Compression ignition engine - sources of pollution

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Abstract. The high reliability and efficiency of the compression ignition engine as well as its low operating costs turned this engine into the preferred propulsion system for both cars and heavy vehicles. At the same time, the harmfulness of its pollutant emissions gave him the unpleasing status of First Culprit for the many health problems of the population in the metropolis. Currently, the compression ignition engine is mainly responsible for the release of five types of pollutant emissions into the atmosphere: carbon monoxide-CO, hydrocarbons-HC, mechanical particles-PM, sulphur dioxide-SO2 and nitrogen oxides-NOx. Thus, while emissions of carbon monoxide-CO and hydrocarbon-HC are low, due to the fact that this engine usually works with lean mixtures, high emissions of nitrogen oxides-NOx and mechanical particles-PM raise serious pollution problems worldwide.

1. Introduction
From de beginning of the XX century, human activities have played a major role in the earth’s climate shaping. The greenhouse effect represents the consequence of these activities. Especially, burning fossil fuels have contributed to the increase of the greenhouse gases in the Earth atmosphere at the global level, leading to major climate changes [1].

Carbon dioxide (CO2) is considered to be the principal guilty for global warming, because of his largest rate among the greenhouse gases. According to [2], in 2012, CO2 emissions were about 35,000 million tons per year, throughout the world, and it is expected to rise up to 41,000 million metric tons per year in 2020.

A research of International Energy Agency form 2012 finds that the road transport was the second-largest sector in producing global CO2 emissions with a 22 % percentage, and the main source for NOX emissions with a 42 % percentage, according European Energy Agency [3].

Because of their high energy efficiency and low-operating costs the Diesel engines are more used compared to gasoline engines, and the preferred power sources for road vehicles, trains or industrial off-road vehicles such as mining equipment and excavation machinery.

The higher amount of NOx emissions and particulate matter from the Diesel exhaust gases are responsible for severe environmental and health problems [4]. Beginning with June 2012, the diesel engine is considered carcinogenic to humans, according to the World Health Organization’s International Agency on Research on Cancer (IARC), based on the evidences that exposure to the diesel exhaust gases is associated with an increased risk for lung cancer [5].

We will present in this article a review of the main pollutant emissions from diesel-engine. Five main pollutant emissions (SO2, CO, HC, NOx, and PM) will be explained individually.
2. Diesel exhaust emissions

The compression ignition engine, known as Diesel engine, is an internal combustion engine in which the air is highly compressed inside the cylinder to generate high temperatures and pressures which ignite the fuel when it is injected into combustion chamber. Thus, the chemical energy contained in the diesel fuel is converted into mechanical force.

In the case of complete combustion of fuel inside the diesel engine, would be generated only CO2 and H2O [4]. But, the combustion in the combustion chamber is far from ideal, because of many influence factors: air–fuel ratio, ignition timing, turbulence in the combustion chamber, air–fuel concentration, combustion temperature, etc. Therefore, a large number of harmful products are generated during combustion. The most significant are: CO - carbon monoxide, SO2 - sulphur dioxide, HC - hydrocarbons, NOx – nitrogen oxide, and PM – particulate matter.

The SO2 is produced by the sulphur contained in diesel fuel, therefore the rate of this pollutant in the exhaust gases depends largely on the quality of fuel. To prevent the harmful effect of SO2 (the sulphur dioxide combined with water and air forms sulfuric acid), in the last decades, the concentration of the sulphur in the diesel fuel has dropped significantly – figure 1. As a consequence, the amount of SO2 in Diesel exhaust gases became modest compared with the others pollutant emissions. This is the reason why the international emissions standards are not focused on SO2 restriction.

In the next, we will analyse the pollutant emissions that are the subject of the international emissions standards: CO - carbon monoxide, HC - hydrocarbons, NOx – nitrogen oxide, and PM – particulate matter.

We have presented in the figure 2 the mean values of the products from the diesel exhaust gas according to various sources [7], [8], [9]. It can be observed that the represented pollutant emissions (CO, NOx, HC, PM) have a proportion of less than 1 % in the diesel exhaust gas.

The composition of the pollutant emissions are represented in figure 3. As can be seen, the highest rates in the pollutant emissions are the NOx (59.25 %) and PM (20.63 %). CO has the third highest proportion in pollutant emissions (11.53 %). Comparing with spark ignition engines, diesel engines works with lean mixture, therefore the concentration of HC in the exhaust gases is lower (8.59 %).
2.1. Hydrocarbons (HC)
Diesel engine hydrocarbon emissions contain alkanes, alkenes, alkynes, and aromatic, and the concentrations of these compounds depend on engine operating regime.

HC emissions are actually unburnt hydrocarbons (UHC) resulting from incomplete combustion of fuel. This incomplete combustion is the result of lower air–fuel mixture temperature, near the cylinder wall, therefore small fractions of hydrocarbons survive oxidation during combustion, while other fractions become intermediate combustion products as a result of pyrolysis and partial oxidation.

When the engine operating conditions allow a minimum of 600 °C temperature in the exhaust pipeline, the unburned hydrocarbons continue to react in the exhaust, in the presence of oxygen, therefore the hydrocarbon emissions are significantly lower at the tailpipe than near the exhaust valves [10].

The emission of hydrocarbons in Diesel engine is much higher at light load operating conditions and the main causes of unburnt hydrocarbons appearance are:
- over-mixing of fuel with air, which causes over-lean mixture and difficult combustion especially at low temperatures;
under-mixing which leads to over-rich mixture zones, difficult to ignite;
- flame quenching at low temperature walls which leads to partial burning.

During the ignition delay, some portions of the air-fuel mixture are favourable to auto-ignition; some are too rich to ignite, while others are too lean to support combustion. At the beginning of combustion, high temperature favours rapid oxidation of fuel-air mixture. As the combustion continues we will find inside the cylinder: over-rich portions of mixture as the result of slow mixing of fuel, products of pyrolysis due to high temperature, fuel amounts in the nozzle sac, and in the rifts [11].

All of these factors lead to incomplete combustion, especially at light-load operating conditions, and to hydrocarbons appearance in the exhaust [12].

The effects of the hydrocarbons on environment and human health are very harmful. The hydrocarbon emissions combined with nitrogen oxides and other organic compounds can create ground-level ozone. The ozone in the air we breathe can be harm for human health (toxic for the respiratory tract and can cause cancer) and for vegetation during the growing season [13].

In the figure 4 we have represented the evolution of hydrocarbons and nitrogen oxides limits from Euro 1 to Euro 6 emission standards, for Diesel engines and different road vehicles.

![Figure 4. Evolution of hydrocarbons and nitrogen oxides limits, for Diesel engines and different road vehicles (Emission Standards, European Union)](image)

2.2. Carbon monoxide (CO)

In the case of incomplete combustion inside the cylinder, the oxidation process does not occur completely and carbon monoxide results in the exhaust gas. The concentration of the carbon monoxide depends on the value of air-fuel equivalence ratio ($\lambda$) and it is highest for the rich mixture, when the air-fuel equivalence ratio ($\lambda$) is less than 1.0. Because of air deficiency in the case of combustion of rich mixtures, the carbon cannot convert entirely into CO2, therefore will be produced CO emissions. Small amounts of carbon monoxide (CO) are produced even in the case of operation with lean mixtures, because of chemical kinetic mechanism, characteristic of the oxidation process [19].

Diesel engines run on lean mixtures with a consistently high air–fuel equivalence ratio ($\lambda > 1$), and AFR (air-fuel ratio) between 18:1 and 70:1 Therefore, the amount of CO emissions in diesel engines is minimal. The CO emissions are produced even in the case of a reduced turbulence in the combustion chamber or if the fuel droplets are too large.
Carbon monoxide (CO) is a colourless, odourless, and highly toxic gas. In humans, carbon monoxide it combines with haemoglobin to produce carboxyhaemoglobin, which inhibits its capacity to carries oxygen, and begin ineffective for delivering oxygen to bodily tissues. Therefore, depending on concentration, carbon monoxide can lead to slow reflexes, oxygen deficiency of different organs and even to asphyxiation [19].

In the figure 5, we have represented the evolution of carbon monoxide limits from Euro 1 to Euro 6 emission standards, for Diesel engines and different road vehicles.

![Figure 5. Evolution of carbon monoxide limits, for Diesel engines and different road vehicles (Emission Standards, European Union) [14], [15], [16], [17], [18].](image)

2.3. Nitrogen oxides (NOx)

In the case of diesel engines, the air, mainly composed of oxygen and nitrogen, is sucked into the cylinder and then compressed. The fuel is injected into this compressed air, on the last part of the compression stroke and ignites, due to the high temperature inside the combustion chamber. Under these high temperature conditions (over 1600 °C), nitrogen reacts with oxygen and generates nitrogen oxides emissions. Therefore, we can say that the main factors that influence the amount of nitrogen oxides emissions are the temperature inside the cylinder and the oxygen concentration during the combustion process.

Most NOx are formed at the beginning of the combustion process, when the piston is near the end of compression stroke, due to the high temperature in the combustion chamber, which has the highest values. According to Lee T and Co [20], each increase in temperature by 100 °C generates a triple of NOx emissions.

Nitrogen oxides generated by the diesel engine are nitrogen monoxide (NO) and nitrogen dioxide (NO2). Nitrogen monoxide (NO) accounts for 85 - 95 % of total NOx emissions. Once in the atmosphere, NO is gradually transformed into NO2. There are distinct differences between the two types of gases. Thus, while NO is a colourless and odourless gas, NO2 is a reddish brown gas with a pungent odour.

Road transport is the most important source of urban NOx emissions worldwide, contributing with 40-70 % to total NOx emissions. From different types of road vehicles, vehicles equipped with diesel engines are the most polluting vehicles. Due to the high temperatures in the combustion chamber, diesel
engines are responsible for most NOx emissions. It is estimated that approximately 85% of total NOx emissions from road vehicles come from diesel engines and are mainly in the form of NO [20].

Nitrogen oxide emissions from vehicles are very dangerous to the environment and to health. Nitrogen oxides mainly cause inflammation of the airways. Long-term exposure can lead to decreased lung function and increased allergen sensitivity. Nitrogen oxides also contribute to the formation of smog and ozone at ground level, both of which are associated with adverse effects on health and the environment. The toxicity level of NO2 is five times higher comparing with NO and is one of the main culprits for lung disease. Nitrogen dioxide can irritate the lungs and reduce the resistance to respiratory infections. NOx emissions contribute to the formation of acid rain that can affect terrestrial ecosystems.

Nitrogen dioxide in combination with nitrate contributes to the formation of pollutant mist, which strongly affects visibility [21].

Figure 6. Evolution of nitrogen oxides limits, for Diesel engines and different road vehicles (Emission Standards, European Union) [14], [15], [16], [17], [18].

Considering the harmful effects of this type of pollutant emissions, European emission standards pay particular attention to the levels of NOx emissions. It can be seen in figure 6 the evolution of the maximum limits allowed for NOx emissions, for diesel engine, imposed by European emission standards.

2.4. Particulate matter (PM)

The process of particulate matter formation in the Diesel engine is a consequence of the spray combustion that begins inside the combustion chamber. The incomplete combustion results in volatile organic fractions in the exhaust stream which subsequently condense as particles of organic compound along the expansion, exhaust process and outside the engine. The non-oxidized particles are evacuated as visible soot.

As an experimental study demonstrated [22], the composition of mechanical particles in the case of a heavy-duty diesel engine consists of 41% carbon, 7% unburned fuel, 25% unburned oil, 14% sulphate and water, 13% ash and other components.

Diesel particulate matters are typically spheres, more than 90% of them are smaller than 0.1 µm in diameter. The formation process of PM emissions depends on many factors: engine loads, fuel quality (sulphur and ash content), lubrication oil quality, combustion temperature or exhaust gas cooling [23].
The particulate matter formation process may include the following steps: pyrolysis, nucleation, surface growth, agglomeration (inside the cylinder) and condensation (in the atmosphere).

Diesel particulate matter contains several fractions: sulphates, nitrates, volatile organic fractions, carbon fractions (soot), ash. Sulphates result from the combination of the sulphate ions emitted by the Diesel engine with the metals from the lubricating oil additives, while the nitrates result from the combination of nitrogen oxides (NO2) with water vapour.

![Figure 7. Evolution of Particulate Matter limits, for Diesel engines and different road vehicles (Emission Standards, European Union) [14], [15], [16], [17], [18].](image)

Volatile organic fractions mainly result from unburned or partially burned hydrocarbons, which come from fuel and oil at low loads. Diesel soot particles are formed especially during diffusive combustion while the resulting ash is mainly composed of oxides and phosphates of the metals present in the lubricating oil additives, but also of the burned material of the used engine components [11].

PM emissions have a harmful impact on environment and human health. According to USA Environmental Protection Agency, “the small size of those particles is directly linked to their potential for causing health problem. Exposure to such particles can affect both lungs and heart. Numerous scientific studies have linked particle pollution exposure to a variety of problems, including: premature death in people with heart or lung disease, nonfatal heart attacks, irregular heartbeat, aggravated asthma, decreased lung function.”

The level of particulate matter emissions has been increasingly drastically regulated in recent years. An evolution of the maximum limits imposed by the European legislation can be analyzed in figure 7.

3. Conclusions
The diesel engine remains the preferred energy source for road vehicles and other industrial equipment, due to its low operating costs and high energy efficiency. Despite these advantages, the engine Diesel remains the main pollutant with NOx and particulate emissions. Given the harmful effect of these pollutant emissions, international pollution standards have become more drastic in order to protect human and animal health as well as the environment.

Therefore, the manufacturers of these engines are forced to find increasingly ingenious construction solutions to ensure that diesel engines will continue to play an important role in the economy. In a world
that is increasingly focusing on the use of renewable energy, the use of diesel engines in certain sectors of activity will become uncertain in the near future. Thus, the efficient solutions to reduce the pollutant emissions of these engines will be able to ensure a future for these engines.

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