CONTROL OF EXHAUST EMISSIONS FROM INTERNAL COMBUSTION ENGINED VEHICLES

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Contents

Summary

Vehicles with internal combustion engines provide transportation worldwide. They can be broadly classified as road vehicles and non-road vehicles. In the beginning of the 21st century more than 600 million such vehicles are engaged in ever increasing transportation activities.

Internal combustion engines operate by burning fossil fuel derivatives and produce exhaust emissions, which are their major contribution to environmental pollution. Primary greenhouse gases – carbon dioxide, methane, nitrous oxide and all criteria pollutants – carbon monoxide, nitrogen oxides, sulfur dioxide, non methane volatile organic compounds and particulate matter are major components. Toxic compounds emitted include benzene, butadiene, aldehydes and lately – ethers, methanol, etc. Noise and odor pollution is also created by internal combustion engines.

If all activities related to transportation are considered, many other pollution sources

and pollutants have to be added to those described above. Vehicle production and maintenance, construction and maintenance of roads, stations and ports, emissions from cargo in normal transportation and in accident, disposal of old vehicles and obsolete transportation infrastructure, are major contributors.

A variety of options - engine design modifications, cleaner fuels, post combustion control devices, inspection and maintenance devices, vehicle design, etc. may be employed to increase efficiency and reduce pollution from transportation. This chapter concentrates on the characterization of pollution from internal combustion engine vehicles, the formation of pollutants and the general approaches for their control. Engine modifications for control of exhaust emissions and cleaner fuels are discussed in detail.

1. Introduction.

Internal combustion engines (ICE) operate by burning fossil fuel derivatives. Exhaust emissions are their major contribution to environmental pollution. Typical emissions contain primary greenhouse gases – carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O). All criteria pollutants – carbon monoxide (CO), total nitrogen oxides (NO_x), sulfur dioxide (SO_2), non-methane volatile organic compounds (NMVOC) and particulate matter (PM) are the other major components. Toxic compounds include benzene, butadiene, aldehydes and lately – ethers, methanol, etc. In many countries exhaust emissions still contain lead and/or manganese. Halogen containing gases and hydrocarbons emitted as evaporative emissions are vehicle pollutants, which are not tail-pipe emissions. Other negative effects include odor and noise.

Environmental pollution from internal combustion engine vehicles (ICEV) is not only limited to air pollution. If all activities related to transportation are considered, many other pollution sources and pollutants have to be added to those described above. Pollutants are emitted to air, water and soil. Vehicle production and maintenance, construction and maintenance of roads, stations and ports, pollution from cargo in normal transportation and in accident, from disposal of old vehicles and obsolete transportation infrastructure, etc. are major sources.

This chapter on the topic on pollution from transportation will outline the impact of ICEV on the environment and will present the main features of ICE, the formation of pollutants, their measurement, and estimation. The options for control of exhaust emissions through engine modification and fuel composition will be discussed in detail.

2. Environmental Pollution from Internal Combustion Engine Vehicles.

Emissions from mobile sources constitute a major negative anthropogenic influence on the environment. In 1997, they were roughly 30, 4, and 67 per cent of the generated in the USA CO_2, CH_4, and N_2O. Total emissions of nitrogen oxides (NO_x) from mobile sources represented 49 per cent of national emissions, while CO, NMVOC and SO_2 emissions contributed approximately 81, 40 and 7 per cent, respectively. Emissions of particulate matter in the USA for the same year are reported as particulate matter smaller than 10 microns (PM10) – 2.569 Gg and total particulate matter (PT) – 5.489

Gg.

Table 1 illustrates the relative participation of major vehicles groups to the total air pollution from mobile sources in the US in 1997.

The above data show that even in countries, leading in pollution control and efficiency, vehicles with ICE contribute a significant portion to air pollution. The contribution of the particular vehicle types can also be seen.

Leaded gasoline was banned in the US in 1995. Still, one source cited more than 1270 tons of lead emissions from vehicles in that country in 1994. Brazil and Japan eliminated leaded gasoline in the 1980s. The first European country, which prohibited leaded gasoline (in 1993), was Austria. Most of the countries in Central and Eastern

Fuel/Vehicle type	Air Pollutants				
	CO	NO_x	NMVOC	CH_4	N_2O
Gasoline Highway, Gg	44 225	4629	4528	211	191
Passenger Cars, %	55.1	56.1	54.5	47.4	56.0
Light Duty Trucks, %	37.6	37.2	39.4	43.1	41.9
Heavy Duty Vehicles, %	6.9	6.5	5.4	7.6	2.1
Motorcycles, %	0.4	0.2	0.7	1.9	+
Diesel Highway, Gg	1 368	1 753	217	12	7
Passenger Cars, %	2.0	1.8	5.1	+	+
Light Duty Trucks, %	0.7	0.6	2.3	+	+
Heavy Duty Vehicles, %	97.3	97.6	92.6	91.7	100
Non Highway, Gg	15 201	4 137	2 205	20	9
Ships and Boats, %	11.2	6.6	21.2	15.0	11.1
Locomotives, %	0.7	20.8	2.0	10.0	11.1
Farm Equipment, %	2.0	23.2	5.3	30.0	11.1
Construction Equipment, %	7.1	27.2	9.9	5.0	+
Aircraft [a], %	6.0	3.9	7.8	35.0	66.7
Other [b], %	73.0	18.3	53.8	5.0	+
Total, Gg	60 794	10 519	6 949	242	207

Source: Compiled and adapted from Inventory of U.S. Greenhouse Gas Emissions and Sinks:1990 – 1997

(1999). EPA 236-R-99-003, US Environmental Protection Agency, NC, USA.
[a]– Air craft estimates for CO, NO_x and NMVOC do not include altitude emissions.
[b] – For CO, NO_x and NMVOC. “Other” includes: gasoline powered recreational, industrial, lawn and garden, light commercial, loggin, airport service, other equipment, and diesel powered recreational, industrial, lawn and garden, light construction, airport service. For N_2O and CH_4 “Other” includes: snowmobiles, small gasoline powered utility equipment, heavy-duty gasoline powered equipment, and heavy-duty diesel powered equipment.
+ - Does not exceed 0.5 Gg.

Table 1: Contribution of US Internal Combustion Engine Vehicles to air pollution in 1997

Europe are also banning leaded gasoline. Still around one third of the gasoline consumed worldwide is leaded. In some countries manganese compounds are permitted as substitutes for tetra ethyl lead.

Toxic air pollutants from ICE include benzene, butadiene, aldehydes and lately – ethers (i.e. methyl t-butyl ether – MTBE), methanol, etc. The contribution of vehicles to these emissions in the USA in 1990 was estimated as benzene – 45 per cent, butadiene – 41 per cent, formaldehyde – 37 per cent. There are indications that the presence of MTBE in gasoline decreases benzene and butadiene emissions, but emissions of aldehydes are increased.

Noise pollution is predominantly attributed to heavy-duty diesel vehicles and aircraft. It is concentrated at cites of increased transportation activities – highways, ports and stations, etc.

Environmental pollution from ICEV is not limited to air pollution. If all activities related to transportation are considered, many other pollution sources have to be added. Pollutants are emitted in vehicle production and maintenance, in construction and maintenance of roads, stations and ports, from cargo in normal transportation and in accident, from disposal of old vehicles and obsolete transportation infrastructure, storage of fuels and so on.

For instance, highway pollution of water only from exploitation and maintenance includes that with fugitive dust, with chemicals used for deicing, with leaks of fuels and lubricants, from lead batteries, leaks from air conditioners, spills from cargo, etc. Solid wastes contribution will include hazardous material spilled from accidents, miscellaneous spent vehicle parts, sand used for deicing, broken asphalt pieces and so on. It should be noted that more than 60 per cent of all hazardous material in a country like the US is road transported.

These contributions are not at all insignificant. Only fugitive dust from US highways in 1994, for instance, constituted 29.0 Gg of PM10 released into the air. Figure 1 presents the major sources of highway pollution.

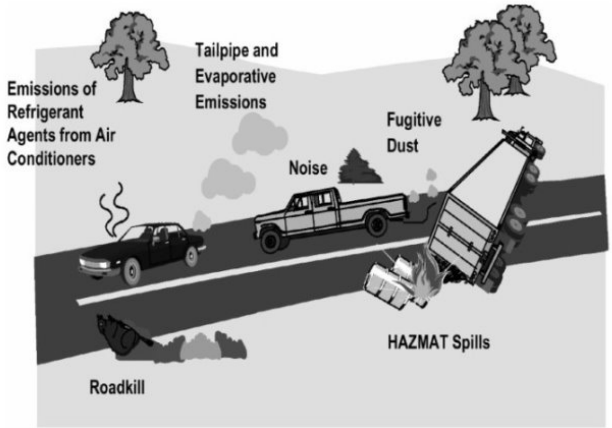

Figure 1: Highway pollution.

In 1994, 71 000 tons of the chlorofluorocarbon CFC-12 – then widely used in air conditioning were released in the USA. Twenty five percent of it was attributed to vehicle air conditioners. Following the Montreal protocol, this greenhouse gas is not produced in the US since 1996. Hydrofluorocarbons became the standard automobile air conditioner refrigerant since 1994. Their emissions grow rapidly as chlorine-containing chemicals disappear from the automobile fleet. The hydrofluorocarbons are unambiguously green house gases but are still not harmless to global warming.

3. Formation of Pollutants and Their Estimation.

Figure 2 illustrates the main sources of air pollution in a passenger car.

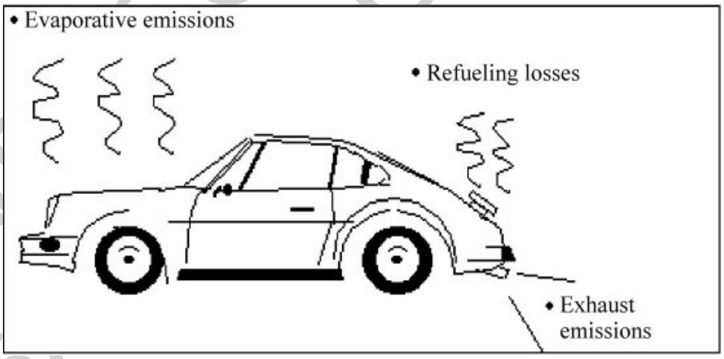

Figure 2: Typical Emission Sources from a Passenger Car.

The relative proportions of the major pollutants in exhaust emissions depend mainly on the specific organization and parameters of the ignition and combustion processes in the ICE. Fuels are usually matched to engines although the full utilization of the advantages of some alternative fuels requires modification of the engine or the development of a new type of engine.

3.1. Internal Combustion Engines.

ICE may be classified by different criteria. For instance, - according to fuel type, to power, to ignition type and so on. An appropriate classification from the point of view of combustion chemistry and air pollution will divide them into two major groups. The first group includes engines in which combustion is performed periodically in a chamber of changing volume (i. e. reciprocating piston engines). In the second group combustion takes place continuously (steady flow) in a chamber of constant volume.

The first group may be further divided into spark ignition (SI) and compression ignition (CI) engines, although there are engines combining both principles. SI engines may be classified as two stroke and four stroke engines, CI engines – as direct and indirect injection engines.

The second group includes the jet engines, which may use a gas turbine, liquid fuel, air as oxidation agent and a turbo compressor (aircraft jet engines), and the rocket jet engines, which have chemical agents as fuels and oxidizers.

Another useful distinction between internal combustion engines is the fact that only in SI engines the fuel is evaporated and mixed with the oxidizing agent before the ignition takes place. In other designs, the fuel is sprayed in the combustion chamber, in the form of drops of different size.

It is not the purpose of this chapter to describe the organization of the combustion processes in the different engines. Its main task is rather to compare the main groups from the point of view of air pollution and describe concisely the mode of formation of major pollutants. Details of combustion systems, combustion processes, efficiencies, etc. can be found in *Pollution Control through Efficient Combustion Technology*.

Modern *SI engines* used in passenger and freight vehicles are four-stroke, although two-stroke passenger cars are still running in some European countries. Two-stroke engines have the important advantages of lower weight and cost per unit of power output. They are widely used in small motorcycles, as outboard motors and other small power equipment.

The main pollutants from four-stroke gasoline engines are hydrocarbons, CO and nitrogen oxides. They are contained in exhaust emissions, but hydrocarbons are contributed both with the exhaust, and with the evaporative emissions. Particulate matter is usually negligible and is produced mainly from oil components brought in the combustion chamber by the piston. Sulfur oxides are typically low and for some time were not considered a problem. New regulations restrict drastically sulfur in gasoline, because of reconsidering its influence on catalysts.

Two-stroke engines emit 20 to 50 per cent of their fuel unburned in the exhaust, but also a considerable amount of oil, which is a component of the air-fuel mixture by design. Air pollution from them is higher and includes a considerable amount of particulate matter. Two-stoke engine designs with advanced fuel injection, lubrication and combustion systems are being developed. They are expected to achieve lower emissions and higher fuel efficiency, while keeping their traditional other advantages.

In *direct injection CI engines,* the fuel is sprayed directly into compressed heated air. It evaporates, and ignites. These engines are typical for medium and larger vehicles. They provide higher power output and better efficiency than engines with indirect ignition, but are noisier. For passenger cars, indirect injection engines are more common, because of lower noise and high performance characteristics. Ignition takes place in a pre-chamber, often by a glow spark, and combustion then spreads into the main chamber. Direct ignition engines with improved noise and efficiency controls are being introduced lately in passenger vehicles as well.

Diesel engines can be also classified as naturally aspired, supercharged or turbo charged, depending on the organization of the airflow and its pressure before spraying the fuel. If properly controlled, emissions from turbo charged engines are smaller than from the other two types.

Compared to the typical gasoline SI engines, both light and heavy duty diesel engines have considerably higher compression ratios and better fuel efficiency, which leads to lower CO and hydrocarbon emissions. Light duty vehicles emit also less nitrogen oxides than comparable gasoline engines, but nitrogen oxides from heavy-duty diesel engines are higher. Particulate matter and the polycyclic carcinogenic hydrocarbons adsorbed on it are eight to ten times as much as in gasoline counterparts and pose a serious problem for diesel engines. They also emit a considerable amount of sulfur compounds due to the presence of more sulfur still allowed in diesel, than in gasoline fuels.

Stratified charge engines are a hybrid between typical gasoline and diesel engines. Indirect injection engines rely on spark for ignition of fuel rich mixture. They utilize non-uniform fuel distribution to improve turbulence mixing, and more efficiently avoid fuel rich zones in which the amount of the fuel is more than the stoichiometric extent. Direct injection engines use a high-pressure injector to create a swirl tangential motion of the fuel towards the spark plug. Stratified charge engines have high fuel efficiency, but use fuels with volatility closer to gasoline, and their emission performance is not very impressive.

Rotary car and motorcycle engines have a triangular rotor, which replaces the piston. They are smaller, lighter and simpler, but their CO and hydrocarbon emissions are higher than from conventional engines, while the NO_x emissions are the same. Stirling engines are capable of higher fuel efficiency and lower emissions, but are impractical for common automotive use, because of high cost, poor transient response and power to weight ratio.

Gas turbine engines are widely used in aircraft, high speed trains, marine vessels and stationary applications, and have been tested without a great success in road vehicles. They use jet fuel, which in volatility is intermediate between gasoline and diesel fuels. The combustion environment and emissions from aircraft gas turbines vary widely with load. At low loads, temperature and NO_x emissions are low, but CO and hydrocarbon emissions are higher. At high loads, CO and hydrocarbon emissions are low, but temperatures and NO_x emissions are high. Soot is also formed at high loads, because of the imperfect mixing and fuel rich zones. The rapid quenching of combustion products in gas turbines promotes the emission of significant quantities of NO_2, which might be comparable to those of nitric oxide, NO. As a whole, the emissions from gas turbine engines per power output are smaller than from the other engines.

Rocket internal combustion engines may use petroleum fractions, alcohols, ammonia, hydrazin, liquid hydrogen, etc. as fuels. The oxidation agents include nitric acid, tetranitromethane, hydrogen peroxide, liquid oxygen, etc. The emissions from rockets, especially those formed from nitrogen compounds are highly toxic.

3.2. Formation of Pollutants.

Chemical elements under ideal reaction conditions should burn to the corresponding oxides, so CO_2 and water are the most likely products to be expected from oxidation of hydrocarbons. However, conditions in engineering applications of combustion reactions are not ideal. The stoichiometric quantity of air needed to burn completely 1 g of gasoline is roughly considered to be around 14.7 g, approximately eleven grams of this being nitrogen. If the air quantity is higher than the stoichiometric proportion the flames are called "lean", if it is lower - "rich". In a real combustion chamber flames may be both, depending on the particular chamber type. Other important factors include flame temperatures, gas residence time at high temperatures and combustion chamber turbulence. None of these factors is at its most favorable values throughout the whole chamber space. The fuels are in fact mixtures of compounds with different molecular masses, volatility, diffusion coefficients, etc. Under the non-ideal conditions in the chamber, they undergo pyrolysis and oxidation pyrolysis, prior to reaching the flame propagation zone. The mode of ignition of the fuel, and the intermediate products through which it passes in combustion reactions are very important for the type and the relative quantity of pollutants formed.

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Biographical Sketch

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