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Wrocław University of Technology

Automotive Engineering

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ECOLOGY OF ROAD TRANSPORTATION

The Logistic System of End-of-Life Vehicles Recycling

Wrocław 2011

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Ecology of road transportation

1. Introduction

The transportation sector is one of the most complex and important direction of world economy development which is strongly correlated with new trends in science and innovation in technologies. The ecology and sustainable development impact on technic and technology progress has been very noticeable in the last decades which makes it impossible to discuss and solve automotive engineering problems without its ecological aspects.

This book is dedicated to technical universities students whose field of study is connected with automotive engineering and transportation. Acquiring essential knowledge about ecology of road transportation prepares students for problem solving during the laboratories, projects and seminars in the range of automotive engineering in the context of powertrain and car vehicle body ecological design and motor car vehicle operating problems.

The book focuses on the selected issues of the ecology of road transportation and is divided into two main parts: engine and vehicle. In the first part the general problems concerning engine combustion process in emission aspect, toxicity estimation of the exhaust gases and the methods of its reduction and emission legislation were discussed. The second part of the book concerns waste management problems and indoor air quality of a car vehicle.

The aim of the book is also to support the Car Ecology and the master studies on Automotive Engineering program. It also presents instructions for the laboratories for classes carried out in The Division of Motor Vehicle and Internal Combustion Engines and Emission Research Laboratory of The Wroclaw University of Technology – where the authors of this paper work.

Fig 1. Division of Motor Vehicles and Internal Combustion Engines

2. Environmental effects of road transportation

In 1956 Ullman in his contribution to Man's Role in Changing the Face of the Earth stated that ''Few forces have been more influential in modifying the earth than transportation.'' Few years later transportation geographers have pointed out the correlation between transportation network expansion and economic development of regions. Nowadays well-known fact is that, since years, the transport sector plays a key role in the World economy. However, transport emissions present a challenge as they are major contributors to global warming and to local air quality problems. The second important environmental issue is End-of-Life Vehicle (ELV's) waste management problem. The car vehicle becomes very important micro-environment of human life that is why indoor measurements of car cabin air quality is also current field of the researches. All those problems are investigated in the aspect of human life and health protection as well as impact on complex ecosystems [1].

Urban transportation is a real concern especially in large cities around the world. The rapid urbanization and motorization in these cities have a direct impact on sustainable development. The transport sector's energy consumption and greenhouse gases emission will likely be doubled by the year 2025. Moreover, the environmental and social impacts of urban transportation are increasingly being seen as a menace to the sustainability of the global ecology [1].

The most transportation efficient cities in the world are facing escalating motorization and mobility demands. Travelling is increasing in virtually all regions of the world, usually at the same or faster than the rate of economic growth, and generally faster in the long run than the rate of reduction of energy and pollution intensity.

The fact is that development of the road transportation is necessary and inevitable and it brings a lot of profits (mostly in sociological and civilizational aspects) but also threats, especially for the environment [2]. In figure 1 the effect of transportation is presented.

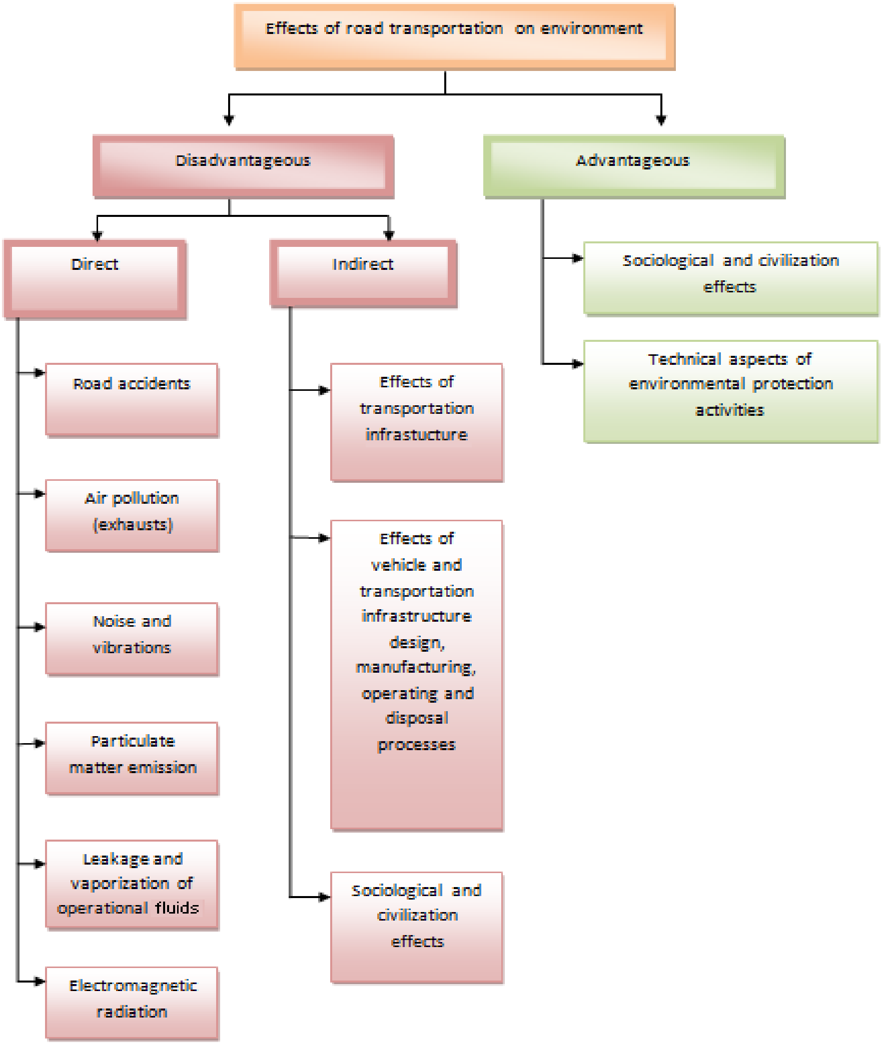


Fig 2. The effects of road transportation on environment [2]

How can the negative impact of automotive industry development be decreased? Improvements can be found in the use of cleaner technologies, alternative fuels and new transport systems as well as in the more efficient use of existing technologies. On the other hand, many questions are still not answered regarding the effectiveness, cost and unwanted side effects [2].

The performance of the modern automobile reflects a number of incremental improvements: reductions in vehicle weight, better aerodynamic design, reductions in tire rolling resistance, reduction in friction losses, new catalytic systems, more efficient engines and drivetrains. But there is one common theme underlying the evolution of the modern automobile: it has become a much more complex system, with a far higher information content than its predecessors. Moreover, it is increasingly linked to its external environment, becoming a subsystem in a yet more complex automotive transportation system. The parable of the modern automobile is increasingly one of systems integration through information generation and linkages, of increased information density in the technology system, of computer and electronic, rather than mechanical, engineering. Internally, mechanical subsystems in older cars were linked mechanically whereas new car systems are linked by sensor networks feeding into multiple computers [3].

Whereas older cars had minimal electronics, newer ones have substantial systems that need to be integrated both physically and functionally. In fact, the numbers of cables and wiring harnesses required by the modern automobile have increased to such an extent that routing them through the vehicle becomes a design problem in itself.

Automobile manufacturers now produce complete advanced engine management systems to balance performance, emissions, fuel consumption, operating conditions (eg. cold starts, stop-and-go conditions). Such systems typically include control units, different sensor systems, and actuators, and utilize complex information topologies to maintain optimal system operation. Reflecting a greatly more complex engineered system, sophisticated multiplexed microcontrollers thus become a necessary component of the modern automobile. In fact, the modern automobile is such an information rich artifact that a complex information hierarchy is required (figure 3).

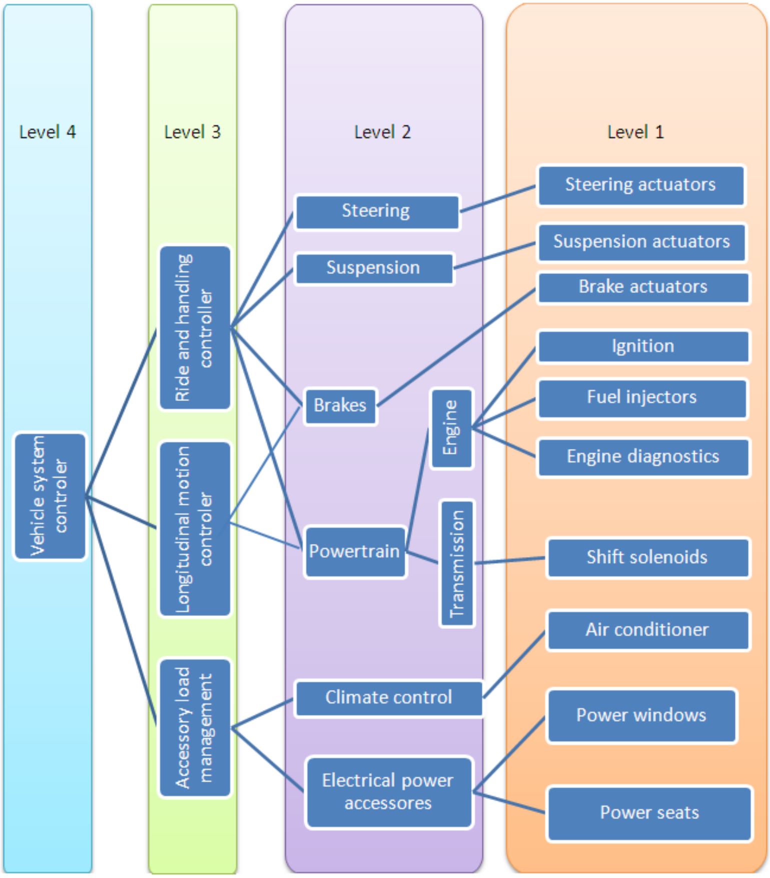


Fig 3. A modern automobile components hierarchy [3]

Producing a more complex system requires, in turn, more sophisticated design tools and manufacturing technologies. For example, lightweighting - reducing the weight of vehicles through better design and material substitution - has been a major contributor to enhanced environmental performance; such designs require precision manufacturing, and the design process becomes a much more information intensive activity. Germany's Audi, for example, believes that only the advent of supercomputing technologies provided the necessary processing power to design the complicated lighter components that have permitted them to lightweight their product. Moreover, difficult design problems are resolved by virtual reality design [1].

In older cars, virtually the only information link between the automobile and the external environment was the driver. Today, sensor systems monitor exhaust systems, the oxygen content of air flows, and road conditions, and newer systems map the car's geographical position, provide up-to-date road conditions and optimal real-time routing options, and pay tolls electronically without the need to stop. The technologies that will permit ongoing communication between road networks and automobiles, in essence integrating the automotive built infrastructure, the automobile, and the driver into one automotive transportation system, which can then be optimized for real-time efficiency by, for example, use sensitive automatic roadway pricing already exist. Cars linked to the internet with speech recognition capabilities, voice-controlled browsers, GPS (Global Positioning System) capabilities, email capability, and their own internal local area networks are on the road. The car is not only an information artifact, it has become an information appliance [1].

3. Ecology of road transportation and its sustainable development

The sustainable development is the ability to make development sustainable— to ensure that it meets the needs of the presence without compromising the ability of future generations to meet their own needs [3]. One of the successes of sustainable development has been its ability to serve as a grand compromise between those who are principally concerned with nature and environment, those who value economic development, and those who are dedicated to improving the human condition. At the core of this compromise is the inseparability of environment and development described by the World Commission on Environment and Development. Thus, much of what is described as sustainable development in practice are negotiations in which workable compromises are found that address the environmental, economic, and human development objectives of competing interest groups [3].

The transportation sector has proven to be particularly difficult territory for the advancement of sustainable development policy. Transportation is a complex and porous social, technical, and economic system, difficult to address comprehensively . This complexity derives from the pluralism of its hardware (infrastructure and vehicles) and of the people and organizations involved [4]. The complexity is multiplied by the existence and roles of different modes, regulatory and legislative bodies, service providers, builders, financing systems, technologies, land-use patterns, and, most importantly, human behavior. The consequences of transportation use are both positive and negative and are addressed in considering the sustainability of the transportation system. Among these consequences are safety, congestion, fuel consumption, vehicle emissions, and access [5].

In the transportation sector, however, it is always a question to answer exactly which resources are of concern when the term ‘sustainable’ is used; different groups may have different resources in mind. To be sure, the transportation sector does consume resources like: energy, human and ecological habitats, atmospheric carbon loading capacity, and individuals’ available time. But solutions that reduce depletion of one of these may exacerbate depletion of another one. Moreover, transportation decisions tend to be made in the service of larger policy goals: economic growth and job creation, the character and intensity of land use, and socioeconomic and geographic transfers of wealth.

Energy consumption is one of the most important factors indicated on sustainable development of the road transportation sector. In most analyzed countries the energy consumption increased dramatically in the period between 1990 and 2004. The change in energy consumption in this period caused by road transportation sector is shown in figure 4.

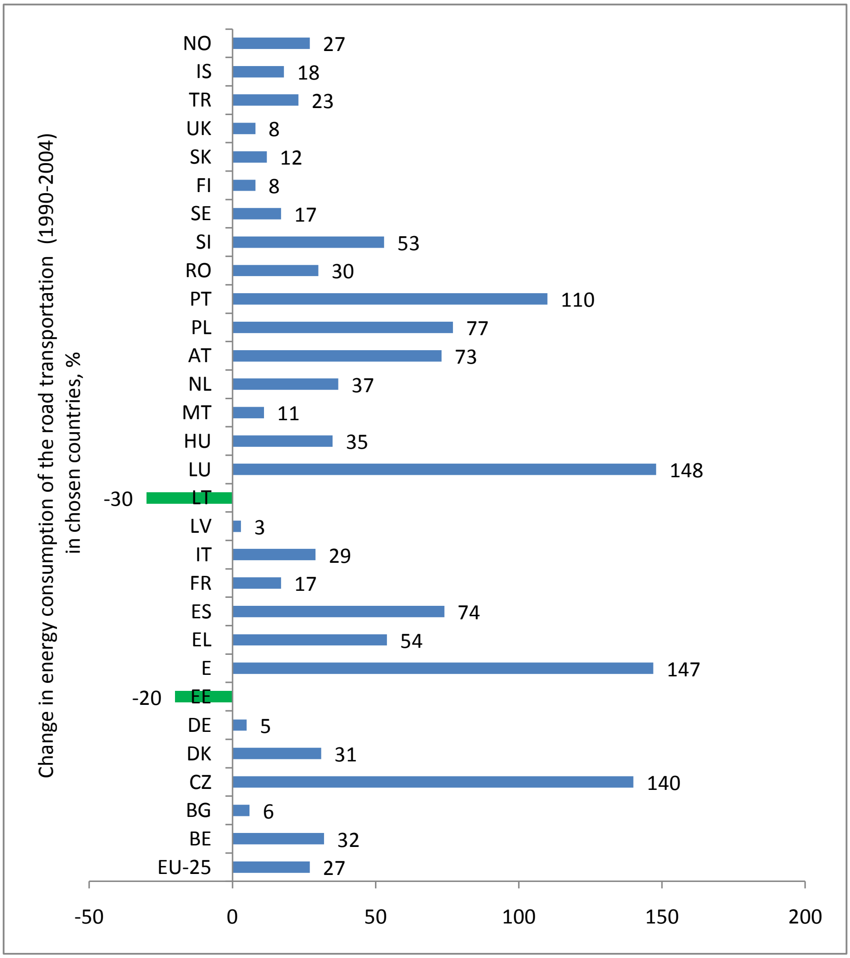


Fig. 4. Energy consumption change, %, by transport mode, 1990-2004 (authors analysis based on [4])

During fourteen years (since 1990 to 2004) in 4 of 29 analyzed countries the energy consumption increased over 100%, in 7 countries over 70% and in 9 countries over 50%. Average change in energy consumption in current European Union countries increased about almost 30%. Only in case of two countries (Estonia and Lithuania) the energy consumption decrease was observed.

The phenomena of increasing energy consumption in road transportation sector is caused by the rapid growth of car vehicle number in European countries. The number of car vehicle per inhabitant in 1990 and 2007 in Europe is shown in figure 5.

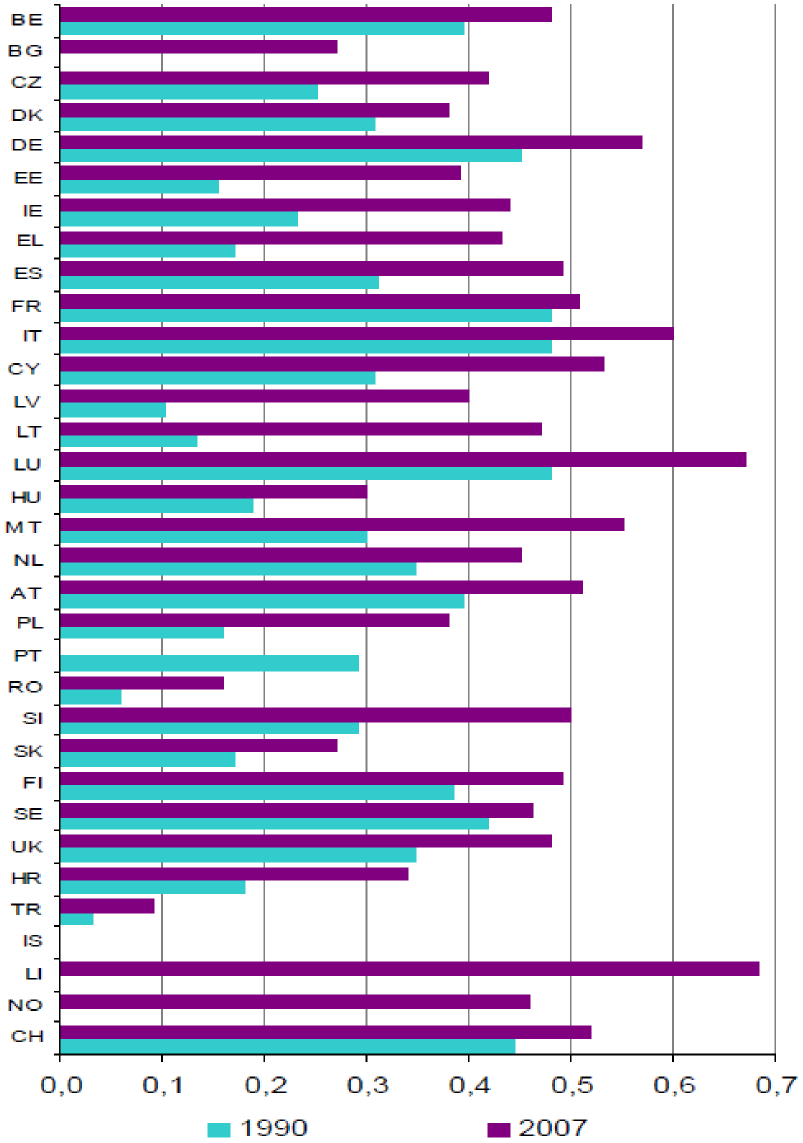


Fig 5. Number of passenger cars per inhabitant, 1990 and 2007 [7]

There are a lot of other factors (technological, economical and sociological) whose impacts on energy consumption by car vehicles are i.e.:

- Age structure of the vehicles,
- New technologies implementation,
- Transportation infrastructure development,
- Fuels prices.

ENGINE

4. Combustion engine as a source of air pollution

4.1. Impact of the engine combustion process on exhaust composition

The internal combustion engines use atmospheric air and hydrocarbon fuel (gasoline, diesel, bio-fuels or gas fuels like: LPG or CNG) and through the process of combustion releases the chemical energy stored in the fuel. Of the total energy relisted by the combustion process, about 30 % is used to propel the vehicle, the remaining 70 % is lost to friction, aerodynamic drag, accessory operation and simply wasted as heat transferred to the cooling system or with exhaust (fig 6).

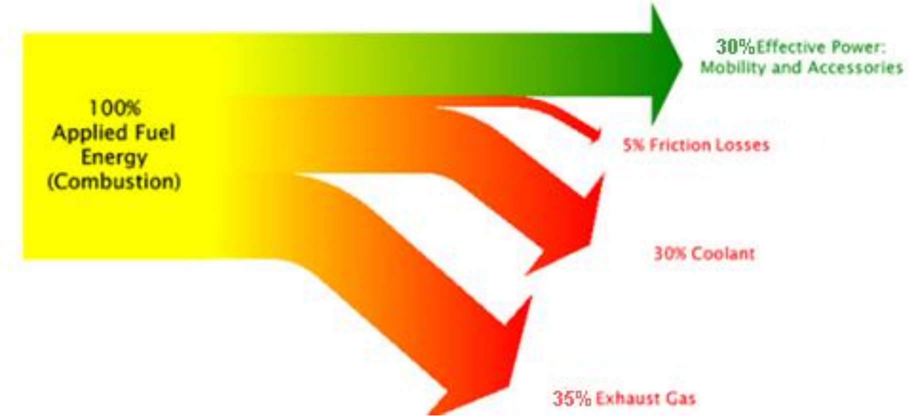
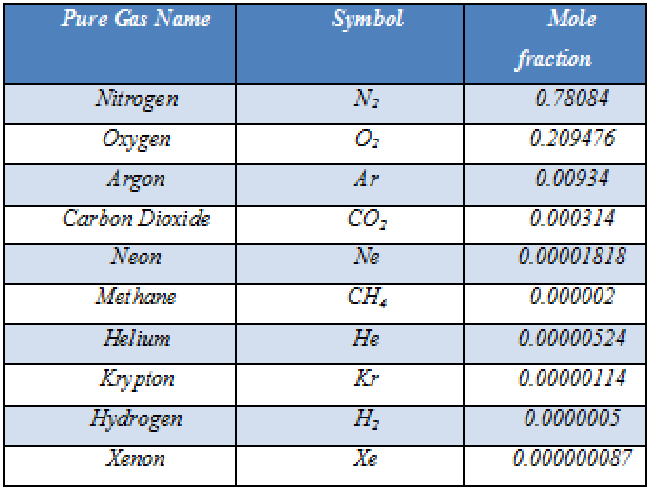


Fig. 6. Simplified, typical energy split in internal combustion engines

The substrates in the typical engine combustion process are fuel and air (as a source of oxygen) that is why the products of the process are compounds which are chemical combination of those substances. The fuel is a mixture of hydrocarbons and its composition is very differentiated – depends on the engine type, source (fossil fuel, biomass), producing company and distributor (additions) etc. The air composition is also changeable and depends i.e. on natural or anthropogenic pollution but it mainly consists of nitrogen, oxygen and carbon dioxide. The air composition is presented in table 1.

Table 1. The air composition [2]



Pure Gas Name	Symbol	Mole fraction
Nitrogen	N_2	0.78084
Oxygen	O_2	0.209476
Argon	Ar	0.00934
Carbon Dioxide	CO_2	0.000314
Neon	Ne	0.00001818
Methane	CH_4	0.000002
Helium	He	0.00000524
Krypton	Kr	0.00000114
Hydrogen	H_2	0.0000005
Xenon	Xe	0.000000087

For combustion of each portion of delivered fuel a certain dose of oxygen is required. It is taken from atmospheric air which is sucked through the intake manifold and suction valve to the combustion chamber. The amount of air needed to burn 1 kg of fuel is described by the reaction [2]:

$$L_t = \frac{1}{0.21}\left(\frac{c}{1} + \frac{h}{4} - \frac{o}{32}\right) kmol / kg$$

Where:

c – mass share of carbon

h – mass share of hydrogen

o – mass share of oxygen

After multiplication by molecular mass of air, a theoretical amount of air in kg per kg of fuel is achieved (table 2) [2]:

$$L_t' = 28.95 \cdot L_t$$

Table 2. Theoretical air demand for combustion of basic liquid fuels

Type of fuel	**Theoretical air demand**	
	L_t kmol/kg of fuel	L_t’ kmol/kg of fuel
Gasoline	0.512	14.8
Diesel fuel	0.495	14.3

Excess air ratio is the ratio of real air mass needed for fuel combustion to the amount required for oxidation of total portion of fuel (stoichiometric amount). This ratio can be calculated using the formula [2]:

$$\lambda = \frac{L}{L_t}$$

Where:

L – amount of air delivered to the cylinder during one operation

L_t – theoretical amount of air required for complete combustion of fuel consisted in the delivered mixture

Typical values of the λ coefficient for nominal operational conditions of engines [2]:

- λ = 0.85 to 1.10 – spark ignition engines,
- λ = 1.40 to 1.65 – self ignition engines with direct fuel injection,
- λ = 1.15 to 1.40 - self ignition engines with indirect fuel injection.

Complete reaction of fuel oxidation is an ideal chemical model where the only products are carbon dioxide, water and energy. The amount of formed CO_2 and the value of heat of combustion depend on the molecular structure of hydrocarbon and especially the ratio of hydrogen atoms to atoms of carbon. Summary equation of the reaction is [2]:

$$C_nH_m + \left(n + \frac{m}{4}\right)O_2 \rightarrow nCO_2 + \frac{m}{2}H_2O$$

Where:

n – number of atoms of carbon

m - number of atoms of hydrogen

The products of complete reaction of hydrocarbon combustion in example of butane oxidation:

$$2C_4H_{10}\ (g) + 13O_2\ (g) \rightarrow 8CO_2\ (g) + 10H_2O\ (g) + \text{Energy}$$

are only energy, carbon dioxide and water steam. In short only harmless elements would remain and enter the atmosphere. Although modern engines produce much lower emission levels then their precursors they still inherently produce some level of harmful emission output (fig. 7).

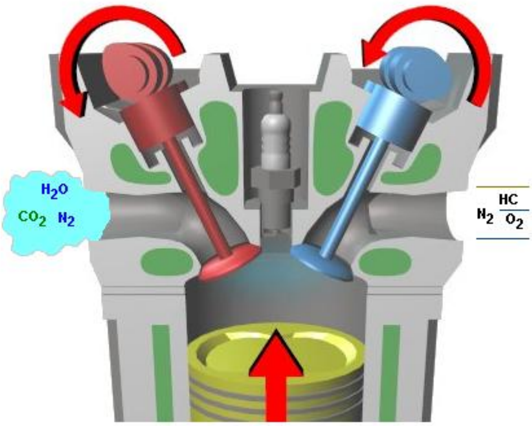


Fig 7. The theoretical complete engine combustion process [11]

In reality this phenomenon is impossible to achieve because there are several conditions in the combustion chamber which prevent perfect combustion and cause unwanted chemical reactions to occur [2]:

- temperature and pressure variation,
- local oxygen deficiency,
- oil present in combustion chamber,
- fuel contaminants and additives,
- air pollution.

Unfortunately even the most technologically advanced, contemporary internal combustion engines inherently produce some level of harmful emission output (fig. 8).

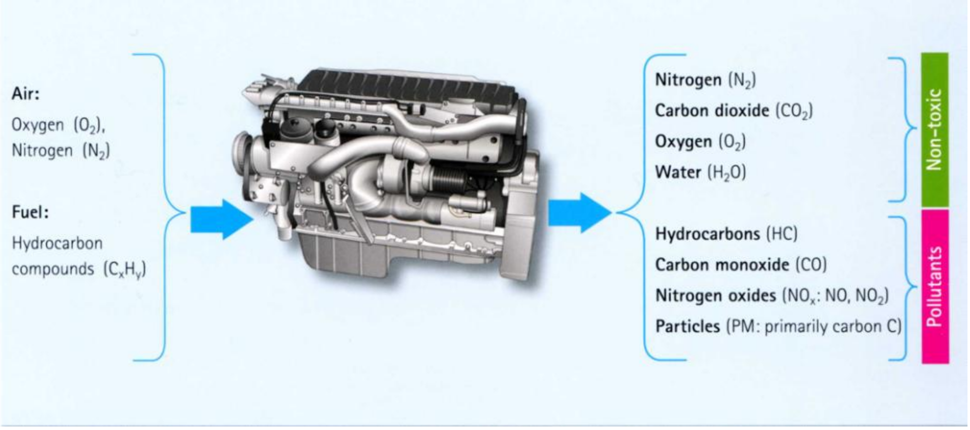


Fig. 8. Engine combustion process – toxic and nontoxic emissions [28]

An example of an incomplete reaction of butane oxidation is shown below:

$$C_4H_{10}\ (g) + 5O_2\ (g) \rightarrow 2CO_2\ (g) + 5H_2O\ (g) + CO\ (g) + C\ (s) + \text{Energy}$$

As a result of combustion processes in internal combustion engine (ICE) there are a lot of substances which are more or less toxic and harmful for the environment.

The engine exhausts gasses generation during the combustion process can be simply described according to the scheme shown in figure 9.

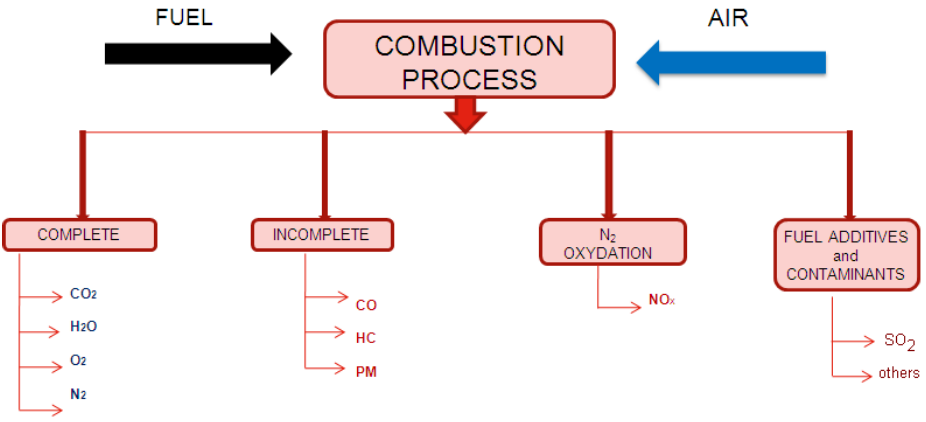
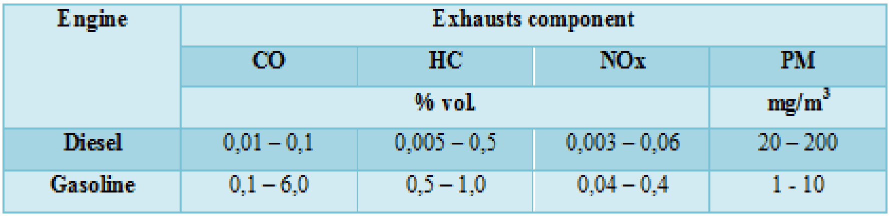


Fig. 9. The simplified structure of combustion gas components formation in car engines [4]: HC – total hydrocarbons , PM – particulate matter

As it is shown in the figure, toxic compounds of the exhausts are generated because of incomplete combustion process.

The exhaust gas composition is influenced not only by the fuel type but also by the combustion process. The fuel combustion process inside the engine cavity differs depending on the ignition type, that is why exhaust gases combination in case of spark ignition engines (SI) and compression ignition engines (CI) will differ as well. The approximate chosen exhaust gases content from SI an CI engines is presented in table 3.

Table 3. The approximate chosen exhaust gases content from SI and CI engines [2]



Engine	**Exhausts component**			
	CO	**HC**	**NOx**	**PM**
	% vol.			**mg/m^3**
Diesel	0,01 – 0,1	0,005 – 0,5	0,003 – 0,06	20 – 200
Gasoline	0,1 – 6,0	0,5 – 1,0	0,04 – 0,4	1 - 10

Although compression ignition (CI) engines are thought to be more environment friendly, the control of particular matter (PM), dangerous, not fully burnt hydrocarbon appearing in an adsorbed form on the dust cells or in a gas form, still causes big problems.

Motorization, being a civilization factor, influences all the environment components, like air, soil, water, ecosystems and landscape. Transportation means are the main reason of the atmosphere pollution. Combustion engines emit nitric oxide, carbon monoxide, hydrocarbon and particulate matter. All the changes that engine fuels underwent within the last tens of years dramatically minimized, once at the global scale, sulphur dioxide and led dioxide emission. The motorization sources share in the overall emission of chosen substances is presented in figure 10.

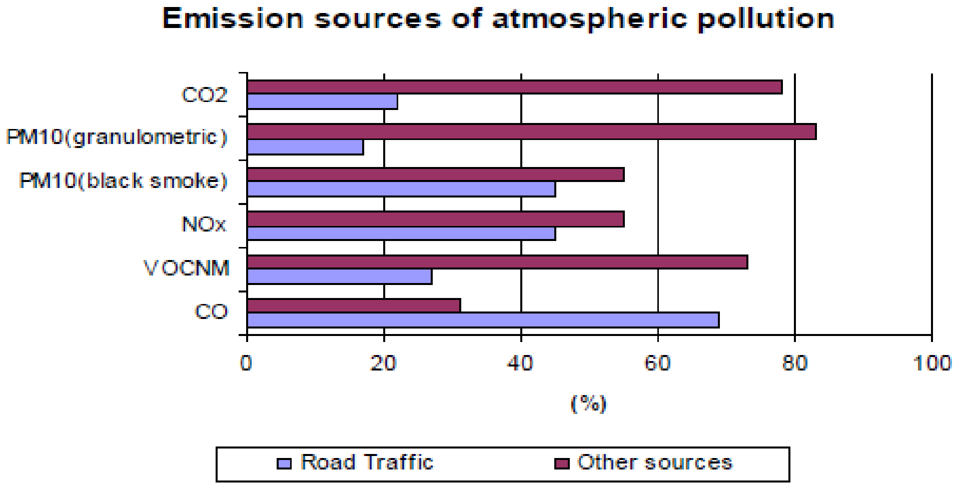


Fig. 10. The motorization sources share in the overall emission of particular substances: nitric oxide (NOx), particle matter (PM10), non-methane volatile organic compounds (VOCNM), carbon monoxide (CO), and carbon dioxide (CO_2) [8]

Internal combustion engine exhausts consists of over 200 individual hazardous chemical components which when combined, can result in as many as 10,000 chemical compounds. According to International Agency of Research on Cancer (IARC) a large majority of these compounds are listed as being cancer causing or suspected carcinogenic.

A recent study estimated that approximately 64,000 people just in the United States die from heart or lung disease every year because of air pollution (more people than die each year in car accidents) [9].

Except emission of toxic compounds the transport sector is responsible also for significant emission of greenhouse gases – especially carbon dioxide. Between 1990 and 2008, transport emissions increased by 34% while emissions from other sectors decreased by 14% [13]. The carbon dioxide emission in European Union form 1990 to 2007 is presented on figure 11.

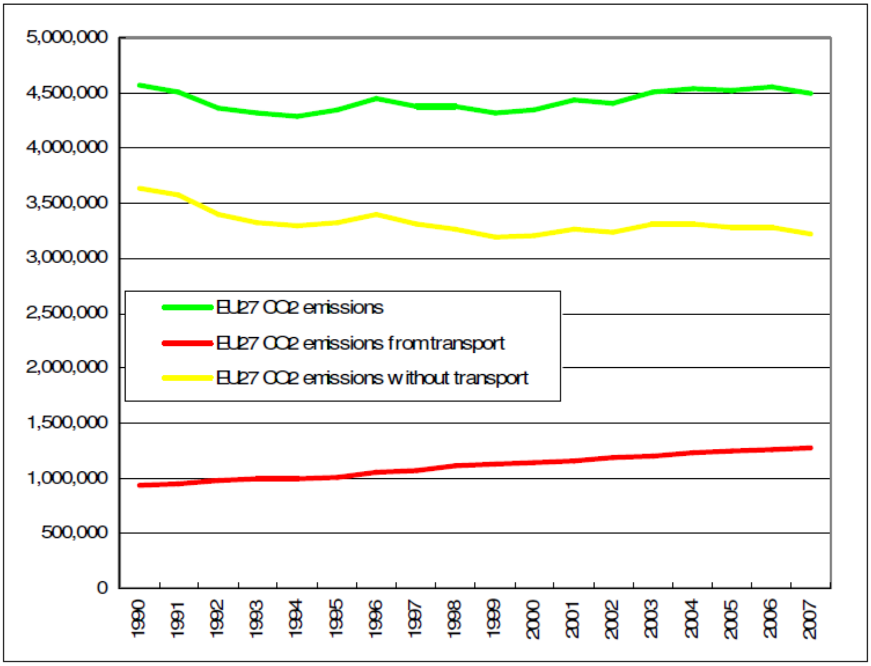


Fig 11. The CO$_2$ emission in EU-27 countries from 1990 to 2007 [13]

As one could have suspected with the 83 % share of transport energy consumed by road transport this mode remains by far the largest single emitter. According to the European Environment Agency, 93 % of greenhouse gas emissions from transport came from road transport in 2004 (fig. 12) [12].

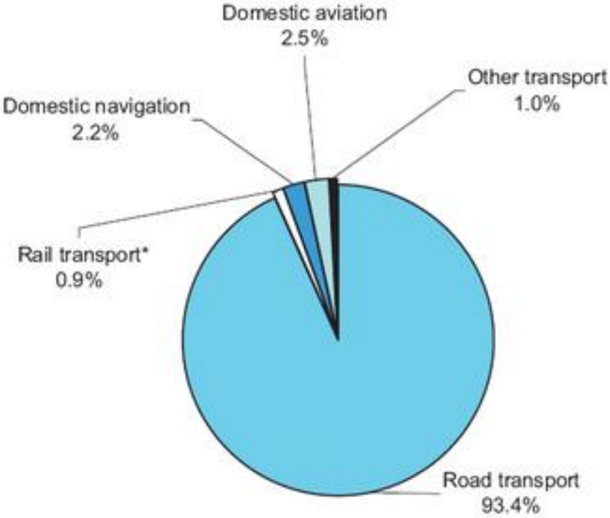


Fig 12. Greenhouse gas emissions from transport by transport mode, EU-25, 2004 [12]

4.2 Toxic emission causes in internal combustion engines

4.2.1 Carbon monoxide

Carbon oxide (CO) is byproducts of incomplete combustion and is in fact partially burned fuel. If the air/fuel mixture does not have enough oxygen present during combustion, it will not burn completely. When combustion takes place in the oxygen starved environment, there is not enough oxygen present to fully oxidize the carbon atoms into carbon dioxide (CO_2). When carbon atoms bond with only one oxygen atom carbon monoxide (CO) forms (fig. 13) [11].

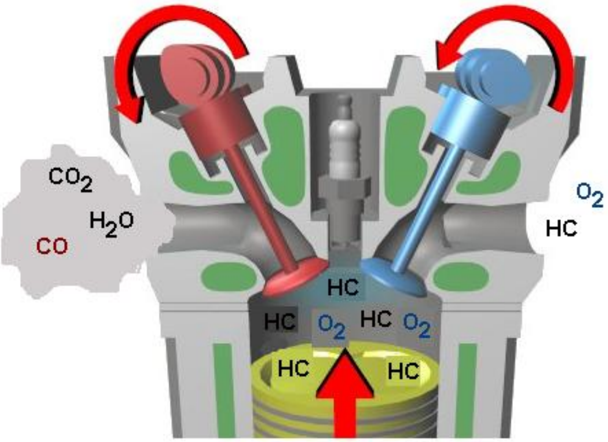


Fig 13. Carbon monoxide emission - oxygen starved conditions [11]

During combustion with rich A/F ratio, the carbon from HC only partially oxidizes, resulting in carbon monoxide (CO) rather than carbon dioxide (CO_2). An oxygen starved combustion environment occurs as a result of air/fuel ratios which are richer then stoichiometry - for example, during cold operation, warm-up, and power enrichment. It is, therefore normal for higher concentrations of CO to be produced under these operating conditions. Causes of excessive CO includes leaky injectors, high fuel pressure, improper closed loop control, etc. The effect of A/F ratio on carbon monoxide emission is shown in figure 14.

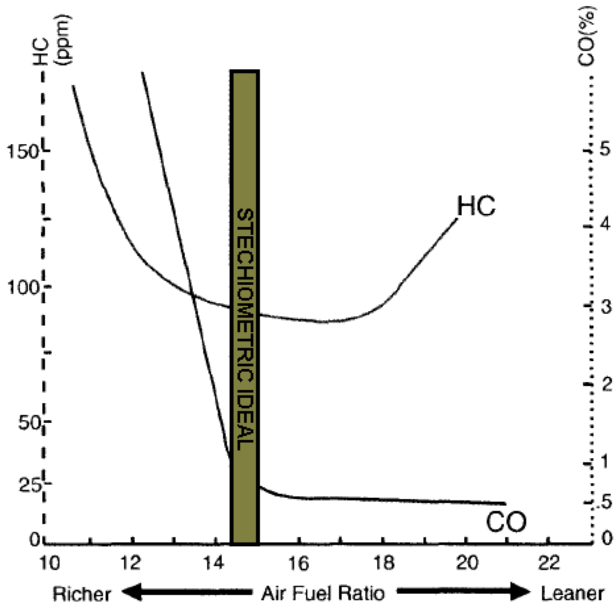


Fig. 14. Effect of A/F Ratio on exhausts CO [11]

Exhaust CO is lowest when A/F ratio is leaner than stoichiometric, however CO increases dramatically with richer mixtures. When the engine is at warm idle or cruise, very little carbon monoxide is produced because there is sufficient oxygen available during combustion to fully oxidize the carbon atoms. This results in higher levels of carbon dioxide (CO_2) the principal by-products of efficient combustion [11].

4.2.2 Oxides of nitrogen (NOx) emission

High cylinder temperature and pressure which occur during the combustion process can cause nitrogen to react with oxygen to form oxides of nitrogen (NO_x). Although there are various forms of nitrogen-based emission that comprise NOx, nitric oxide (NO) makes up majority, about 98% of all NOx emission produced by the engine (fig. 15)

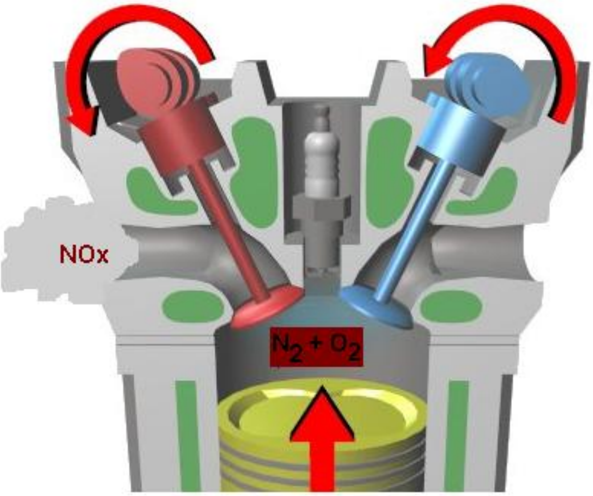


Fig 15. Nitric oxides emission [11]

Generally the largest amount of NO_x is produced during moderate to heavy load conditions when combustion pressures and temperatures are the highest. However, small amount of NO_x can also be produced during cruise and light load, light throttle operation. Common causes of excessive NOx include faulty of EGR (Exhaust Gases Recirculation) system operation, lean air/fuel mixture, high temperature intake air, overheated engine, excessive spark advance, etc [11].

The effect of A/F ratio on NOx emission is presented in figure 16.

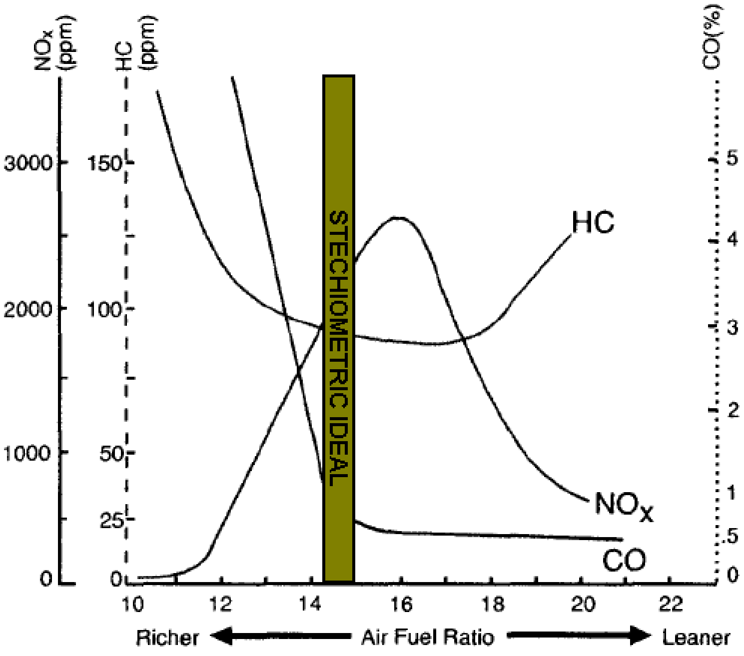


Fig 16. Effect of A/F Ratio on NO_x emission [11]

4.2.3 Sulfur oxides

The formation of Sulphur Oxides (SO_x) in exhaust gases is caused by the oxidation of the sulphur in the fuel into SO_2 and SO3 during the combustion process. The amount of SO_x formed is a function of the sulphur content of the fuel used and therefore the only effective method of reducing SO_x is by reducing the sulphur content of the fuel. Unfortunately, low-sulphur fuels are more expensive to purchase (10 to 20% greater cost, when switching from 3.5% to 1% sulphur) and there is a practical lower sulphur limit desired as desulphurisation of fuel lowers the lubricity of the fuel which can lead to increase wear on fuel pumps and injectors. The regulation of SO_x is predominately a regional issue, however, international pressure is growing for the oil producers to reduce the sulphur content of all fuels in order to control this problem at the source. The current EU Directive is that the sulphur content of fuels must remain below 0.2% with the aim of reducing this limit to 0.1% by the year 2008. Presently, most navies use 1% low-sulphur fuels. Special Areas have been set up, such as the Baltic, where the use of low sulphur fuels is mandatory [22].

If required, desulphurisation of diesel exhaust gases can be achieved by wet scrubbing. The flue gas is first passed through a quencher where it is cooled down to saturation temperature. The SO_x is subsequently washed out with a neutralising agent (calcium bound in lime-milk or seawater) in a scrubber. SO_x formed from diesel exhaust is corrosive and in part is neutralised by an engines lubricating oil which is typically base. In the atmosphere however, SO_x combines with moisture to form H_2SO_4, which then falls as acid rain, and has been linked to environmental damage [22].

4.2.4 Hydrocarbons

Hydrocarbons are elements of unburned fuel (in simple words). When combustion does not take place at all, as misfire, large amounts of hydrocarbons are emitted from the combustion chamber.

A process called wall **quenching** occurs as the combustion flame front burns to the relatively cool walls of the combustion chamber. This cooling extinguishes the flame before all of the fuel is fully burned, leaving a small amount of hydrocarbons to be pushed out the exhaust valve (fig 17).

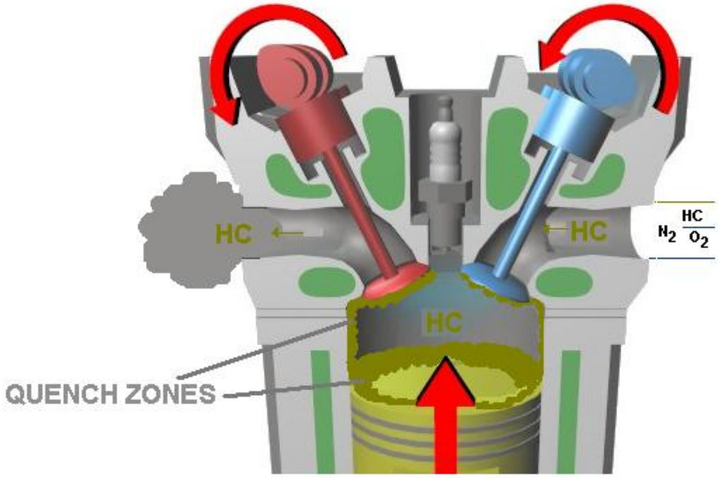


Fig 17. Hydrocarbons emission - quenching effect

Another cause of excessive hydrocarbons emission is related to combustion chamber deposits. Because these carbon deposits are porous, hydrocarbon is forced into these pores as the air/fuel mixture is compressed. When combustion takes place, this fuel does not burn, however , as a piston begins its exhaust stroke, these hydrocarbons are released into the exhaust steam [11].

The most common cause of the excessive hydrocarbons emission is misfire which occurs due to ignition, fuel delivery, or air induction problems. Depending on how severe the misfire, inadequate spark or noncombustible mixture (either too rich or too lean) will cause hydrocarbons to increase to varying degrees. For example a total misfire due to a shorted spark plug wire will cause hydrocarbons to increase dramatically. Conversely, a slight lean misfire due to a false air entering the engine, may cause hydrocarbons to increase only slightly [11].

Excess hydrocarbons can also be influenced by the temperature of the air/fuel mixture as it enters the combustion chamber. Excessively low intake air temperatures can cause poor mixing of fuel and air, resulting partial misfire (fig 18).

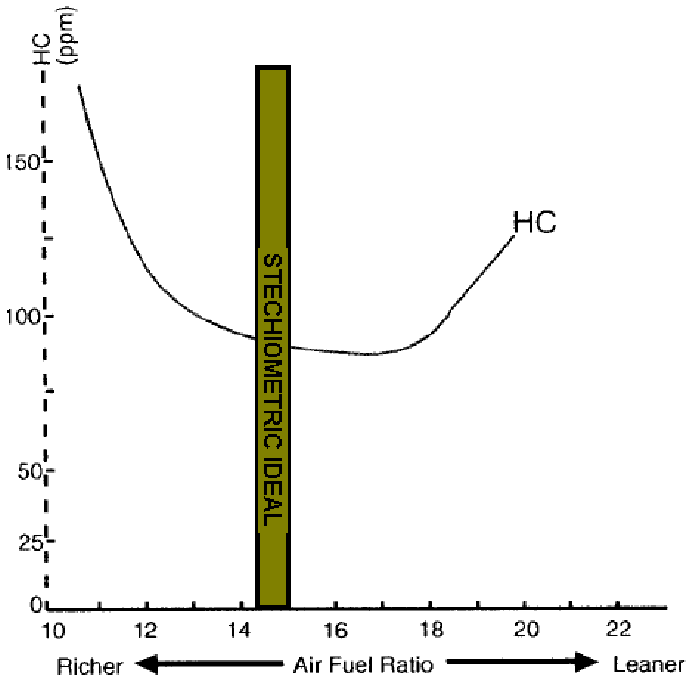


Fig 18. Hydrocarbons emission – impact of the air/fuel ratio [11]

As shown exhaust HC production is the lowest when air/fuel ratio is slightly leaner then stoichiometric, however HCs increases dramatically when the mixture becomes too rich or too lean to the point of misfire [11].

4.2.5 Particulate Matter (PM) and soot

Particulates, alternatively known to as particulate matter (PM) or fine particles and also called soot, are tiny subdivisions of solid matter suspended in a gas or liquid. In contrast, aerosol refers to particles and/or liquid droplets and the gas together [27].

Among the most common categorizations imposed on particulates are those with respect to size, referred to as fractions. As particles are often non-spherical (for example, asbestos fibers), there are many definitions of particle size. The most widely used definition is the aerodynamic diameter. A particle with an aerodynamic diameter of 10 micrometers moves in gas like a sphere of unit density (1 gram per cubic centimeter) with a diameter of 10 micrometers. PM diameters range from less than 10 nanometers to more than 10 micrometers. These dimensions represent the continuum from a few molecules up to the size where particles can no longer be carried by gas.

The notation PM_{10} is used to describe particles of 10 micrometers or less and $PM_{2.5}$ represents particles less than 2.5 micrometers in aerodynamic diameter [25].

But because no sampler is perfect in the sense that no particle larger than its cutoff diameter passes the inlet, all reference methods allow a high margin of error. These are also sometimes referred to with other equivalent numeric values. Everything below 100 nm, down to the size of individual molecules is classified as ultrafine particles (UFP or UP) [26].

The PM fractions and their size range is presented in table 4.

Tab. 4. Fraction of the particulate matter (PM)

Fraction	Size range
PM_{10} (thoracic fraction)	<=10 μm
$PM_{2.5}$ (respirable fraction)	<=2.5 μm
PM_1	<=1 μm
Ultrafine (UFP or UP)	<=0.1 μm

Particulate matter (PM), from the combustion engine measurements point of view, can be defined as total of all the solid and liquid, organic or inorganic mass, that accumulates on a filter with 99% efficiency, after the air thinned fumes pass through the inlet face 52 ^{0}C. The mass molecule form and size depends on the interception point.

The particulate matter emission is definitely higher in spontaneous ignition engines comparing to spark ignition ones, which results from the SI combustion process.

The composition and properties of the particulates varies greatly with engine design and is therefore difficult to define. The approximated PM composition of heavy-duty diesel engine is presented on figure 19.

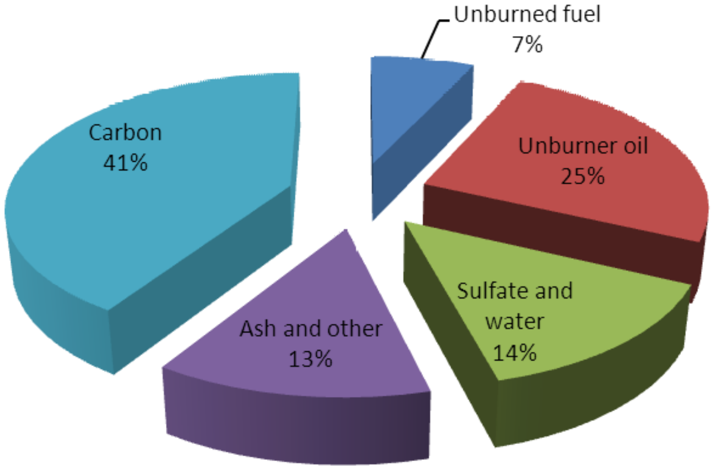


Fig 19. Approximated particulate matter composition of heavy-duty diesel engine [24]

Furthermore, there is not a quantitative relationship between the smoke opacity and the particulate emission. Particle emissions from diesel engines can originate from:

- agglomeration of very small particles of partly burned fuel;
- partly burned lubricant oil;
- ash content of fuel oil and cylinder lubricant oil; or
- sulphates and water.

The correlation between soot emission and the fuel composition shows tendency of soot forming as following [29]:

PARAFFINS[1] → MONOOLEFINS[2] → DIOLEFINS[3] → BENZENE → NAFTALENE

where:

[1] paraffin is a term that can be used synonymously with "alkane", indicating hydrocarbons with the general formula C_nH_{2n+2}.

[2] monoolefine is an unsaturated chemical compound containing one carbon-to-carbon double bond

[3] diolefine is an unsaturated chemical compound containing two carbon-to-carbon double bond

The mechanism of soot formation has been widely disused by scientists but in general the theory of HACA mechanism (H-abstraction/C_2H_2 addition sequences) is accepted. The simple scheme of for soot formation in homogeneous mixtures is presented in figure 20.

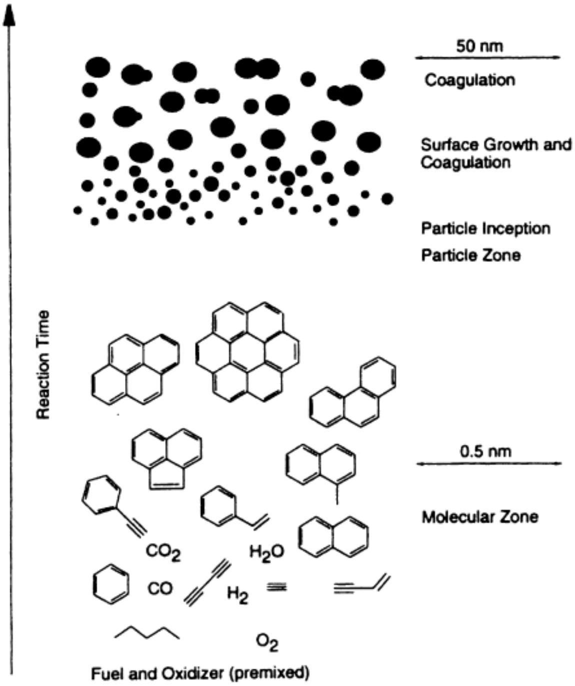


Fig. 20. A rough picture for soot formation in homogeneous mixtures (premixed flames) [14]

According to the several hypothesis of soot formation mechanism there are three main ones:

- nucleus formation,
- nucleus growth and soot molecule formation,
- molecules join into bigger units.

The typical forms of PM present in diesel exhausts are presented in figure 21.

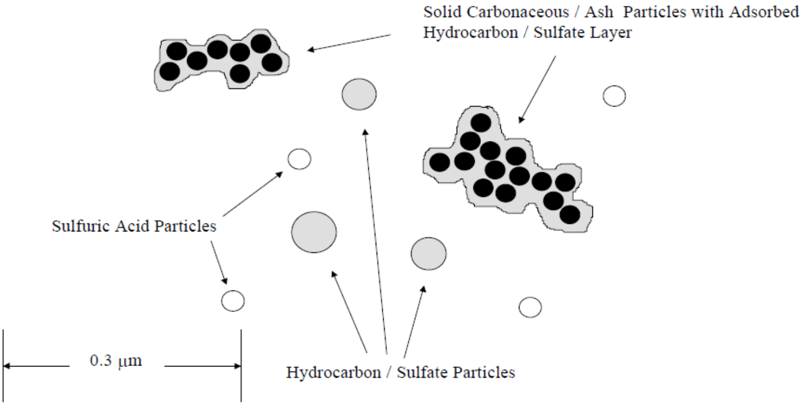


Fig 21. Forms of particulate matter (PM) in diesel engine exhausts [24]

The most hazardous for human health are nanoparticles (NPs). Because of their nano-size they can easily infiltrate to the human respiratory system and cause its serious damages. The formation and evolution of nanoparticles in the engine exhaust diluting in the atmosphere is shown in figure 22. The engine exhaust experiences two distinct dilution stages: (1) tailpipe-to-road and (2) road-to-ambient.

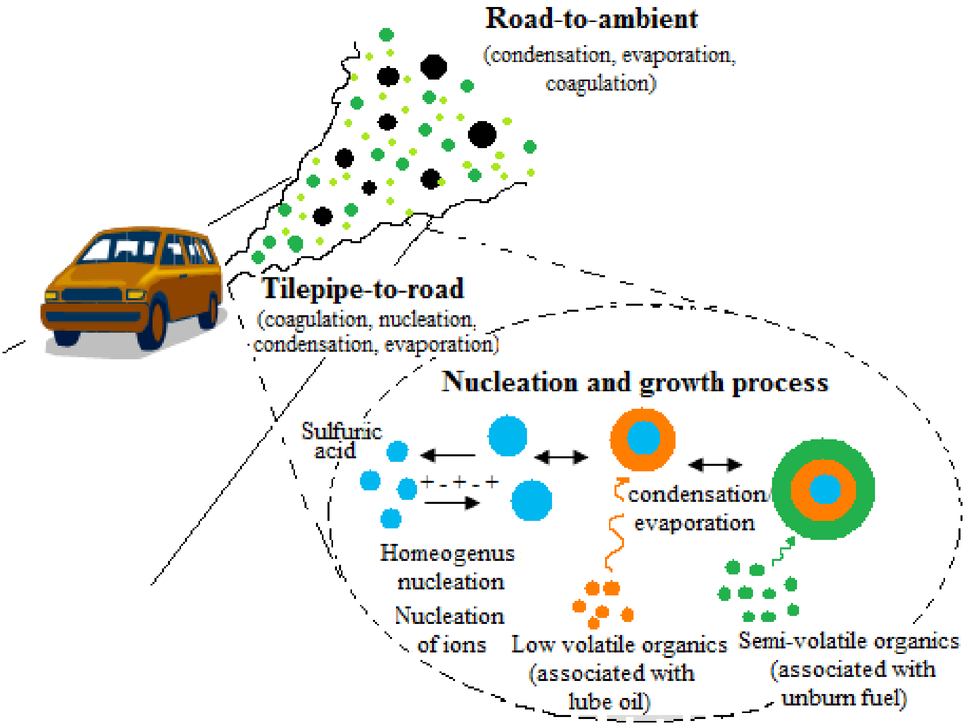


Fig. 22. Schematic illustration of the formation and evolution processes of engine-generated nanoparticles in the atmosphere [30]

In the first stage, tailpipe-to-road dilution, the exhaust is diluted by strong turbulence generated by moving traffic, and dilution ratio reaches around 1000 in 1-5 s. In the second stage, road-to-ambient dilution, the exhaust is further diluted by a factor of around 10 in 200-600 s by atmospheric turbulence induced by wind and atmospheric instability [30].

3.2.6. Summary

The main (typical) sources of toxic components emission from internal combustion engines are presented in table 6.

Table 5. Sources of toxic components emission from internal combustion engines [22]

Exhaust compound	Source
Carbon monoxide (CO)	Function of the air excess ratio and combustion temperature and air/fuel mixture.
Nitric oxides (NOx)	Function of peak combustion temperatures, oxygen content and residence time.
Sulfur dioxide (SO_2)	Function of fuel oil sulphur content
Hydrocarbons (HC)	Very engine dependent but a function of the amount of fuel and lubricant oil left unburned during combustion.
PM/soot	Originates from unburned fuel, ash content in fuel and lubricant oil.

4.3. Hydrocarbons in engine exhaust

Like all previously mentioned compounds, hydrocarbons are being created during the incomplete process of fuel oxidation. Until now scientists discovered over 200 but the actual number is estimated about 1000. Hydrocarbon formation is elevated by low temperature of cylinder walls and lack of oxygen. Those yield to reaction disturbances and blanking of the flame. After incomplete combustion, the unburned fuel leaves the engine through exhaust system. [2]

As shown in figure 23, hydrocarbons is a very wide family of chemicals on which comprise many different chemical compounds [23].

In terms of the toxic emission from internal combustion engines and its impact on the human health and environment two groups of substances are most important:

- Volatile Organic Compounds (VOC's),
- Polycyclic aromatic hydrocarbons (PAHs).

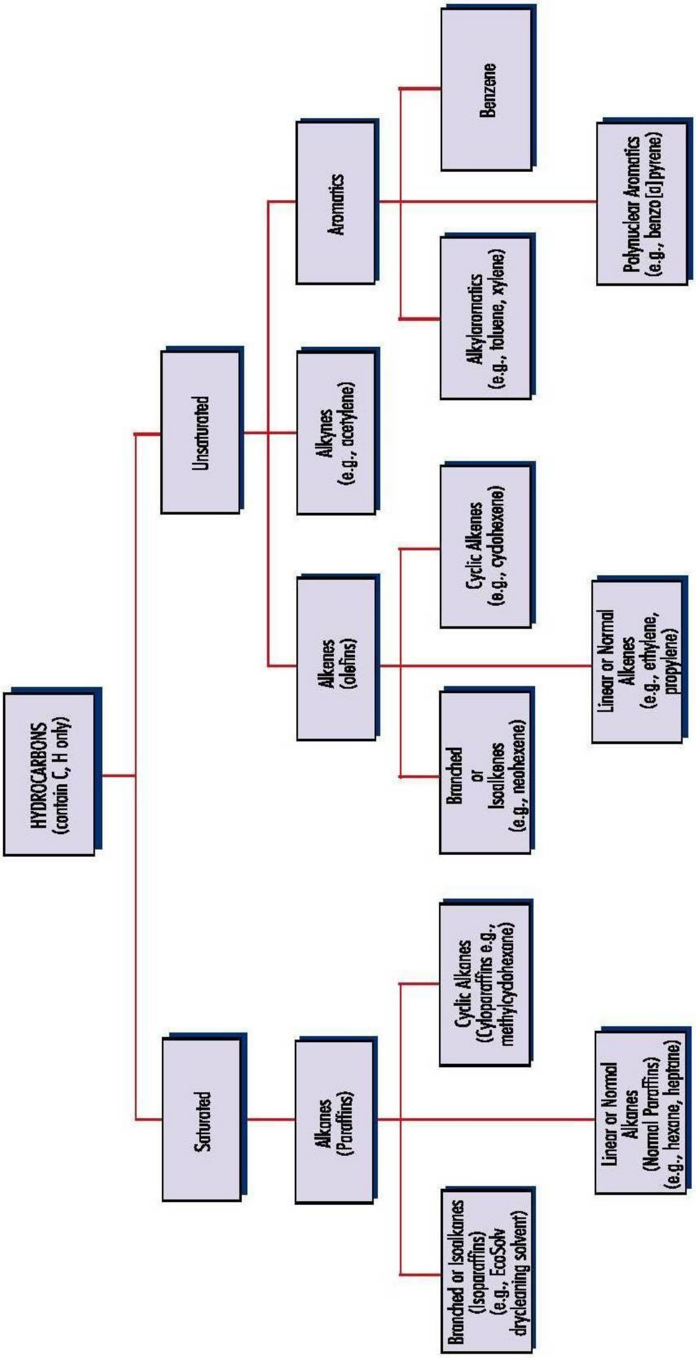


Fig. 23. Types of hydrocarbons [23]

4.3.1. Volatile organic compounds

Volatile organic compounds are significant group amid 200 identified compounds in diesel engine exhaust (mainly aldehydes but also alcohols, ketons, esters, paraffin and aromatic hydrocarbons). In the group of VOC's the most toxic and common in human environment are particularly: benzene, formaldehyde (methanal) and acrolein [9].

Volatile organic compounds (VOCs), which is often referred to as reactive organic gases (ROGs), play a major role in the formation of photochemical oxidants in the atmosphere. The reaction of VOC with ultraviolet energy from sunlight in the presence of NOx could produce ozone (O_3), a federal criteria pollutant as listed by the US Environmental Protection Agency (US EPA). Not all identified VOC are ROG, some are non-reactive hydrocarbons which may not significantly contribute to ozone formation. Most of the measured individual VOC are expressed as the sum of non-methane hydrocarbons, and these measurements do not give information on the photochemical reactivity of the hydrocarbon mixtures [15].

Several anthropogenic activities lead to volatile organic compounds emission into the atmosphere. One of the most important is motorization. VOC's emitted from combustion engines are very often hazardous compounds for human and environment [16]. In the atmosphere, VOC's contribute to tropospherical ozone formation, stratospheric ozone layer depletion and to the greenhouse effect [16]. Inside the human body these organic compositions are able to resolve in fat and to cumulate in tissues.

The volatile organic compounds (VOC’s) are significant group f air pollution emitted during fuel combustion in diesel engines. Because a fact that most of VOC’s are listed as being toxic a problem of reduction of their concentration in diesel engines exhausts is considered necessary to be solved. In atmosphere, because of ultraviolet radiation, VOC’s can be able to formation into secondary pollutions (photochemical reactions) [16].

In group of VOC’s the most toxic and common in human environment are particularly [16]:

- Benzene – the simplest organic compound in group of hydrocarbons. Because of its high volatile and commutation ability (in some conditions) in atmospheric air, benzene is one from the most toxic industrial poisons. It is known from its mutagenic and carcinogenic properties. Benzene is absorbed mainly from respiratory system and alimentary canal. Benzene and its metabolites (i.e. phenol) are able to fixate with liver proteins, bone marrow, kidney, blood, muscles and lien proteins. It causes devastation of nervous system and bone marrow (causes leukemia).
- Formaldehyde (methanal) – the simplest organic compound from aldehydes. It is formed during incomplete combustion of substances with contain carbon. In normal conditions formaldehyde is gas which has very characteristic, suffocating odour. It is known as toxic, hazardous and mutagenic substance.
- Acrolein – even in a low level of concentration in air causes eyes and respiratory system irritations. It is known as very hazardous even deadly, compound.

4.3.2. Polycyclic aromatic hydrocarbons

PAHs are a type of hydrocarbons which are produced during incomplete oxidation of all hydrocarbons except methane. Another source is any process of heavy heat treatment of organic compounds. Both processes are present in internal combustion engines which are ones of the main sources of worlds polycyclic aromatic hydrocarbons emission. The most harmful to environment are compression-ignition engines (diesel engines) due to highest emitted amount of PAHs. In a spark ignition engine injected fuel is compressed and at highest point of the piston a spark is induced between center and side electrodes. Thus electric spark is the beginning of fuel oxidation process. When the amount of oxygen inside combustion chamber is too low the process is called incomplete combustion. Detailed information about process of formation of Polycyclic aromatic hydrocarbons was not yet discovered. Scientists think that during the short period of time of combustion, organic radicals are formed. Next they merge into PAHs with small number of circles and after joining more radicals transform into more complex compounds. These particles have higher molar mass than typical hydrocarbons because they comprise of more carbon atoms. Carbon atoms form circles, which are surrounded by atoms of hydrogen. [30]

Polycyclic aromatic hydrocarbons formed in internal combustion engines can usually be found rather in soil or sediments than in water due to their lower volatile and water soluble properties. They are one of the most prevalent organic pollutants. Common feature is that PAHs rarely exist separately, usually they form groups. Their influence on human health and natural environment depends on the type of isomer of the hydrocarbon. Different kinds of particles with the same molecular structure affect other organisms in differently [31].

The subject of large number of books and articles around the world is how PAHs affect human health and natural environment. The reason is that these substances are highly generated in wide spectrum of industry and other human activities. From burning all kinds of fossil fuels for energy creation, through production lines of many goods, and ending with a simple barbeque. What is more Polycyclic aromatic hydrocarbons can reach inside of human body through [31]:

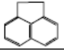
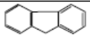
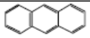
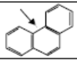
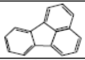
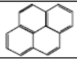
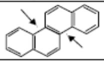
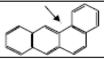
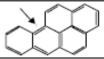
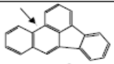
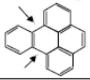
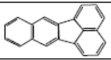
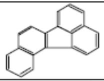
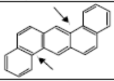
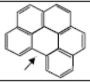
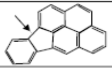
- inhalation exposure,
- oral exposure,
- dermal exposure.

When any of the mentioned above occurs it can cause damages to internal organs, multiple diseases and eventually even death. Those compounds are harmful in many ways, with regard to their chemical properties. PAHs can be divided into two groups: alternant and nonalternant. This division was formed basing on the electron density related to the molecule. Altenant compounds have an equally distributed electron density, while nonalternant PAHs seem to act like they were two separate molecules as a result of an uneven distribution of electron density from one dose of the molecule to another. The toxicological property of this dissimilarity is that either alternant and nonalternant PAHs appear to behave differently, for instance, from the point of view of the process of metabolism inside living organism which eventually transform them into carcinogens. Until now over 200 polycyclic aromatic hydrocarbons were discovered, but only 17 were proved to be a reason of deterioration of human health condition. Those toxic compounds are (tab. 6) [31]:

- Acenaphthene
- Acenaphthylene

- Anthracene
- Benz[a]anthracene
- Benzo[a]pyrene
- Benzo[e]pyrene
- Benzo[b]fluoranthene
- Benzo[g,h,i]perylene
- Benzo[j]fluoranthene
- Benzo[k]fluoranthene
- Chrysene
- Dibenz[a,h]anthracene
- Fluoranthene
- Fluorene
- Indeno[1,2,3-c,d]pyrene
- Phenanthrene
- Pyrene

Table 6. Construction and physical properties of carcinogenic PAHs [32]

No	Polycyclic aromatic hydrocarbon	Molecular formula	Structural formula	Molecular mass	Boiling point °C
1.	Acenaften	$C_{12}H_{10}$		154.2	96.2
2.	Acenaftylen	$C_{12}H_8$		154.2	265-275
3.	Fluoren	$C_{13}H_{10}$		166.2	295
4.	Antracen	$C_{14}H_{10}$		178.2	342
5.	Fenantren	$C_{14}H_{10}$		178.2	340
6.	Fluoranten	$C_{16}H_{10}$		202.3	375
7.	Piren	$C_{16}H_{10}$		202.3	404
8.	Chryzen	$C_{18}H_{12}$		228.3	448
9.	Benz(a)antracen	$C_{18}H_{12}$		228.3	437.5
10.	Benzo(a)piren	$C_{20}H_{12}$		252.3	310-312
11.	Benzo(b)fluoranten	$C_{20}H_{12}$		252.3	481.2
12.	Benzo(e)piren	$C_{20}H_{12}$		252.3	492.3
13.	Benzo(k)fluoranten	$C_{20}H_{12}$		252.3	480
14.	Benzo(j)fluoranten	$C_{20}H_{12}$		252.3	480
15.	Dibenz(a,h)antracen	$C_{22}H_{14}$		278.4	269-270
16.	Benzo(g,h,i)perylen	$C_{22}H_{12}$		276.3	500
17.	Indeno(1,2,3-cd)piren	$C_{22}H_{12}$		276.3	530

From mentioned 17 harmful to human organism polycyclic aromatic hydrocarbons the most dangerous is benzo[a]pyrene.

It has been included to the priority pollutant list Publisher by the U.S. Environmental Protection Agency (EPA). As any other PAH BaP is formed during incomplete combustion of crude oil derivatives, coal or organic matter. It can be found in smoke, water and soil which makes it very susceptible to absorption by human or other living organism [31].

Exposure to high concentrations of benzo[a]pyrene for even a short time may effect in red blood cell damage. This in turn is likely lead to anemia and failures of immune system. Tumors were observed to appear in laboratory animals organisms when fed with nourishment consisting of benzo[a]pyrene. Similar results were achieved after application of the chemical directly on the skin. Effects increased when skin covered by BaP reached contact with sunlight or ultraviolet light. Humans subjected to BaP in high concentration for long periods of time were found to develop cancer cells. In pregnant animals tested in relatively similar conditions sterility occurred as well as birth defects in their offspring and decreased body weight. Benzo[a]pyrene was also observed to affect skin and body fluids. Cases of injured digestion system, bladder and other internal organs damage were found. Repeated exposure can result in bronchitis and respiratory system cancer [31].

4.4. Toxicity estimation of exhaust gasses

4.4.1. Methods of exhaust gases toxicity estimation

The ability of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effect. As with other pollutants, the extent and nature of the health effect will depend on many factors including the level of exposure and length of time exposed. Eye and respiratory tract irritation, headaches, dizziness, visual disorders, and memory impairment are among the immediate symptoms that some people have experienced soon after exposure to some organics. Many organic compounds are known to cause cancer in animals; some are suspected of causing, or are known to cause, cancer in humans [17].

The methods of investigation of substance toxic activity can be general divided as [18]:

- estimation of substance toxicity based on relation between chemical structure of substance and its biological activity (new direction of toxicology science),
- investigation of substance toxicity based on tests on animals (the most popular method),
- alternative methods based on rule 3R (replacement, reduction, refinement) which aim is to eliminate or reduce of animal suffer.

Concentration toxicometry investigations are usually applied to determine safe for humans level of the substance (the quantitative assessment of toxicity and hazards of potentially toxic substances).Concentration limits of potential toxic substances have various applications. The most popular are [18]:

- Recommended Maximum Concentration Limit (RMCL) for air and workstand, averaged for various time periods,
- Allowable Daily Intake (ADI),
- Allowable Week Intake (AWI).

For toxicity estimation and analysis of the group of substances usually data for one representative and common compound occurring in environment are used (i.e. benzo(a)pirene for PAHs). The intensity of mutagenic, carcinogenic, irritant or sensitize activity of other compounds from the group is counted in relation to the representative compound. This method can be used to determin Relative Toxicity (mutagenic, carcinogenic, irritant or sensitize) Coefficient (RTC) for all substances from the group. RTC can be evaluated on the bases of empirical or modeling researches.

4.4.2. Estimation of VOCs toxicity

Volatile organic compounds (VOC's) effects on human health range from odour problems to toxic or carcinogenic effects. As a consequence, more stringent legislation on VOC emission has been implemented worldwide. To comply with this legislation, the use of processes which inherently cause little or no VOC's emission is preferable [17].

A motorization is one of the most important anthropogenic source of VOC’s emission. Combustion engines are responsible for benzene, formaldehyde or acriolein emission – those substances belong to VOC’s group and they are known from their mutagenic and carcinogenic properties. Because of the fact that most of volatile organic compounds are listed as being toxic not only a problem of their concentration in exhausts is considered necessary to be solved but also it is very important to monitor their toxic influence on human health. The second problem is very complicated and it strongly depends on the VOC’s group composition in emitted exhaust gases. Estimation of toxic influence of particular compounds in VOC’s group is also very problematic because for many substances their toxic properties are unknown. For some substances Recommended Maximum Concentration Limit (RMCL) is settled in governmental directives what constitute a base for VOC’s mixture toxicity estimation by using Toxicity Equivalent Factors (TEF) [17].

The most important group of substances from motorization source which are known to have mutagenic and carcinogenic effect on humans are polycyclic aromatic hydrocarbons (PAHs) (their main source are diesel engines).

4.4.3. Estimation of PAHs toxicity

The Relative Carcinogenic Coefficients (RCCs) for polycyclic aromatic hydrocarbons determined by different authors are shown in table 8.

Tab. 7. Relative Carcinogenic Coefficients (RCC) determined by difference authors [18]

No.	PAH	EPA (1984)	Chu i Chen (1984)	Clemens (1986)	Thorslund (1990)	**Nisbet and LaGoy (1992)**
1	Naftalene	0	n.d.*	n.d.*	n.d.*	**0,001**
2	Acenaphthalene	0	n.d.*	n.d.*	n.d.*	**0,001**
3	Acenaphthene	0	n.d.*	n.d.*	n.d.*	**0,001**
4	Fluorene	0	n.d.*	n.d.*	n.d.*	**0,001**
5	Fenantrene	0	n.d.*	n.d.*	n.d.*	**0,001**
6	Antracene	0	n.d.*	0,32	n.d.*	**0,010**
7	Fluoranthene	0	n.d.*	n.d.*	n.d.*	**0,001**
8	Piren	0	n.d.*	0,0810	n.d.*	**0,001**
9	Benzo(a)antracene	1	0,0130	0,1450	0,1450	**0,100**
10	Chryzene	1	0,0010	0,0044	0,0044	**0,010**
11	Benzo(j,b)fluoranthene	1	0,0800	0,1400	0,1200	**0,100**
12	Benzo(k)fluoranthene	1	0,0040	0,0660	0,0520	**0,100**
13	**Benzo(a)pirene**	**1**	**1**	**1**	**1**	**1**
14	Indeno(1,2,3-cd)pirene	1	0,0017	0,2320	0,2780	**0,1**
15	Dibenzo(a.h)antracene	1	0,6900	1,1000	1,1100	**1**
16	Benzo(ghi)perylene	0	n.d*	0,0220	0,0210	**0,010**
* n.d. – no data						

In recent researches [18, 19, 20, 21] on PAHs RCC determined mainly by Nisbet and LaGoy with modeling method based on toxicology experiments were used.

Samples consisting of hydrocarbons extracted from the exhaust gases can be put into in-vitro toxicity tests. The testes for cytotoxicity are carried out in standardized cell-culture system (i.e. human lung cell line) in special assay tests. Cell growth, cell morphology and cell viability are used as parameters to determine the cytotoxicity of the hydrocarbons from diesel engine exhausts.

Samples of the tested samples contain hydrocarbons from the exhausts are added to prepared cells, which are then incubated usually for 24h, 48h. The cytotoxicity are often defined as the highest dilution of a test samples that causes 50% or greater destruction of cells. The example of the visible result of the test in vitro (polycyclic hydrocarbons from the engine exhaust estimation) are presented in figure 24.

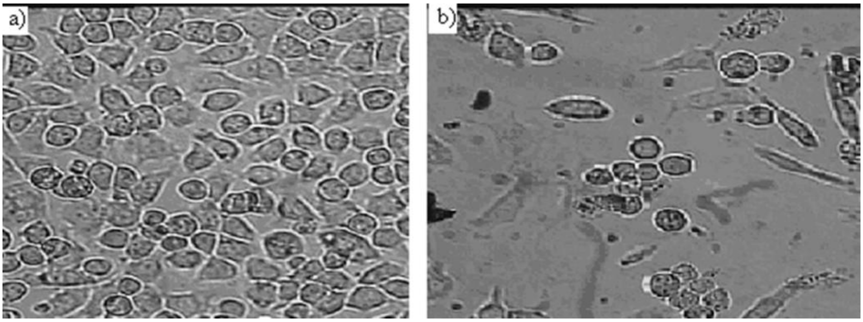


Fig 24. The example of the visible result of the test in vitro: a) human lung cells: control sample, b) human lung cells: sample after contact with aromatic hydrocarbons extracted from exhaust gases

4.5. Methods of chemical compounds marking in the exhausts

The fumes composition analysis can be carried out using chemical or physical methods. The devises designed to analyze fumes composition are usually built as multifunctional, in practice the mostly commonly used are analyzers based on the following types of methods [33]:

- Non-Dispersive Infrared Analyzers (NDIR),
- Flame Ionization Detector (FID),
- Chemiluminescent Detector (CLD),
- Chromatographic Methods: gas chromatography (GC) and liquid chromatography (LC).

4.5.1 Non-Dispersive Infrared Analyzers (NDIR)

The method is a referential method to measure the CO, CO_2, NO, HC, O_2 content in fumes. NDIR uses a spectrometric method, consisting in measuring the total radiation absorption in quite narrowly ranged wave length, specific for a particular compound, using a photometer [36].

Gas and vapour molecules, comprised of different atoms, like CO_2, NO, SO_2, O_2, and some hydrogens (eg. methane CH_3) are characterized by a constant or induced dipole moment. Those molecules, exposed to an electromagnetic radiation of certain frequency, may develop valence or deformation vibrations, absorbing some of the radiation energy at the same time. That absorbed radiation energy causes the tested gas temperature to increase. The temperature or resulting pressure increase may be used to assess the amount of absorbed energy and, at the same time, the density of that particular gas. The described method is called the Non-dispersive Method. NDIR structure is shown in figure 25 .

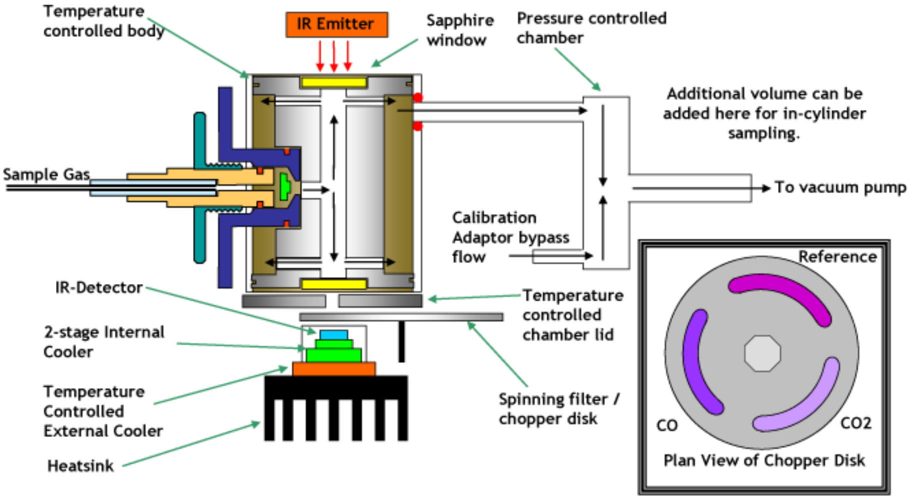


Fig. 25. Non-dispersive infrared analyzer structure [35]

The radiation source is an electric filament, behind which there are narrowband optical filters, letting through only specified wavelength radiation. Those filters are prepared from specially prepared glass. As a replacement a glass tray can be used, filled with adequately selected gases. There are also sets of glass-gas filters used. The selected wavelength radiation beams (specific for the analyzed gas) go through two trays, one goes through a comparative tray, filled with gas that does not absorb present radiation (most frequently it is nitrogen or argon), and the other goes through a measuring tray, conveying the analyzed gas with a constant speed. In the latter one, part of the stream gets absorbed by the analyzed gas. Next, the radiation of both streams gets absorbed by gas (similar to the tested one) that fills up the detector chambers. Those are separated by an elastic diaphragm, which also serves as a movable cover inside the condenser. The amount of energy absorbed inside both of the chambers equals only when the measuring tray does not contain the determined gas [36].

4.5.2. Flame Ionization Detector (FID)

The method is a referential to measure the total number of hydrocarbon compounds (HC) and methane (CH_4) in fumes and air. FID analyzer works by ionizing flames (resistance change between cold and warm electrodes) which is proportional to the number of carbon atoms added within a certain unit of time. To calculate the total amount of all hydrocarbons found in fumes (esp. in compression-ignition engines) it is recommended to use analyzers that heat up the gas in the system up to 180-200^{0}C. Flame ionization detectors are used to determine the total amount of HC, often called THC (Total Hydrocarbons), and methane (CH_4) in fumes and air. FID analyzers ionize the hydro-oxygen flame by introducing hydrocarbon atoms into it [36].

The ionization, not caused by carbon-oxygen compounds (CO and CO_2 do not affect the process), is proportional to the number of carbon atoms, added to the flame within a certain unit of time. The analyzed gas, containing hydrogen at specific flow intensity (3-5 ml/min), goes into the flame-ionization chamber, in which there is a hydroxyl blowpipe 3 (fig. 26), powered by hydrogen and air.

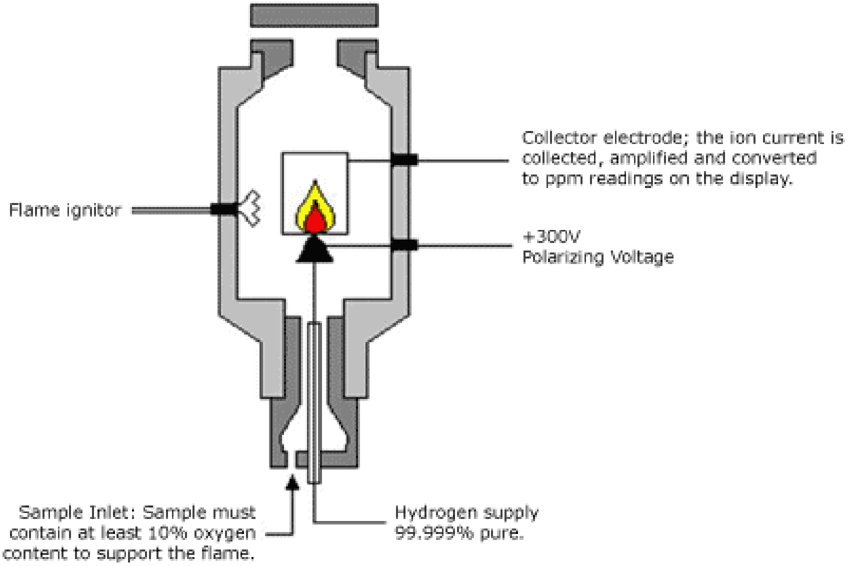


Fig. 26. Flame Ionization Detectors structure [37]

Burning hydrogen does not cause ionization but burning hydrocarbon causes the flame ionization, which changes the electric circuit conductivity. A fuse consists of two electrodes located inside the flame ionizing chamber: cold 4 and hot 5. The electric signal from the electrodes 4 and 5 gets amplified in the converter 7, goes into the gauge calibrated to show the total hydrogen density per specified compound (the same number of carbon atoms C), most frequently propane C_3H_8 (when, eg. 100 ppm C_3H_8 = 300 ppm C) or hexane C_6H_4 (called n-hexane), used in FID calibration [36].

In practice, the tested gas may not even contain any of propane or hexane. . To calculate the total amount of all hydrocarbons found in fumes (esp. in compression-ignition engines) it is recommended to use analyzers that heat up the gas in the system up to 180-200^{0}C (so called H-FID = Heated FID).

All the analyzer internal leads and valves, the whole fume exit shaft from the engine have to be heated up, otherwise the heavy hydrocarbons will condense inside the leads and will not reach the analyzer. To make the measurement as accurate as possible it is vital to use clean air and hydrogen. Analyzer sensitivity can be around 0,1 ppm [36].

4.5.3. Chemiluminescence Detector (CLD)

The method is a referential to measure the total NO and NO_2 concentration in exhaust gas. CLD uses the electromagnetic radiation emission which is a result of nitric oxide (NO) reacting with ozone (O_3) – generated by an ozone generator. This reaction is possible only in the environment close to the absolute vacuum, generated by a vacuum pomp. To calculate the number of NO_2, that is neutral to O_3, NO_2 is broken down into NO and O_2 using a thermal convector at 650^0C. The thermal convector can also be used to calculate the number of NOx as per NO. Figure 27 shows the CLD structure [36].

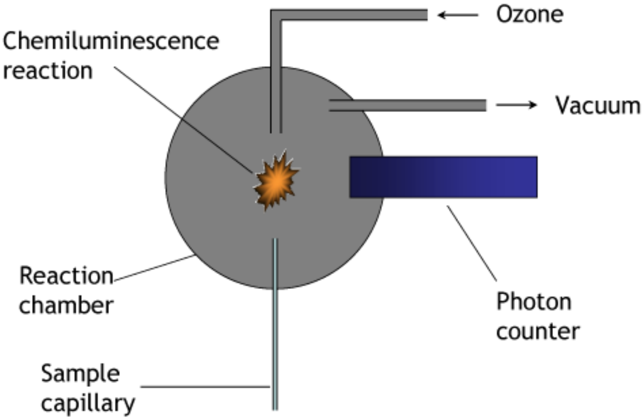


Fig. 27. Chemiluminescence Detector (CLD) Structure [38]

A vacuum pomp keeps the absolute pressure at a low level inside the reactor. The tested gas and ozone O3, produced in the generator - the vital part of the whole device, are connected to that reactor at a constant, very low flow intensity. In such environment NO and O3 atoms react

$$NO + O_3 \text{->} NO_2 + O_2 + h\nu$$

combined with electromagnetic radiation emission hv. Using the photomultiplier that emission is converted into electric signal, which, amplified, is directed to the gauge or logger. Keeping the temperature and flow at a constant level results in the radiation intensity being linearly dependant on nitric oxide concentration. Another part of CLD is the thermal convector, which, by heating up the tested gas to 650 °C decomposes NO_2 as follows

$$2NO_2 \text{->} 2NO + O_2$$

The converter is positioned parallel to the shaft that brings fumes directly to the CLD. That is how the NO and NO_2 concentration in fumes is measured.

Chemiluminescent method is very precise and allows to identify even trace concentration, despite other fumes components.

4.5.4. Chromatographic Methods

Chromatography is the only method which allows to educe individual hydrocarbons from the exhaust gas. In each of the chromatographic techniques the first step is to separate the tested mixture, next, all the individual components are detected. As all chromatographic separations are carried out using a mobile and a stationary phase, the primary classification of chromatography is based on the physical nature of the mobile phase. The mobile phase can be a gas or a liquid which gives rise to the two basic forms of chromatography, namely, gas chromatography (GC) and liquid chromatography (LC). The classification of chromatographic methods is presented in table 9 [36].

Table 8. Chromatographic methods classification

MOBILE PHASE	GAS PHASE
GAS **Gas chromatography (GC)**	**LIQUID** Gas-liquid chromatography (**GLC**)
	SOLID Gas-solid chromatography (**GSC**)
LIQUID **Liquid chromatography (LC)**	**LIQUID** Liquid-liquid chromatography (**LLC**)
	SOLID Liquid-solid chromatography (**LSC**)

The equipment for chromatographic analysis is chromatograph. It is constructed from [36]:

- Sample injection system,
- Column,
- Mobile phase dozers system,
- Detector (i.e. FID, CLD or other),

- Data acquisition system (PC).

A scheme of the gas chromatogram example is shown in a figure 28.

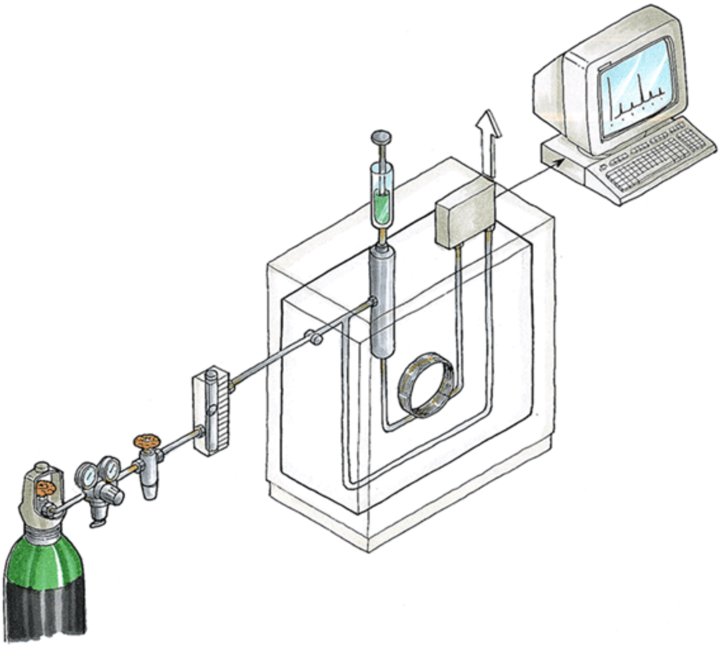


Fig. 28. Gas chromatograph construction [39]

Mixture separation is done by passing the tested mixture solution through specially prepared stationary phase. The stationary phase consists of sorptive substances and substances differently affecting flowing substances. When the eluent passes through the stationary phase, all the adsorbed substances get eluted and some of the components stay in the phase longer and some shorter (fig. 29). That leads to their separation. The time during which the component remain in the phase is called retention time.

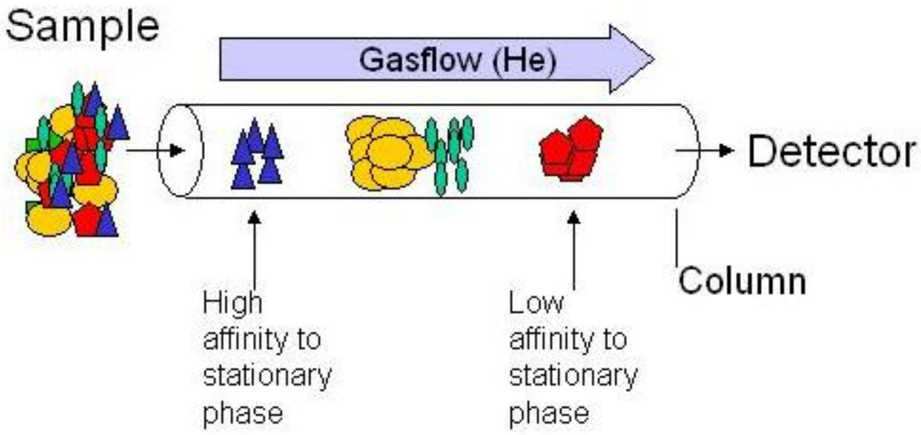


Fig 29. Principle of the chromatographic analysis [40]

The chromatographic method is a comparative method and therefore, for individual spike identification and specific compound concentration determination, it is necessary to introduce a formula for every researched compound with the known concentration (ideally of similar value to the defined compound), to determine the **retention time** and the spike **area or height** which depend on the detection signal strength (determining the constant of proportionality for concentration and area) in the same chromatographic separation conditions. To avoid any mistakes, if the spikes appear close to one another on the chromatograph, the internal standard method is applied to calibrate it by introducing the defined compound formula into the tested sample. As a result the researched compound spikes distinctively and that allows a definite identification. An exemplary of chromatograph (the chromatographic analysis results) is shown in figure 30 [36].

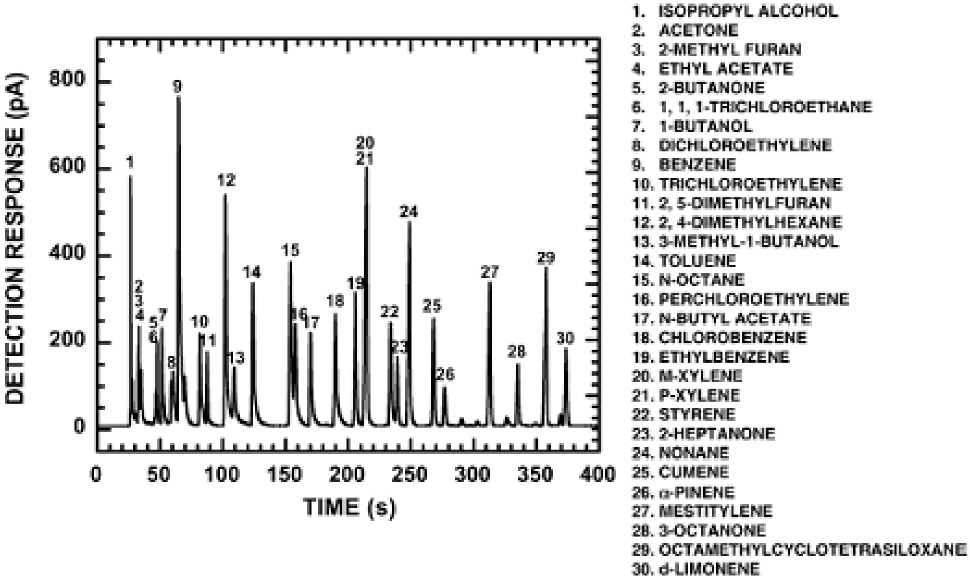


Fig. 30. Result of gas chromatographic analysis: chromatogram – example [41]

4.6. The methods of the combustion engine toxic emissions reduction

4.6.1. Classification of the exhaust compounds reduction methods

When the number of motor vehicles on the roads is rising, the only way to reduce the amount of emitted pollutants is to improve vehicles power train and exhaust system. Improvement methods can be divided into three groups:

- Limit the toxic substances formation,
- Increase of total efficiency of the engine,
- Exhaust gas purification.

Generally the methods of pollution reduction form ICE can be divided into pre-treatment (before combustion), primary (impact during the combustion process) and secondary (after-treatment). Simplified scheme of the emission reduction is presented on figure 31.

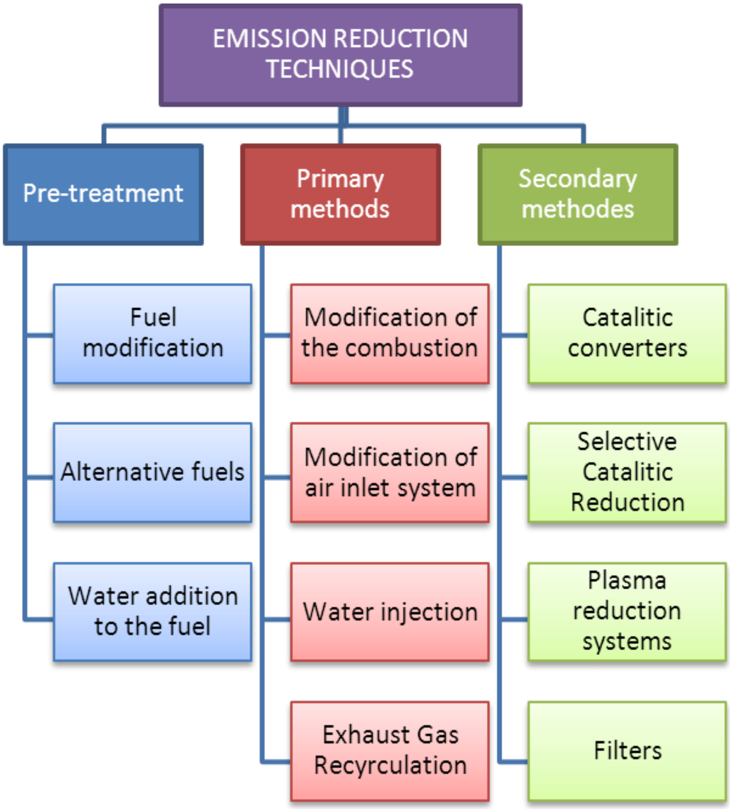


Fig 31. Simplified scheme of the emission reduction methods

In the figure 32 the methods of the particular exhausts gases compounds are presented.

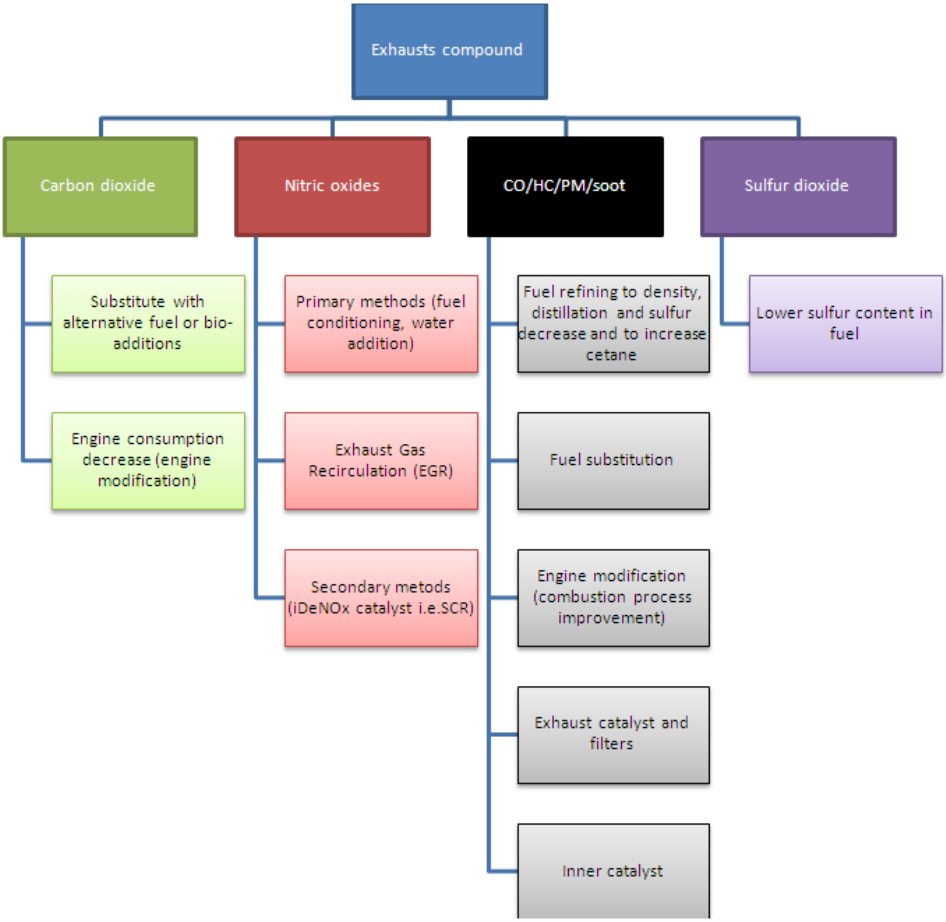


Fig. 32. Methods of the engine egxaust gasses harmful emission reduction

Catalysis is the process in which the rate of a chemical reaction is either increased or decreased by means of a chemical substance known as a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself. The catalyst may participate in multiple chemical transformations. The general feature of catalysis is that the catalytic reaction has a lower rate-limiting free energy change (lower activation energy, Ea, of the reaction) to the transition state than the corresponding uncatalyzed reaction, resulting in a larger reaction rate at the same temperature (fig. 33) [42].

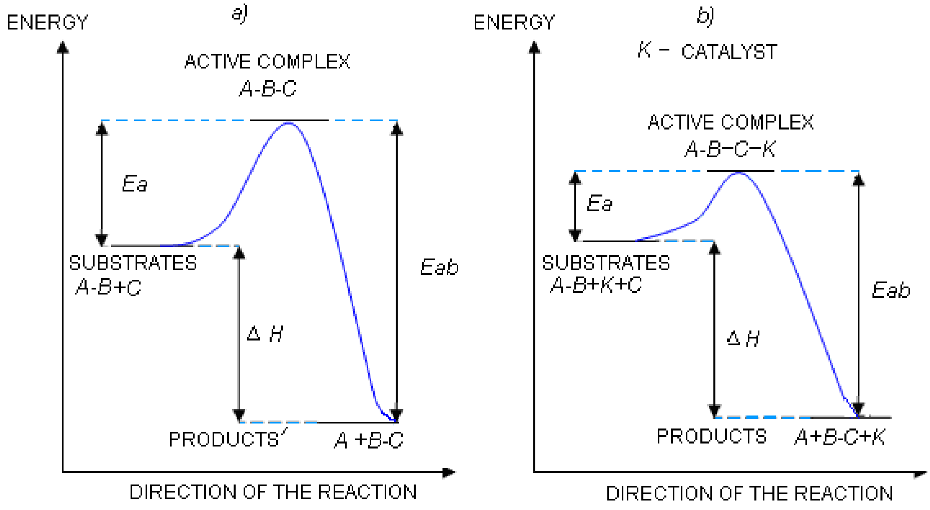


Fig 33. The reaction proceeding a) without a catalyst, b) with a catalyst

Catalysts work by providing an (alternative) mechanism involving a different transition state and lower activation energy. Consequently, more molecular collisions have the energy needed to reach the transition state. Hence, catalysts can enable reactions that would otherwise be blocked or slowed by a kinetic barrier. The catalyst may increase reaction rate or selectivity, or enable the reaction at lower temperatures [33].

Catalysts do not change the extent of a reaction: they have no effect on the chemical equilibrium of a reaction because the rate of both the forward and the reverse reaction are both affected (see also thermodynamics). The fact that a catalyst does not change the equilibrium is a consequence of the second law of thermodynamics. Suppose there was such a catalyst that shifted an equilibrium. Introducing the catalyst to the system would result in reaction to move to the new equilibrium, producing energy.

Catalysts can be either heterogeneous or homogeneous, depending on whether a catalyst exists in the same phase as the substrate. Heterogeneous catalysts are those which act in a different phases than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. Homogeneous catalysts function in the same phase as the reactants, but the mechanistic principles invoked in heterogeneous catalysis are generally applicable. Typically homogeneous catalysts are dissolved in a solvent with the substrates [16].

A catalytic processes are very useful for improving combustion reactions (oxidation processes) like fuel combustion in combustion engines.

A catalytic converter is commonly used to eliminate the harmful, toxic exhaust gas compounds such as carbon monoxide (CO), nitric oxide (NOx) and hydrocarbon (HC). A catalytic converter is the key to all the standard requirements allowing vehicles and machines with combustion engines on the roads [33].

Catalytic converters were first used in the 70's and the dynamic electronic fuel injection system development encouraged widespread use in cars with spark ignition engines.

There are a few types of catalytic neutralisers that can work with a combustion engine:

- oxidation converters,
- reduction converters;
- three-way converters: reduction – oxidation.

Oxidation converters cause the oxidation of carbon monoxide (CO) and hydrocarbons (H_nC_m) [33]:

$$2\,CO + O_2 \rightarrow 2\,CO_2$$

$$H_nC_m + (m + n/4)\,O_2 \rightarrow m\,CO_2 + (n/2)\,H_2O$$

These reactions occur when there is oxygen in the fumes, which characterizes the air-fuel mixture with $\lambda > 1$ and λ is the excess air factor.

With engines working on rich mixture with $\lambda < 1$, extra air needs to be connected up to the converter. Oxidation converters usually do not influence the NOx concentration in fumes.

The second type are reduction converters. They reduce nitrogen oxides (2NO),present in fumes, to free nitrogen (N). The reduction factor is carbon monoxide (CO).

$$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2$$

There should be no oxygen in fumes for the reduction reactions to occur, so the engine should be running on the rich mixture ($\lambda < 1$).

The third type is reduction - oxidation converters, so called three-way converters.

Using reduction - oxidation converters, which, based on just one catalyst bed, allow the oxidation reaction on both hydrocarbon and carbon monoxide with the reduction reaction on nitrogen oxides at the same time, became possible only by installing in a spark ignition engine an electronic fuel injection (EFI). EFI controls the fuel mixture using signals from a lambda sensor, which measures the oxygen concentration in fuel. This system keeps the air-fuel mixture in the entire engine as close to the stoichiometric ratio as possible ($\lambda = 1$). Stoichiometric mixture fumes composition allows to remove the pollutants with one process, without dividing the converter into reduction and oxidation part and without connecting up extra oxygen source. The essential element of a catalytic exhaust gas purification system is a ceramic or metal monolithic carrier, which has an active agent layer. The construction of the monolithic carrier provides possibly the biggest extended surface per volume. In cross-section it resembles a honeycomb.

The carrier should have good mechanical qualities as well as be resistant to thermal shock. The body perfect plastic qualities allow to print monolith with the wall thickness of app. 0,15mm, or even bellow 0,1 mm.

Metal carriers in converters are made of rolled corrugated steel foil, app. 0,05 mm. thick. It is welded, which prevents the carrier from exhaust gas damage. On the metal carrier surface there is also a transitional ceramic layer and active catalyst phase, similar to the ceramic carriers.

Under the active metals layer on the monolith surface, there is a transitional aluminium oxide (Al_2O_3) layer which contains catalyst effect intensifying substances. The transitional layer has a highly developed internal surface (100 cm^2/cm^3) which, once the active metals are on it, gives monolith with very good catalytic qualities. Most often used converters are the ones with the active phase containing well-proportioned platinum, palladium and rhodium mixture. Compounds of copper, manganese, nickel and others are also used. The active phase composition depends on the converter type.

To build a converter suitable for engine exhaust system installation, a carrier with the active catalyst layer is placed in a stainless steal converter (fig.34.) [33]

The converter shape has to not only allow for the monolith shape but also take into account the space given by the underbody structure, as well as proper exhaust gas direction towards the frontal monolith surface. The circular sectioned monoliths are perfect for this purpose.

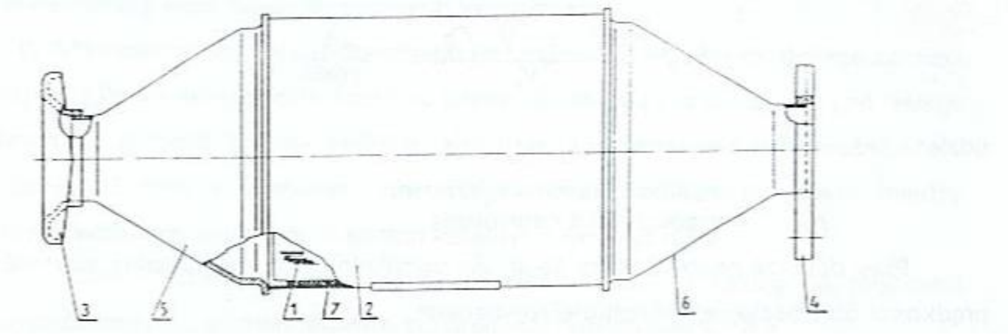


Fig.34. The catalytic converter structure: 1-ceramic monolith, 2- casing/shell, 3-inlet flange, 4-outlet flange, 5-inlet cone, 6-outlet cone, 7-ceramic layer

Using the ceramic monolith, it is important not to put it directly in the metal converter casing, as the vibrations will lead to its destruction. To avoid that, monolith gets wrapped into a special heat-resistant mat, which protects it from any damage.

The catalytic exhaust gas purification system efficiency depends on:

- temperature,
- time during which exhaust gas was in contact with the converter surface,
- toxic ingredients concentration in the exhaust gas.

Because the catalyst bed temperature is difficult to determine, the fumes temperature inside the converter is measured, considering how thin the carrier walls are (sometimes, depending on the type, app. 0,05 ÷ 0,15 mm), in the set testing conditions the temperature disparity between the flowing flumes and the catalyst bed is small.

The time during which exhaust gas was in contact with the converter surface depends on cubical speed, therefore mainly on engine speed.

The toxic component concentration in fumes mainly depends on engine parameters, like the engine load or engine speed.

The converter efficiency evaluation is done by calculating the change course for the carbon monoxide (CO), nitric oxide (NOx) and hydrocarbon (HC) conversion, in order to calculate the engine load and engine speed.

To establish the conversion level for the fumes toxic components, the toxic substances concentration is tested in front of and behind the converter, and after that the individual conversion levels are calculated accordingly [33]:

$$\boldsymbol{\eta = (C_p - C_z)/ C_p}$$

given: η – conversion level (converter efficiency), C_p – particular component concentration in front of the system, C_z – particular component concentration behind the system.

After combustion of fuel in diesel engines the content of exhaust gas is relatively rich in NO_x. Selective Catalytic Reduction is the most effective method of reduction of the post combustion toxic pollutant. It is mounted after catalytic converter in exhaust system of a diesel fueled internal combustion engine. Its task is to utilize a chemical reaction which yields to conversion of NO_x in exhaust gas into nitrogen and water. [43]

When exhaust gas leaves the cylinder through exhaust manifold, it usually still consists of some toxic ingredients. Catalyst is a device that is used for reducing the engine emissions so they match demanded emission standards forced in the region of destination. This process must proceed without drastically influencing engines performance and fuel economy. This refers to toxic compounds such as HC, CO and NO_x, although NO_x is the one that especially depends on the catalytic converter in case of fulfilling the emission standards. There were two main types of catalytic converters [43]:

- Two-way Catalytic Converter,
- Three-way Catalytic Converter (TWC).

Inside every catalytic converter there is a chemical substance called catalyst. It is not subject to transformation during chemical reaction but it significantly influences the process. This takes place as a result of changing the level of the free activation energy of chemical reaction. There are two main types of catalysts [44]:

- „Positive” catalyst,
- „Negative” catalyst (inhibitor).

Due to the presence of the positive the pace of chemical reaction elevates, while usage of the negative catalyst slows the reaction down. During the chemical process the catalyst creates a temporary compounds which break apart after the reaction finishes. Process of catalysis using constant porous catalysts consists of following stages [19, 57]:

- Leading reagents from the inside of gaseous stream,
- Reagent diffusion in pores of catalytic grains,
- Reagent adsorption on the surface of the catalyst,
- Chemical reaction on the surface of the catalyst,
- Desorption of the products of chemical reaction with the catalyst surface,
- Products diffusion in pores of catalytic grains,
- Drainage of the reaction products to the gaseous stream.

Two-way Catalytic Converter (fig. 35.) is a commonly used device in spark ignition engines until 1981 when a Three Way Catalytic Converter was elaborated. Its task is to oxidize carbon monoxide and hydrocarbons, but it is unable to remove NO_x from exhaust gas due to lack of reductive material. Nowadays it is still applied to vehicles powered by diesel motors.

Fig. 35. Two way Catalytic Converter [45]

Reduction catalysts are not used in case of compression-ignition engines because the oxygen contained in the exhaust gas would react with the catalyst before nitrogen oxides. Problem of the presence of NO_x in exhaust gas is coped with other systems, for example EGR (Exhaust Gas Recirculation) Two oxidation reactions take place during operation of a Two Way Catalytic Converter [46]:

Oxidation reaction of carbon monoxide:

$$2CO + O_2 \rightarrow 2CO_2$$

Oxidation reaction of hydrocarbons:

$$C_xH_2x + 2 + [(3x+1)/2]\ O_2 \rightarrow xCO_2 + (x+1)\ H_2O$$

Three-way Catalytic Converter (Fig. 21.) introduced in 1981 solved this problem. Inside there is an insert coated with a substance called catalyst. Those can be divided into two groups [46]:

- Reduction catalysts,
- Oxidation catalysts.

Reduction catalysts divide NO_x into separate particles of O_2 and N_2. Oxidation catalysts elicit an oxidation reaction of HC and CO with oxygen that are left after fuel combustion into $CO_2 + H_2O$ [43].

Construction of Three-way Catalytic Converter

There are two types of catalytic converter structure. Older devices were built of tightly packet pellets coated with certain active elements. Pellets consist of porous cavities approximately 3 mm in diameter. Every single pellet has maximum of 10 mm^2 of internal surface area. The total internal surface are of one dm^3 of pellets can equal even 500,000 m^2. Pellets are usually made of alumina (aluminum oxide, Al_2O_3). By applying a careful oxidation of organic additives and also incomplete sintering, the grand internal porosity is achieved [48]. The scheme of the TWC construction is presented in figure 36.

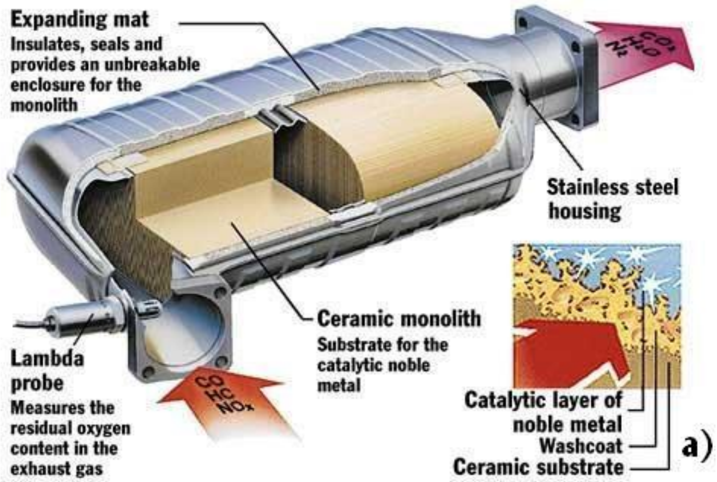


Fig. 36. TWC construction [47]

More advanced models of catalytic converters comprise of honeycomb structured inserts. Honeycomb monoliths contain 1,000 to 2,000 longitudinal pores not bigger than one mm. Each pore surrounded by very thin wall. The material is usually a magnesium aluminosilicate ($Mg_2Al_4Si_5O_{18}$) called cordierite. One of its essential properties is low thermal expansion. The honeycomb structure is coated with a wash of alumina, which imbeds the platinum particles. Pellet inserts are much cheaper than monolith type, however they create higher pressure drop along exhaust system. They are also less effective because of their much smaller internal surface area. Unfortunately both structures are sensitive to vibrations due to their friability. Both devices need a precise sealing, which moreover will not create any external stresses [48].

Several heavy elements are used as catalytic coating of ceramic inserts. Among them are [43,48]

- Platinum,
- Palladium,

- Rhodium,
- Ruthenium,
- Cerium,
- Manganese oxide,
- Chromium oxide,
- Copper oxide,
- Rhenium,
- Silver,
- Osmium,
- Iridium,
- Gold.

The most efficient element used as reduction catalyst is rhodium. To perform toxic ingredients oxidation usually platinum and palladium are applied [49].

Operation of Three Way Catalytic Converter

As exhaust gas reaches the catalytic converter, it flows through pores of the insert. The gas becomes in contact with active layer of catalyst and involves into chemical reaction, either oxidation or reduction. Certain temperature is a starting impulse of the following reactions [48].

Oxidation reaction of hydrocarbons:

$$HC + O_2 \rightarrow CO_2 + H_2O$$

Oxidation reaction of carbon monoxide:

$$2CO + O_2 \rightarrow 2CO_2$$

Reduction reaction of nitrogen:

$$2NO \rightarrow N_2 + O_2$$

There are two factors which significantly influence the converters efficiency: feed gas composition and operating temperature. When the temperature reaches 280°C the chemical processes start and after exceeding 400°C, operation approaches its nominal efficiency. For both chemical processes to occur certain amount of oxygen in exhaust gas must be present. Oxidation reaction takes place only if enough of free O_2 has left. Whereas reduction process occurs merely in absence or with presence of very low amount of free oxygen. Therefore both processes can not occur simultaneously at their highest efficiency. A roper mixture is necessary for optimal operation of catalytic converter. The efficiency of reduction is satisfactory when the oxygen part in exhaust gas is low. To fulfill this criterion there is a need for rich fuel-air mixture. On the other hand for undisturbed run of oxidation process, there appears a demand for high oxygen content. This is possible only with delivery of lean mixture. Three way catalysts contain cerium which has an ability of oxygen storage. When needed, oxygen is released and complements content of this element in exhaust gas [43].

Converting NOx from the engine to nitrogen requires a chemical reduction. Diesel exhaust is an oxidising, not a reducing, environment. The SCR method utilises the fact that NOx can be converted with ammonia into nitrogen and water in a catalyst. Currently, the most critical problems inherent with this method are the toxicity of the reagent in a marine environment, the investment and operational costs, and the space and weight problems of implementing this solution. However, the reward is up to a 95% reduction in NOx. This is the area that is presently receiving an enormous amount of research in order to make this method as practical in all respects as possible and to minimise the amount of ammonia slip experienced during transient responses.

Superimposing the numerous primary methods available will not have a significant effect on the total amount of NOx, which can be eliminated from the exhaust, and doing so will lead to a significant engine cost increase.

A scheme of Selective Catalytic Reduction system is shown in figure 37.

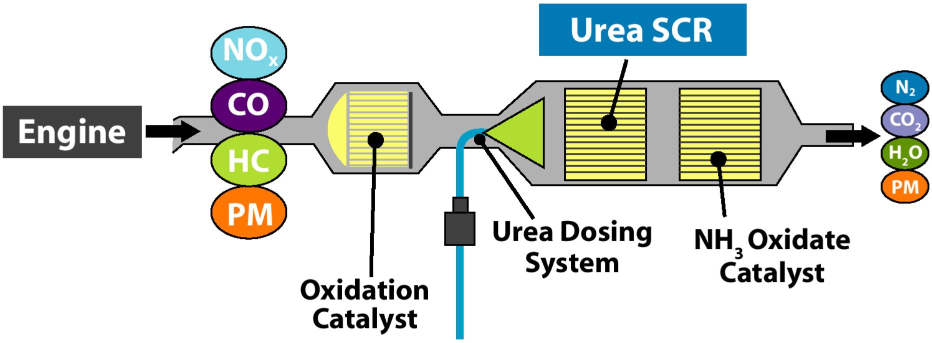


Fig 37. SCR construction scheme [50]

The urea dozer precisely meters a low amount of urea and delivers it to the exhaust system. In the SCR Catalyst and NH_3 Oxidation Catalyst NO_x are divided into nitrogen and water according to following reactions [45, 46]:

- $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$
- $4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O$

After division N_2 and H_2O leave the system freely through exhaust pipe. The catalysts are made of Cu-Zn/ZSM-5 washcoated ceramic monolith inserts (fig. 38). Thanks to application of microporous or mesoporous materials internal surface can be enhanced to even 40 m^2/g.

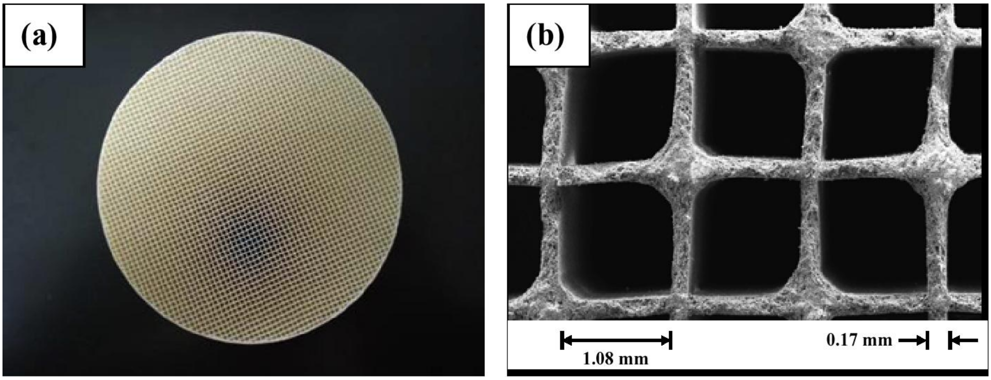


Fig. 38. Monolith insert: a) normal view, b) enlarged image [51]

The method was named „selective" because the reduction substance is more likely to react with nitrogen not with oxygen at certain temperature [52].

Applications of SCR results in significant reduction in emission of toxic compounds. It was found to remove up to 90% of NO_x along with simultaneous removal of hydrocarbons and carbon monoxide in amount of 50-90%. The system might be combined with particulate filters for increase of particulate matter capturing [50].

The SCR catalysts usually is equipped in an oxidation catalyst, often called a slip catalyst, at the end as a guard to ensure that no ammonia is emitted. The SCR construction model is presented in figure 39.

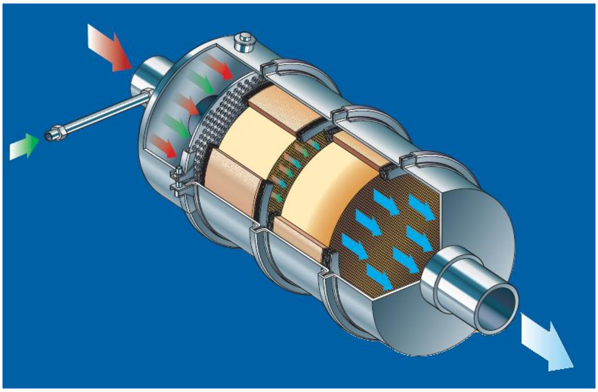


Fig 39. SCR construction model [50]

4.6.4. Exhaust gas recirculation (EGR)

Another solution of reducing the amount of toxic particles in exhaust gas is exhaust gas recirculation. It is basically the most effective way of NO_x emission reduction. Diesel engine operates on a lean mix, which is characterized by high ratio of fresh air to portion of fuel. Such mixture yields to achieving high temperatures in the cylinder. Reducing the combustion temperature helps preventing the occurrence of nitrogen oxides thus these compounds are being formed during fuel oxidation when temperatures exceed 1370°C. The EGR method significantly decreases the number of NO_x particles, which are one of the most toxic particles among generated during internal combustion engines operation. The task of EGR is to return a part of the exhaust gases to the intake manifold, instead of some volume of the fresh-air and reducing the engine's combustion temperature to lower NO_x formation. The system works because recirculated exhaust gas mixes with oxygen, which absorbs part of the combustion energy, slowing down the whole chemical process. The higher is the amount of EGR the lower is the NO_x output. However excessive EGR volume delivers not enough oxygen to combustion chamber, which yields to incomplete combustion and eventually raises the particulate levels. To achieve full operation, exhaust gas recirculation process flow needs to equal following parameters [53]:

- High EGR flow – essential when the vehicle is cruising or accelerates with medium speed, therefore temperatures inside combustion chamber reach high levels,
- Low EGR flow – useful together with low velocity and insignificantly loaded propulsion system,
- No EGR flow – should be introduced along engines’ operation periods when EGR participation might noticeably influence engines efficiency or vehicles operation (i.e. idling, engines warming up, full throttle).

Exhaust gas is directed when it leaves the cylinder, just upstream of the turbocharger turbine. Here a by-pass valve controlled by an electric motor sends the certain volume of gas through the catalyser. Next the fluid is directed to intake manifold downstream from the turbocharger. The Exhaust gas recirculation system accurately regulates the flow rate of returned exhaust gases to maintain the most beneficial performance and emission level along changes of the loads of the engine.

From numerous sensors it receives information about loads and speed of the engine, intake temperature and intake pressure, air flow rate and water temperature. After calculations computer shows the volume of exhaust gases that later on is delivered to intake manifold. It sometimes drastically differs in a period of time as operating conditions change. The EGR system is constantly balancing between low NO_x emissions and best performance. When volume of exhaust gas delivered into cylinder is bigger than optimal, engine performance descends. On the other hand if the mentioned volume is too small, it might cause engine knocking and undesired higher emission of NO_x as well as other toxic compounds. In theory the metered amount of recirculated exhaust gas is called the EGR ratio. Fig. 40. presents the value of the EGR ratio in relation to engines working conditions [53].

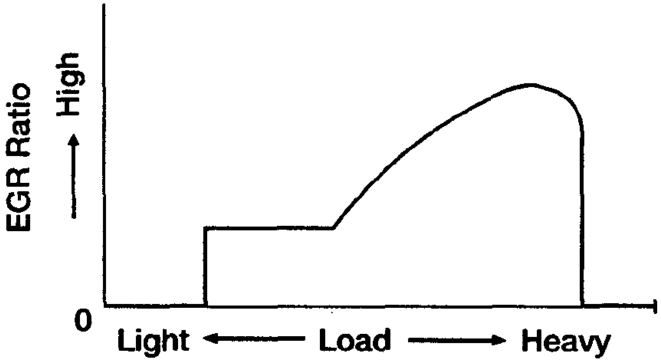


Fig. 40. EGR ratio in relation to engines working conditions [53]

Elements of EGR System

To deliver desired exhaust gas recirculation output, EGR system comprises of number of elements (fig. 41.).

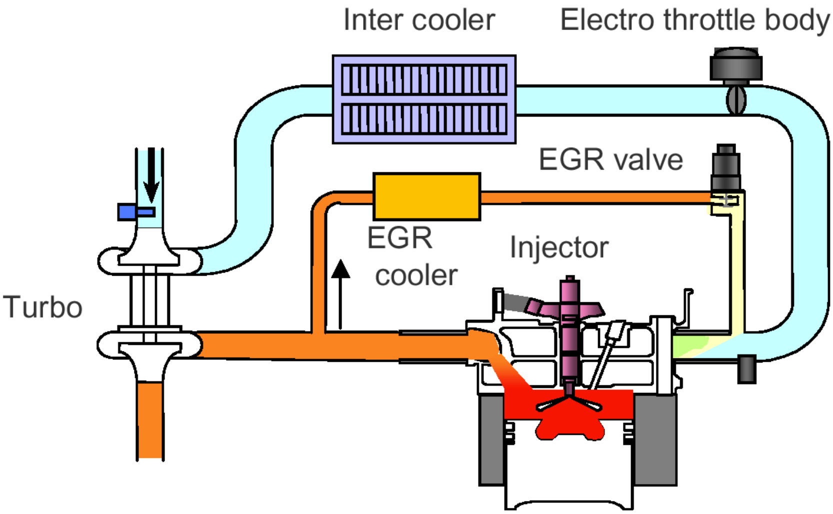


Fig. 41. EGR construction and operation [54]

- Vacuum Actuated EGR Control Valve,
- EGR cooler,
- Injector.

EGR Control Valve

This device regulates the flow of exhaust gas directed into the intake manifold. It is performed with usage of a pintle valve which is fastened to the valve diaphragm. A ported vacuum signal and calibrated spring on the first side of the membrane are balanced against atmospheric pressure that acts on the second side of the membrane. When the vacuum signal applied to the valve reaches certain value, the valve is moved further away from its previous position. The essential part that allows the EGR metering accurately is the exhaust gas recirculation modulator set. This assembly with high precision regulates the strength which the emitted vacuum signal has [53].

EGR Vacuum Modulator

As the engine loading increases, the exhaust backpressure changes similarly. In such manner the EGR vacuum modulator controls precisely the power of the vacuum signal that is sent to ERG valve. Typically system controlling the EGR makes use of two ported vacuum signals achieved from the throttle assembly. Primal phase of the process is at the Port E and secondly ported vacuum signal reaches Port R. Signal opens or closes the throttle valve. After applying vacuum from Port E, the power of vacuum signal sent to the EGR valve depends on the value of exhaust pressure on the side of chamber A of the vacuum modulator. In case of applying the vacuum at Port R, the power of vacuum signal sent to the EGR valve is not affected by amount of exhaust backpressure signal. In such a situation, the power of EGR signal depends only on vacuum signal obtained from Port E of the throttle body. The EGR Vacuum Modulator enables accurate adjusting the part of EGR flow to the engine loading conditions [53].

ECM Controlled Vacuum Switching Valve (VSV)

Along with EGR modulator, the ECM Controlled VSV task is to suppress EGR operation, in cases when it might significantly influence either engines or vehicles functioning. The device could be opened and closed in a normal way and placed in the series of connections between the EGR Modulator and EGR Valve or placed at second port on the EGR Valve. ECM Controlled Vacuum Switching Valve regulates the atmospheric bleed which suppresses the work of exhaust gas recirculation anytime when a number of ECM parameters are faced [53].

4.6.5. PM filters

Particulate filters are used to trap Particulate Matter (PM). Catalysts are needed to burn the PM collected in the trap, maintaining the performance of the system. There are two ways that catalysts can be used to keep Diesel Particulate Filters (DPFs) clean, and these are often used together. Nitrogen dioxide (NO_2) and oxygen (O_2) can both be used to combust the soot trapped in a filter. NO_2 has the advantage that it reacts with soot at the temperatures found in diesel exhaust. The O_2 reaction requires higher temperatures, but is much faster (fig. 42) [33].

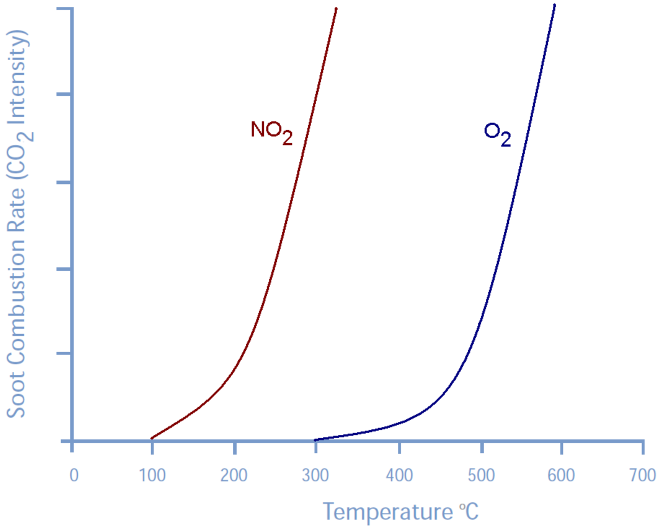


Fig 42. Soot combustion rate - oxidizer: NO_2 and O_2

NO_2 reacts with soot trapped in a filter, making NO and CO_2. This reaction can occur from 200°C, so the temperatures found in diesel exhaust streams are sufficient and no additional energy is required. Some of the NO_X emitted by an engine is NO_2 and more can be made by an oxidation catalyst designed to oxidize NO to NO_2.

Particulate matter collected in a filter can be oxidized very quickly using the oxygen (O_2) in the exhaust gases. This reaction requires temperatures which are higher (>550°C) than the ones reliably found in most diesel engine applications, so some mechanism is required to raise the temperature of the exhaust periodically. An oxidation catalyst placed before the filter is a very efficient way of doing this. When the filter needs regenerating, the hydrocarbon content of the exhaust stream is increased. The catalyst burns the hydrocarbon, producing the heat required. The catalyst can also be designed to make NO_2 during normal operation to provide additional regeneration. The hydrocarbon enrichment can be achieved in-cylinder using electronic fuel systems, or by injecting fuel directly into the exhaust system [33].

4.6.6. Alternative fuels

Fossil fuels are nowadays the primary source of energy in vehicles. Unfortunately usage of the resource is harmful to the environment and moreover eventually all sources will be depleted. At the same time energy demand rapidly increase. For that reason new types of fuels are introduced and sometimes the ones ignored for decades are now revived. Those substances need to be easily available, produce lower amount of toxic ingredients during oxidation and provide better engine performance. Fig. 43 shows the division of vicarious fuels which can be used in internal combustion engines in regard to the physical state.

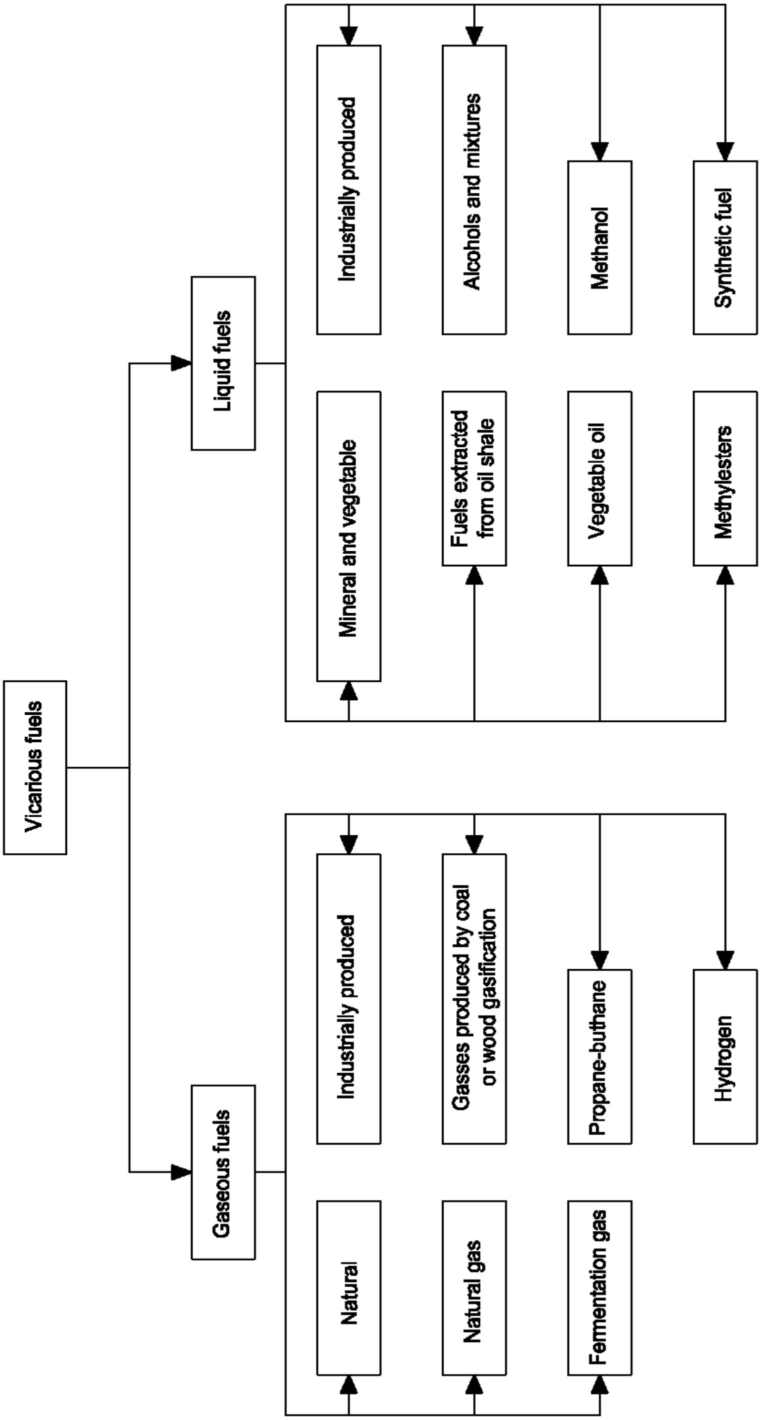


Fig 43. Classification of alternative fuels

However each of them is not suitable for all types of the motors. The classification of ecologic fuels in regard of the type of application is shown below:

Liquid fuels for diesel engines:

- Esters,
- Oils.

Liquid fuels for spark ignition engines:

- Alcohols (mainly ethanol).

Gaseous fuels:

- Liquefied Petroleum Gas (LPG),
- Natural gas,
- Hydrogen.

Biodiesel

Older types of diesel engines are suitable for combustion of vegetable oil. Unfortunately it is a problem for modern units unless they are especially prepared. Glycerin contained in the oil transforms under influence of high temperature into acrolein which tends to deposit in the engine and hoses. This sludge causes excessive abrasive wear of the components. In a process called transestrification the glycerin is removed. Products of the process are esters of fatty acids of which a good example is FAME [55].

The fuel is a liquid with density of 0.88 g/cm3 in 15°C and viscosity similar to diesel fuel equal to 6.5-7 mm2/s in 20°C. It has a yellowish color and characteristic smell. Its temperature of combustion is lower than 150°C.

Cetane number of methyl ester ranges from 56-58, while mineral diesel fuel has the number as high as 54 only after addition of proper refiners. Ability to self combustion effects in better operational characteristics and more complete oxidation of fuel. Temperature of cold filter plugging point (CFPP) of FAME is similar to diesel fuel and in temperatures lower than -20 needs an addition of antifreeze substances [55].

Usage of biodiesel reduces emission of all toxic compounds in comparison to diesel fuel. It contains vestigial amount of sulfur oxides, content of hydrocarbons, carbon monoxide is much lower. Methyl ester eliminates particulate matter concentration in exhaust gas and as a result it reduces the black cloud and smog formation [55, 56].

Ethanol

In search for an alternative for gasoline scientists turned to ethanol. It requires little or no engine modification, although specially designed systems are needed for optimal operation. The fuel might be applied in two forms [57]:

- Native state - E100 (pure ethanol),
- An additive to gasoline in different ratios (E25 meaning 25 units of ethanol per 0 units of gasoline).

Ethanol is formed by fermentation of natural substances rich in carbohydrate for example corn, cellulose etc. Gasoline has been widely used for the last couple of decades and capabilities of ethanol were not fully exploited. Many of its significant properties are superior to gasoline. Oxidation of this fuel produces lower amount of toxic emissions. Exhaust gas comprises of carbon monoxide, water and carbon monoxide, whose level is much lower. Its latent heat of vaporization is higher, as well as the octane number and rating. Higher octane rating leads to better performance of the engine. In spite of ethanol lower heating value being 40% lower than in gasoline, it is compensated by high latent heat of vaporization equal to 839.686 kJ/kg. The last parameter is nearly twise as high as in case of gasoline (325.64 kJ/kg). Mentioned properties yield to similar volumetric efficiency of both fuels when burned in proper stoichiometric ratios. Unfortunately a mixture richer in gasoline is necessary to start an ethanol fuelled engine during winter.

In year 2006 global production of ethanol exceeded 45 billion liters, where 19 in USA and 15 in Brazil [57].

Liquefied Petroleum Gas (LPG)

Due to constantly rising gasoline prices in recent several years LPG extremely gained in popularity. Crucial criterion was the cost per unit of the fuel which back then was twice cheaper than gasoline or diesel fuel [58].

Liquefied petroleum gas is a liquefied mixture of multiple gases. Main ingredients are propane, n-butane and izobutane which has the same composition but different molecular construction. Other ingredients are small amounts of ethane, butane isomers and higher hydrocarbons [58].

Propane and butane occur alone but they usually also accompany crude oil deposits. Gases are side products of gasoline production, hydrogenation of coal (production of liquid fuels out of coal), cracking and hydrogenation of crude oil. After condensation the fuel contains multiple contaminants like carbon oxysulphide, carbon dioxide and hydrogen sulfide which are needed to be removed before the distribution process [58].

Density of LPG in normal conditions ranges from 1.5 to 2 times higher than air and depends on the content of each ingredient. It hardly dissolves in air and gathers near ground. It is invisible or in the form of white fog when in higher concentration. Contents of liquefied petroleum gas are almost odorless therefore an unpleasant smell needs to be added for safety reasons [58].

LPG heat of combustion is about 24 MJ/dm3 and 46 MJ/dm3 while gasoline is respectively 32.8 MJ/dm3 and 43.5 MJ/dm3. The octane number of liquefied petroleum gas varies along differences of composition, however it is higher than in case of gasoline and oscillates around 100 [58].

Liquefied petroleum gas is stored in vehicles in tanks (Fig. 11) under pressure ranging from 600 kPa to 1050 kPa depending on the tank type. Refueling is a bit different because it proceeds under high pressure and requires proper sealing.

LPG can be delivered to the intake manifold in gaseous or liquid state. Usage of gaseous system yields to variation of operational conditions of the engine due to changes of concentration of the fuel contents. Propane is lighter than butane therefore it is located above it inside the tank. The fuel pump captures only part of those two substances and eventually the ratio of their amounts differs from the initial. In case of liquid fuel delivery dissection of propane and butane is restricted and the problem is much more significant [58].

The emission of toxic substances during combustion of liquefied petroleum gas is lower than in case of gasoline due to more simple composition of the fuel. It contains only vestigial amounts of polycyclic aromatic hydrocarbons which are the most dangerous pollutants. As well as other toxic chemical compounds like NOx and CO occur in lower concentrations in exhaust gas [58].

Natural gas

Physical and chemical properties of methane gas lead to its employment as a good and ecological fuel. Excessive storing of the resource is not required due to its common availability. Its price is much lower in comparison to other liquid fuels, also when properly treated the gas does not contain aggressive substances. The density of methane is nearly twice as low as density of air, therefore if any leakages in the system appear, the fuel dissolves in the atmosphere instead of accumulating near ground surface. Foregoing property enables vehicles equipped in gas installation to park in very commonly built underground garages, which is forbidden for automobiles using propane-butane as a fuel. Natural gas might be applied to vehicles in two forms [59].

- Compressed Natural Gas (CNG),
- Liquefied Natural Gas (LNG).

The technological processing of CNG bases on compressing and drying. The main flaw of the system is lower density of stored energy per one volume unit, in spite of compression of the gas to pressures reaching about 20 MPa. This yields to construction of containers having large volumes and weights. The fuel is intended to be used in any spark ignition engine and even diesel engines after introducing some proper changes in the design [58].

The problem of the low density of accumulated energy inside the tank was eliminated with the invention of another method of gas storage. In the process of liquefaction methane is cooled down to the temperature of -161.15°C. This results in significant reduction of volume equal to approximately 630 times and elevating the energy density to very high levels. Along with decreasement of temperature, the gas is carefully purified of carbon dioxide, propane-butane, nitrogen and water vapor. The fuel is characterized by high octane number reaching 130 and insignificant amount of pollutants. Higher calorific value of fuel enables reaching higher compression ratios. Refueling procedure of LNG is not much different from pouring traditional fuels, however to maintain stable temperature a cryogenic tank is required. This strongly impede storing of the fuel and creates design problems [58].

In case of natural gas there is no need of any special chemical processing except purification and sulfur removal, however this process is very expensive and requires significant amount of energy. The removal of CO_2 is necessary as it can be dangerous to the system. carbon dioxide has strong corrosive properties. It is also not combustible, therefore any amount of it in natural gas lowers its efficiency as a fuel. Natural gas has higher melting temperature than carbon dioxide, so any presence of unwanted gas might cause obstructions in transferring lines. CO_2 freezes and unables the fuel to flow. When the blockage is grand in size it creates elevation of pressure and leads to damage of the pipelines [60].

During the test conducted on a bus diesel engines, the emission of toxic ingredients shown significant differences in comparison to usage of diesel fuel and CNG. The amount of CO fell to 41%, NOx to

37%, HC 16% and PM to only 2%. It was mostly caused by methane very simple structure of particles [59].

Usage of compressed natural gas can be very beneficial for future vehicle operation. Main advantages of this type of fuel are [59]:

- Vestigial sulfur content,
- Minimal presence of particulate matter,
- Low amount of fuel vapor in exhaust gas,
- Reduced emission of carbon dioxide,
- Limited pollutants emission after cold start,
- High calorific value of fuel (130 octane),
- Extended combustibility,
- Lower combustion temperature leading to limited NOx emission,
- Lower HC emission, nearly complete elimination of benzene and 1-3 butadiene,
- Less noise during engine operation,
- Low tendency of smog creation.

Disadvantages:

- Low energy density impede storing,
- Gas usage requires prior compression,
- Limited range of vehicle,
- Expensive treatment process,
- Purification consumes high amount of energy,
- Necessity of massive containers usage,
- Hindered catalytic afterburning of methane,

- Risk of methane reaching atmosphere (the gas itself is a pollutant,)
- Need of humidity removal,
- Longer refuelling time,
- Lower engine performance,
- Possibility of flame backflow,
- Requires removal of CO_2.

It is expected for the CNG fuel usage to extend in near future. According to the ENGVA (European Natural Gas Vehicles Association) in the year 2020, number of European vehicles powered by CNG derived from renewable sources will reach 20% [59].

Hydrogen

Hydrogen is hoped to be one of the basic type of fuel in future. As a renewable and commonly available energy source, it delivers the possibility of a stable development especially in the transportation branch of industry. Engines operating on hydrogen are found to be more advantageous at some points in comparison to engines using fossil fuels. The amount of pollutants concentration which remain in exhaust gas after combustion process in the lowest among all types of fuels. Hydrogen combustion process can be described using an equation [42].

$$2H_2 + O_2 \rightarrow 2H_2O$$

When the temperature of combustion is high, nitrogen oxides are formed:

$$H_2 + O_2 + N_2 \rightarrow H_2O + N_2 + NOx$$

In some cases low amount of carbon monoxide is present as a result of oil burning along with fuel. Another advantage is a possibility of lean air-fuel mixture delivery to combustion chamber due to hydrogen's wide flammability limits and high speed flame propagation. For simple usage of the fuel it is not required to use any special equipment or devices that are not used in typical fuel system of a vehicle.

Hydrogen has the best energy-to-weight ratio among all fuels, therefore it has been used in space rockets. Combustive properties of hydrogen can be described by few parameters [61]:

- Wide range of flammability,
- Low ignition energy,
- Small quenching distance,
- High autoignition temperature,
- High flame speed at stoichiometric ratios,
- High diffusivity,
- Very low density.

Wide range of flammability

In comparison with other fuels hydrogen has a wide range of flammability, hence the combustion process is possible when the content of fuel in air ranges very widely. Consequently the engine is capable of operating on a lean mixture. This is beneficial because along with lowering the amount of fuel in the mixture, fuel economy rises and the oxidation reaction is more complete. Wide range of flammability also lowers the temperature which reduces pollutants formation i.e. nitrogen oxides. Also it facilitates starting up the engine [61].

Low ignition energy

This designation means that certain portion of hydrogen needs a small amount of energy for combustion process to start. In fact it is approximately one order of magnitude lower than necessary for gasoline to oxidize. This property, similarly to wide range of flammability, enables hydrogen motors to operate on lean air fuel mixture and also secures immediate ignition. Unfortunately, the low ignition energy creates a possibility for the mixture to ignite unexpectedly. This may occur as an effect of hot spots on the cylinder which can act as combustion starters. It results in premature ignition and flashback. Preventing the appearance of the phenomena is one of the main challenges during design of hydrogen fuelled engines [61].

Small Quenching Distance

Quenching distance informs about intensiveness of a flame. Hydrogen flames are harder to extinguish than gasoline. Due to that it travels closer to the cylinder wall, which may result in backfires when the flame passes in the vicinity of closed intake valve [61].

High Autoignition Temperature

High autoignition temperature of hydrogen is a very important factor, because it determines the compression ratio that is obtained in combustion chamber. Higher autoignition temperature effects in higher compression ratio. During ignition process the temperature rises according to the equation [61]:

$$T_2 = T_1 \cdot \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$

V1/V2 = compression ratio
T1 = absolute initial temperature
T2 = absolute final temperature
γ = ratio of specific heats

Due to high autoignition temperature, hydrogen fueled engines is characterized by larger compression ratio than fueled with hydrocarbons. Higher compression elevates the engines thermal efficiency, however it is difficult to use hydrogen in a diesel type units [61].

High Flame Speed

Hydrogen flame is almost an order faster gasoline flame, thus hydrogen fueled motors operate closer to the ideal engine cycle in a thermodynamical sense. Value of speed descends when a lean mixture is delivered [61].

High Diffusivity

Due to high diffusivity, an air fuel mixture fills the combustion chamber faster and more evenly if it contains hydrogen instead gasoline. This property results in higher performance of the engine [61].

Low Density

Hydrogen has the lowest molar mass among all discovered elements. This indicates low energy density of the fuel, thus an increased size of tank is required to provide appropriate vehicle range. Refueling (fig. 44) is similar to LPG due to high pressure of the fluid [61].

Fig. 44. Hydrogen fuelled car refueling [62]

Mixtures

There is a possibility of hydrogen usage as an additive to commonly applied fuels.

Hydrogen is often mixed with high pressure natural gas as both gases can be poured into one tank. Usually, due to its lower density, H_2 requires a separate container and is mixed in intake manifold before combustion. A fuel known as Hythane comprises of 20% of hydrogen and of 80% natural gas. Application of this fuel does not require any modifications to a natural gas engine, and research have shown emission reduction along increasing the amount of hydrogen, however some changes in the engine are necessary [61].

4.7. Car vehicle emission legislation

4.7.1. Emission and its units

Emission is the term used to describe the pollution (gaseous, liquid, solid) and which is put into the environment (air, water, soil) or emitted by various sources. There are many sources of emissions. These have been grouped into four categories: point, mobile, biogenic, and area [63]:

- Point sources include things like factories and electric power plants.
- Mobile sources include cars and trucks, of course, but also lawn mowers, airplanes and anything else that moves and puts pollution into the air.

The emission is often mistaken for concentration, which is the measure of how much of a given substance there is mixed with another substance.

The unit of emission is unit of a mass (ng, µg, mg, g, kg, Mg) per unit of:

- time (i.e. h),
- energy (i.e. kWh),
- distance (i.e. km).

Vehicular emission can be divided into three groups [64]:

- Exhaust (tail-pipe) emissions from the vehicle’s engine as it is driven,
- Cold Start emissions are additional emissions from the vehicle when started from cold,

- Evaporative emissions are evaporation of petroleum from the vehicles’ fuel system, engine, and fuel tanks.

Evaporation from vehicle refuelling and the supply of fuels is calculated elsewhere.

In general emissions are estimated using the following equation [64]:

$$\text{Emission} = \sum_{abcd} (\text{EF}_{\text{abcd}} \bullet \text{Activity}_{\text{abcd}}) + \sum_{b} \text{Cold}_{\text{b}} + \sum_{b} \text{Evaporation}_{\text{b}}$$

Where:

Emission: Total emissions from road transport

EF: Emission factor, as mass per unit of activity rate

Activity: activity rate (fuel consumed or distance travelled)

Cold: Extra emissions due to cold starts

Evaporation: extra emissions due to evaporation (NMVOCs)

a: fuel type (petrol, diesel, LPG, etc)

b: vehicle type (passenger car, light-duty truck, bus etc)

c: emission control

d: road type or vehicle speed

4.7.2. European emission standards

In simply words the emission standards are requirements that set specific limits to the amount of pollutants that can be released into the environment.

"Tailpipe" emission standards specify the maximum amount of pollutants allowed in exhaust gases discharged from a diesel engine. The tailpipe emission standards were initiated in California in 1959 to control CO and HC emissions from gasoline engines. Today, emissions from internal combustion engines are regulated in tens of countries throughout the world. The regulated diesel emissions include [28]:

- Diesel particulate matter (PM), measured by gravimetric methods. Sometimes diesel smoke opacity measured by optical methods is also regulated,
- Nitrogen oxides (NOx), composed of nitric oxide (NO) and nitrogen dioxide (NO2). Other oxides of nitrogen which may be present in exhaust gases, such as N2O, are not regulated,
- Hydrocarbons (HC), regulated either as total hydrocarbon emissions (THC) or as non-methane hydrocarbons (NMHC). One combined limit for HC + NOx is sometimes used instead of two separate limits,
- Carbon monoxide (CO).

Emissions are measured over an engine or vehicle test cycle which is an important part of every emission standard. Regulatory test procedures are necessary to verify and ensure compliance with the various standards. These test cycles are supposed to create repeatable emission measurement conditions and, at the same time, simulate a real driving condition of a given application. Analytical methods that are used to measure particular emissions are also regulated by the standard [28].

Emission cycles are a sequence of speed and load conditions performed on an engine or chassis dynamometer. Emissions measured on vehicle (chassis) dynamometers are usually expressed in grams of pollutant per unit of traveled distance, e.g., g/km or g/mi. Emissions measured according to an engine dynamometer test cycle are expressed in grams of pollutant per unit of mechanical energy delivered by the engine, typically g/kWh or g/bhp-hr.

Depending on the character of speed and load changes, cycles can be divided into steady state cycles and transient cycles. Steady state cycles are a sequence of constant engine speed and load modes. Emissions are analyzed for each test mode. Then the overall emission result is calculated as a (weighted) average from all test modes. In a transient cycle the vehicle (engine) follows a prescribed driving pattern which includes accelerations, decelerations, changes of speed and load, etc. The final test results can be obtained either by analysis of exhaust gas samples collected to plastic bags over the duration of the cycle or by electronic integration of a fast response, continuous emission measurement.

Regulatory authorities in different countries have not been unanimous in adopting emission test procedures and many types of cycles are in use. Since exhaust emissions depend on the engine speed and load conditions, specific engine emissions which were measured on different test cycles may not be comparable even if they are expressed or recalculated into the same units of measure. This should be kept in mind whenever comparing emission standards from different countries.

Tailpipe emission standards are usually implemented by government ministries responsible for the protection of environment, such as the EPA (Environmental Protection Agency) in the USA. The duty to comply with these standards is on the equipment (engine) manufacturer. Typically all equipment have to be emission certified before it is released to the market.

European Union emission regulations for new light duty vehicles (passenger cars and light commercial vehicles) were once specified in Directive 70/220/EEC with a number of amendments adopted through 2004. In 2007, this Directive has been repealed and replaced by Regulation 715/2007 (Euro 5/6). Some of the important regulatory steps implementing emission standard for light-duty vehicles were [28]:

- Euro 1 standards (also known as EC 93): Directives 91/441/EEC (passenger cars only) or 93/59/EEC (passenger cars and light trucks),
- Euro 2 standards (EC 96): Directives 94/12/EC or 96/69/EC
- Euro 3/4 standards (2000/2005): Directive 98/69/EC, further amendments in 2002/80/EC,
- Euro 5/6 standards (2009/2014): Regulation 715/2007 ("political" legislation) and Regulation 692/2008 ("implementing" legislation).

Emission standards for light-duty vehicles are applicable to all vehicles category M1, M2, N1 and N2 with a reference mass not exceeding 2610 kg (Euro 5/6). EU regulations introduce different emission limits for compression ignition (diesel) and positive ignition (gasoline, NG, LPG, ethanol,...) vehicles. Diesels have more stringent CO standards but are allowed higher NOx. Positive ignition vehicles were exempted from PM standards through the Euro 4 stage. Euro 5/6 regulations introduce PM mass emission standards, equal to those for diesels, for positive ignition vehicles with DI engines [28].

Fuels. The 2000/2005 standards were accompanied by an introduction of more stringent fuel regulations that require minimum diesel cetane number of 51 (year 2000), maximum diesel sulfur content of

350 ppm in 2000 and 50 ppm in 2005, and maximum petrol (gasoline) sulfur content of 150 ppm in 2000 and 50 ppm in 2005. “Sulfur-free” diesel and gasoline fuels (≤ 10 ppm S) must be available from 2005, and became mandatory from 2009 [28].

Emission Testing. Emissions are tested over the NEDC (ECE 15 + EUDC) chassis dynamometer procedure. Effective year 2000 (Euro 3), that test procedure was modified to eliminate the 40 s engine warm-up period before the beginning of emission sampling. This modified cold start test is referred to as the New European Driving Cycle (NEDC) or as the MVEG-B test. All emissions are expressed in g/km [28].

The Euro 5/6 implementing legislation introduces a new PM mass emission measurement method (similar to the US 2007 procedure) developed by the UN/ECE Particulate Measurement Programme (PMP) and adjusts the PM mass emission limits to account for differences in results using the old and the new method. The Euro 5/6 legislation also introduces a particle number (PN) emission limit in addition to the mass-based limits [28].

EU emission standards are summarized in tables 9 and 10. All dates listed in the tables refer to new type approvals. The EC Directives also specify a second date—one year later, unless indicated otherwise—which applies to first registration (entry into service) of existing, previously type-approved vehicle models.

Table 9. EU Emission Standards for Passenger Cars (Category M1)*

EU Emission Standards for Passenger Cars (Category M_1*)

Stage	**Date**	**CO**	**HC**	**HC+NOx**	**NOx**	**PM**	**PN**
		g/km					#/km
Compression Ignition (Diesel)							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	0.14 (0.18)	-
Euro 2, IDI	1996.01	1.0	-	0.7	-	0.08	-
Euro 2, DI	1996.01[a]	1.0	-	0.9	-	0.10	-
Euro 3	2000.01	0.64	-	0.56	0.50	0.05	-
Euro 4	2005.01	0.50	-	0.30	0.25	0.025	-
Euro 5a	2009.09[b]	0.50	-	0.23	0.18	0.005[f]	-
Euro 5b	2011.09[c]	0.50	-	0.23	0.18	0.005[f]	6.0×10^{11}
Euro 6	2014.09	0.50	-	0.17	0.08	0.005[f]	6.0×10^{11}
Positive Ignition (Gasoline)							
Euro 1†	1992.07	2.72 (3.16)	-	0.97 (1.13)	-	-	-
Euro 2	1996.01	2.2	-	0.5	-	-	-
Euro 3	2000.01	2.30	0.20	-	0.15	-	-
Euro 4	2005.01	1.0	0.10	-	0.08	-	-
Euro 5	2009.09[b]	1.0	0.10[d]	-	0.06	0.005[e,f]	-
Euro 6	2014.09	1.0	0.10[d]	-	0.06	0.005[e,f]	-

*** At the Euro 1..4 stages, passenger vehicles > 2,500 kg were type approved as Category N_1 vehicles**

† Values in brackets are conformity of production (COP) limits

a - until 1999.09.30 (after that date DI engines must meet the IDI limits)

b - 2011.01 for all models

c - 2013.01 for all models

d - and NMHC = 0.068 g/km

e - applicable only to vehicles using DI engines

f - 0.0045 g/km using the PMP measurement procedure

Table 10. EU Emission Standards for Light Commercial Vehicles

EU Emission Standards for Light Commercial Vehicles								
Category†	**Stage**	**Date**	**CO**	**HC**	**HC+NOx**	**NOx**	**PM**	**PN**
			g/km					#/km
Compression Ignition (Diesel)								
N$_1$, Class I ≤1305 kg	Euro 1	1994.10	2.72	-	0.97	-	0.14	-
	Euro 2 IDI	1998.01	1.0	-	0.70	-	0.08	-
	Euro 2 DI	1998.01[a]	1.0	-	0.90	-	0.10	-
	Euro 3	2000.01	0.64	-	0.56	0.50	0.05	-
	Euro 4	2005.01	0.50	-	0.30	0.25	0.025	-
	Euro 5a	2009.09[b]	0.50	-	0.23	0.18	0.005[f]	-
	Euro 5b	2011.09[d]	0.50	-	0.23	0.18	0.005[f]	6.0×10^{11}
	Euro 6	2014.09	0.50	-	0.17	0.08	0.005[f]	6.0×10^{11}
N$_1$, Class II 1305-1760 kg	Euro 1	1994.10	5.17	-	1.40	-	0.19	-
	Euro 2 IDI	1998.01	1.25	-	1.0	-	0.12	-
	Euro 2 DI	1998.01[a]	1.25	-	1.30	-	0.14	-
	Euro 3	2001.01	0.80	-	0.72	0.65	0.07	-
	Euro 4	2006.01	0.63	-	0.39	0.33	0.04	-
	Euro 5a	2010.09[c]	0.63	-	0.295	0.235	0.005[f]	-
	Euro 5b	2011.09[d]	0.63	-	0.295	0.235	0.005[f]	6.0×10^{11}
	Euro 6	2015.09	0.63	-	0.195	0.105	0.005[f]	6.0×10^{11}
N$_1$, Class III >1760 kg	Euro 1	1994.10	6.90	-	1.70	-	0.25	-
	Euro 2 IDI	1998.01	1.5	-	1.20	-	0.17	-
	Euro 2 DI	1998.01[a]	1.5	-	1.60	-	0.20	-
	Euro 3	2001.01	0.95	-	0.86	0.78	0.10	-
	Euro 4	2006.01	0.74	-	0.46	0.39	0.06	-
	Euro 5a	2010.09[c]	0.74	-	0.350	0.280	0.005[f]	-
	Euro 5b	2011.09[d]	0.74	-	0.350	0.280	0.005[f]	6.0×10^{11}
	Euro 6	2015.09	0.74	-	0.215	0.125	0.005[f]	6.0×10^{11}
N$_2$	Euro 5a	2010.09[c]	0.74	-	0.350	0.280	0.005[f]	-
	Euro 5b	2011.09[d]	0.74	-	0.350	0.280	0.005[f]	6.0×10^{11}
	Euro 6	2015.09	0.74	-	0.215	0.125	0.005[f]	6.0×10^{11}
Positive Ignition (Gasoline)								
N$_1$, Class I ≤1305 kg	Euro 1	1994.10	2.72	-	0.97	-	-	-
	Euro 2	1998.01	2.2	-	0.50	-	-	-
	Euro 3	2000.01	2.3	0.20	-	0.15	-	-
	Euro 4	2005.01	1.0	0.1	-	0.08	-	-
	Euro 5	2009.09[b]	1.0	0.10[g]	-	0.06	0.005[e,f]	-
	Euro 6	2014.09	1.0	0.10[g]	-	0.06	0.005[e,f]	-

N_1, Class II 1305-1760 kg	Euro 1	1994.10	5.17	-	1.40	-	-	-
	Euro 2	1998.01	4.0	-	0.65	-	-	-
	Euro 3	2001.01	4.17	0.25	-	0.18	-	-
	Euro 4	2006.01	1.81	0.13	-	0.10	-	-
	Euro 5	2010.09[c]	1.81	0.13[h]	-	0.075	0.005[e,f]	-
	Euro 6	2015.09	1.81	0.13[h]	-	0.075	0.005[e,f]	-
N_1, Class III >1760 kg	Euro 1	1994.10	6.90	-	1.70	-	-	-
	Euro 2	1998.01	5.0	-	0.80	-	-	-
	Euro 3	2001.01	5.22	0.29	-	0.21	-	-
	Euro 4	2006.01	2.27	0.16	-	0.11	-	-
	Euro 5	2010.09[c]	2.27	0.16[i]	-	0.082	0.005[e,f]	-
	Euro 6	2015.09	2.27	0.16[i]	-	0.082	0.005[e,f]	-
N_2	Euro 5	2010.09[c]	2.27	0.16[i]	-	0.082	0.005[e,f]	-
	Euro 6	2015.09	2.27	0.16[i]	-	0.082	0.005[e,f]	-

† For Euro 1/2 the Category N_1 reference mass classes were Class I ≤ 1250 kg, Class II 1250-1700 kg, Class III > 1700 kg.
a - until 1999.09.30 (after that date DI engines must meet the IDI limits)
b - 2011.01 for all models
c - 2012.01 for all models
d - 2013.01 for all models
e - applicable only to vehicles using DI engines
f - 0.0045 g/km using the PMP measurement procedure
g - and NMHC = 0.068 g/km
h - and NMHC = 0.090 g/km
i - and NMHC = 0.108 g/km

Except for HDD non-road legislation all other applications will effectively mandate wall flow diesel particulate filter systems through the introduction of particulate number limits. NO_X emission limits will require highly effective NO_X reduction aftertreatment technologies. Increased demand for exhaust aftertreatment and limited space make highly integrated systems, which combine multiple functions on one component, very desirable. As engines/vehicles become cleaner, the majority of the emissions inventory shifts to older engines. Efficient retrofit exhaust aftertreatment systems are required to clean up the legacy fleet [28].

The emission standards for New Light Duty Vehicles in chosen World regions in comparison to European standards are presented in figure 44.

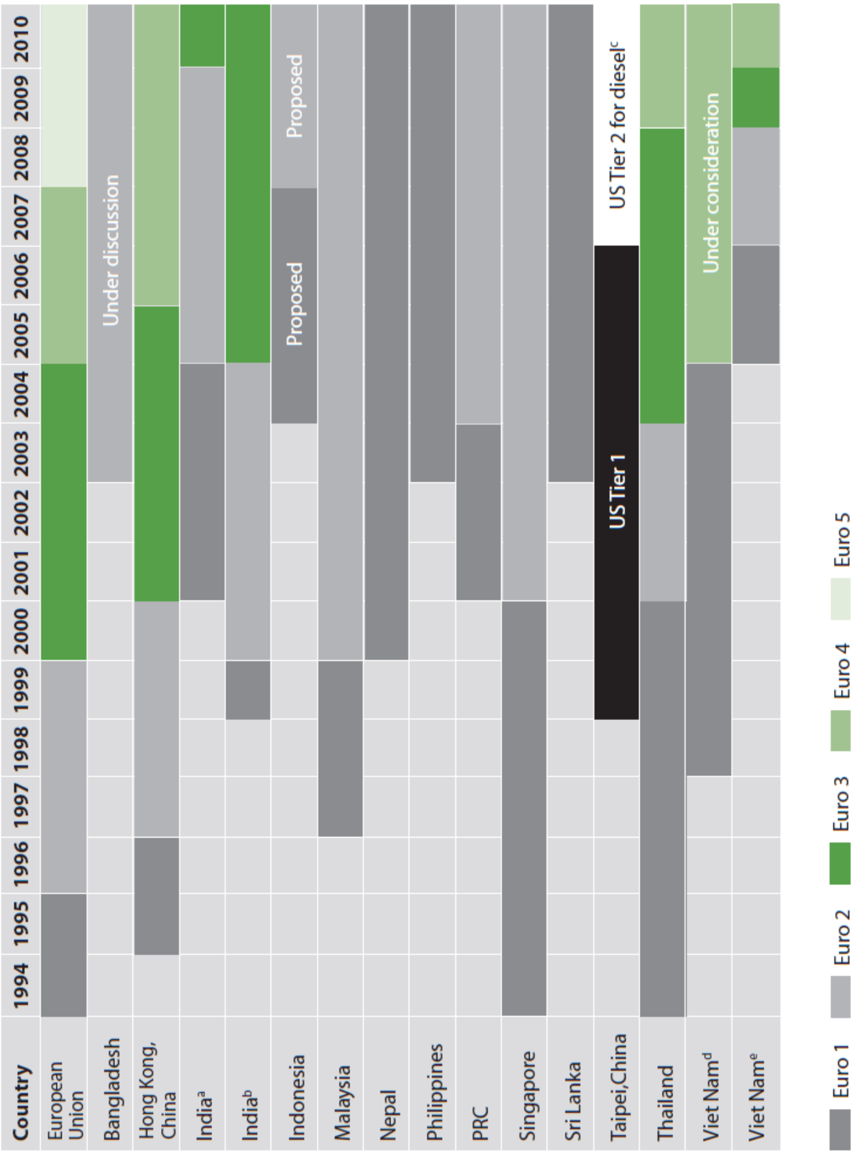


Fig. 44. Emission Standards for New Light Duty Vehicles: a) Entire country b) Delhi and other cities; Euro 2 introduced in Mumbai, Kolkata and Chennai in 2001; Euro 2 in Bangalore, Hyderabad, Kanpur, Pune and Ahmedabad in 2003; Euro 3 to be introduced in Delhi, Mumbai, Kolkata, Chennai, Bangalore, Hyderabad and Ahmedabad in 2005 c) Gasoline vehicles under consideration d) For gasoline vehicles e For diesel vehicles [65]

The development of new vehicle standards will require active dialogue between the motor and oil industries to ensure that required fuels will be available. Policymakers should encourage such a dialogue.

As new vehicle standards are tightened, in-use vehicle standards should also be tightened and these in turn should form the basis for routine vehicle inspections.

Vehicle

5. Vehicle as a source of environmental pollution

5.1. Eco-design

Since the last decade automobile industry is redefining their product improving the engine performance as well as rending the new models more comfortable, safer, easier to drive, and getting them environmental friendliness. And they do this by means of simultaneous engineering methods that enhance eco-design approach from materials selection to the end of life vehicles treatment. This new design approach represents a means of integrating environmental criteria on product development as part of competitive corporate strategy. Eco-design practices are changing the way automobiles are being conceived enabling car companies to cope with the most restrict environmental regulations and even to anticipate them. In this context environmental friendliness has become an important criterion for materials selection. Clean and recyclable materials are responsible for automobile environmental quality, which is becoming a critical issue for the near future. Materials selection is one of the strongest environmental drives to which engineering design seek to respond [67].

According to Ashby “the four main factors upon which the designers relies when considering materials choice are the relationship between materials specifications and technical performance of the product, the economic performance of the product, the environmental performance of the product the practice of industrial design embedded in the product and its functionality”. For automobile industry optimizing end of life vehicle recycling is a complex task since automobile is a multicomponents products in which more than twenty thousand of different parts, made of a number of raw materials, are assembled by a wide spectrum of processes and techniques [67].

And at the end of its life vehicles will represent a buck of multi-component materials that cannot directly be reconverted into new auto parts. So the complex interconnected materials cycles originating from recycled cars have to be optimized from a technological as well as an economic point of view. The most important factors which indicates on car vehicle optimizing on design stage are presented in figure 45 [67].

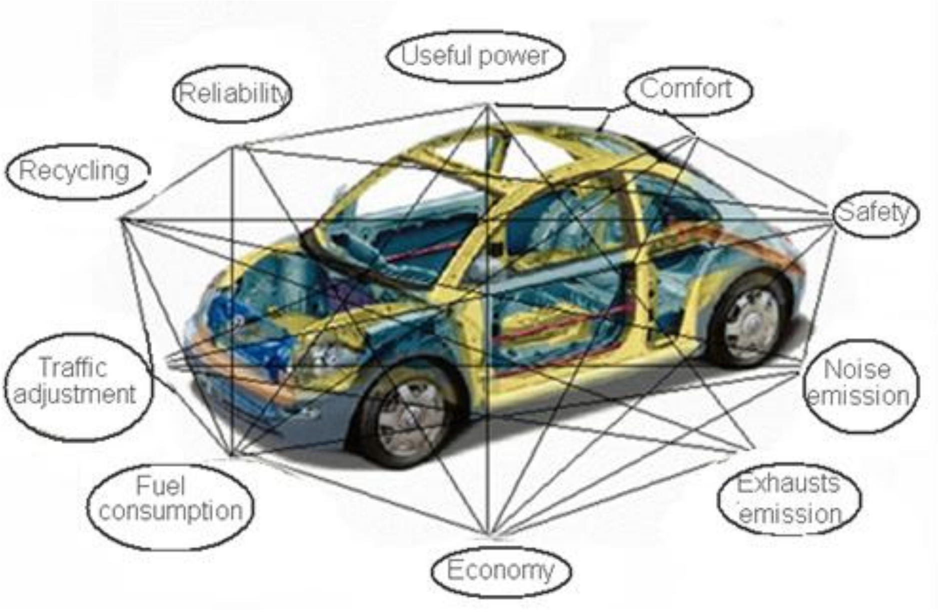


Fig 45. Key-fields of car vehicle design optimizing

The materials selection environmental oriented is the first step to facilitate end of life vehicles dismantling and an efficient materials recovery. Nevertheless materials selection for environment is not as simple as it seems at first sight [67].

Eco-design is sometimes referred to as Clean Design or Design for Environment –DFE- or Sustainable Design, which means that the term is not yet clearly defined or well known. Clean Design most important concern is air pollution. It is about green cars in terms of low or zero emissions. DFE and Sustainable Design are more broader view since they are supposed to enlarge product life cycle from the raw materials and energy production up to final disposal and recycling. But, according to Tischner, sustainable design is more than eco-design "as it integrates social and ethical aspects of the product‘s life cycle alongside environmental and economic considerations.“ Eco-design for instance is to get design activities environmental oriented from the first step of a product project up to its production and consumption phases. Recently this last phase was enlarged to cope with recycling end of life product. Eco-design is about to integrate environmental criteria on project and product development. Which means to balance environmental requirements with the basic project requirements as cost, quality, security, delay, since the products are firstly conceived to be produced and to be efficiently used by theirs customers and secondly to be dismantling and recycled. So eco-design a product as complex as a car aiming to minimize its environmental impact over its whole life cycle is not an easy task. But car companies in Europe have to do it to encompass environmental legislation standards such as the ELV Directive and ISO 14000 (EU environmental management standards). And they are definitely putting a great effort on partnerships with not only their traditional supplier but also with materials producers and recyclers. In this sense they are codesigning new models sharing integrated software and data basis [67].

In short, cars are produced to be a means of transportation, to provide people a better way of life, a place to live in, to work in, or even to be used for leisure. Made of about twenty thousand parts, and these parts are not only articulated but also integrated in a synergic way so every little detail affects the final result. So eco-design requires specific tools to assure car global sustainability. So each car manufacture has to develop its own tools to integrate environmental concerns into project activities in order to guide an environmental friendly materials choice without jeopardizing the main functions of the vehicle.

In the car industry environmental legislation are fostering eco-design practices strongly based on materials selection.

Ecodesign and materials recycling which can be summed up as follow [67]:

- Eco-design methods automobile industry is improving car environmental friendliness;
- Creating and developing eco-tools car designers are enabling the integration of environmental criteria in car projects from the materials selection to end of life vehicles recycling, and;
- Simplifying assembly for make easier and faster disassembling steps for recycling they are getting economic and technical advantages as well.

5.2. Wastes

5.2.1. Car vehicle lifecycle

When designing and manufacturing a product i.e. car vehicle nowadays it is necessary to consider its life cycle - time from the product manufacture to its recycling or disposal. The scheme lifecycle of a car vehicle is presented in figure 46.

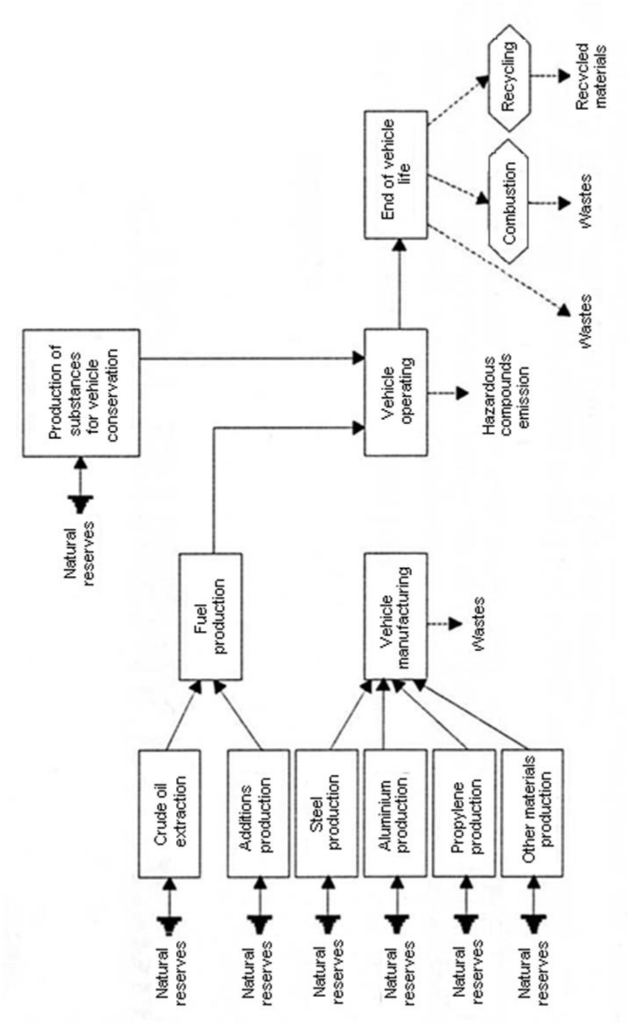


Fig 46. Scheme of car vehicle lifecycle

The input in the car lifecycle are energy (mechanical, electrical, thermal) and operating and additional fluids. The lifecycle outputs are wastes, sewages, heat and pollution (air, water, soil) (fig. 47)

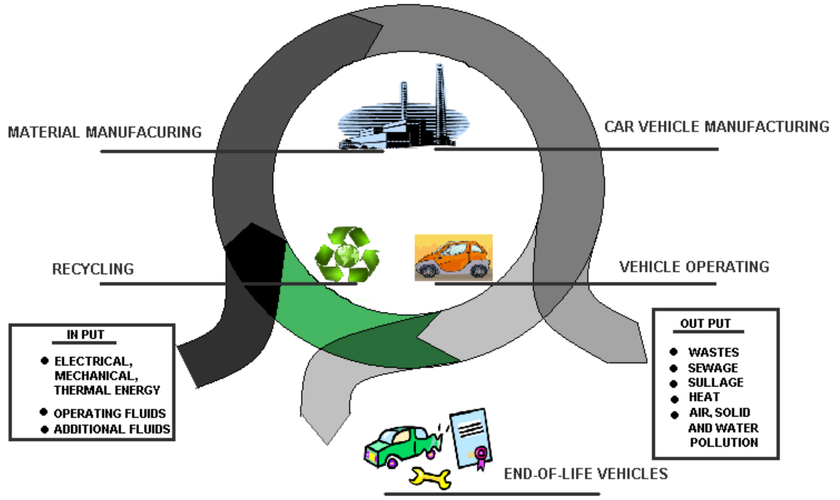


Fig 47. Car vehicle lifecycle: inputs and outputs

5.2.2. Morphology of car vehicle

Car consists of many parts and materials. The breakdown materials by weight diagram below shows that metal are a dominant material (68% ferrous metal and 8% non-ferrous metal). The average composition of a car vehicle is presented in figure 48 [68].

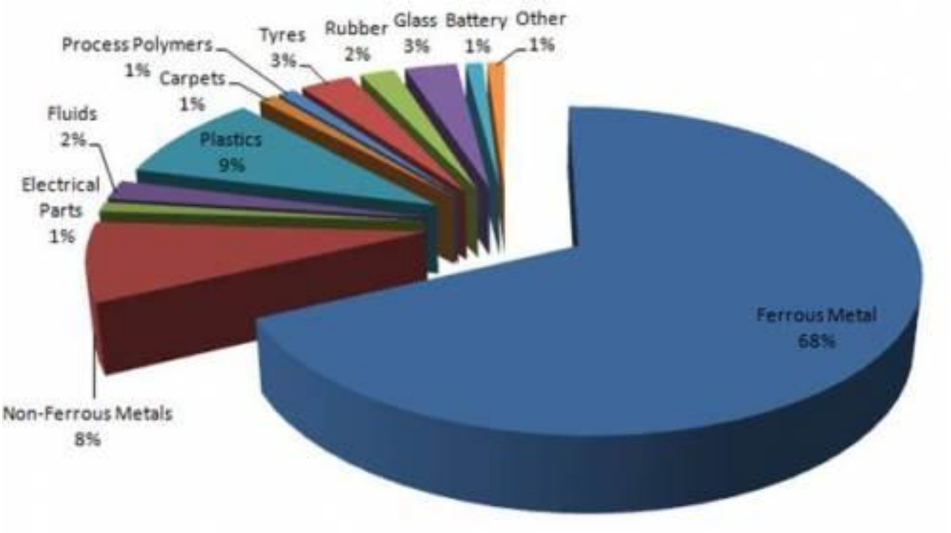


Fig 48. Car vehicle material composition [68]

Metal (76%)

Metal dominates around 76% of a car weight. Currently, 98% of metal in a car are recovered by steel industry and re-smelting plants. One of good news is that automotive manufacturing companies historically redesign car with reducing the weight of metals in a car. This reducing can support eco labelling product and environmental friendly product because it can reduce the total weight of car. Hence, the consumption of fuel is also reduced [68].

Plastic and Polymers (10%)

Plastic and polymers contribute roughly 10% of a car weight. Car manufactures use plastics increasingly from 1980s until today. In addition, utilizing plastics in a car for changing metal is more environmental friendly. Apart from a low cost, using plastics can decrease weight that has impact in decreasing the consumption of fuel. Automotive usually use polypropylene (PP), polyethylene (PE), polyurethane (PU) and polyvinylchloride (PVC). PP is common use in bumpers, dashboards, engine component, interior trim moulding, and wheel arch liners. Then, PE and PU are common use in seat foam and seat belt. The rest of plastics parts are PVC [68].

PP, PE, and PU categorize plastics which are easily recycled. Plastic waste is chopped into flakes or pellets, and then it becomes the raw material of plastics. It can be melted into new product of plastics. In contrast, PVC is difficult to recycle. Alternative disposal method of PVC is incineration, but it is connected with environmental concerns. The emission during incineration is dioxin and phthalate plasticisers which are thought to be disruptions of hormone system. Currently, car manufactures are doing research to change PVC [68].

Tyre, Rubber, and Carpet (6%)

Tyre, rubber, and carpet obtain approximately 6% of a car weight. Number of options for reuse, recycling, and recovery are following [68]:

- Scrapped and vulcanized to reuse treys in good condition.
- Tyre can be shredded and the rubber granulated for use in other products, sports surfaces, paints, flooring, etc.,
- Tyre can be recycled by cryogenic fragmentation. First, tyres are shredded and cooled to below -80°C. Then, The resultant rubber granules can be used for athletics tracks, carpet underlay, playground surfaces and rubberised asphalt for road surfaces,

- Tyres are broken by microwave prototype into their original component. The steel is recoverable. The carbon and oil also can be reused,
- Pyrolysis is heating tyres without air; then the gas, oil and carbon can be reprocessed. In big capacity, this process also produces energy that can provide electricity,
- Tyre are incinerated to extract energy,
- Tyre can be used as a fuel in the manufacture of cement. 25% of the coal, replaced up from tyre, can be used in cement kilns and reduce nitrogen oxide emission.

Glass (3%)

Glass possesses approximately 3% of vehicles weight. Two types of glass are commonly used in the automotive industry; toughened glass and laminated glass. Toughened glass is easy to remove from vehicles. Laminated glass need to be removed manually. It is crushed into cullet (small pieces) and melted, then moulded to make new product like bottle and jar. Majority, the most of glass waste are sent to landfill because the value of glass is relatively low to recover. Most of industries are not interesting in glass recycling because it is profitless [68].

Fluids (2%)

The problem of fluids like engine oil is not only for end of life vehicles but also for vehicles during service or maintenance. Wrong treatment to dispose fluids can pollute clean water. Three options of oil disposal are reuse, recovery, and recycle. First, oil can recover as mucky lubricant for simple use. Second, oil can be used as a fuel burnt in heavy industry and power stations. Third, oil can refine as clean/base lubricant for the raw material of lubricating oil. The first treatment is boiling oil to remove water and remove metal particles [68].

Battery (1%)

Currently, the recycling rate for car batteries is estimated to exceed 90%. If the electrical component like lead anode and cathode pole and the plastic case do not broken, battery can be used again with refilling acid and distilled water. Battery consists of 4 materials that can be recycled. First, plastic battery cases can be recycled to be raw material. Second, lead cathode and anode can be melted down to be raw material of lead. Third, acid can be treated and neutralized. Forth, distilled water can be purified and used again [68].

Electrical Parts (1%)

Electrical parts are relatively too complicated to be recycled because it contains many different types of parts. Two options can be chosen to recycle electrical parts. First, the electrical component disposal can be sold back to the electrical part supplier to be repaired, reused or recycled. Second, electrical parts actually are assembled from raw material like plastics, metal, glass, rubber, and so on. Hence, it is recycled with breaking down the component and recycles separately based on the material [68].

Other Components (1%)

A car is supported by approximately 1% additional groups of components. It consists of leather, foam, cloth, and so on. Because of this component in a small portion of car, it can be more profitable if company sells back to the supplier to be reused or recycled [68].

The possibilities of car elements transformation in specific branches of industry are presented in figure 49.

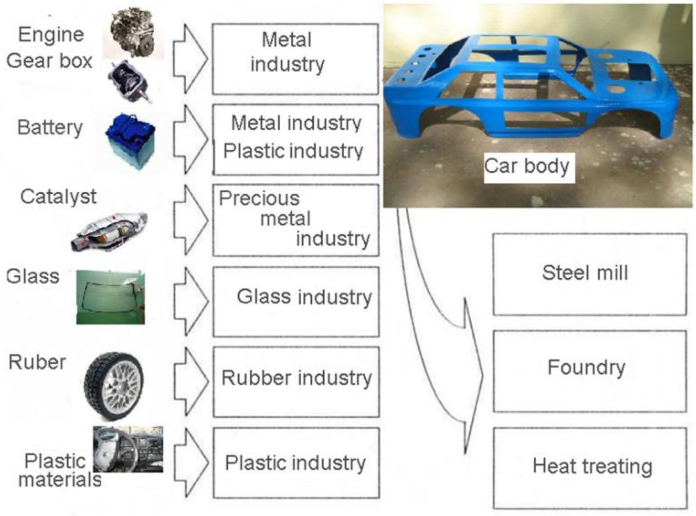


Fig. 49. possibilities of car elements transformation in specific branches of industry

The number of car vehicles in EU has been increasing since years. Despite the fact that the number of EU inhibitats increased very slightly in last 20 years (about 0,7 %) the number of cars for inhibitant increased approximately 40%. In figure 50 the number of cars per 1000 inhibitants in chosen European countries is shown [69].

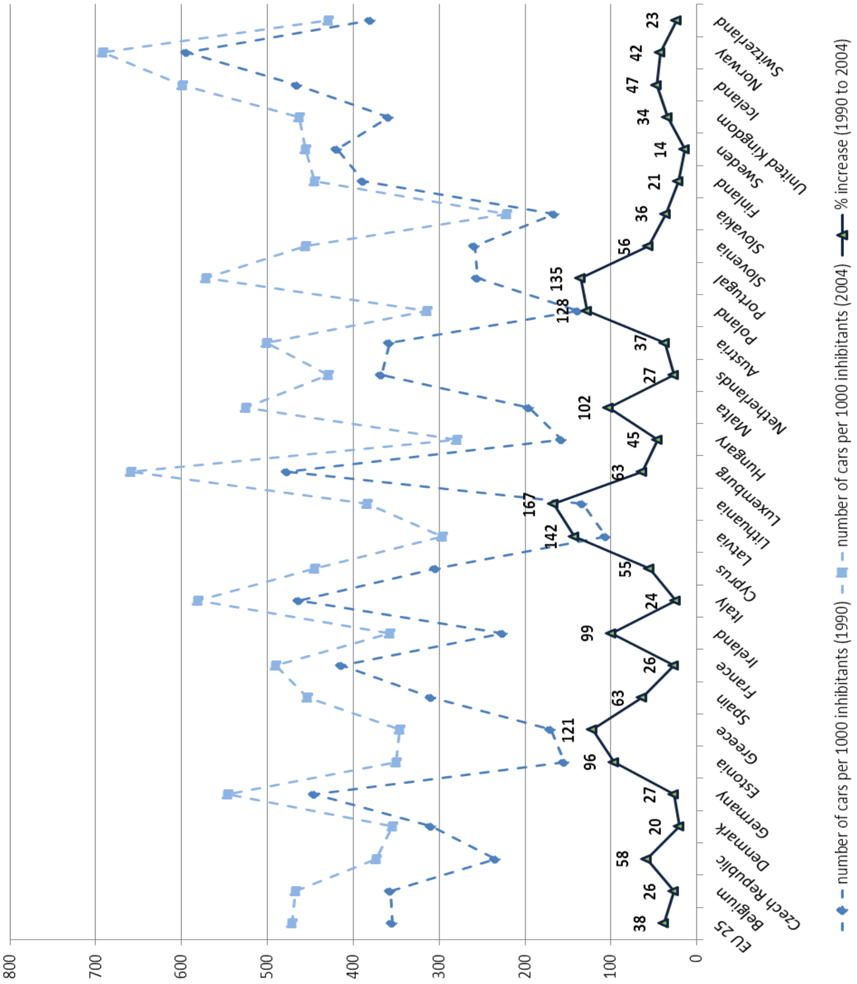


Fig. 50. Number of car vehicles in European Union [69]

The rapid growth of a registered car number and the fact that the average age of driven passenger cars in the increased from 6 years in 1980 to 10 years in 2009 indicates on the End-of-Life Vehicles management problem [70].

The average car vehicle age can vary widely between countries depending on their general economic conditions. For instance, the effects from scrappage schemes implemented in Greece and Denmark in the 1990s can be seen in figure 51 [70].

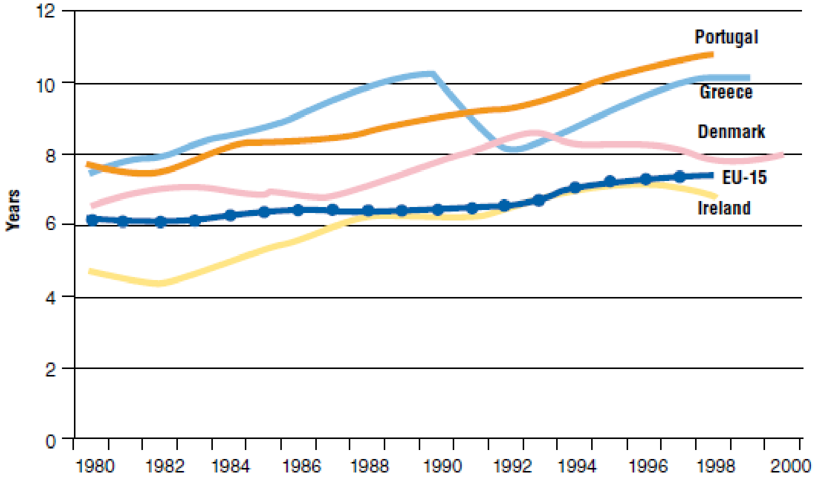
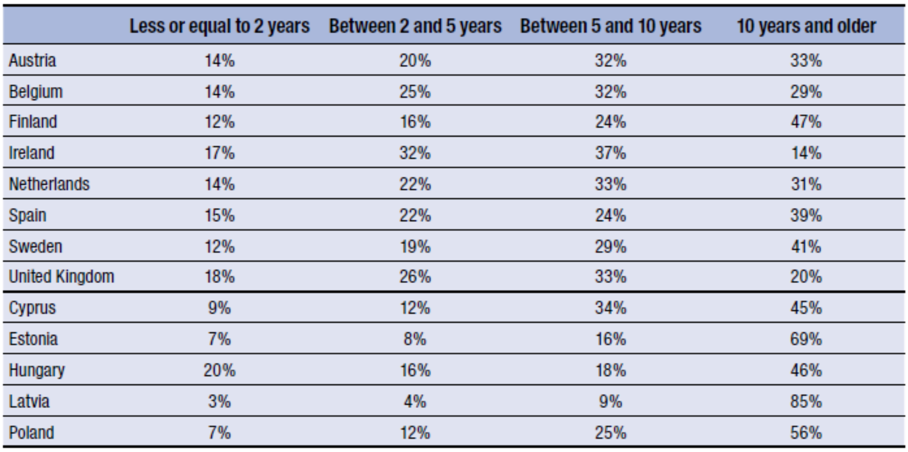


Fig.51. Average age of the car fleet in the EU (1980-2000)

Table 11 displays the composition of the car fleet in 2005. The statistics show that in 2004 cars more than 10 years old were generally more prominent in the new Member States than in the EU [70].

Table 11.Composition of the car fleet in terms of age



	Less or equal to 2 years	Between 2 and 5 years	Between 5 and 10 years	10 years and older
Austria	14%	20%	32%	33%
Belgium	14%	25%	32%	29%
Finland	12%	16%	24%	47%
Ireland	17%	32%	37%	14%
Netherlands	14%	22%	33%	31%
Spain	15%	22%	24%	39%
Sweden	12%	19%	29%	41%
United Kingdom	18%	26%	33%	20%
Cyprus	9%	12%	34%	45%
Estonia	7%	8%	16%	69%
Hungary	20%	16%	18%	46%
Latvia	3%	4%	9%	85%
Poland	7%	12%	25%	56%

Poland

In 2008 the Polish car fleet grew by 12.9 percent to over 21 million vehicles versus 2007. High growth rate was triggered by massive purchases of passenger cars. 13.46 percent more passenger cars versus 2007 were registered for the first time in 2008. New registrations went up by 9 percent in 2007 [71, 72].

Data of the Central Statistical Office of Poland indicate that the number of new registrations in 2008 stood at 1,553,9 tousand motor vehicles (1,1376.7K the year before), including 1,280,6K passenger cars (1,128,7K in 2007) as well as 185,3K trucks and road tractors (176,6K in 2007). Importers sold 319,9K new passenger cars in 2008, whereas second hand imports accounted for 1,103,9K vehicles. With massive used car imports, there were 422 passenger cars per 1,000 inhabitants in Poland in 2008, whereas the figure for the previous year stood at 383. Huge import of second hand cars triggered negative effects, too. Private import is mainly focused on vehicles aged 10 years and over (42 percent last year), what contributes to ageing of the Polish car fleet.

Barely 12 percent of all cars were 5 years old or under. In 2003, prior to Poland’s accession to the EU when limits on imports of older models were still in force, the number of the newest cars aged 5 years and under stood at over 18 percent. Almost a half of all passenger cars registered in Poland was from six to 15 years old (47.5 percent), whereas 40.5 percent of the fleet was from 16 to 30 years old. There were more over 31 year old cars in Poland in 2008 than vehicles under two years of age! Consequences of maintaining ageing car fleet do not only affect vehicle owners (who are forced to pay more expensive repair bills) but the entire society. Old cars are less safe and eco-friendly – their worn out engines demonstrate higher emission of noxious substances than new models [72].

CEPiK data indicate that over 20,000 vehicles are being declared off the road every year. 218,201 plates were surrendered in 2009 (versus 229,406 in 2008). The age structure (according to Polisch CSO, 2008) of car vehicles, buses and heavy-duty vehicles in Poland is presented in figure 52. Polish Vehicle Recycling Forum Members estimates that the average age of a vehicle disposed for scrappage stand at 16 years [72].

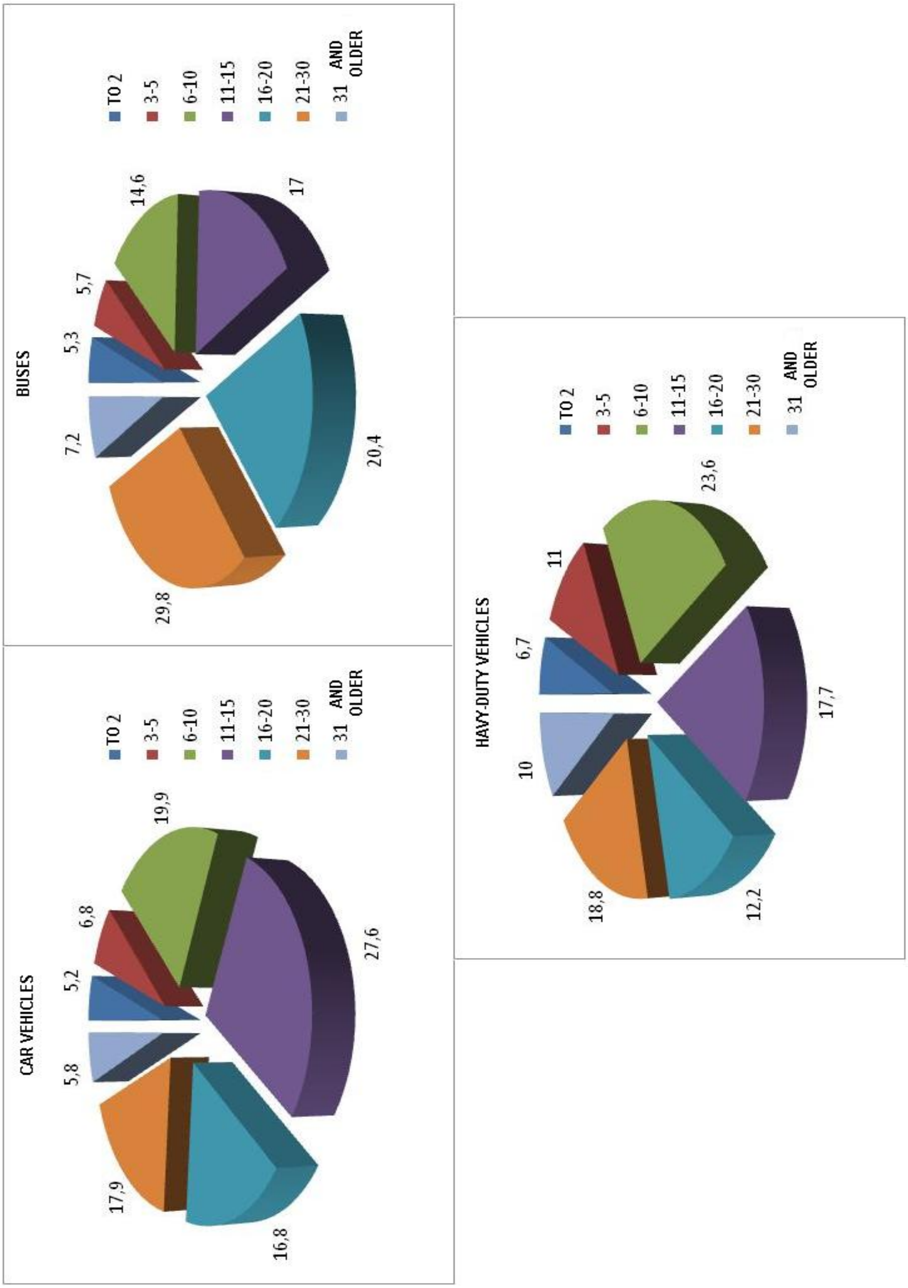


Fig 52. Age structure of car vehicles, buses and heavy-duty vehicles in Poland (2008) Source: [71]

CEPiK data indicate that over 20,000 vehicles are being declared off the road every year. 218,201 plates were surrendered in 2009 (versus 229,406 in 2008). Vehicle Recycling Forum argues that the average age of a vehicle disposed for scrappage stand at 16 years. In line with requirements of the act on recycling of ELV vehicles (ELV – End of Life Vehicle), Poland is home to a network made up of vehicle collection facilities and associated dismantling facilities. Entities which import more than a thousand vehicles into the territory of Poland are committed to establish nation-wide recycling networks. The system is not operating correctly [72].

Current regulations enforce establishment of excessively dense networks, what proves to be unprofitable in areas inhabited by small populations where few vehicles are handed over to dismantling facilities. In such regions, cars are usually abandoned at parking sites, courtyards or in forests, and legislation fails to prosecute such practises. Since the number of registration plates surrendered annually is relatively small as compared to the fleet size, it is highly possible that dismantling has fallen into grey market, which undermines financial foundations of dismantling facilities. Scrappage sub-fund of the National Environmental Protection and Water Economy Fund raised PLN 230 million in 2009, of which PLN 51.5 million was allocated by the Ministry of Environment to support dismantling stations and PLN 3.1 million to assist communes in implementation of junk car removal schemes [72].

The change in number of vehicles declared off the road from 2007 to 2009 is shown on figure 53.

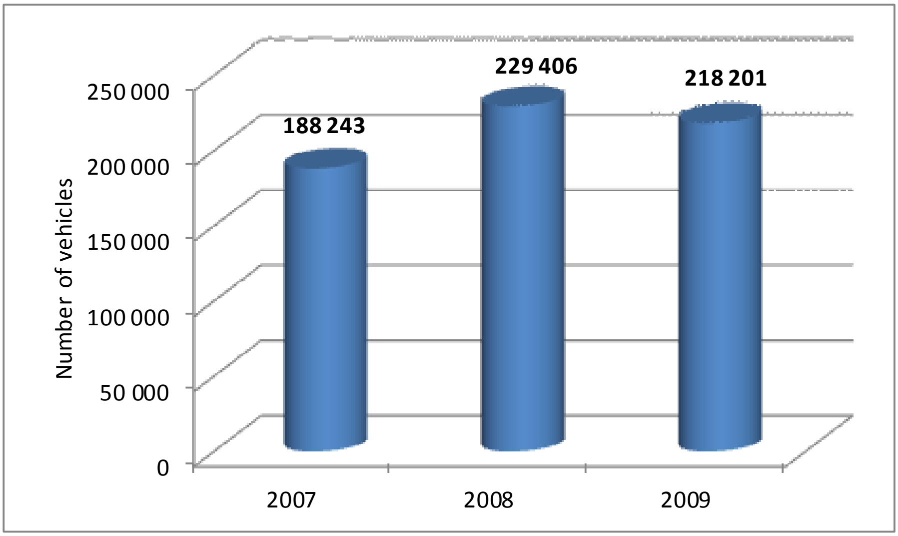


Fig 53. the number of vehicles declared off the road [72]

5.2.3. The model of car vehicle recycling system according to EU EVLs Policy

The legislation of European EVLs treatment is defined on it base on general rules of waste management preferences (fig. 54).

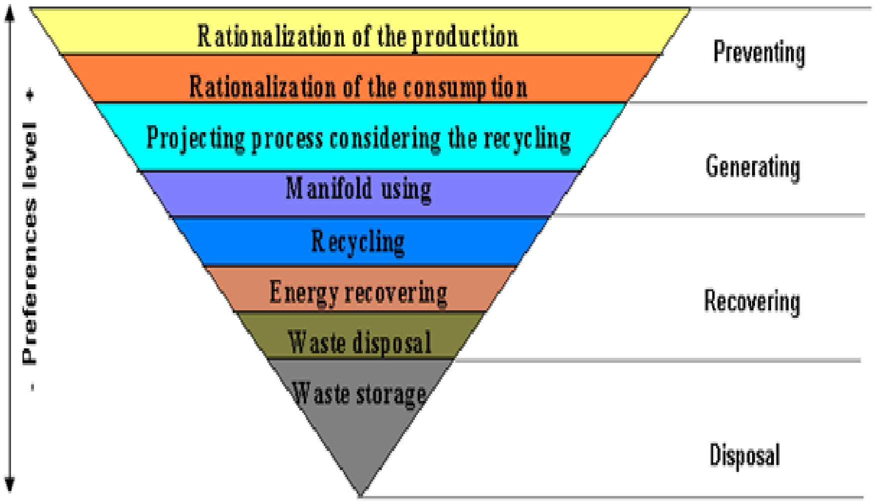


Fig 54. General waste management preferences [73]

According to the Directive minimizing the environmental impact of ELVs should be based on [74]:

- Reduce the final disposal,
- Improve environmental performance of economic operators,
- Ensuring proper functioning of the internal market and avoid distortions of competition.

The vehicle recycling can be divided to 3 main stages:

- Stage I. Disassembling and vehicle drying. From vehicle every usable parts, catalyst, gas reservoir, oil filter, battery. Also vehicle drying (exploiting liquids removing) is provided,
- Stage II. Shredding. After disassembling process the vehicles are shredded. The batch scrap metal is separated (magnetic methods) which is the highest quality raw material for steel production. The rest part of the material compose automotive shredder residue (ARS),
- Stage III. Automotive shredder residue management. In this stage row material recover is steal proceed on special technological lines for waste segregation. This technology enable to recover: residual metal fraction, scale (granular fraction of ferric oxides, mineral fraction and glass) and also rubber, plastic, fibres and wood.

Objectives of the ELV Directive are [74]:

- Minimising the environmental impact of ELVs:
  - Reduce the final disposal,
  - Improve environmental performance of economic operators.
- Ensuring proper functioning of the internal market and avoid distortions of competition.

In Article 3 of The Directive the prevention actions are proposed:

- Limit the use of hazardous substances in vehicles,
- Design new vehicles taking into account dismantling, reuse and recycling,
- Develop market for recycled materials in vehicles,
- Substance ban:

– Pb, Hg, Cd, CrVI,
– Materials and components of vehicles (also spare parts),
– Applies since 1 July 2003,
– List of exemptions in Annex II.

The Directive treats about problem of ELV’s collection giving proposals of the solution of [74]:

- Economic operators to set up collection systems,
- Member States to guarantee adequate availability of collection facilities,
- End-user needs certificate of destruction for deregistration of ELV,
- Producer responsibility.

The producer responsibilities concern [74]:

- End-user can return ELV free of charge,
- Producers pay for all or significant part of take-back costs, in case ELV has a negative value,

- Take-back is not fully free of charge, if: ELV does not contain essential components such as engine or coachwork, ELV contains added wastety should be able to take-back ELVs free of charge.

The Directive also sets the short and long-term targets [74]:

- Targets to be reached as from 2006:
  - Minimum reuse and recovery: 85%
  - Minimum reuse and recycling: 80%
- Targets to be reached as from 2015:
  - Minimum reuse and recovery: 95%
  - Minimum reuse and recycling: 85%
- Lower targets for vehicles produced before 1980:
  - Minimum reuse and recovery: 75%
  - Minimum reuse and recycling: 70%

Future developments on the targets are also define as [74]:

- Revision of the targets:
  - EP and Council to re-examine the 2015 targets,
  - Basis of the revision - Commission report on development of material composition of vehicles.
- Commission to promote dismantability, recoverability and recyclability of vehicle,
- EP and Council to establish targets beyond 2015.

The EU targets according to the ELV's Directive are presented in figure 55.

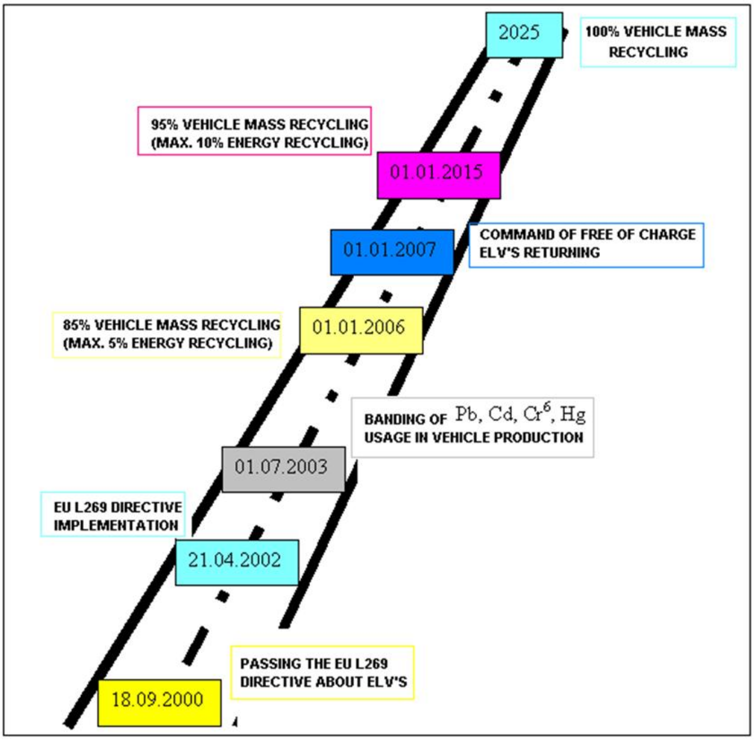


Fig 55. EU targets according to the ELV’s Directive [74]

5.2.5. After shredding residues (ARS) problem

According to the Directive 2000/53/EC of the European Parliament (18 September 2000) on end-of life vehicles ‘shredder’ means any device used for tearing into pieces or fragmenting end-of life vehicles, including for the purpose of obtaining directly reusable metal scrap. A scheme of a shredding installation is presented in figure 56.

Fig 56. Scheme of a shredding installation

A view of the shredding installation of the one of the polish companies is presented in figure 57.

Fig. 57. Shredding installation of Centrozlom S.A.

As the effect of the shredding process After Shredding Residues (ARS) appears (fig. 58).

Fig. 58. After Shredding Residues - view

Recovered materials are transformed in special installations and become the products for many technologies. Hazardous wastes are disabled in proper centers. In companies equipped with shredders a problem with after shredder fraction management (ARS) appears (fig. 59).

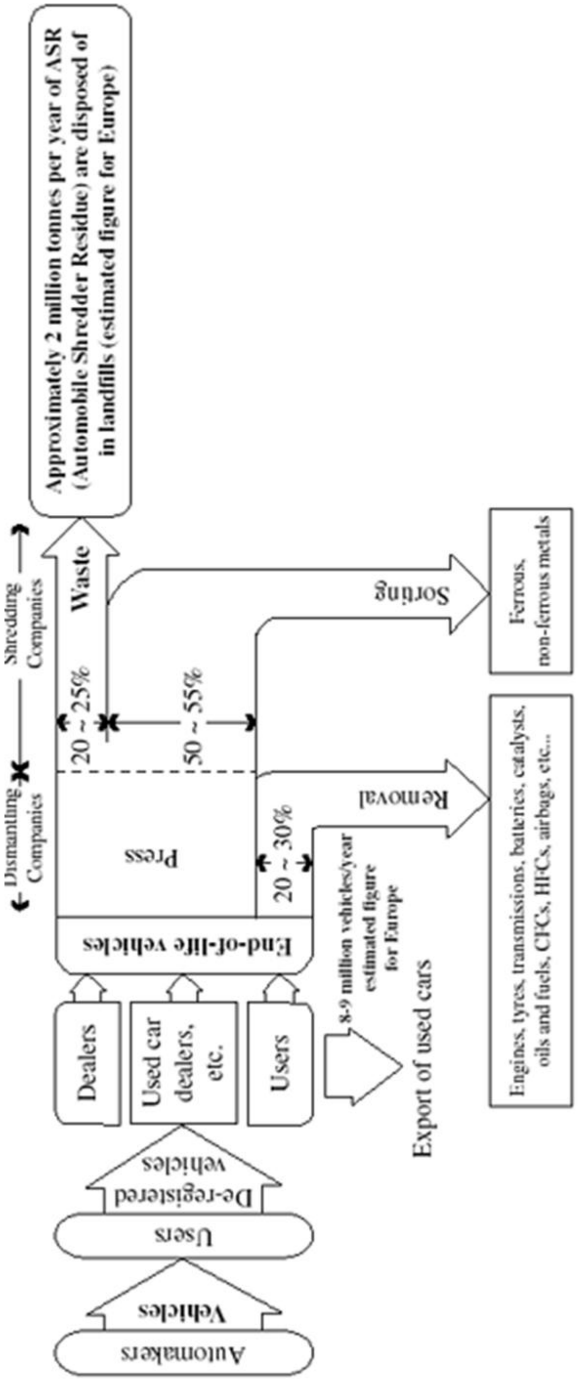


Fig 59. Scheme of ARS genesis

The ARS are a mixture of fibers, ferrous and non-ferrous metal light fractions and plastic materials. In figure 60 an example of ARS composition is presented [75].

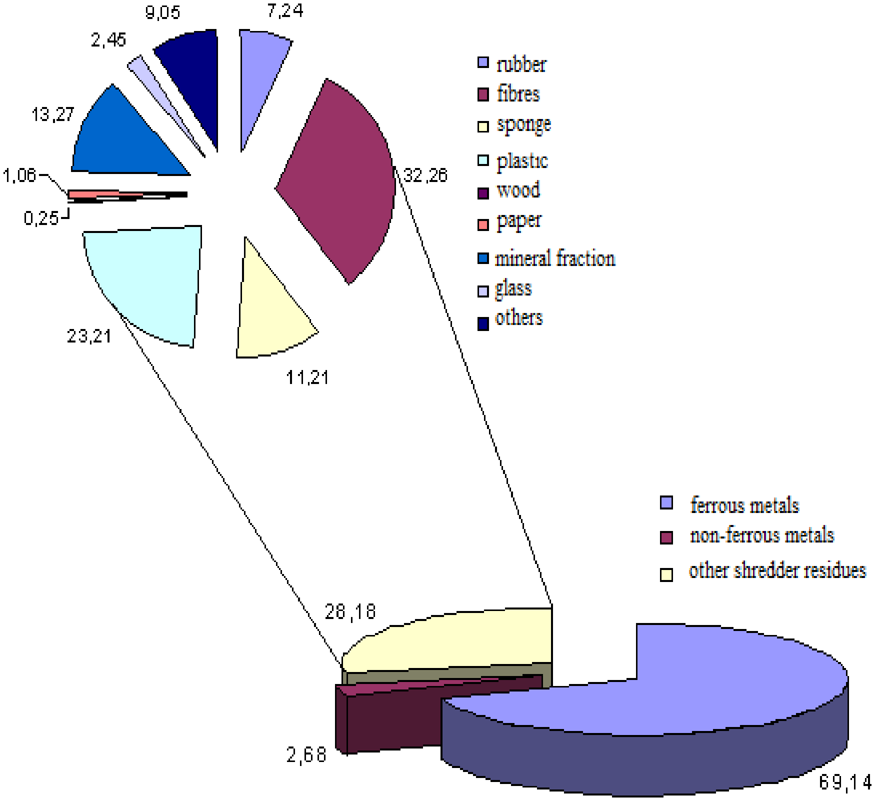


Fig 60. The ARS composition (a statistic probe) [75]

After sorting lines where most of metallic fraction are separated, ASR are mostly magazine on a company area where wastes are waiting for future treatment. The automotive shredder residue, because of potential of hazardous elements should be stored only in special conditions, define in the directive, because of the possibility of natural environment contamination [75].

Indoor air quality has become a public health issue of increasing concern during the last decades. since the concentrations of air pollutants are known to be frequently higher indoors than outdoors often exceeding by up to five times the outdoor levels and because most people spend an average of 87% of their time within enclosed buildings living, working and studying. Also the inner atmosphere of a car vehicle became one of the most important environments of human life [76-79].

It has been consequently acknowledged that the inhalation of indoor air is the major determinant of human exposure to many pollutants. One of the most hazardous for human health is Volatile organic compounds (VOC's) group.

As it was presented in chapter 3.3.1. VOC's effects on human health range from odour problems to toxic or carcinogenic effects. As a consequence, more stringent legislation on VOC emission has been implemented worldwide. To comply with this legislation, the use of processes which inherently cause little or no VOC's emission is preferable [79].

Because of a fact that most of volatile organic compounds are listed as being toxic not only the problem of their concentration in environment is considered necessary to be solved but also it is very important to monitor their toxic influence on human health. The second problem is very complicated and it strongly depends of the VOC's group composition in indoor air [80]

A significant impact on VOC's concentration has vehicle cabin equipment and quality of applied materials. The internal sources of the pollution are elements of cabin equipment (textiles, foams, plastic materials), solvents in glues, paints, lacquers and car cosmetics [78].

In the ambient air, traffic is the dominating source for these compounds that’s why the indoor air load of VOC’s compounds inside of a car cabin originates in part from the outdoors. Another part is created by human activities indoors, like smoking, cleaning, fumigation and the use of varnish and solvents [78].

The VOC’s propagation inside of a vehicle cabin strongly depends on velocity distribution. The example of velocity distribution in vehicle car cabin is shown in figure 61.

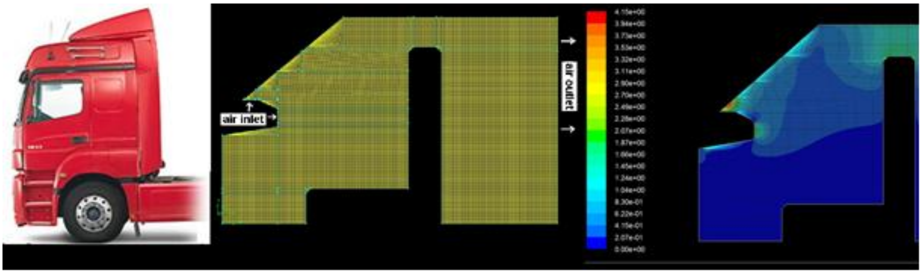


Fig 61. Contour of velocity magnitude [m/s] in vehicle cabin – example; Fluent Software, author: M.Tkaczyk

BTX (Benzene – Toluene - Xylene) compounds are known as markers for the exposure to volatile organic compounds [78].

Dictionary

A/F Ratio - air/fuel ratio

ADI - Allowable Daily Intake

Alternative Fuels - also known as non-conventional or advanced fuels, are any materials or substances that can be used as fuels, other than conventional fuels

AWI - Allowable Week Intake

benzo[a]pyrene (BaP)- PAHs indicator - the most dangerous compound from PAHs group.

CI engine - compression ignition engine

CLD - chemiluminescence detector

Eco-design -This new design approach represents a means of integrating environmental criteria on product development as part of competitive corporate strategy

Ecology - is the scientific study of the relation of living organisms with each other and their surroundings.

Ecosystem - is a biological environment consisting of all the organisms living in a particular area, as well as all the nonliving, physical components of the environment with which the organisms interact, such as air, soil, water and sunlight

EGR - Exhaust Gases Recirculation

ELV's - end-of-life vehicles

Emission -is the term used to describe the pollution (gaseous, liquid, solid) and which is put into the environment (air, water, soil) or emitted by various sources

Emission units - The unit of emission is unit of a mass (ng, µg, mg, g, kg, Mg) per unit of: time, energy, distance"

EURO - EU emission standards

FID - flame ionization detector

GC -gas chromatography

Greenhouse effect - is a process by which thermal radiation from a planetary surface is absorbed by atmospheric greenhouse gases, and is re-radiated in all directions. Since part of this re-radiation is back towards the surface, energy is transferred to the surface and the lower atmosphere. As a result, the temperature there is higher than it would be if direct heating by solar radiation were the only warming mechanism.

Greenhouse gasses - gases cause greenhouse effect

HC - hydrocarbons

ICE - internal combustion engine

LC - liquid chromatography

Lightweighting - reducing the weight of vehicles through better design and material substitution

NDIR - Non-Dispersive Infrared

NMHC - non-methane hydrocarbons

NPs - nanoparticles

PAHs - Polycyclic aromatic hydrocarbons, also known as poly-aromatic hydrocarbons or polynuclear aromatic hydrocarbons, are potent atmospheric pollutants that consist of fused aromatic rings and do not contain heteroatoms or carry substituents. Naphthalene is the simplest example of a PAH. PAHs are a type of hydrocarbons which are produced during incomplete oxidation of all hydrocarbons except methan. eare known to have mutagenic and carcinogenic effect on humans (their main source are diesel engines). The most dangerous of PAHs is benzo[a]pyrene.

PAHs - polycyclic aromatic hydrocarbons

PM - Particulates, alternatively known to as particulate matter (PM) or fine particles and also called soot, are tiny subdivisions of solid matter suspended in a gas or liquid

PM 10 - is used to describe particles of 10 micrometers or less

PN - particles number

Quenching effect - a process called wall quenching occurs as the combustion flame front burns to the relatively cool walls of the combustion chamber. This cooling extinguishes the flame before all of the fuel is fully burned, leaving a small amount of hydrocarbons to be pushed out the exhaust valve

RCC - Relative Carcinogenic Coefficient

RMCL - Recommended Maximum Concentration Limit

ROGs - reactive organic gases, play a major role in the formation of photochemical oxidants in the atmosphere

RTC - Relative Toxicity (mutagenic, carcinogenic, irritant or sensitize) Coefficient

SCR - Selective catalytic reduction

SI engine - spark ignition engine

Sustainable development - is the ability to make development sustainable—to ensure that it meets the needs of the presence without compromising the ability of future generations to meet their own needs

TEF - toxicity equivalent factor

THC - total hydrocarbons

Theoretical air demand - theoretical amount of air required for complete combustion of fuel consisted in the delivered mixture

Transportation - is a complex and porous social, technical, and economic system . This complexity derives from the pluralism of its hardware (infrastructure and vehicles) and of the people and organizations involved.

The complexity is multiplied by the existence and roles of different modes, regulatory and legislative bodies, service providers, builders, financing systems, technologies, land-use patterns, and, most importantly, human behavior

TWC - Three Way Catalytic Converter

VOCs -volatile organic compounds

Volatile Organic Compounds - are significant group amid 200 identified compounds in diesel engine exhaust (mainly aldehydes but also alcohols, ketons, esters, paraffin and aromatic hydrocarbons)

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Figures and tables index

FIGURES

TABLES

Exercise 1 - *Engine Test Bed*

ECOLOGY AND ENVIRONMENT PROTECTION OF ROAD TRANSPORTATION – LABORATORY

1. Objectives

The purpose of this exercise is to learn the construction of a test bed station which is used to research the environment-friendly characteristics of a combustion engine as well as the effectiveness of emission control systems.

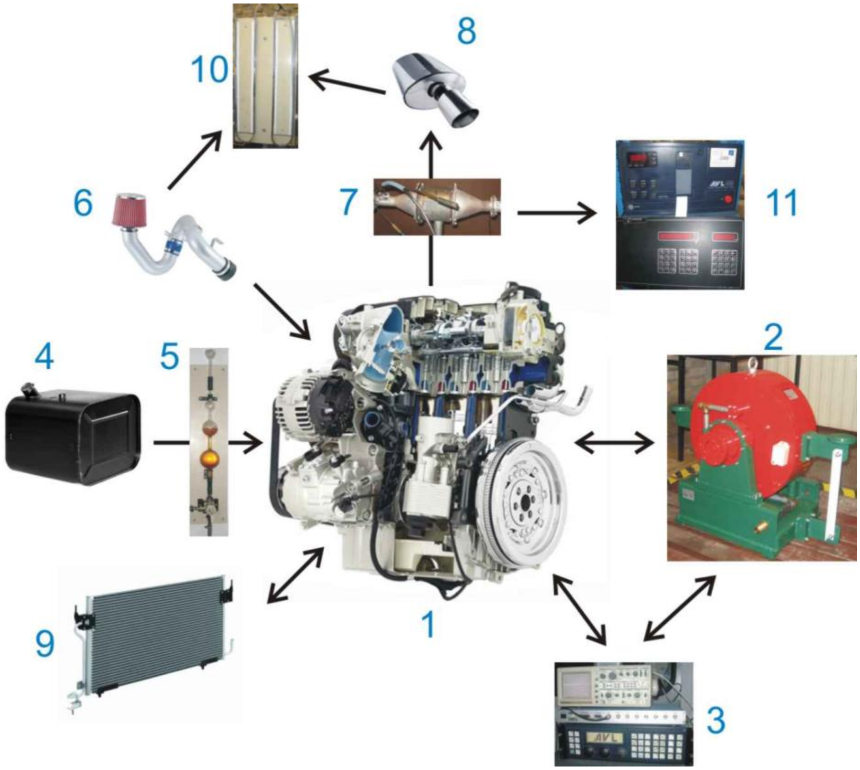
2. Engine Test Bed Construction

Internal combustion engines can be tested along with the machine they power (eg. a car tested on the road or on the chassis dynamometer) or separately in an engine test house. A test bed is the only devise that measures an engine parameters, including its actual power. During a test bed testing the main energy receiver is brakes. There are two types of engine brakes:

- hydraulic brakes (also called water brakes because the medium used is most commonly water),
- electrical brakes: generator and eddy current.

Mechanical energy, that powers an internal combustion engine, inside brakes (hydraulic and eddy current brakes) changes into heat and is removed by coolant, or into electric power (generator brakes) which can be put back in the system.

While testing an engine on a test bed it is possible to apply any load and precisely measure the revolutions and torque. Figure below shows the engine test bed structure:



1 - engine, 2 - dynamometer, 3 – steering system, 4 – fueling system, 5 – fuel consumption measurement system, 6 – air inlet system, 7 – catalyst/filter, 8 – exhaust system, 9 – cooling system, 10 – pressure measurement system, 11 – exhaust gas analyzers

3. Implementation

Demonstration exercise: introduction to the structure and basic maintenance of engine test beds.

ECOLOGY AND ENVIRONMENT PROTECTION OF ROAD TRANSPORTATION – LABORATORY

1. Objectives

The purpose of this exercise is to learn about the measuring devices and methods used to calculate the concentration of particular elements of combustion gas, especially those, that are potentially harmful to humans and the environment: CO, CO_2, NO_x, HC (including PAHs and VOCs), PM.

Requisite knowledge: **chapters 4.2, 4.3 and 4.5**

2. Implementation

Demonstration exercise: introduction to the structure and basic handling of the exhaust gas analyzers used at the test beds:

- NDIR analyzer
- Smoke matter analyzer
- CLD analyzer

Also PAHs and VOC's sampling method (active coal samplers) is presented and chromatographic analytics.

ECOLOGY AND ENVIRONMENT PROTECTION OF ROAD TRANSPORTATION – LABORATORY

1. Objectives

The purpose of this exercise is evaluation of exhaust gas pollution basing on the measurements done at a test bed station.

Many of the substances emitted by combustion engines are toxic to a human organism. Even though, the toxic influence of most of those substances is well known (basing on that data, the allowable concentration of those substances in the environment is established), it is important to remember that those compounds appear in fumes as mixture with diverse composition. Toxic influence of such mixtures on a living organism is very often only indirectly related to toxic qualities of the individual compounds.

The problem of reducing the toxic substances emission has become extremely important also in terms of strict law requirements imposed on the vehicle users. Despite the improvement in all the construction and material solutions applied to modern combustion engines, complying with the current and future emission standards becomes a challenge for engine manufacturers as well as for emission control systems.

Requisite knowledge: **chapters 2 and 4.7**

2. Implementation

2.1. Health and Safety Training

The Health and Safety training at a work station is to be conducted before commencing any work or testing.

2.2. Test Bed station preparation.

Prior to the work start:

- check the engine oil level,
- check the engine coolant level,
- check the connection between the measuring probe and measuring apparatus,
- remove all the redundant items from the work station,
- check the fuel delivery system – fuel consumption measurement system should be full, the fuel should be connected.

2.3. Measuring

- Before the start of the exercise, consult with the teacher the measuring plan, the measuring supervisor and choose the apparatus operator
- The engine is to be started only by the teacher. Next, the measuring apparatus is switched on and checked,

- After the test bed station is started, the teacher allows the start of the testing. The results are to be recorded on a measuring sheet provided, according to the measuring plan,
- Any observed irregularities are to be reported to the teacher immediately.

2.4. Test end

The teacher is to be informed after the measuring is finished. Only the teacher is allowed to switch off the measuring apparatus. .

2.5. Test results analysis

After the exercise is over, the results are to be analyzed and presented during the following classes in a form of a report.

ECOLOGY AND ENVIRONMENT PROTECTION OF ROAD TRANSPORTATION – LABORATORY

1. Objectives

The purpose of this exercise is the analysis and evaluation of the exhaust gas pollution versus engine load and engine speed point of view, based on the measuring done at the dynamometer station

Requisite knowledge: **chapter 4.1**

2. Implementation

2.1. Health and Safety Training

The Health and Safety training at a work station is to be conducted before commencing any work or testing.

2.2. Test Bed station preparation.

Prior to the work start:

- check the engine oil level,
- check the engine coolant level,

- check the connection between the measuring probe and measuring apparatus,
- remove all the redundant items from the work station,
- check the fuel delivery system – fuel consumption measurement system should be full, the fuel should be connected.

2.3. Measuring

- Before the star of the exercise, consulting with the teacher, the measuring plan, the measuring supervisor and the apparatus operator is chosen.
- The engine is to be started only by the teacher. Next, the measuring apparatus is switched on and checked.
- After the test bed station is started, the teacher allows to start the testing. The results are to be recorded on a measuring sheet provided, according to the measuring plan.
- Any observed irregularities are to be reported to the teacher immediately.

2.4. Test end

The teacher is to be informed after the measuring is finished. Only the teacher is allowed to switch off the measuring apparatus. .

2.5. Test results analysis

After the exercise is over, the results are to be analyzed and presented during the following classes in a form of a report.

ECOLOGY AND ENVIRONMENT PROTECTION OF ROAD TRANSPORTATION – LABORATORY

1. Objectives

The purpose of this exercise it to evaluate the catalytic exhaust gas purification system based tests performed at the test bed station.

Requisite knowledge: **chapters 4.6.1, 4.6.2. and 4.7**

2. Implementation

3.1. Health and Safety Training

The Health and Safety training at a work station is to be conducted before commencing any work or testing.

3.2. Test Bed station preparation.

Prior to the work start:

- check the engine oil level,
- check the engine coolant level,

- check the connection between the measuring probe and measuring apparatus,
- remove all the redundant items from the work station,
- check the fuel delivery system – fuel consumption measurement system should be full, the fuel should be connected.

3.3. Measuring

- Before the start of the exercise, consulting with the teacher, the measuring plan, the measuring supervisor and the apparatus operator is chosen.
- The engine is to be started only by the teacher. Next, the measuring apparatus is switched on and checked.
- After the test bed station is started, the teacher allows the start of the testing. The results are to be recorded on a measuring sheet provided, according to the measuring plan.
- Any observed irregularities are to be reported to the teacher immediately.

3.4. Test end

The teacher is to be informed after the measuring is finished. Only the teacher is allowed to switch off the measuring apparatus. .

3.5. Test results analysis

After the exercise is over, the results are to be analyzed and presented during the following classes in a form of a report.

ECOLOGY AND ENVIRONMENT PROTECTION OF ROAD TRANSPORTATION – LABORATORY

1. Objectives

The purpose of this exercise is to evaluate the effectiveness of the particulate matter filter basing on the test bed measurements.

Requisite knowledge: **chapters 4.6.1, 4.6.5. and 4.7**

2. Implementation

2.1. Health and Safety Training

The Health and Safety training at a work station is to be conducted before commencing any work or testing.

2.2. Test Bed station preparation.

Prior to the work start:

- check the engine oil level,
- check the engine coolant level,
- check the connection between the measuring probe and measuring apparatus,
- remove all the redundant items from the work station,
- check the fuel delivery system – fuel consumption measurement system should be full, the fuel should be connected.

2.3. Measuring

- Before the start of the exercise, consulting with the teacher, the measuring plan, the measuring supervisor and the apparatus operator is chosen.
- The engine is to be started only by the teacher. Next, the measuring apparatus is switched on and checked.
- After the test bed station is started, the teacher allows the start of the testing. The results are to be recorded on a measuring sheet provided, according to the measuring plan.
- Any observed irregularities are to be reported to the teacher immediately.

2.4. Test end

The teacher is to be informed after the measuring is finished. Only the teacher is allowed to switch off the measuring apparatus.

2.5. Test results analysis

Ater the exercise is over, the results are to be analyzed and presented during the following classes in a form of a report.

L 269/34 EN Official Journal of the European Communities 21.10.2000

DIRECTIVE 2000/53/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 18 September 2000

on end-of life vehicles

THE EUROPEAN PARLIAMENT AND THE COUNCIL OF THE EUROPEAN UNION,

Having regard to the Treaty establishing the European Community, and in particular Article 175(1) thereof, Having regard to the proposal from the Commission (1), Having regard to the opinion of the Economic and Social Committee (2), Having consulted the Committee of the Regions, Acting in accordance with the procedure referred to in Article 251 of the Treaty in the light of the joint text approved by the Conciliation Committee on 23 May 2000 (3),

Whereas

(1) The different national measures concerning end-of life vehicles should be harmonized in order, first, to minimize the impact of end-of life vehicles on the environment, thus contributing to the protection, preservation and improvement of the quality of the environment and energy conservation, and, second, to ensure the smooth operation of the internal market and avoid distortions of competition in the Community.

(2) A Community-wide framework is necessary in order to ensure coherence between national approaches in attaining the objectives stated above, particularly with a view to the design of vehicles for recycling and recovery, to the requirements for collection and treatment facilities, and to the attainment of the targets for reuse, recycling and recovery, taking into account the principle of subsidiarity and the polluter-pays principle.

(3) Every year end-of life vehicles in the Community generate between 8 and 9 million tonnes of waste, which must be managed correctly.

(4) (4) In order to implement the precautionary and preventive principles and in line with the Community strategy for waste management, the generation of waste must be avoided as much as possible.

(5) It is a further fundamental principle that waste should be reused and recovered, and that preference be given to reuse and recycling.

(6) Member States should take measures to ensure that economic operators set up systems for the collection, treatment and recovery of end-of life vehicles.

(7) Member States should ensure that the last holder and/or owner can deliver the end-of life vehicle to an authorized treatment facility without any cost as a result of the vehicle having no or a negative, market value. Member States should ensure that producers meet all, or a significant part of, the costs of the implementation of these measures; the normal functioning of market forces should not be hindered.

(8) This Directive should cover vehicles and end-of life vehicles, including their components and materials, as well as spare and

replacement parts, without prejudice to safety standards, air emissions and noise control.

(9) This Directive should be understood as having borrowed, where appropriate, the terminology used by several existing directives, namely Council Directive 67/548/EEC of 27 June 1967 on the approximation of laws, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances (4), Council Directive 70/156/EEC of 6 February 1970 on the approximation of the laws of the Member States relating to the type-approval of motor vehicles and their trailers (5), and Council Directive 75/442/EEC of 15 July 1975 on waste (6).

(10) Vintage vehicles, meaning historic vehicles or vehicles of value to collectors or intended for museums, kept in a proper and environmentally sound manner, either ready for use or stripped into parts, are not covered by the definition of waste laid down by Directive 75/442/EEC and do not fall within the scope of this Directive.

(11) It is important that preventive measures be applied from the conception phase of the vehicle onwards and take the form, in particular, of reduction and control of hazardous substances in vehicles, in order to prevent their release into the environment, to facilitate recycling and to avoid the disposal of hazardous waste. In particular the use of lead, mercury, cadmium and hexavalent chromium should be prohibited. These heavy metals should only be used in certain applications according to a list which will be regularly reviewed. This will help to ensure that certain materials and components do not become shredder residues, and are not incinerated or disposed of in landfills.

(12) The recycling of all plastics from end-of life vehicles should be continuously improved. The Commission is currently examining the environmental impacts of PVC. The Commission will, on the basis of this work, make proposals as appropriate as to the use of PVC including considerations for vehicles.

(13) The requirements for dismantling, reuse and recycling of end-of life vehicles and their components should be integrated in the design and production of new vehicles.

(14) The development of markets for recycled materials should be encouraged.

(15) In order to ensure that end-of life vehicles are discarded without endangering the environment, appropriate collection systems should be set up.

(16) A certificate of destruction, to be used as a condition for the de-registration of end-of life vehicles, should be introduced. Member States without a de-registration system should set up a system according to which a certificate of destruction is notified to the relevant competent authority when the end-of life vehicle is transferred to a treatment facility.

(17) This Directive does not prevent Member States from granting, where appropriate, temporary deregistrations of vehicles.

(18) Collection and treatment operators should be allowed to operate only when they have received a permit or, in case a registration is used instead of a permit, specific conditions have been complied with.

(19) The recyclability and recoverability of vehicles should be promoted.

(20) It is important to lay down requirements for storage and treatment operations in order to prevent negative impacts on the environment and to avoid the emergence of distortions in trade and competition.

(21) In order to achieve results in the short term and to give operators, consumers and public authorities the necessary perspective for the longer term, quantified targets for reuse, recycling and recovery to be achieved by economic operators should be set.

(22) Producers should ensure that vehicles are designed and manufactured in such a way as to allow the quantified targets for reuse, recycling and recovery to be achieved. To this end the Commission will promote the preparation of European standards and will take the other necessary measures in order to amend the pertinent European vehicle type-approval legislation.

(23) Member States should ensure that in implementing theprovisions of this Directive competition is preserved, in particular as regards the access of small and mediumsized enterprises to the collection, dismantling, treatment and recycling market.

(24) In order to facilitate the dismantling and recovery, in particular recycling of end-of life vehicles, vehicle manufacturers should provide authorised treatment facilities with all requisite dismantling information, in particular for hazardous materials.

(25) The preparation of European standards, where appropriate, should be promoted. Vehicle manufacturers and material producers should use component and material coding standards, to be established by the Commission assisted by the relevant committee. In the preparation of these standards the Commission will take account, as appropriate, of the work going on in this area in the relevant international forums.

(26) Community-wide data on end-of life vehicles are needed in order to monitor the implementation of the objectives of this Directive.

(27) Consumers have to be adequately informed in order to adjust their behaviour and attitudes; to this end information should be made available by the relevant economic operators.

(28) Member States may choose to implement certain provisions by means of agreements with the economic sector concerned, provided that certain conditions are met.

(29) The adaptation to scientific and technical progress of the requirements for treatment facilities and for the use of hazardous substances and, as well as the adoption of minimum standards for the certificate of destruction, the formats for the database and the implementation measures necessary to control compliance with the quantified targets should be effected by the Commission under a Committee procedure.

(30) The measures to be taken for the implementation of this Directive should be adopted in accordance with Council Decision 1999/468/EC of 28 June 1999 laying down the procedures for the exercise of implementing powers conferred on the Commission (1).

(31) Member States may apply the provisions of this Directive in advance of the date set out therein, provided such measures are compatible with the Treaty,

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(1) OJ C 337, 7.11.1997, p. 3, andOJ C 156, 3.6.1999, p. 5.

(2) OJ C 129, 27.4.1998, p. 44. (4) OJ 196, 16.8.1967, p. 1. Directive as last amended by Commission

(3) Opinion of the European Parliament of 11 February 1999 (OJ C Directive 98/98/EC (OJ L 355, 30.12.1998, p. 1). 150, 28.5.1999, p. 420), Council Common Position of 29 July 1999 (OJ C 317, 4.11.1999, p. 19) and Decision of the European Parliament of 3 February 2000 (not yet published in the Official Journal). Council Decision of 20 July 2000 and Decision of theEuropean Parliament of 7 September 2000. (5) OJ L 42, 23.2.1970, p. 1. Directive as last amended by Directive 98/91/EC of the

European Parliament and of the Council (OJ L 11, 16.1.1999, p. 25). (6) OJ L 194, 25.7.1975, p. 39. Directive as last amended by Commission Decision 96/350/EC (OJ L 135, 6.6.1996, p. 32).

HAVE ADOPTED THIS DIRECTIVE:

Article 1

Objectives

This Directive lays down measures which aim, as a first priority, at the prevention of waste from vehicles and, in addition, at the reuse, recycling and other forms of recovery of end-of life vehicles and their components so as to reduce the disposal of waste, as well as at the improvement in the environmental performance of all of the economic operators involved in the life cycle of vehicles and especially the operators directly involved in the treatment of end-of life vehicles.

Article 2

Definitions

For the purposes of this Directive:

1. ‘vehicle’ means any vehicle designated as category M_1 or N_1 defined in Annex IIA to Directive 70/156/EEC, and three wheel motor vehicles as defined in Directive 92/61/EEC, but excluding motor tricycles;
2. ‘end-of life vehicle’ means a vehicle which is waste within the meaning of Article 1(a) of Directive 75/442/EEC;
3. ‘producer’ means the vehicle manufacturer or the professional importer of a vehicle into a Member State;

4. ‘prevention’ means measures aiming at the reduction of the quantity and the harmfulness for the environment of end-of life vehicles, their materials and substances;
5. ‘treatment’ means any activity after the end-of life vehicle has been handed over to a facility for depollution, dismantling, shearing, shredding, recovery or preparation for disposal of the shredder wastes, and any other operation carried out for the recovery and/or disposal of the end-of life vehicle and its components;
6. ‘reuse’ means any operation by which components of end-of life vehicles are used for the same purpose for which they were conceived;
7. ‘recycling’ means the reprocessing in a production process of the waste materials for the original purpose or for other purposes but excluding energy recovery. Energy recovery means the use of combustible waste as a means to generate energy through direct incineration with or without other waste but with recovery of the heat;
8. ‘recovery’ means any of the applicable operations provided for in Annex IIB to Directive 75/442/EEC;
9. ‘disposal’ means any of the applicable operations provided for in Annex IIA to Directive 75/442/EEC;
10. ‘economic operators’ means producers, distributors, collectors, motor vehicle insurance companies, dismantlers, shredders, recoverers, recyclers and other treatment operators of end-of life vehicles, including their components and materials;
11. ‘hazardous substance’ means any substance which is considered to be dangerous under Directive 67/548/EEC;
12. ‘shredder’ means any device used for tearing into pieces or fragmenting end-of life vehicles, including for the purpose of obtaining directly reusable metal scrap;

13. ‘dismantling information’ means all information required for the correct and environmentally sound treatment of end-of life vehicles. It shall be made available to authorized treatment facilities by vehicle manufacturers and component producers in the form of manuals or by means of electronic media (e.g. CD-ROM, on-line services).

Article 3

Scope

1. This Directive shall cover vehicles and end-of life vehicles, including their components and materials. Without prejudice to Article 5(4), third subparagraph, this shall apply irrespective of how the vehicle has been serviced or repaired during use and irrespective of whether it is equipped with components supplied by the producer or with other components whose fitting as spare or replacement parts accords with the appropriate Community provisions or domestic provisions.
2. This Directive shall apply without prejudice to existing Community legislation and relevant national legislation, in particular as regards safety standards, air emissions and noise controls and the protection of soil and water.
3. Where a producer only makes or imports vehicles that are exempt from Directive 70/156/EEC by virtue of Article 8(2)(a) thereof, Member States may exempt that producer and his vehicles from Articles 7(4), 8 and 9 of this Directive.
4. Special-purpose vehicles as defined in the second indent of Article 4(1)(a) of Directive 70/156/EEC shall be excluded from the provisions of Article 7 of this Directive.
5. For three-wheel motor vehicles only Articles 5(1), 5(2) and 6 of this Directive shall apply.

Article 4

Prevention

1. In order to promote the prevention of waste Member States shall encourage, in particular:
   (a) vehicle manufacturers, in liaison with material and equipment manufacturers, to limit the use of hazardous substances in vehicles and to reduce them as far as possible from the conception of the vehicle onwards, so as in particular to prevent their release into the environment, make recycling easier, and avoid the need to dispose of hazardous waste;
   (b) the design and production of new vehicles which take into full account and facilitate the dismantling, reuse and recovery, in particular the recycling, of end-of life vehicles, their components and materials;
   (c) vehicle manufacturers, in liaison with material and equipment manufacturers, to integrate an increasing quantity of recycled material in vehicles and other products, in order to develop the markets for recycled materials.
2. (a) Member States shall ensure that materials and components of vehicles put on the market after 1 July 2003 do not contain lead, mercury, cadmium or hexavalent chromium other than in cases listed in Annex II under the conditions specified therein;
   (b) in accordance with the procedure laid down in Article 11 the Commission shall on a regular basis, according to technical and scientific progress, amend Annex II, in order to:

(i) as necessary, establish maximum concentration values up to which the existence of the substances referred to in subparagraph (a) in specific materials and components of vehicles shall be tolerated;

(ii) exempt certain materials and components of vehicles from the provisions of subparagraph (a) if the use of these substances is unavoidable;

(iii) delete materials and components of vehicles from Annex II if the use of these substances is avoidable;

(iv) under points (i) and (ii) designate those materials and components of vehicles that can be stripped before further treatment; they shall be labelled or made identifiable by other appropriate means;

(c) the Commission shall amend Annex II for the first time not later than 21 October 2001. In any case none of the exemptions listed therein shall be deleted from the Annex before 1 January 2003.

Article 5

Collection

1. Member States shall take the necessary measures to ensure:

— that economic operators set up systems for the collection of all end-of life vehicles and, as far as technically feasible, of waste used parts removed when passenger cars are repaired,

— the adequate availability of collection facilities within their territory.

2. Member States shall also take the necessary measures to ensure that all end-of life vehicles are transferred to authorized treatment facilities.

3. Member States shall set up a system according to which the presentation of a certificate of destruction is a condition for

deregistration of the end-of life vehicle. This certificate shall be issued to the holder and/or owner when the end-of life vehicle is transferred to a treatment facility. Treatment facilities, which have obtained a permit in accordance with Article 6, shall be permitted to issue a certificate of destruction. Member States may permit producers, dealers and collectors on behalf of an authorised treatment facility to issue certificates of destruction provided that they guarantee that the end-of life vehicle is transferred to an authorised treatment facility and provided that they are registered with public authorities. Issuing the certificate of destruction by treatment facilities or dealers or collectors on behalf of an authorised treatment facility does not entitle them to claim any financial reimbursement, except in cases where this has been explicitly arranged by Member States. Member States which do not have a deregistration system at the date of entry into force of this Directive shall set up a system according to which a certificate of destruction is notified to the relevant competent authority when the end-of life vehicle is transferred to a treatment facility and shall otherwise comply with the terms of this paragraph. Member States making use of this subparagraph shall inform the Commission of the reasons thereof.

4. Member States shall take the necessary measures to ensure that the delivery of the vehicle to an authorised treatment facility in accordance with paragraph 3 occurs without any cost for the last holder and/or owner as a result of the vehicle's having no or a negative market value. Member States shall take the necessary measures to ensure that producers meet all, or a significant part of, the costs of the implementation of this measure and/or take back end-of life vehicles under the same conditions as referred to in the first subparagraph. Member States may provide that the delivery of end-of life vehicles is

not fully free of charge if the end-of life vehicle does not contain the essential components of a vehicle, in particular the engine and the coachwork, or contains waste which has been added to the end-of life vehicle. The Commission shall regularly monitor the implementation of the first subparagraph to ensure that it does not result in market distortions, and if necessary shall propose to the European Parliament and the Council an amendment thereto.

5. Member States shall take the necessary measures to ensure that competent authorities mutually recognise and accept the certificates of destruction issued in other Member States in accordance with paragraph 3. To this end, the Commission shall draw up, not later than 21 October 2001 the minimum requirements for the certificate of destruction.

Article 6

Treatment

1. Member States shall take the necessary measures to ensure that all end-of life vehicles are stored (even temporarily) and treated in accordance with the general requirements laid down in Article 4 of Directive 75/442/EEC, and in compliance with the minimum technical requirements set out in Annex I to this Directive, without prejudice to national regulations on health and environment. L 269/38 EN Official Journal of the European Communities 21.10.2000
2. Member States shall take the necessary measures to ensure that any establishment or undertaking carrying out treatment operations obtains a permit from or be registered with the competent authorities, in compliance with Articles 9, 10 and 11 of Directive 75/442/EEC. The

derogation from the permit requirement referred to in Article 11(1)(b) of Directive 75/442/EEC may apply to recovery operations concerning waste of end-of life vehicles after they have been treated according to Annex 1(3) to this Directive if there is an inspection by the competent authorities before the registration. This inspection shall verify:

(a) type and quantities of waste to be treated;

(b) general technical requirements to be complied with;

(c) safety precautions to be taken, in order to achieve the objectives referred to in Article 4 of Directive 75/442/EEC. This inspection shall take place once a year. Member States using the derogation shall send the results to the Commission.

3. Member States shall take the necessary measures to ensure that any establishment or undertaking carrying out treatment operations fulfils at least the following obligations in accordance with Annex I:

(a) end-of life vehicles shall be stripped before further treatment or other equivalent arrangements are made in order to reduce any adverse impact on the environment. Components or materials labelled or otherwise made identifiable in accordance with Article 4(2) shall be stripped before further treatment;

(b) hazardous materials and components shall be removed and segregated in a selective way so as not to contaminate subsequent shredder waste from end-of life vehicles;

(c) stripping operations and storage shall be carried out in such a way as to ensure the suitability of vehicle components for reuse and recovery, and in particular for recycling. Treatment operations for depollution of end-of life vehicles as referred to in Annex I(3) shall be carried out as soon as possible.

4. Member States shall take the necessary measures to ensure that the permit or registration referred to in paragraph 2 includes all

conditions necessary for compliance with the requirements of paragraphs 1, 2 and 3.

5. Member States shall encourage establishments or undertakings, which carry out treatment operations to introduce, certified environmental management systems.

Article 7
Reuse and recovery

1. Member States shall take the necessary measures to encourage the reuse of components which are suitable for reuse, the recovery of components which cannot be reused andthe giving of preference to recycling when environmentally viable, without prejudice to requirements regarding the safety of vehicles and environmental requirements such as air emissions and noise control.
2. Member States shall take the necessary measures to ensure that the following targets are attained by economic operators:
   (a) no later than 1 January 2006, for all end-of life vehicles, the reuse and recovery shall be increased to a minimum of 85 % by an average weight per vehicle and year. Within the same time limit the reuse and recycling shall be increased to a minimum of 80 % by an average weight per vehicle and year; for vehicles produced before 1 January 1980, Member States may lay down lower targets, but not lower than 75 % for reuse and recovery and not lower than 70 % for reuse and recycling. Member States making use of this subparagraph shall inform the Commission and the other Member States of the reasons therefor;

(b) no later than 1 January 2015, for all end-of life vehicles, the reuse and recovery shall be increased to a minimum of 95 % by an average weight per vehicle and year. Within the same time limit, the re-use and recycling shall be increased to a minimum of 85 % by an average weight per vehicle and year. By 31 December 2005 at the latest the European Parliament and the Council shall re-examine the targets referred to in paragraph (b) on the basis of a report of the Commission, accompanied by a proposal. In its report the Commission shall take into account the development of the material composition of vehicles and any other relevant environmental aspects related to vehicles. The Commission shall, in accordance with the procedure laid down in Article 11, establish the detailed rules necessary to control compliance of Member States with the targets set out in this paragraph. In doing so the Commission shall take into account all relevant factors, inter alia the availability of data and the issue of exports and imports of end-of life vehicles. The Commission shall take this measure not later than 21 October 2002.

3. On the basis of a proposal from the Commission, the European Parliament and the Council shall establish targets for reuse and recovery and for reuse and recycling for the years beyond 2015.
4. In order to prepare an amendment to Directive 70/ 156/EEC, the Commission shall promote the preparation of European standards relating to the dismantlability, recoverability and recyclability of vehicles. Once the standards are agreed, but in any case no later than by the end of 2001, the European Parliament and the Council, on the basis of a proposal from the Commission, shall amend Directive 70/156/EEC so that vehicles type-approved in accordance withthat Directive and put on the market after three years after the amendment

of the Directive 70/156/EEC are re-usable and/or recyclable to a minimum of 85 % by weight per vehicle and are re-usable and/or recoverable to a minimum of 95 % by weightper vehicle.

5. In proposing the amendment to Directive 70/156/EEC relating to the ability to be dismantled, recoverability and recyclability of vehicles, the Commission shall take into account as appropriate the need to ensure that the reuse of components does not give rise to safety or environmental hazards.

Article 8

Coding standards/dismantling information

1. Member States shall take the necessary measures to ensure that producers, in concert with material and equipment manufacturers, use component and material coding standards, in particular to facilitate the identification of those components and materials which are suitable for reuse and recovery.
2. Not later than 21 October 2001 the Commission shall, in accordance with the procedure laid down in Article 11 establish the standards referred to in paragraph 1 of this Article. In so doing, the Commission shall take account of the work going on in this area in the relevant international forums and contribute to this work as appropriate.
3. Member States shall take the necessary measures to ensure that producers provide dismantling information for each type of new vehicle put on the market within six months after the vehicle is put on the market. This information shall identify, as far as it is needed by treatment facilities in order to comply with the provisions of this Directive, the different vehicle components and materials, and the

location of all hazardous substances in the vehicles, in particular with a view to the achievement of the objectives laid down in Article 7.

4. Without prejudice to commercial and industrial confidentiality, Member States shall take the necessary measures to ensure that manufacturers of components used in vehicles make available to authorised treatment facilities, as far as it is requested by these facilities, appropriate information concerning dismantling, storage and testing of components which can be reused.

Article 9

Reporting and information

1. At three-year intervals Member States shall send a report to the Commission on the implementation of this Directive. The report shall be drawn up on the basis of a questionnaire or outline drafted by the Commission in accordance with the procedure laid down in Article 6 of Directive 91/692/EEC (1) with a view to establishing databases on end-of life vehicles and their treatment. The report shall contain relevant information on possible changes in the structure of motor vehicle dealing and of the collection, dismantling, shredding, recovery and recycling industries, leading to any distortion of competition between or within Member States. The questionnaire or outline shall be sent to the Member States six months before the start of the period covered by the report. The report shall be made to the Commission within nine months of the end of the three-year period covered by it. The first report shall cover the period of three years from 21 April 2002. Based on the above information, the Commission shall publish a

report on the implementation of this Directive within nine months of receiving the reports from the Member States.

2. Member States shall require in each case the relevant economic operators to publish information on:
   — the design of vehicles and their components with a view to their recoverability and recyclability,
   — the environmentally sound treatment of end-of life vehicles, in particular the removal of all fluids and dismantling,
   — the development and optimisation of ways to reuse, recycle and recover end-of life vehicles and their components,
   — the progress achieved with regard to recovery and recycling to reduce the waste to be disposed of and to increase the recovery and recycling rates. The producer must make this information accessible to the prospective buyers of vehicles. It shall be included in promotional literature used in the marketing of the new vehicle.

Article 10

Implementation

1. Member States shall bring into force the laws, regulations and administrative provisions necessary to comply with this Directive by 21 April 2002. They shall immediately inform the Commission thereof. When Member States adopt these measures, these shall contain a reference to this Directive or shall be accompanied by such reference on the occasion of their official publication. The methods of making such a reference shall be laid down by Member States.

2. Member States shall communicate to the Commission the text of the main provisions of domestic law, which they adopt in the field governed by this Directive.

3. Provided that the objectives set out in this Directive are achieved, Member States may transpose the provisions set out in Articles 4(1), 5(1), 7(1), 8(1), 8(3) and 9(2) and specify the detailed rules of implementation of Article 5(4) by means of agreements between the competent authorities and the economic sectors concerned. Such agreements shall meet the following requirements:

   (a) agreements shall be enforceable;

   (b) agreements need to specify objectives with the corresponding deadlines;

   (c) agreements shall be published in the national official journal or an official document equally accessible to the public and transmitted to the Commission;

   (d) the results achieved under an agreement shall be monitored regularly, reported to the competent authorities and to the Commission and made available to the public under the conditions set out in the agreement;

   (e) the competent authorities shall make provisions to examine (1) OJ L 377, 31.12.1991, p. 48. the progress reached under an agreement; L 269/40 EN Official Journal of the European Communities 21.10.2000

   (f) in case of non-compliance with an agreement Member States must implement the relevant provisions of this Directive by legislative, regulatory or administrative measures.

Article 11

Committee procedure

1. The Commission shall be assisted by the committee established by Article 18 of Directive 75/442/EEC, hereinafter referred to as ‘the Committee’.
2. Where reference is made to this Article, Articles 5 and 7 of Decision 1999/468/EC shall apply, having regard to the provisions of Article 8 thereof. The period laid down in Article 5(6) of Decision 1999/468/EC shall be set at three months.
3. The Committee shall adopt its rules of procedure.
4. The Commission, according to the procedure laid down in this Article, shall adopt:
   - (a) the minimum requirements, as referred to in Article 5(5), for the certificate of destruction;
   - (b) the detailed rules referred to in Article 7(2), third subparagraph;
   - (c) the formats relating to the database system referred to in Article 9;
   - (d) the amendments necessary for adapting the Annexes to this Directive to scientific and technical progress.

Article 12

Entry into force

1. This Directive shall enter into force on the day of its publication in the Official Journal of the European Communities.
2. Article 5(4) shall apply:
   — as from 1 July 2002 for vehicles put on the market as from this date,

— as from 1 January 2007 for vehicles put on the market before the date referred to in the first indent.

3. Member States may apply Article 5(4) in advance of the dates set out in paragraph 2.

Article 13

Addressees

This Directive is addressed to the Member States. Done at Brussels, 18 September 2000.

For the European Parliament: The President N. FONTAINE

For the Council The President: H. VÉDRINE

ANNEX I

Minimum technical requirements for treatment in accordance with Article 6(1) and (3)

1. Sites for storage (including temporary storage) of end-of-life vehicles prior to their treatament:
   - — impermeable surfaces for appropriate areas with the provision of spillage collection facilities, decanters and cleanser-degeasers,
   - — equipment for the treatment of water, including rainwater, in compliance with health and environmental regulations.
2. Sites for treatment:
   - — impermeable surfaces for appropriate areas with the provision of spillage collection facilities, decanters and cleanser degreasers,

— appropriate storage for dismantled spare parts, including impermeable storage for oil-contaminated spare parts,

— appropriate containers for storage of batteries (with electrolyte neutralisation on site or elsewhere), filters and PCB/PCT-containing condensers,

— appropriate storage tanks for the segregated storage of end-of-life vehicle fluids: fuel, motor oil, gearbox oil, transmission oil, hydraulic oil, cooling liquids, antifreeze, brake fluids, battery acids, air-conditioning system fluids and any other fluid contained in the end-of-life vehicle,

— equipment for the treatment of water, including rainwater, in compliance with health and environmental regulations,

— appropriate storage for used tyres, including the prevention of fire hazards and excessive stockpiling.

3. Treatment operations for depollution of end-of-life vehicles:

— removal of batteries and liquified gas tanks,

— removal or neutralisation of potential explosive components, (e.g. air bags),

— removal and separate collection and storage of fuel, motor oil, transmission oil, gearbox oil, hydraulic oil, cooling liquids, antifreeze, brake fluids, air-conditioning system fluids and any other fluid contained in the end-of-life vehicle, unless they are necessary for the re-use of the parts concerned,

— removal, as far as feasible, of all components identified as containing mercury.

4. Treatment operations in order to promote recycling:

— removal or catalysts,

- — removal of metal components containing copper, aluminium and magnesium if these metals are not segregated in the shredding process,
- — removal of tyres and large plastic components (bumpers, dashboard, fluid containers, etc), if these materials are not segregated in the shredding process in such a way that they can be effectively recycled as materials,
- — removal of glass.

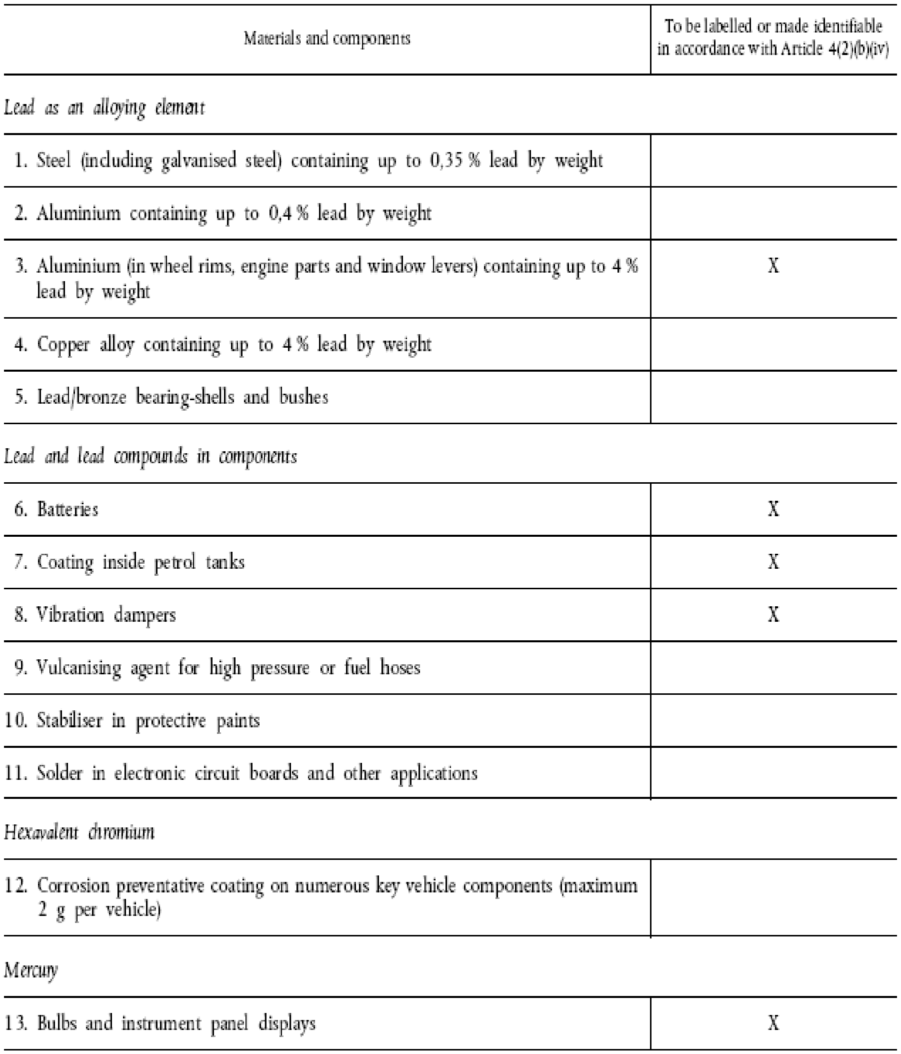
5. Storage operations are to be carried out avoiding damage to components containing fluids or to recoverable components and spare parts.

L 269/42 EN Official Journal of the European Communities 21.10.2000

Materials and components To be labelled or made identifiable in accordance with Article 4(2)(b)(iv)

ANNEX II

Materials and components exempt from Article 4(2)(a)



Materials and components	To be labelled or made identifiable in accordance with Article 4(2)(b)(iv)
Lead as an alloying element	
1. Steel (including galvanised steel) containing up to 0,35 % lead by weight	
2. Aluminium containing up to 0,4 % lead by weight	
3. Aluminium (in wheel rims, engine parts and window levers) containing up to 4 % lead by weight	X
4. Copper alloy containing up to 4 % lead by weight	
5. Lead/bronze bearing-shells and bushes	
Lead and lead compounds in components	
6. Batteries	X
7. Coating inside petrol tanks	X
8. Vibration dampers	X
9. Vulcanising agent for high pressure or fuel hoses	
10. Stabiliser in protective paints	
11. Solder in electronic circuit boards and other applications	
Hexavalent chromium	
12. Corrosion preventative coating on numerous key vehicle components (maximum 2 g per vehicle)	
Mercury	
13. Bulbs and instrument panel displays	X

Within the procedure referred to in Article 4(2)(b), the Commission shall evaluate the following applications:

— lead as an alloy in aluminium in wheel rims, engine parts and window levers

— lead in batteries

— lead in balance weights

— electrical components which contain lead in a glass or ceramics matrix compound

— cadmium in batteries for electrical vehicles as a matter of priority, in order to establish as soon as possible whether Annex II is to be amended accordingly. As regards cadmium in batteries for electrical vehicles, the Commission shall take into account, within the procedure referred to in Article 4(2)b and in the framework of an overall environmental assessment, the availability of substitutes as well as the need to maintain the availability of electrical vehicles.