EMISSION PURIFICATION TECHNOLOGIES

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Contents

Summary

During the last hundred years the demand for combustion-generated power has increased exponentially. The proliferation of combustion systems resulted in large emissions of combustion byproducts, which caused air pollution. Over the second half of the 20th century a large effort was undertaken to make combustion systems cleaner. Currently, combustion engineers pay attention to the emissions of a combustor, along with its performance and fuel efficiency. Improvements in the design, the materials and the operating parameters of combustion chambers are quite effective in reducing the emissions of pollutants. So are improvements in the physical and chemical properties of fuels and lubricants. However, most situations need exhaust flow treatment before it is released to the atmosphere. Exhaust purification technologies have been developed to bring the combustion effluent in contact with liquids or solids capable at selectively removing gaseous pollutants, and often to pass the exhaust through devices capable at capturing particulate matter.

Initially, an overview of combustion-generated pollutants is presented, both from stationary and from mobile power-generation sources. Section 2 deals with the emissions of internal combustion engines and their control. Since engines are predominately used in transportation, the volume and the weight of the exhaust after-treatment devices must be kept low. Engines typically burn highly refined gaseous or

liquid fuels and their major pollutant emissions are carbon monoxide, unburned hydrocarbons, nitrogen oxides and particulates. Section 3 deals with stationary furnaces that deliver power (electricity) and/or heat to industrial and residential consumers. In such applications the volume and the weight of exhaust after-treatment devices is less important. Stationary furnaces often burn unrefined liquid and solid fuels. Thus, in addition to the emissions of the aforementioned pollutants, they emit other chemical species in gaseous and condensed forms (sulfur oxides, metal fumes, ash). This requires additional control techniques such as compounded or integrated flue gas after-treatment systems.

1. Introduction to Combustion-Generated Pollutants

Combustion of fossil fuels is used for heat or power generation, either in stationary units or in mobile units found in transportation applications. Fossil fuels are hydrocarbons, composed of hydrogen and carbon, and often include other elements, such as oxygen, sulfur, nitrogen, chlorine, etc. Fossil fuels can be found in all three phases: gaseous, liquid and solid. Heavy liquid fuels and, particularly, solid fuels include many metallic and non-metallic elements as impurities. Elements may also be deliberately introduced to fuels as additives. Fuels are burned in furnaces of various designs. In such furnaces, fuels are brought in contact with air and, upon ignition, react with oxygen and burn exothermically. Thus, the internal energy of fuels is converted to heat. Heat may be used directly to meet the needs of residential or industrial applications, or it may be converted to work by external combustion engines, such as steam engines. Fuels may also be burned inside engines; such internal combustion engine devices directly convert the released heat to work, with thermodynamic efficiencies typically well under 50 percent.

As fuels react with oxygen and burn, new molecules are formed, the products of combustion. Such products are primarily carbon dioxide (CO_2) and water vapor (H_2O). Both of these species are harmless, with the exception of the contributions of the former to the likely global warming phenomenon (see *Greenhouse Gases and Global Warming*). For instance, complete combustion of gasoline, approximated below as liquid hydrocarbon iso-octane (C_8H_{18}), is as follows:

$$C_8H_{18} + 12.5\,(O_2 + 3.76\,N_2) \Rightarrow 8\,CO_2 + 9\,H_2O + 47\,N_2 \qquad (1)$$

In the molar proportions shown above combustion of iso-octane is stoichiometric and corresponds to approx. 15 kg of air per 1 kg of fuel or, roughly, 15 000 liters of air per 1 liter of fuel. Carbon monoxide (CO) may form, either when there is insufficient oxygen for completing the oxidation of carbon to carbon dioxide, i.e., locally fuel-rich conditions, or by partial decomposition of carbon dioxide at elevated flame temperatures. At regions in the combustor where fuel-rich conditions prevail, typically by incomplete mixing with air, pyrolysis of fuel results in the release of unburned hydrocarbons (HC). Such hydrocarbons may be fuel components themselves (petrogenic) or may have formed by pyrosynthesis in high-temperature flame regions (pyrogenic). Polycyclic aromatic hydrocarbons (PAHs) are often formed and are eventually released, or they are further dehydrogenated in the combustor and condensed to soot (carbon). At high combustion temperatures (above 1800 K) a small fraction of atmospheric nitrogen, which is normally inert, may react with oxygen atoms and form oxides of nitrogen, i.e., "thermal-NO_x", the major component of which is nitrogen monoxide (NO) and the minor nitrogen dioxide (NO_2) (see *Oxidized and Reduced Nitrogen in the Atmosphere*. Carbon monoxide, the most abundant pollutant, is an asphyxiating agent; light hydrocarbons may be toxic and some participate in atmospheric chemistry that leads to formation of smog (see *Formation and Effects of Smog*); PAHs are toxic and some are suspected carcinogens; soot forms smoke and causes pulmonary and cardiovascular ailments (see *Suspended Particulate Material (SPM)*). Nitrogen oxides, particularly nitrogen dioxide, cause respiratory health effects. In warm and sunny climates oxides of nitrogen participate, along with unburned hydrocarbons, in the formation of photochemical smog (see *Formation and Effects of Smog*), whereas in cold and humid climates they contribute to the formation of acid rain (see *Acid Deposition*).

Fuels that contain heteroatoms, such as nitrogen, sulfur and chlorine, result in the release of additional amounts of oxides of nitrogen, called "fuel-NO_x", and traces of other nitrated species, sulfur compounds (predominately sulfur dioxide and hydrogen sulfide) (see *Sulfur Dioxide and Sulfur Cycles*), and hydrogen chloride (HCl). All of these species contribute to acid rain and are toxic; upon inhalation, they inflame the respiratory tract and cause pulmonary ailments. Often, there are synergistic activities between these pollutants and particulates. Under certain atmospheric conditions, the above primary pollutants give rise to secondary pollutants such as photochemical oxidants, which include ozone (O_3) and oxygenated hydrocarbons (see *Tropospheric Ozone Pollution*, *Gas-Phase (Photo-) Chemical Processes in the Troposphere*). Mineral inclusions in coal and in other heavy fuels may be vaporized or otherwise released during the combustion process as fine aerosols. These include metals, such as beryllium (Be), chromium (Cr), manganese (Mn), nickel (Ni), cadmium (Cd), mercury (Hg), lead (Pb), arsenic (As), antimony (Sb) and selenium (Se). While most are released as condensed-phase particles, forming aerosols, a large fraction of mercury, a sizable fraction of selenium and minor fractions of others are released in the vapor phase. Fumes of heavy metals are detrimental to the health of living organisms. Moreover, fuel additives often contain minerals that are health hazardous. A notable example is lead which was added to gasoline, for the most part of last century (1900's), in the form of tetraethyl lead ($(C_2H_5)_4Pb$), in order to raise the auto-ignition temperature of gasoline and suppress engine knock. Currently, leaded gasoline is being phased out worldwide.

2. Control of Pollutants from Internal Combustion Engines

There are three main categories of engines: (a) spark-ignition, reciprocating (Otto) or rotary (Wankel) engines that mostly burn liquid light-hydrocarbon blends (gasoline, alcohols, etc.) but, also, burn gaseous hydrocarbons (such as natural gas); (b) compression-ignition reciprocating engines (Diesel) that mostly burn liquid middle-distillate hydrocarbon blends (diesel fuel) but, also, gaseous hydrocarbons in conjunction with diesel fuel pilot ignition; (c) gas turbines (Brayton) which burn liquid kerosene-based fuels (such as aviation fuel Jet A, JP-8, etc.) and gaseous fuels (natural gas, synthesis gas). Most engines are used in transportation applications and the fuels they burn are typically hydrocarbons that contain only traces of heteroatoms. Thus, the combustion-generated pollutants are mostly carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NO_x) and soot. Estimates in the USA put the road vehicle contribution to the total emissions as follows: 56 percent of the total CO, 32 percent of the total HC and 30 percent of the total NO_x; in urban environments such contributions are much higher.

2.1. Spark-Ignition Engines

Spark-ignited engines traditionally burn a premixed fuel-air charge at a predetermined equivalence ratio, ϕ, where

$$\phi = (m_{\text{fuel}}/m_{\text{air}})_{\text{actual}}/(m_{\text{fuel}}/m_{\text{air}})_{\text{stoichiometric}} \tag{2}$$

Modern engines operate at a stoichiometric equivalence ratio, $\phi = 1$, where flame temperatures are near-maximum. Carbon monoxide emissions are low and typically originate from equilibrium dissociation of carbon dioxide (CO_2). Unburned hydrocarbons (HC) have been found to result mostly from fuel pushed into the crevices of the combustion chamber (around the piston rings, spark-plug, head-gasket, etc.), from absorption/desorption by the film of lubricating oil on the cylinder walls as well as by porous carbon deposits, and from flame quenching at the cooled cylinder walls. Oxides of nitrogen form in the hot burned-gas region, behind the high-temperature flame front.

There are three strategies for reducing emissions from spark-ignited engines: (1) modification of engine design and operation parameters, (2) exhaust after-treatment, and (3) fuel modifications. Engine parameters, such as the compression ratio, the combustion chamber geometry, the placement and number of the spark plugs, the spark timing, the placement and number of valves, the valve timing, etc., can be altered to reduce some emissions. However, there are trade-offs among the emissions of the aforementioned pollutants as well as the engine performance and economy. Thus, while optimization of the engine design and operation parameters is instrumental, the pollutants are best controlled with exhaust after-treatment techniques and fuel modifications. The exhaust pipes of modern automobiles are equipped with three-way catalytic converters that can destroy all three major pollutant categories, after being formed: CO, HC and NO_x, see Figure 1.

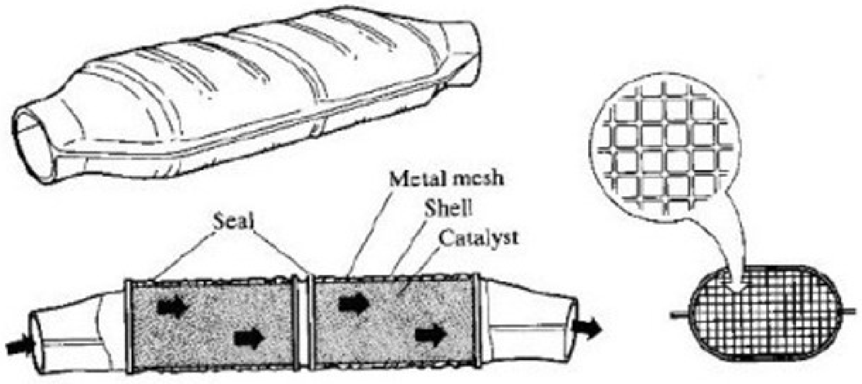

Figure 1: Catalytic converter, fitted with a ceramic monolith for spark-ignition engine emission control *(adapted from Haywood, J.B. (1988) "Internal Combustion Engine Fundamentals" McGraw-Hill, New York)*

These catalytic converters are typically comprised from a porous ceramic substrate (most often cordierite, an aluminosilicate compound) with large surface area, in the form of a honeycomb monolith or pellets. The substrate is coated with an activated alumina (Al_2O_3) layer, called the washcoat. Dispersed in the washcoat are small amounts of small particles (<50 nm) of noble metal catalysts, typically platinum (Pt), rhodium (Rd) and palladium (Pd). Platinum is the principal metal for the removal of unburned HC and CO; rhodium is the principal metal for the removal of NO. Catalysts are sensitive to lead, thus, they must be used with unleaded gasoline. The molecules of CO, HC and NO react with each other at normal operating exhaust temperatures of 400-600 °C and form mostly benign products; for example:

$$CO + NO \Rightarrow CO_2 + ½ N_2 \qquad (3)$$

Any remaining CO and hydrocarbons are removed through oxidation reactions to form carbon dioxide and water. A three-way catalytic converter functions properly only if the exhaust composition corresponds to nearly stoichiometric combustion conditions (±1 percent), see Figure 2. At such conditions the right proportion of the pollutants in the effluent enters the catalyst. A close loop control with an oxygen sensor (lambda sensor) is used to determine the actual fuel-air ratio, and adjust the electronically-controlled fuel injectors so that the engine operates in a narrow range about the stoichiometric set-point.

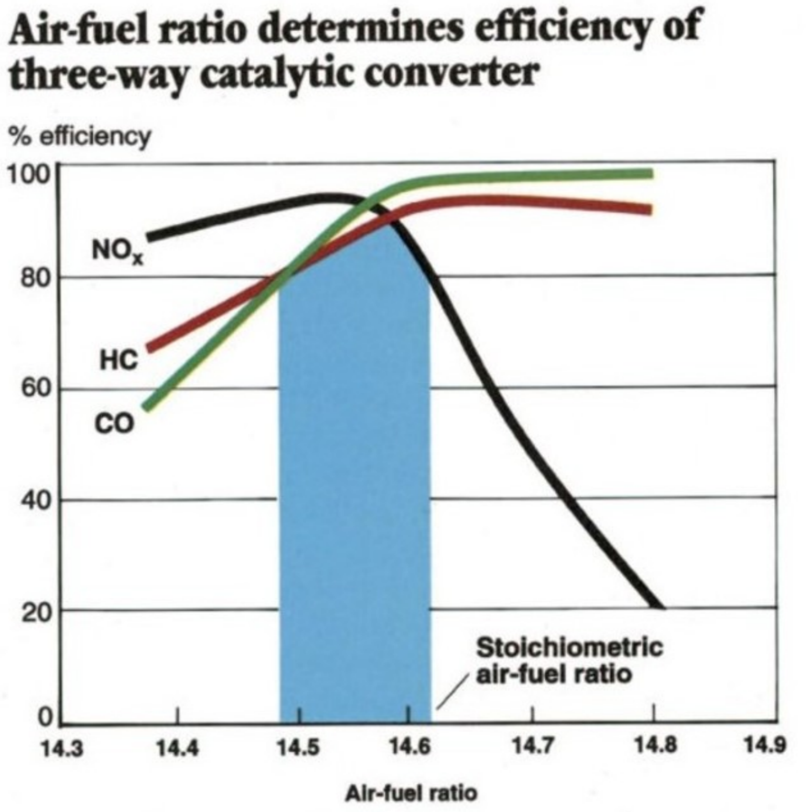

Figure 2: Conversion effectiveness of fully-warmed up three-way catalysts
(adapted from C&EN magazine, September 7, 1992)

However, for chemical reactions to occur, the catalyst must be warmed up to a certain temperature range. The temperature at which the catalytic converter becomes 50 percent efficient is defined as the light-off temperature. In typical current catalyst formulations the light-off temperature for CO is approx. 220 °C while that for HC is about 270 °C. When the converter is fully warm (approaching 400 °C), high conversion efficiencies can be reached: 98 percent for CO, 95 percent for HC, as illustrated in Figure 2. The main problem with catalytic converters is that they need time to warm up (several minutes), and it is during this warm-up period that untreated emissions are released to the atmosphere. Short trips and cold weather exacerbate this problem. In recent years, almost 90 percent of HC emissions resulted from vehicle operation during the warm-up period (the “cold-start” phenomenon). Research is ongoing to device acceptable ways of preheating the catalyst, or to lower the light-off temperature of the converter by improving on the catalyst formulation, or to temporarily store hydrocarbons in a medium upstream of the converter until the catalyst warms up.

Research is also being conducted to improve the fuels themselves to result in lower emissions. In the USA, the Clean Air Act of 1990 set up two programs, an oxygenated fuels program and a reformulated fuels program. The oxygenated fuels program was set to reduce CO and HC levels in approx. 40 major cities during the winter months. It mandates that gasoline contains a minimum of 2.7 percent oxygen, see Table 1. The reformulated gasoline (RFG) program is used on a year-round basis to reduce excessive ozone levels. Reformulated gasoline (Phase 2, mandated in California in 1996) has a minimum oxygen content level of 2 percent and a benzene upper level of 1 percent. The use of reformulated gasoline in a certain group of fleet vehicles was reported to decrease emissions as follows: HC by 26 percent, non-methane-HC by 27 percent, CO by 30 percent and NO_x by 18 percent. The principal oxygenates used are methyl tertiary-butyl ether (MTBE, $H_3COC_4H_9$) and ethanol (C_2H_5OH). However, future use of MBTE is questionable since during storage and handling it has been found to contaminate drinking water supplies (see *Soil Chemistry*). As sulfur has an adverse effect on the performance of catalytic converters, and promotes formation of hydrogen sulfide (H_2S) and sulfuric acid (H_2SO_4), reformulated gasoline specifications call for a sulfur level down to 30 parts per million (ppm) by mass, see Table 1.

Alternative fuels, such as propane, natural gas (either compressed (CNG) or liquefied (LNG)), hydrogen (H_2), methanol (CH_3OH) and ethanol (C_2H_5OH) are currently in use throughout the world, depending on availability. For instance, in Brazil about half of the vehicles use “alcool”, an ethanol-based fuel prepared from fermentation of biomass. Alternative fuels have many benefits and have lower stoichiometric carbon dioxide emissions on an equivalent energy content of the fuel basis than gasoline; ethanol: 1 percent lower, methanol: 4 percent, propane (C_3H_8): 10 percent, and natural gas: 24 percent lower. Combustion of hydrogen, obviously, does not emit CO_2. There are still issues with infrastructure, delivery and on-board storage of many of these fuels. Emissions of major pollutants (CO, HC, NO_x) are mostly lower when compared to those from gasoline-burning engines. Emissions of toxic byproducts, such as benzene (C_6H_6) and 1,3-butadiene (C_4H_6) are also reported to be much lower. However, alcohols emit much higher quantities of the oxygenated intermediates formaldehyde ($HCHO$) and acetaldehyde (CH_3CHO), which are photochemical smog agents (see *Formation and Effects of Smog*).

Content (volume %)	**Industry Average Gasoline**	**MBTE Oxygenated Gasoline**	**Phase 1 Reformulated Gasoline**	**Phase 2 Reformulated Gasoline**	**Gasohol**
Aromatics	28.6	25.8	23.4	25.4	23.9
Olefins	10.8	8.5	8.2	4.1	8.7
Benzene	1.6	1.6	1.3	0.93	1.6
MBTE	0	15	11	11.2	0
Ethanol	0	0	4	0	10
Sulfur (mass ppm)	338	313	302	30	305

Table 1: Content of Gasoline Fuels
Adapted from the US-Environmental Protection Agency (EPA) publication 420-F95-007, http://www.epa.gov

Particulate emissions from spark ignition engines are rather insignificant, however, they are a concern with the new direct-injection spark-ignited engines, currently under development. These are typically two-stroke engines, which have much cleaner emissions than their crankcase-scavenged carburated ancestors that produced excessive unburned HC emissions. A current limitation of the direct-injection two-stroke engine is the inability to control its NO_x emissions catalytically because of its very lean air/fuel ratio. Lean NO_x catalysts are being developed.

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Biographical Sketch

Dr. Levendis holds a B.S. (1980) and an M.S. (1982) in Mechanical Engineering from the University of Michigan and a Ph.D. in Environmental Engineering from the California Institute of Technology (Caltech) (1987), where he also was a postdoctoral research engineer (1987-1988). He joined the Northeastern University faculty in 1988, and he is currently a Professor in the Department of Mechanical and Industrial Engineering. Dr. Levendis' current research is dealing with topics related to Combustion, Air Pollution, Acid Rain Prevention, Incineration of Municipal Wastes, Engine Performance and Emissions, Combustion Diagnostics and Pyrometry, Fire Prevention and Extinction, Carbonaceous Material Synthesis and Characterization, and Polymeric Coatings. He is an authority in the fields of combustion/emissions of waste tires, combustion/emissions of waste polymers, combustion/emissions of coal and emissions from diesel engines. He has developed chemical/physical methods for reducing toxic emissions. These techniques range from high-temperature filtration to development of novel SO_2, and HCl sorbents as well as NO_x reductions agents. Dr. Levendis has published 150 technical papers and holds 10 US and International patents. He is a member of the engineering honorary societies ΤΒΠ, ΠΤΣ, ΦΚΦ, as well as the professional societies American Society of Mechanical Engineers (ASME), Society of Automotive Engineers (SAE), Society of Automotive Engineers (SME), the Combustion Institute and the American Chemical Society (ACS).