions is to lower the combustion temperature. A number of conceptually similar techniques operate by introducing water into the combustion process. These are often used in conjunction with exhaust gas recirculation (EGR). General drawbacks of these systems are that they require additional treatment and mixing apparatus and many require freshwater storage. Many are still at a development stage.

3.3.1.2.1 Direct Water Injection (DWI)

In this system, developed by Wärtsilä, a calibrated amount of water is introduced into the combustion chamber. To avoid effects on engine operation, if the water is stopped, the water injection apparatus is independent from that of the

fuel. The water to fuel ratio is typically 0.4–0.7 and NO_x reduction of 50–60 % is achieved. The main drawbacks are a significant increase in both fuel consumption and particulate emissions. The system is not suitable for high-sulphur fuels and residual oils, and it is expensive, due to the need to have freshwater storage and treatment systems as well as the need to frequently substitute the injector.

3.3.1.2.2 Combustion Air Saturation System (CASS)

This is a similar system developed by Wärtsilä, in which water is injected into the combustion air and enters the combustion chambers as steam. This can result in a 30–50 % decrease in NO_x emissions.

3.3.1.2.3 Water in Fuel Emulsion, Water-Fuel Emulsion (WiFE, WFE)

The WiFE method is a well-established technology which has been the subject of attention for marine engines over the last 20 or so years. The water and fuel are mixed before the injection to form a micro-emulsion in which small water droplets are surrounded by the fuel. The injection produces a fine spray in which the droplets explode due to rapid water evaporation, thereby increasing the air/fuel mixing. This reduces NO_x formation, with a simultaneous reduction in CO, PM and HC formation. The NO_x and PM emission reductions observed are proportional to the water content in the fuel. The general consensus seems to be that the reductions achievable depend on the water percentage of the emulsion, with a 1:1 ratio in the case of NO_x and a 1:2 to 1:3 ratio in the case of PM (i.e., 30 % of water reduces NO_x by 30 % and PM by 60–90 %). The technique is limited by an upper limit of water which can be effectively employed, which is approximately 30 %. The process also results in an increase in fuel consumption.

3.3.1.2.4 Humid Air Motor Technology (HAM)

Developed by MAN, combustion temperature reduction and elimination of temperature spikes are both achieved by the addition of steam to the inlet air. To reach significant reductions, the amount of steam introduced must be at least three times higher than the amount of fuel. Importantly, seawater can be used in this system. The main disadvantages are the costs and complexity of the steam plant. This solution is cheaper than the costly ammonia SCR approach to NO_x abatement (vide infra). However, HAM technology can reach 70 % NO_x reduction, while SCR reaches 90 % (see Table 5).

3.3.1.2.5 Exhaust Gas Recirculation (EGR)

EGR is a well-established method of pollution abatement in the automotive sector which can be applied to any engine. The exhaust is filtered and reintroduced into the combustion chamber after cooling. Due to the higher thermal capacity of

Table 5 Estimated emission reduction efficiencies of various deNO_x techniques

Measure	% Emissions reduction (–)/increase (+) per vessel			
	NO _x (%)	SO ₂ (%)	PM (%)	VOC (%)
Basic IEM (2 stroke slow speed only)	–20	0	0	0
Advanced IEM	–30	0	0	0
Direct water injection	–50	0	0	0
Humid air motors	–70	0	0	0
Exhaust gas recirculation ^a	–35	–93	≥63 ^b	± ^c
Selective catalytic reduction (2.7 % residual oil (RO))	–90	0	0	0
Selective catalytic reduction (1.5 % RO)	–90	–44	–18	±
Selective catalytic reduction (0.1 % marine distillate (MD))	–90	–96	≥63 ^d	±

Data reproduced from de Jong et al. (2005)

^aAssumed switch from 2.7 % sulphur residual oil (RO) to marine diesel (MD) for technical reasons

^bUS EPA 2003 outline that a switch from 2.7 % sulphur RO to 0.3 % MD reduces PM by 63 %. The PM reduction to 0.1 % MD will therefore be slightly higher than 63 %

^c± no or not conclusive information available

^dPM reductions estimated in the same way as for EGR

the exhausts, the combustion temperature, and consequently the emitted NO_x, is reduced. The main problem is related to PM removal because its introduction in the chamber can lead to the formation of solid deposits, to lubricating oil contamination, to valve fouling, etc. Due to the difficulty to remove or reduce PM emission for HFO, the system should be applicable only with low-sulphur fuel (LSF) and distillate fuel.

3.3.1.3 NO_x Reduction Through the Use of Alternative Fuels

The possible use of alternative fuels has also received attention in recent years and the main fuels studied are methanol and liquefied petroleum gas (LPG). The potential use of methanol is still at a research stage because of the great differences in density, viscosity, heat capacity and ignition temperature between methanol and oil fuels. LPG is a more developed alternative because its characteristics are more similar to marine fuel oil. The use of LPG can result in significant decreases in NO_x emission, but security problems related to fuel storage are an issue.

The abatement efficiencies of the various prevention measures discussed above are summarised in Table 5. The efficiency of ammonia SCR (vide infra) is included in the comparison to offer an overall comparison of the efficiencies of the various deNO_x methods discussed.

3.3.1.4 Selective Catalytic Reduction

SCR with urea has been successfully transferred from stationary and automotive sources to the marine sector and is, thus far, the only commercial post-combustion deNO_x solution applied on board ships. The on-board SCR was pioneered by Haldor-Topsøe A/S and MAN B&W Diesel A/S which lead, in 1989, to the installation of the first marine SCR deNO_x unit on a 37,000 tdw deep-sea bulk carrier the Pacific Princess. The system was installed for the first time on a ferry, the M/S Stena Jutlandica, in 1997, on all main as

well as auxiliary engines. Other commercially available SCR system are the Siemens SINO_x system and the Munters Diesel Emission Control Selective Catalytic Reduction (DEC SCR) Converter System, which was first delivered in 1991. An on-board SCR system is analogous to that described for heavy-duty diesel applications, the differences being mainly related to the scale. The catalyst housing usually replaces the silencer in the exhaust uptake as SCR systems also effectively reduce noise. The SCR catalyst can be fitted with the optional of an oxidation catalyst, which can effectively reduce emissions of VOCs from the exhaust. Cooper and Gustafsson report that 45 % of ships on international routes which are fitted with an SCR system also have an oxidation catalyst (Cooper and Gustaffson 2004). Catalyst formulations are similar to those used in stationary sources (sect. 2.2.1.2).

3.3.1.4.1 Advantages and Disadvantages of Ammonia SCR

The SCR technique has a number of advantages which render it particularly suitable for installation in seagoing vessels (see below). The disadvantages associated with this technology are mostly the same as those which encountered for on-road diesel engines, with some differentiation due to scale, disadvantages which have not been overcome but which must be accepted. There are, however, a number of specific problems related to the marine sector that must be considered. The most important aspect is the high content of sulphur in the marine fuel which detrimentally affects the activity of the SCR catalyst, particularly those based on V₂O₅ (Huang et al. 2002, 2003). As a matter of fact, SO₂ is easily oxidised to SO₃ and this species tends to strongly bind to the surface. Both ammonia sulphates and bisulphates may form at low reaction temperature which, being solid, leads to pore plugging and catalyst deactivation. Furthermore, the ammonia that reacts is not used for the reduction process, leading to a decrease of the efficiency of ammonia

utilisation. Despite these disadvantages, urea-SCR offers one of the very few established post-combustion techniques to achieve significant NO_x reductions in the marine sector.

Flexibility

It has no effect on engine operation or design and can be easily fitted on a new engine or retrofitted on an existing engine, with no apparent limitation on ship or engine type.

Catalyst Lifetime

SCR catalysts are not resistant to sulphur poisoning. While catalyst formulations can be varied to strike a balance between high SCR activity and tolerable SO_2 resistance, catalyst performance invariably does degrade upon sulphur exposure and catalyst lifetime can be prolonged by using low-sulphur content fuels. Thus, the optimum situation, from the point of view of catalytic performance, is an SCR system running with such a fuel. However, these fuels are considerably more expensive. On the other hand, the use of more expensive fuels with low sulphur and other impurities may reduce overall costs by less frequent catalyst substitution, so the situation must be carefully evaluated. The experience gained indicates that with $<1.5\%$ sulphur, the reactor may have to be replaced every 4–5 years, while with 2.7% sulphur replacement may be necessary every 3 years (de Jong et al. 2005; Lovblad and Fridell 2006). With this information, the costs of catalyst replacement and fuel switching can therefore be compared and optimised.

A further significant problem in the case of marine diesel engines is pore blockage through deposition of calcium sulphate (CaSO_4) which forms after the combustion chamber. This drastically reduces the number of active sites available to the gas and will eventually result in a complete loss of activity. Other potential poisons include oxides of potassium, sodium, calcium, arsenic and phosphorous. The problem of deactivation of the catalyst through deposition of solid matter, in particular at the front of the catalyst, can be rather effectively attenuated by the incorporation of dust blowing systems into the catalytic system. Another technological option to prevent this problem is incorporation of filters before the catalyst.

Operating Materials

Aqueous solutions of urea are used as the source of ammonia. Urea solutions are commonly available, so supply is not a problem and cost is relatively low. In addition, they are non-poisonous and odourless and are considered relatively safe to transport and store at ambient temperature and pressure. However, at low ambient temperatures, the solution may freeze, which necessitates suitable storage conditions.

Space and Weight

SCR installations have considerable space and weight requirements: In addition to the space required for the SCR system (and the oxidation catalyst, if installed), large urea storage tanks are necessary.

Installation and Operation Costs

From a commercial point of view, the cost of installing the SCR plant is one of the biggest disadvantages. In addition to the basic investment for the system, other costs include the raw materials needed to operate the system, the higher fuel consumption due to the added weight of the catalytic reactor and urea storage tank and the need to dedicate specialised personnel to operate and maintain the system, which usually include sophisticated control systems. Routine maintenance, such as cleaning of the urea spray nozzles, is particularly important as their blockage can result in ammonia slip. As always, the issue of cost/benefit is often intangible and difficult to assess. However, the fact that SCR systems are now rather well established removes much of the guesswork.

Variables in Operating Costs

The concentration of the solution is an important consideration, and, from the point of view of minimising on-board storage space requirements, which in turn affects operational costs, very concentrated solution would clearly be preferred. However, there are limitations. A 40% solution can be stored and used where the temperature remains above 0°C . A 35% solution, on the other hand, can be stored at temperatures down to -15°C . Thus, in colder seas, such as the Baltic Sea SECA, 35% solutions must be used. If it is necessary to use very large amounts of ammonia, such as in the case of longer voyages, another option is to store urea in the form of pellets and prepare the urea solution on-board. The cost of these possibilities must be evaluated on a case-by-case basis.

Catalyst Warm-Up

As discussed in Sect. 2, this is a problem common to many depollution catalysts. SCR catalysts have a minimum useful operational temperature (in the case of SCR catalysts, about 270°C). However, as the heating process is normally achieved by the exhaust gases themselves, there is a time delay between start-up and adequate functioning of the catalyst. This results in a warm-up time (around 20–30 min), during which the NO_x reduction is non-existent or low. This may be a problem in a harbour, where the lowest emissions possible are necessary.

Urea Economy and Ammonia Slip

Urea reaction economy indicates the actual amount of used urea, with respect to reaction stoichiometry. In particular, it has been reported that the formation of various types of ammonium sulphates and bisulphates, as well as the polymers

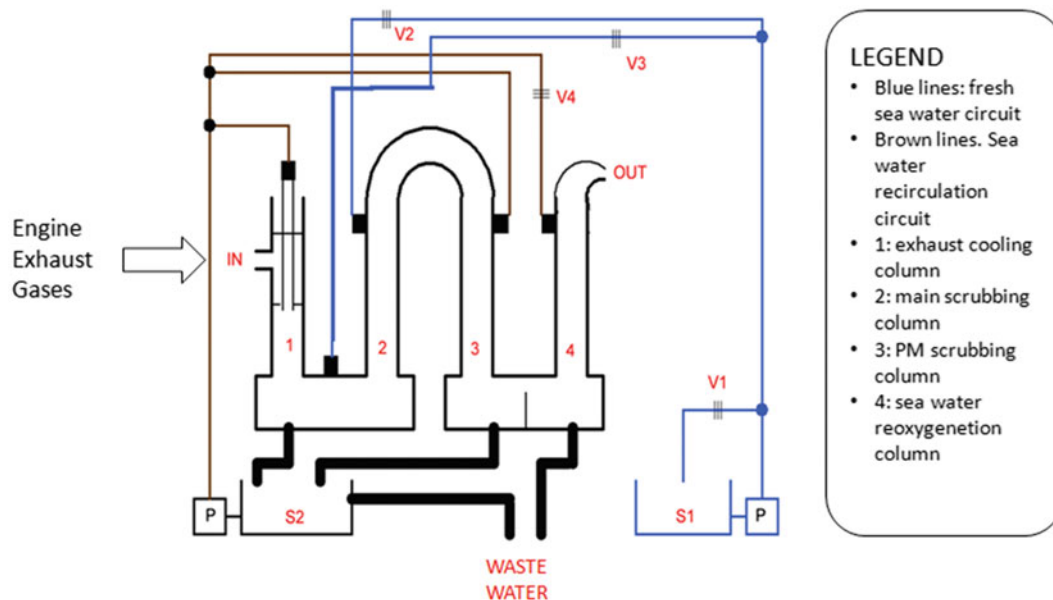


Fig. 16 Schematic representation of an on-board seawater scrubbing system

mentioned above (sect. 2.2.1.2), decreases the NO_x conversion to N_2 . To maximise the conversion, an excess of urea is generally used. This varies in function of the sulphur content in the fuel. Ratios of 1.2:1 or higher are usually used.

Under normal operating conditions, the problem of ammonia slip is most likely to occur with load variations. The consequent odour problems are especially unwelcome in the case of passenger ships. The phenomenon can also result in downstream corrosion problems. Although SCR systems incorporate a feedback control loop to address the issue of correct dosage of the urea solution, brief episodes of ammonia slip can still occur due to control response factors. The possibility of ammonia slip is enhanced at higher space velocities, even when the system is operating correctly. Another possible source of ammonia slip is incorrect or inadequate maintenance of the urea injection system. Ensuring that the urea injection nozzles do not become blocked is a vital part of the maintenance procedures.

3.3.2 SO_x Reduction Methods

Two main options are considered as potential SO_x reduction methods in marine applications:

1. Fuel switching
2. Seawater scrubbing (SWS)

The fuel switching option includes both the reduction of fuel sulphur content and the practice of on-board fuel switching when necessary, for example, when entering a port or a SECA. Reducing sulphur content represents a concrete preventative abatement measure which is immediately applicable. However, there are a number of disadvantages associated with this approach. The high costs associated with a switching from high-sulphur content residual oils

(ROs) to the low-sulphur content marine distillates (MDs) make such measures unattractive from an economic point of view for the shipowners, even though such option can be attractive on a global scale (Wang et al. 2007). In addition, for application of on-board fuel switching, significant changes to the ship would be required: extra fuel tanks and modifications to fuel pumps, fuel circuits and even to the engine. This overall increase of complexity of the system, along with the concomitant necessity of more expensive maintenance, is another economic drawback. Finally, fuel switching has only a moderate effect in the case of NO_x emissions, which means that separate solutions need to be found for this pollutant.

Several pollution control techniques have been evaluated for shipping (Farrell et al. 2002), but seawater scrubbing is the only technological option considered suitable. In general, SO_x scrubbing is a consolidated technology which has been used for many years in flue gas desulphurisation (FGD) applications (Rajendran et al. 1999; Srivastava et al. 2001). A number of options are available: the limestone/gypsum system, the spray dry system, the Wellman-Lord process and seawater scrubbing. The first large-sized FGD process was installed at the Battersea in London in 1930. The first seawater scrubber was introduced in 1988 at the Statoil refinery in Mongstad, Norway. Seawater scrubbing installations are now quite common all around the world.

The transfer of the SWS process from land-based applications to marine applications is a process in an advanced state of development. Commercial on-board SWS systems are now available, such as the Krystallon Seawater Scrubber (BP Marine and Kittiwake Developments Ltd). A schematic representation of a SWS system is illustrated in Fig. 16. It is clear that the overall systems are complicated and

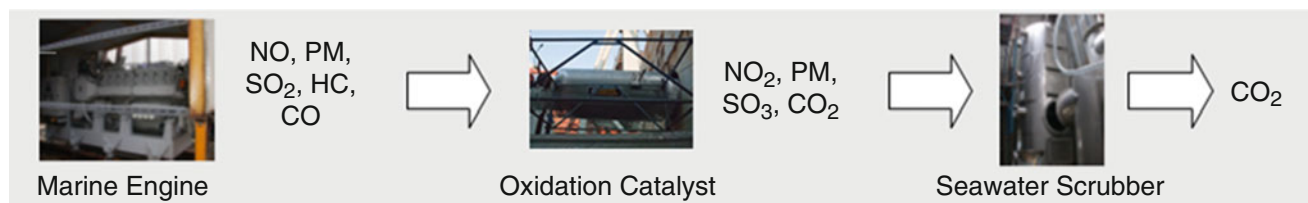


Fig. 17 Scheme of the strategy adopted in the ECOMOS project, aimed at developing an integrated method for abatement of the main pollutants emitted from a marine engine

involve elaborate systems for water treatment and process control. The common factor in all seawater scrubbing systems is intimate contact between the exhaust gas and seawater, during which the SO₂ present is transferred to the seawater.

3.3.2.1 Advantages and Disadvantages of Seawater Scrubbing

Very high SO_x and PM abatement efficiencies can be achieved using the SWS technique. An important characteristic of seawater is its pH: Seawater is naturally basic with a pH which ranges from 8.0 to 8.2. It is therefore a more effective scrubbing medium than freshwater. The capacity of the scrubbing water can be increased by addition of alkaline (usually lime), but this has added cost and space requirements.

Formation of sulphuric acid mists is a potential problem associated with sulphur scrubbing processes. Their formation depends on the concentrations of SO₃ and water vapour in the gas stream as well as the temperature. The process is a well-known phenomenon in SO₂ scrubbing processes *after* the scrubbing step, where the temperature of the flue gas is below the sulphuric acid dew point. A number of consolidated countermeasures, above all droplet separators, are available to combat the problem.

The main environmental concern surrounding seawater scrubbing is the quality of the water discharged from the scrubbing unit. Factors which must be considered include the pH of the discharged liquid, the presence of sulphites and the presence of other potentially harmful species. Due to the high quantity of sulphates already present in seawater, it is commonly considered that sulphates which remain in the used scrubbing water can be safely discharged into the sea without significant environmental impact. The IMO OILPOL fixes a maximum concentration of petroleum hydrocarbons which can be discharged overboard at 15 ppm (IMO 2013). The IMO has not specified limits for other components and characteristics of discharge water, such as pH, suspended solids and heavy metals. Ideally, the discharge water should not significantly affect the pH of seawater (a very sensitive parameter for sea life), but it should be oxygenated to ensure that the chemical oxygen demand (COD) is not high (thus, sulphite discharge should

be avoided) and PM discharge is undesirable. With regard to pH, seawater contains a natural carbonate buffer system and the indications from the test results are that dilution of the used water does not result in significant pH variations. Water treatment procedures are incorporated in the commercial systems to ensure both oxygenation of the scrubbing liquid and PM abatement (see Fig. 16).

3.3.2.2 Integrated NO_x/SO_x Abatement Systems

Integrated systems are not commercially available. An early demonstration of a seawater scrubber in conjunction with a selective catalytic reduction unit and particle eductor has been reported. This was installed in 1993 and showed an SO₂ removal efficiency of 90 %, with the conclusion that there was potential for even more efficient abatement (Ritchie et al. 2005b). It is not clear why this approach has not been pursued, but it is not difficult to imagine high costs, both for installation and operation, especially with the two technologies in their infancy from the point of view of ship-board application. However, such systems are the subject of current research. We have, in fact, within the ECOMOS¹ project analysed feasibility of an integrated process using an abatement strategy illustrated in Fig. 17. The process was scaled up from laboratory to a pilot plant and showed promising results: removal efficiencies for PM, CO, HC and SO_x of over 90 % and for NO_x of over 35 % could be achieved, highlighting the possibility of integrating the catalytic technology into seawater scrubber pollution control devices, which could make the use of SCR technology on-board ships unnecessary.

¹ The ECOMOS project (Ecological compatibility of ships cruising the motorways of the sea) was cofunded by the Italian Ministry of Education (MIUR) and accomplished by a Consortium lead by Fincantieri C. N.I. and RAM (Mediterranean Network of Motorways of the Sea). Project partners are CETENA (Italian Ship Research Centre), INCA (Inter-university Consortium "Chemistry for the Environment"), University of Genoa, RINA Services, I.M.-C.N.R. ("Engines Institute"-National Research Council), ISSIA - CNR (Institute of intelligent systems for automation), ISMAR - CNR (Institute of Marine Sciences) and CONSAR (Shipowners Research Consortium).

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