Chapter 14

Vehicle Emissions: What Will Change with Use of Biofuel?

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Additional information is available at the end of the chapter

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1. Introduction

In urban areas, large concentrations of chemical compounds are emitted into the atmosphere by industries, vehicles and other human activities. Nearly 3000 different compounds, mostly organic, resulting from human activity have been identified in the atmosphere. This complex mixture of pollutants can have impacts on health and the environment. Thus, the systematic determination of air quality should be, for practical reasons, limited to a restricted number of pollutants, defined in terms of their importance and the human and material resources available to identify and measure them. Generally, pollutants chosen to serve as indicators of air quality are the currently regulated and universally occurring compounds: sulfur dioxide (SO_2), particulate matter (PM), carbon monoxide (CO), ozone (O_3) and nitrogen oxides (NO_x). They are chosen due to their frequency of occurrence and adverse effects on the environment. Thus, the effects of air pollution can be characterized by a deterioration of good quality environmental conditions and the exacerbation of existing problems, which can manifest themselves in health, population welfare, vegetation, fauna, and urban structures. The attention of regulatory authorities and researchers must not only look to the standards of air quality. There are compounds that despite being unregulated deserve attention because of the damage they cause to the environment and, especially, to human health.

The search for alternative fuels to reduce dependence on petroleum and emission of pollutants into the atmosphere has stimulated many scientific studies. The goal is to develop fuels that can be used in existing vehicles without the need for major changes in their engines. A term often used for fuel derived from renewable sources is 'biofuel', which has strong links with the concept of sustainability, whereby the use of natural resources to meet current needs should not compromise the needs of future generations. In this way, the purpose of this chapter is to answer the question about vehicle emissions: what will change with use of biofuel?

2. Emission sources of pollutants to the atmosphere

Air quality in urban atmospheres depends on several related factors: primary pollutant's emissions (emitted directly from sources to the atmosphere), secondary pollutant's emissions (resulting from the chemical reactions occurring in the atmosphere and which involve some primary pollutants) and consumption, geographical and meteorological factors.

Primary pollutants can be emitted by natural and anthropogenic sources. The pollutants emitted from both sources may be in two physical states: adsorbed in the particulate or in the gas phase. In this context, the primary particles emitted by many natural and anthropogenic sources include combustion processes, volcanic eruptions, forest fires, fumes created by certain industrial activities and roadways, the "marine spray" and some biological materials [1]. The pollutants frequently found in the atmosphere are: CO, NO_x, sulfate oxides (SO_x), PM, volatile organic compounds (VOC), O_3 and; some Greenhouse Gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFC) andnitric acid (HNO_3).

In many areas of the developed and developing world, the concentration of tropospheric pollutants has increased to levels significantly affecting various aspects of the environment. Reducing the amount of solar radiation reaching the ground has the potential for important effects on climate by reducing ground temperature, and increasing cloud albedo and stability, which result in global cooling. Increased pollutants in the atmosphere reduce visibility, and have important effects on human health leading to respiratory diseases by inhalation and to rickets due to inadequate sunlight for the production of vitamin D. Reduced solar radiation and changes in atmospheric stability have important effects on atmospheric photochemistry and modeling [2].

In recent decades, there have been concerns with the increase of anthropogenic pollution that can be seen through the initiation of programs aimed at improving air quality in cities around the world. One of the strategic actions to reduce the emission of pollutants in urban environments is the displacement of local industries from urban to non-urban areas [3]. Thus, the improved control of industrial emissions resulted in the current situation, where in large cities vehicles are the main source of emissions of air pollutants, especially CO, hydrocarbons (HC), NO_x, aldehydes and metals [4-7]. Although there are actions and programs that encourage the reduction and control of air pollutants, there are cities where some of these pollutants routinely exceed local air quality standards. Table 1 shows some general pollutants emitted and their sources such as human activity, industrial uses and transportation systems.

Pollutants	Sources
CO	Traffic (especially vehicles without catalytic converters) and Industries.
NO_x	Traffic and General industry (resulting from the combustion of the higher or lower temperatures).
SO_x	Traffic (vehicles using fuel with high sulfur content) and Industry (chemical industry, pulp and paper, refineries and boilers using fuel with high sulfur content, for example, fuel oil).
PM	Traffic, Industries (cement, refineries, steel, paper pulp, chemical industry, inter alia), Construction work and agricultural practices.
Pb (Lead)	Traffic (Leaded fuels) and Industries (manufacturing process from raw materials that integrate Pb).
VOC	Chemical Industry, traffic, Storage of Fuel and petrol stations, Car workshops, Construction Materials, and other activities, involving handling of solvents.
O_3	Is formed at ground level as a result of chemical reactions established between some primary pollutants, such as NO_x, VOC or CO. These reactions occur in the presence of light sunlight, so that higher levels of ozone occur during the emission of primary pollutants in the summer. The sources of primary pollutants that have influence on atmospheric ozone concentration are: Traffic; Industries, Landfills, Paints and solvents (VOC); forests; and Other sources (gas stations, equipment that uses this fuel, etc.).
CO_2	Use of fóssil fuels, deforestation and Change of land use.
CH_4	Production and consumption of energy, Farming and livestock, Landfills and wastewater.
N_2O	Fertilizer use, Production of acids and Burning of biomass and fossil fuels .
CFC	Industry, refrigeration, aerosols, propellants, Expanded foams and Solvents.
HNO_3	Combustion of wood, Fossil fuels, the chemical composition of fertilizersand microbes.

Table 1. Main sources of air pollutants.

The transportation sector can be considered the major source of atmospheric pollutants. In the evaluations of the vehicular emission impacts, measurements have been limited to regulated pollutants such as suspended PM, HC, CO, NO_x and O_3, with this last one being an important secondary product formed by photochemical reactions in the atmosphere. However, some specific compounds, which are not regulated by law to be monitored, have a significant toxic potential. Thus, one can highlight the polycyclic aromatic hydrocarbons (PAHs), Nitro PAHs and the VOC, which result from incomplete combustion, as having a double influence on air quality. These molecules can act as primary toxic pollutants and play a role of precursor in the formation of photochemical oxidant species.

Emission studies of controlled substances have already been done extensively. However, there is a current need for the study of non-regulated emissions. Some studies on unregulated substances, such PAHs, nitro HPAs, carbonyl compounds (CC) and both vapor and particulate of light aromatic hydrocarbons, showed a lower amount of mutagenic compounds being emitted when using biofuels [8]. However, there are some contradictory results [9], which point to the need for further studies of such substances.

In the last three decades CC, aldehydes and ketones, have received a great deal of attention due to their strong influence on photochemical smog formation and their recognized adverse human health effects. Carbonyl compounds are directly emitted into the atmosphere by combustion sources and also produced from photochemical oxidation of hydrocarbons and other organic compounds.

3. Vehicle emissions

The transportation sector has an active role in rising pollution levels, especially in large urban centers in regions where transport is based on roads, i. e., much of the transportation of goods is done by trucks, and transportation of people is primarily done by bus or car. The gases resulting from complete combustion of fuel used in vehicles are CO_2, H_2O (usually in gaseous state) and nitrogen (N_2). In this reaction, the only product that has concern from environmentalists is the CO_2, due to impacts on the greenhouse effect and global warming. However, as seen before, the reactions that occur in vehicle engines emit other compounds into the atmosphere. Due this fact, the combustion process of vehicles is considered incomplete. Moreover, it is important to note that vehicle emissions are not only those emitted during the combustion process. Emissions of pollutants arising from the use of vehicles can be divided into the following categories [10]:

- Emissions of gaseous and particulates by tailpipe of the vehicle (byproducts released to the atmosphere by combustion exhaust pipe);
- Fuel evaporative emissions (released into the atmosphere through evaporation of the hydrocarbon fuel);
- Emissions of gases from the crankcase of the engine (combustion by products that passing through the piston rings of the engine and the oil vapors lubricant);
- Particulate emissions from wear of tires, brakes and clutch;
- Resuspension of dust and soil;
- Evaporative emissions in the fuel transfer operations fuel (associated with storage and fuel supply).

The main pollutants emitted into the atmosphere by the vehicles are from the process of incomplete combustion in which fuel injected into the cylinder doesn´t find the required amount of air for its burning. So, these primary pollutants are emitted directly by the automotive exhaust (CO, NO_x, SO_x, alcohols, CC, HC, PAHs and PM). These pollutants can interact with each other or with the aid of light to form secondary pollutants (O_3, nitrates peroxiacetila - PAN, among others). The latter may be much more harmful to the environment than the primary pollutants.

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The PM from engines has three major components: soot formed during combustion, heavy hydrocarbon condensed or absorbed on the soot, and sulfates. Particle size is also an important variation in terms of vehicular emissions, as it has been associated with an increase in health conditions. Ultrafine particles (< 0.01 μm), generated in great amounts mainly by diesel exhaust, have special toxicity due to their ability to penetrate into the cardiovascular system and other organs [11-13].

Even with the technological evolution of vehicle exhaust systems, these emissions remain a serious air pollution problem in many regions. Several reasons can be highlighted [14]:

- Significant increase in size of vehicle fleet and its use;
- High fuel consumption because of lower prices in some countries, the characteristics of the vehicles and driving conditions;
- Malfunction of emission control systems reducing the effectiveness of control;
- Accelerated degradation of components of the car that has a direct impact on increasing the emissions such as design flaw and / or use of inappropriate materials, or also by misuse of the vehicle;
- Lack of care in the maintenance of the vehicles by their owners;
- Lack of preparedness in a considerable number of vehicle repairshops to offer technically appropriate maintenance services;
- Deliberate withdrawal of emissions control devices by the owners of vehicles or inadequate repair services;
- Adulteration of fuel;
- Existence of old vehicles in circulation or vehicles in poor condition, with very high levels of emissions;
- Lack of measures to popularize and encourage the use of public transport, to contain the increasing use of automobiles as a means of individual transportation.

In this context, the factors mentioned above have contributed to overtake the air quality standards in major metropolitan areas. They should be prioritized over the effects of other sources of pollutant emissions such as power plants and industries. Vehicle emissions are an important contributor to the formation of photochemical smog and overall emissions.

Light vehicles (Otto cycle) are becoming more numerous in large urban centers with the main regulated pollutants emitted from these vehicles being: CO, HC and NO_x. On the other hand, diesel vehicles emit the largest amount of the regulated pollutants: PM and NO_x (Table 2).

Among unregulated pollutants, several authors study the emission of individual HC [15,16] and especially those of methane, a gas with a strong greenhouse effect. However, the total contribution of light vehicles (Otto cycle) to global methane emissions is estimated to be very low, not more than 0.3-0.4% of the total methane emissions[17].

Kind of vehicle		Fuel	Emission (%)			
			CO	HC	NOx	PM_{10} [a]
		Gasoline	46.65	14.47	5.72	-
Light vehicles		Ethanol	8.60	4.13	1.37	-
(cars, etc)		Flex (Gasoline/Ethanol)	13.27	6.81	2.46	-
Commercial vehicles		Gasoline	5.42	1.76	0.72	-
		Ethanol	0.78	0.38	0.13	-
		Flex (Gasoline/Ethanol)	0.60	0.30	0.11	-
		Diesel	0.29	0.34	2.84	1.42
Trucks	Light	Diesel	0.16	0.23	1.77	1.35
	Medium		0.81	1.15	8.74	6.55
	Heavy		2.92	3.36	32.00	15.90
Buses	Urban	Diesel	1.87	2.30	19.94	12.01
	Road		0.43	0.53	4.72	2.77
Motorcycles		Gasoline	15.56	12.92	1.15	-
		Flex (Gasoline/Ethanol)	0.04	0.04	0.01	-

[a]Contribution study as a model recipient for inhalable particles (< 10 µm).

Table 2. Estimation of emission sources of air pollution in a Brazilian urban center (São Paulo) in 2010 [10].

Studies have shown that amongst the total gas phase non-methane hydrocarbons emitted for gasoline burning, 75–93% are aromatics species, 6–18% linear and substituted alkanes, 1.2–4.3% alkenes and alkynes, and 0.1–2% CC. The analysis for a diesel engine showed 54–75% of species analyzed are aromatics, 18–31% linear and substituted alkanes, 3–6% alkenes and 2–6.4% CC.In the case of vehicles with diesel engines, the abundance of CC is more significant than Otto cycle engines; and should be related to the composition of the fuel[18].

An important global emission, VOC, is observed at different levels in light vehicles (Otto cycle) compared to diesel vehicles. Generally, depending on vehicle technology and vehicle year, make and model, aromatics compounds are the major species but with a somewhat weaker contribution for diesel cars. Saturated hydrocarbons with weaker percentages which are about 20% for diesel cars are the second most common and 12% for gasoline cars. The CC displayed very low concentration (0.5% for gasoline and 10% for diesel)[18].

4. Profile of vehicular emissions with the use of biofuel

Biofuels are derived from biomass, the name given to the organic matter in an ecosystem or a plant or animal population. Because plants and animals can reproduce continuously, one

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can assume that they are renewable sources of energy. Plants, through photosynthesis, convert solar energy they receive into biomass, and animals generate energy by eating organic matter (plants or other animals). There are several types of biofuels that can be produced from biomass, such as alcohol (ethanol and methanol), biodiesel, biokerosene, H_2 and others. The sources for its production can be through animal (for example, tallow fat or chicken), vegetable (e.g., vegetable oils and cane sugar) and biomass materials [19].

All biomass materials can be converted to energy via thermochemical and biological processes. Biomass gasification attracts the reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases [20]. Biomass gasification can be considered as a form of pyrolysis, which takes place in higher temperatures and produces a mixture of gases with H_2 content ranging 6–6.5% [21]. Hydrogen may be an alternative to gasoline, gas-oil and biofuels for the automotive sector. Hydrogen can be used in internal combustion engines or in fuel cells. However, this chapter will discuss more about biodiesel and ethanol biofuels emission profiles.

Ethanol can be produced from a number of crops including sugarcane, corn (maze), wheat and sugar beet. In general, ethanol is produced through fermentation of sugar derived from corn or cellulosic biomass. Moreover, technically speaking, biodiesel is the alkyl ester from fatty acids, made by the transesterification of oils or fats, from plants or animals, with short chain alcohols such as methanol and ethanol. Glycerine is, consequently, a by-product from biodiesel production [22].

The ethanol obtained from sugar cane is the biofuel with the most energy efficiency: each joule (unit of energy) used in its production allows the return of about seven joules. Brazil developed technologies for producing ethanol and gasoline engines adapted to it, but alcohol is considered by many a luxury fuel, being used only in light vehicles. One great challenge is to develop technologies that enable the use of ethanol as fuel in large vehicles (buses and trucks) and aviation [19].

Over the past 10 years, the number of scientific and technological studies on biofuels has grown exponentially. A refined search done in a scientific database [23] using as keywords: "biodiesel emission" and "ethanol emission", revealed that interest in research on biofuel emissions has increased each year and studies of emissions from burning of ethanol and biodiesel have similar trends, although there was a greater interest for research on ethanol (Figure 1). This fact is justified because ethanol is a biofuel that has been used in the energy matrix since the 70's and biodiesel in the last 10 years. For this reason (Figure 2) the production of ethanol is roughly more than four times the world production of biodiesel.

In this context, there are several reasons for biofuels to be considered a relevant technology for both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The following sections will discuss the results obtained from research evaluating the emission of pollutants when biofuels are used.

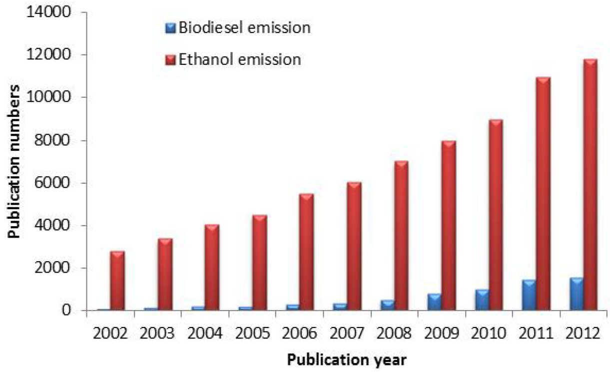
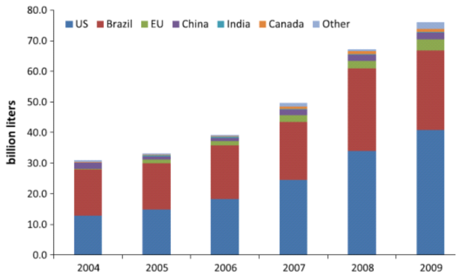
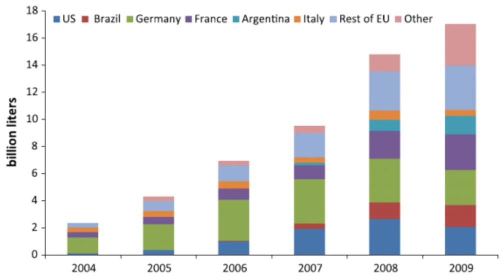


Figure 1. Publication numbers of research about both biodiesel and ethanol emission topics from 2002 to 2012 [23].



(a)



(b)

Figure 2. World Ethanol (a) and Biodiesel (b) Production from 2004 to 2009 [24].

4.1. Otto cycle vehicles (gasoline/ethanol)

In general, biofuels are considered climate friendly, even when based on a life-cycle analysis. Ethanol use in gasoline has tremendous potential for a net reduction in atmospheric CO_2 levels. CO_2 is released into the atmosphere when ethanol (like other fuels) is burned in an engine and is also recycled into organic tissues during plant growth [25].

A study was done about the direct vehicle emission impact on the future use of ethanol as a fuel for gasoline cars in Denmark arising from the vehicle specific fuel consumption and emission differences between neat gasoline (E0) and E5/E85 gasoline-ethanol fuel blends derived from emission tests. For vehicles using E5 rather than E0, the average fuel consumption and emission differences are small. For CO, VOC and NO_x the derived average differences are 0.5%, -5% and 7%, respectively. For using E85 rather than E5, the emission differences become even smaller for VOC and NO_x, but greater for CO. The de-

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rived average emission differences are in this case 18%, -1% and 5% for CO, VOC and NO_x, respectively [26].

Already, in field studies conducted regarding the use of 10% ethanol additions to gasoline on pollutant formation concluded that PM and CO emissions are significantly reduced. For some of the vehicles tested, CO_2 emissions were also significantly reduced and overall it led to a small deterioration in fuel economy (although this was not significant at 95% confidence level). NO_x emissions were not significantly influenced. However, for some of the vehicles tested, acetaldehyde emissions significantly increased [27].

CO, formed by the incomplete combustion of fuels, is produced most readily from petroleum fuels, which contain no oxygen in their molecular structure. Since ethanol and other ''oxygenated'' compounds contain oxygen, their combustion in automobile engines is more complete. The result is a substantial reduction in CO emissions. Research shows that reductions range up to 30%, depending on type and age of engine/vehicle, the emission control system used, and the atmospheric conditions in which the vehicle operates [27].

Because of its high octane rating, adding ethanol to gasoline leads to reduction or removal of aromatic HC's (such as benzene), and other hazardous high-octane additives commonly used to replace tetra ethyl lead in gasoline [28]. Adding ethanol to gasoline can potentially increase the volatility of gasoline. However, some studies have identified divergent results about NO_x emissions, showing the ethanol concentration in the fuel increased anywhere from 0% to 20%. So, the ethanol addition can reduce CO and HC, aldehydes and unburned ethanol emissions. NO_X results can vary depending on the operating condition, spark advance timing and other parameters [29].

Adding ethanol to gasoline does emit slightly greater amount of aldehydes during combustion. However, the resulting concentrations are extremely small and are effectively reduced by the three-way catalytic converter in the exhaust systems of all modern vehicles. Generally, benzene and toluene emissions decrease by ethanol addition to gasoline, although this beneficial effect of ethanol was eliminated after the operation of the catalyst. Acetic acid was detected in exhaust gases in some cases only for the base and the 3% ethanol blend fuel [30,31].

There are other toxic emissions (unregulated), which should be considered to ascertain the impact of ethanol blended fuels, such as: acetaldehyde, formaldehyde, propionaldehyde and acrolein, benzene, ethylbenzene, 1-3 butadiene, hexane, toluene, xylene, and fine particulates. Studies indicate a reduction of benzene emission up to 50% with the ethanol-blended fuels. Emissions of 1,3-butadienes were also substantially decreased, with reduction ranging from 24% to 82%. Isolated trends were noted for certain PAHs. There was a decrease in 1-nitrobenzene with use of ethanol in all cases. There was also a general increase in the proportion of heavy PAHs in the particulate phase with ethanol use, and although less pronounced, general decreases in light PAHs in the particulate phase [32].

In summary, it can be said that ethanol produces generally less pollution than gasoline and diesel. Alcohol has a tolerance combustion with excess air, which allows a more complete burn with lower emissions of CO and PM. Moreover, there is an increase in the emission of aldehydes. Under certain conditions (cold start), alcohols are oxidized to aldehydes, especially formaldehyde (in the case of methanol) and acetaldehyde (in the case of ethanol) [33].

4.2. Diesel cycle Vehicles (diesel / biodiesel / ethanol)

Among the biofuels discussed above, we can highlight the use of biodiesel and ethanol in vehicles with diesel engines. In the specific case of biodiesel, this has viscosity close to mineral diesel. These vegetable oil esters contain 10–11% oxygen by weight, which may encourage more combustion than hydrocarbon-based diesel in an engine. Furthermore, biodiesel can form blends with diesel in any ratio, and thus could replace partially, or even totally, diesel in combustion engines that could bring a number of environmental, economic and social advantages. However, biodiesel can be produced from different types of raw material and this can directly influence the final composition of the biofuel and consequently in the emission of pollutants.

Thus, the investigation discovered that biodiesel impacts on emissions varied depending on the type of biodiesel (soybean, rapeseed, or animal fats) and on the type of conventional diesel to which the biodiesel was added. There is one minor exception: emission impacts of biodiesel did not appear to differ by engine model year [34].

The United States Environmental Protection Agency has conducted a comprehensive analysis of the emission impacts of biodiesel using publicly available data. This investigation made use of statistical regression analysis to correlate the concentration of biodiesel in conventional diesel fuel with changes in regulated and unregulated pollutants. The majority of available data was collected on heavy-duty highway engines and this data formed the basis of the analysis. The average effects are shown in Figure 3.

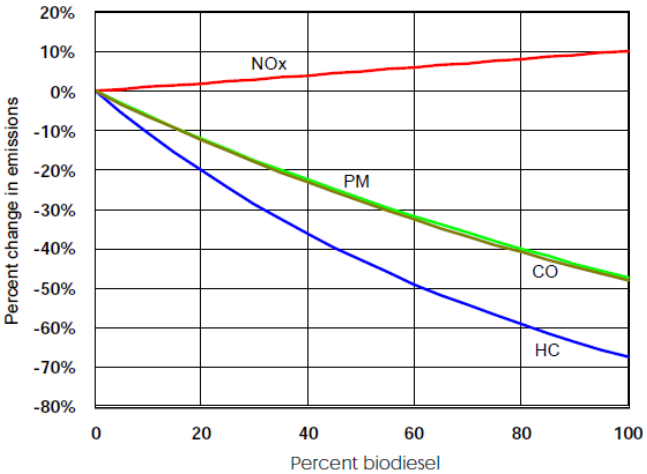

Figure 3. Average emission impacts of biodiesel for heavy-duty highway engines [34].

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Increasing the level of biodiesel in the fuel blend increased NO_x while reducing PM. Proportionally, the PM reduction was slightly more than the increase in NO_x, on a percentage basis. The reduction in CO and HC was linear with the addition of biodiesel for the blends tested. These reductions indicate more complete combustion of the fuel. The presence of oxygen in the fuel was thought to promote complete combustion [35,36].

The NO_x forms by oxidation of atmospheric nitrogen at sufficiently high temperatures. Kinetics of NO_x formation is governed by Zeldovich mechanism, and its formation is highly dependent on temperature and availability of oxygen. There are several reported results of slight increase in NO_x emissions for biodiesel [37]. It is quite obvious, that with biodiesel, due to improved combustion, the temperature in the combustion chamber can be expected to be higher and a higher amount of oxygen is also present, leading to formation of a higher quantity of NO_x in biodiesel-fueled engines. However, biodiesel's lower sulfur content allows the use of NO_x control technologies that cannot be otherwise used with conventional diesel.

Biodiesel is free from sulfur, hence less sulfate emissions, and reduced PM is reported in the exhaust. Due to the near absence of sulfur in biodiesel, it helps reduce the problem of acid rain caused by emission of pollutant from fuels burning. The lack of aromatic hydrocarbon (benzene, toluene etc.) in biodiesel reduces unregulated emissions as well as ketone, benzene etc. Breathing particulate matter has been found to be hazardous for human health, especially in terms of respiratory system problems. PM consists of elemental carbon (~31%), sulfates and moisture (~14%), unburnt fuel (~7%), unburnt lubricating oil (~40%) and potential remaining metals and others substances [27].

Regarding environmental concerns, many studies have shown that pure biodiesel, biodiesel/diesel and biodiesel/ethanol/diesel blends may reduce emissions of regulated substances (CO, CO_2, SO_x, HC and PM) [38-40]. However, there is an increasing interestin studying emissions of some unregulated substances, such as carbonyl compounds, PAHs, nitro-PAHs and other toxics that are of concern from both environmental and human health standpoints [22]. Among CC, both formal dehyde and acetaldehyde were the major contributors to the observed total CC levels in diesel and diesel/biofuels blends emissions. Except for acrolein and formaldehyde, all CC showed a clear trend of reduction in emissions when using biodiesel/diesel blends [41].

In general, the addition of higher concentrations of biodiesel to diesel make an improvement in the carbonyl concentration profile at places with high circulation of heavy-duty vehicles, bringing profiles down to levels found at sites less impacted by these kind of vehicles [42].

However, concerning CC emissions, there are some divergences when considering the results obtained using pure diesel and biodiesel blends. Depending upon the author, biodiesel could contribute to increase or decrease in the CC emissions [43-47]. Furthermore, comparing these studies is not straightforward since different authors have used different biofuel sources, engines, and especially, different sampling methodologies or protocols.

Experimental results showed no significant difference in engine function, damage from deposits inside the chamber or the inferior condition of engine oil for 300 h (18,000 km) of engine operation when using biodiesel/diesel blends. The emissions of HC and CO increased with operation time but the emissions of NO_x and PAHs decreased with operation time between 0 and 300 h (18,000 km). The use of biodiesel/diesel blends can reduce the emissions of total PAHs significantly [48]. Other studies on unregulated emissions with use of biodiesel/diesel blend found that, besides reducing PAH emission, there was also a reduction of nitro-PAHs, carbonyl compounds and light aromatic hydrocarbons when this mixture is compared with pure diesel results [44].

PAH concentrations in the samples from a bus station were associated with atmospheric PM, mass size distributions and major ions (fluorite, chloride, bromide, nitrate, phosphate, sulfate, nitrite, oxalate; fumarate, formate, succinate and acetate; lithium, sodium, potassium, magnesium, calcium and ammonium). Results indicate that major ions represented 21.2% particulate matter mass. Nitrate, sulfate, and ammonium, respectively, presented the highest concentration levels, indicating that biodiesel may also be a significant source for these ions, especially nitrate. Dibenzo[a,h]anthraceneandindeno[1,2,3,-cd]pyrene were the main PAH found, and a higher fraction of PAH particles was found in diameters lower than 0.25 μm in a bus station. The fine and ultrafine particles were dominant among the PM evaluated, suggesting that biodiesel decreases the total PAH emission. However, it does increase the fraction of fine and ultrafine particles when compared to diesel [49].

The direct application of ethanol in diesel engines requires changes in the constitution of the engine and the use of additives to improve the ignition. However, diesel/ethanol blends are a more viable alternative and require little or no change in conventional engines. The use of ethanol combined with diesel can significantly reduce the emission of toxic gases and particulate matters when compared to pure diesel. However, there are critical barriers to commercial use of diesel/ethanol blends, as the addition of ethanol to diesel affects properties such as lubricity, viscosity, energy content, cetane number, and, mainly, stability and volatility. The solubility of ethanol in diesel depends, among other factors, on the composition of diesel, the water content in the mixture, and the temperature [50].

Despite the technical problems presented by the use of pure ethanol in diesel cycle vehicles, many studies have been developed using ethanol blended with diesel. Thus, no modification is required in the engines of these vehicles. E-diesels (blends of ethanol in diesel) are currently being used in fleet vehicles in the European Union and the United States. Studies carried out with E-diesel indicated significant reductions of PM, sometimes up to 40%, depending on the test methods and operating conditions. The CO and NO_x emissions were significantly lower when a 20% blend of E-diesel was used in a constant-speed stationary diesel engine, as opposed to diesel fuel. The addition of ethanol to diesel may result in a volumetric reduction in sulphur, by as much as 20%, thus significantly reducing SO_2 emissions [51]. The major drawback in E-diesel is that ethanol is immiscible in diesel over a wide range of temperatures [52].

The diesel/ethanol/biodiesel blends have also emerged as an alternative fuel to reduce emissions in diesel engines. The biodiesel can help the miscibility of ethanol in diesel fuel. Researches have shown that the use of these blends can substantially reduce emissions of CO, HC, and PM[53, 54]. The mixtures (v/v/v) were used in the emission study: diesel/ethanol –

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90/10%, diesel/ethanol/soybean biodiesel – 80/15/5%, diesel/ethanol/castor biodiesel – 80/15/5%, diesel/ethanol/residual biodiesel – 80/15/5%, diesel/ethanol/soybean oil – 90/7/3%, and diesel/ethanol/castor oil – 90/7/3%. The diesel/ethanol fuel showed higher reduction of NO_x emission when compared with pure diesel. The combustion efficiencies of the diesel can be enhanced by the addition of the oxygenate fuels, like ethanol and biodiesel/vegetable oil, resulting in a more complete combustion in terms of NO_x emission. In the case of CO_2 decreases were observed. Meanwhile, no differences were observed in CO emission. Among CC studied, formaldehyde, acetaldehyde, acetone, and propionaldehyde showed the highest emission concentrations [50].

There are a great number of previously published studies comparing diesel with biodiesel and ethanol blends. These biofuels have a good energy return because of the simplicity of its manufacturing process, and has significant benefits in emissions as well. It could also play an important role in the energy economy if higher crop productivities are attained.

5. Burning biofuel vs toxicology

Considerable populations are exposed to fuel exhaust in everyday life, whether through their occupation or through the ambient air. People are exposed not only to engine vehicle exhausts but also to exhausts from burning sources such as from other modes of transport (trains and ships) and from power generators.

Increasing environmental concerns over the past two decades have resulted in regulatory action in North America, Europe and elsewhere with successively tighter emission standards for both diesel and gasoline engines. There is a strong interplay between standards and technology – standards drive technology and new technology enables more stringent standards. For diesel engines, this required changes in the fuel such as marked decreases in sulfur content, changes in engine design to burn diesel fuel more efficiently, reductions in emissions through exhaust control technology with some countries investing in the use of biofuels [55].

However, while the amount of particulates and chemicals are reduced with these changes, it is not yet clear how the quantitative and qualitative changes may translate into altered health effects. In addition, existing fuels and vehicles without these modifications will take many years to be replaced, particularly in less developed countries, where regulatory measures are currently less stringent. It is notable that many parts of the developing world lack regulatory standards, and data on the occurrence and impact of diesel exhaust are limited.

Recently in June 12, 2012 after a week-long meeting of international experts, the International Agency for Research on Cancer (IARC), which is part of the World Health Organization (WHO), classified diesel engine exhaust as carcinogenic to humans (Group 1), based on sufficient evidence that exposure is associated with an increased risk for lung cancer. In this context, the biofuels can be an interesting alternative fuel to reduce health impact of petroleum fuel and pollutant emissions into the atmosphere. However, little is known about health impact and effects, and the air quality impacts of biofuels remain unclear. Significant concern exists regarding biofuel's production impacts on food security and nutrition for the poor [56].

The purpose of this section is to describe research that has been done on the toxicity of vehicular emissions, when fossil diesel is replaced by biofuel or when biofuels are added to petroleum fuel, and what happens in the chemical composition, size distribution and toxicity of the compounds emitted and their damages on health. This section will also discuss how the compounds can damage cells and organs and how the chemical composition and physical proprieties can influence the toxicity of pollutants that affect human health.

5.1. Emissions chemical and physical composition

The most commonly found pollutants from burning fuel emissions are regulated by many countries around the world. These pollutants can harm health and the environment, and cause property damage. Among the pollutants, PM and O_3 are the most widespread health threats. United States Environmental Protection Agency (EPA) calls these pollutants "criteria" air pollutants because it regulates them by developing human health-based and/or environmentally-based criteria (science-based guidelines) for setting permissible levels. The main regulated pollutants emitted during burning fuel and their damages to human health are listed in Table 3.

There are many studies reporting the difference in pollutant emission when comparing fuels with biofuel as described above. In general they report a decrease, similarities or increases in emissions using biofuel comparing with fossil fuels. Studies have indicated a decrease release of CO, SO_x, PM from the combustion process of biodiesel and ethanol. On the other hand, they indicated an increase of NO_x from the combustion process [57,58]. These results are important in terms of human health but do not assume the real effects and damages caused because there are some other pollutants emitted that do not fall under regulated pollutants.

Importantly, there are some air pollutants not regulated that can cause damage to human health. The types of components in the gas and PM phases include single aromatic and PAH and your derived (alkylbenzenes, quinones, oxy and nitro- PAH), alkanes, alkenes, CC, metals, inorganic ions (e.g. sulfates, carbonates), among other chemicals. These compounds are related as potential mutagenic and carcinogenic compounds to humans. Some of these compounds, present in fuel and biofuel exhaust, can induce known toxicity in exposed human populations, even causing cellular effects.

An important group of chemical carcinogens is the PAH which are important in health for several reasons: some are known to be potent carcinogens in man; there is strong epidemiological evidence that exposed groups have increased risks of lung, urinary tract, brain and skin cancers. As heavy-duty vehicles are the main contributors to particle emissions, where this kind of compound is present, the large increase in internal combustion vehicles in big cities has intensified atmospheric pollution and consequently the harmful effects on human health. Studies have indicated a considerable decrease in PAH emission when burning bio-

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diesel when compared to those from burning of diesel fuel [49,59-61]. In the same way, good results are found for ethanol emission when compared to gasoline fuel burning emissions [62]. On the other hand, as biodiesel use can increase NO_x emissions, some of the derived PAH are supposedly increased, as Nitro-PAHs. The high emission of NO_2 from burning of biofuel can lead to the nitration of the available PAH forming Nitro-PAH. Nitro-PAH is a potential worse chemical carcinogen than PAH; it is shown to induce mutations in bacterial and mammalian cells, sister chromatid exchanges and chromosomal aberrations in cultured mammalian cells [63]. In addition, there is evidence for carcinogenicity in rats [64]. However, some studies have shown discordant results about PAH emissions when biofuels are used compared with fossil fuels in vehicle engines. Some hypothesis to this result may be due the influence of biodiesel source material being particularly strong in the formation of these pollutants. Both increases and decreases can be observed in PAH, nitrated PAH and oxygenated PAH compounds with the use of biodiesel blends from different origin [62,65].

Another group of chemical carcinogens is the CC. Taking into account important concerns of CC for atmospheric chemistry and their negative impact on human health, the levels of carbonyls and their diurnal variability can be an effective indicator reflecting the status of local air pollution. In this sense, correlations between major aldehydes emitted by vehicles and the level of pollution of these compounds in sites impacted by this source are still relatively scarce [42]. The most observed toxic effects to human health by some CC are irritation of skin, eyes and nasopharyngeal membranes [66]. More seriously, formaldehyde, which is usually the most abundant carbonyl in the air, is also the one of more concern because it is classified as carcinogenic to humans by the IARC [67]. Epidemiological studies suggest a causal relationship between exposure to formaldehyde and occurrence of nasopharyngeal cancer, although this conclusion is based in a small number of observed and expected cases in the studies [67]. Indeed, studies about CC indicated a substantial increase in CC during the biofuel combustion process. Biodiesel emissions show an increase of formaldehyde and acrolein [41] and ethanol emissions are related to a large increase of acetaldehyde and formaldehyde [67]. These CC are shown to be a carcinogen, mugenic and can lead to onset of pulmonary edema, respiratory disturbance and asthma like symptoms [68]. Nonetheless CC is also a contributor to the formation of O_3, and thus,of photochemical smog. However, observations of increased aldehydes released by biofuel combustion needs to be better understood for its contribution to any adverse health effects.

Moreover, several studies indicate there is a decrease in the concentration of transition metals in biofuels emission. Metals are more abundant in petroleum fuel combustion exhaust than biofuels and they have the ability to generate radicals which likely lead to depletion of antioxidants and increases in DNA and protein adducts. However, elemental metal composition analyzed in PM from biodiesel and diesel exhaust was found to have metal bound to the carbon core [69].

Additionally, some fuels have specific compounds that are emitted in their burning. Biodiesel exhaust composition presents a number of methyl ester, cyclic fatty acids and nitro fatty acids. Fatty acids are considered pulmonary irritants and present dual polarity that can play an important role tampering the membrane structures and lead to cell death [69]. This kind of compound can play an important role as a fuel emission marker.

Air pollutants	Damage to Human Health
CO	CO can cause harmful health effects by reducing oxygen delivery to the body's organs (like the heart and brain) and tissues. At extremely high levels, CO can cause death.
NOx	In the group of NOx, NO_2 is the component of greatest interest and the indicator for the larger group of nitrogen oxides. In addition to contributing to the formation of O_3, and fine particle pollution, NO_2 is linked with a number of adverse effects on the respiratory system as airway inflammation in healthy people and increased respiratory symptoms in people with asthma.
SOx	SO_2 is the main component and is linked with a number of adverse effects on the respiratory system such as bronchoconstriction and increased asthma symptoms, also short-term exposure increases visits to emergency departments and hospital admissions for respiratory illnesses.
O_3	Even relatively low levels of ozone can cause health effects. People with lung disease, children, older adults, and people who are active outdoors may be particularly sensitive to ozone. The exposure to ozone can make it more difficult to breathe deeply and vigorously, cause shortness of breath and pain when taking a deep breath, cause coughing and sore or scratchy throat, inflame and damage the airways, aggravate lung diseases such as asthma, emphysema, and chronic bronchitis, increase the frequency of asthma attacks, make the lungs more susceptible to infection and ozone can continue to damage the lungs even when the symptoms have disappeared.
PM	Exposure to such particles can affect both lungs and heart, especially fine particles - containing microscopic solids or liquid droplets that are so small that they can get deep into the lungs and cause serious health problems. 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, and increased respiratory symptoms, such as irritation of the airways, coughing or difficulty breathing.

Table 3. Air pollutants and their damage to human health [34].

The PM emitted during fuel burning present some special characteristics. They are composed of a carbon core and organic compounds are adsorbed in their surface. The physical characteristic, especially the size of PM emitted during fuel burning is directly linked to their potential to cause health hazards. Small particles (PM_{10}) less than 10 micrometers in diameter (Dp) pose the greatest problems, because they can get deep into the lungs, and some may even get into the bloodstream. EPA is concerned about particles that are 10 micrometers in diameter or smaller because those are the particles that generally pass through the throat and nose and enter the lungs. Once inhaled, these particles can affect the heart and lungs and cause serious health effects. EPA groups regulated particle pollution into two categories: "Coarse particles," which are larger than 2.5 micrometers and “fine particles” which

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are smaller than 10 micrometers in diameter. These particles are deposited into the airways in the head region when inhaled. "Fine particles," are 2.5 micrometers ($PM_{2,5}$) in diameter or smaller and when inhaled they are deposited into lung airways or the tracheobronchial region (Figure 4).

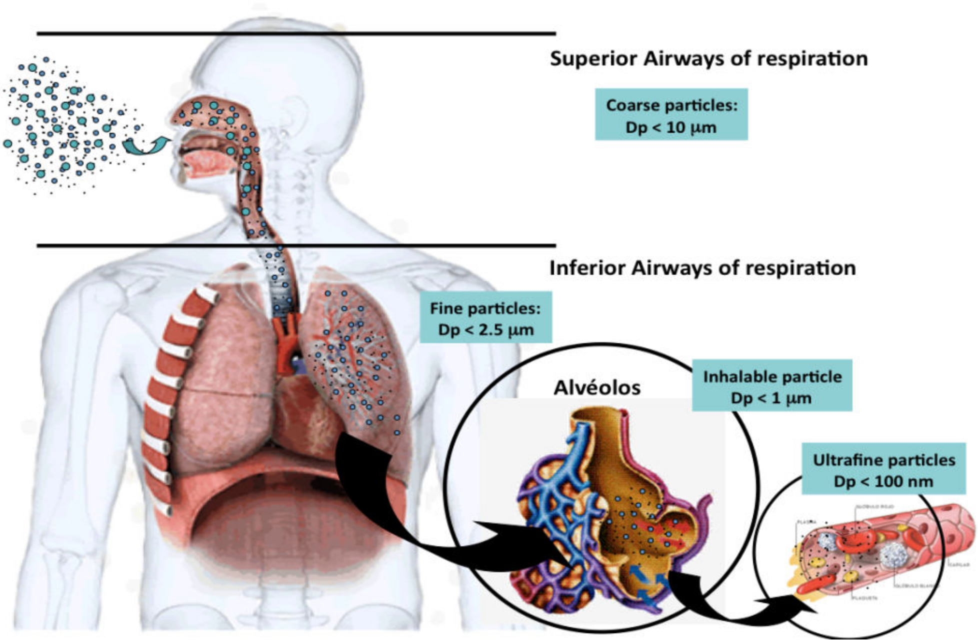

Figure 4. Represents the areas where particulate material from incomplete combustion processes is deposited in the body.

However, researchers consider two other categories as well: “Inhalable particles” are smaller than 1 µm, these particles can deposit into the pulmonary alveoli, and finally the “Ultrafine particles,” such as those found close to emissions source, mainly diesel emissions. These ultrafine particles are 100 nanometers in diameter and smaller. They present a high concentration of organic compounds in their composition and can be deposited in the alveolar region and also get into the bloodstream. So, the uses of biofuel can interfere on size distribution of particles emitted as well as chemical composition. Most of the studies published demonstrate a reduction in PM emissions with biodiesel as compared to diesel fuel. This reduction is mainly caused by reduced soot formation and enhanced soot oxidation [57]. In terms of toxicity this is a good gain for the human health. However, in terms of size distribution studies there are worries that the addition of biofuel to petroleum fuel or the use of pure biofuel will change the particle size distribution. These changes have potential implications for the health impacts of PM emissions from biofuel blends.

The addition of ethanol in gasoline fuel changes the particle size distribution, especially in the accumulation mode (30 nm <Dp< 2.5 μm), and decreases the black carbon and total particulate mass concentrations. The molecular weight distribution of the PAH was found to decrease with added ethanol [70, 71]. Generally these changes in the particle size distribution can happen when volatile materials are in excess, leaving insufficient solid area available for adsorption and condensation promoting the nucleation process.

5.2. Emission exposure and toxic effects

The crucial aim of toxicology studies is to identify possible health effects induced by exposure of both the general population and sensitive or susceptible populations, inducing by determination of the exposure threshold, the level needed to induce health effects. The threshold should include not only a concentration but a duration metric, which could be acute or repeated exposures. The strategies to plan and realize the toxic studies should regard that possible health effects may take years of exposure to discern, e. g., lung cancer, fibrosis, emphysema, and mitigation of the exposure and/or effects may be too late for an individual [69].

There are many factors that influence emissions toxicity and the use of biofuel in recent years in some countries has shown a difference in emission contents reflected in the emission toxicity profile. It is important to understand how and what is changing to be able to identify means to improve human and environmental health. In terms of emission from vehicles, the main line of exposure and toxicity effect is on the respiratory system. This is the main point of human contact with the air pollutant and where the first contact and exposure to the pollutant happens. This system is composed of three main regions: the head airways region, lung airways or tracheobronchial region and the pulmonary or alveolar region. Each region differs markedly in structure, airflow patterns, function, retention time, and sensitivity to gases absorption and particle deposition. Inhaled air follows a flow that goes through a sequence of airway branchings as it travels from the trachea to the alveolar surfaces. The first branchings take place in the tracheobronchial region and the remainder in the gas exchange region (Figure 4). In this mechanism the gases are absorbed in the alveolar region and the particles' contents deposited in the lung for varying time durations, depending on their physicochemical properties, their location within the lung, and the type of clearance mechanism involved [72]. Once the pollutant makes contact with the human tissue it starts a series of mechanisms in which the absorption process, the biotransformation and distribution, and lastly the excretion process occur. Thus, the air contents, the pollutants concentration and the physical proprieties are very important since they will determine the acceptable level of toxic exposure and what health effects and damages are caused.

5.2.1. Lung cancer

Lung cancer is a serious health problem and is the main toxic health effect caused by air pollutants. According to WHO, lung cancer accounts for 1.2 million deaths yearly worldwide, exceeding mortality from any other cancer in developed countries. Though the vast majority is caused by tobacco smoking, environmental causes of lung cancer, including air pollution, have long been a concern as well [73]. WHO recognizes that the exhaust fumes from diesel engines do cause cancer. A panel of experts working from WHO concluded that the exhausts were definitely a cause of lung cancer and may also cause tumors in the bladder [74].

Studies verified that controlled exposures of humans to whole diesel exhaust typically results in lung inflammation as shown with neutrophils entering the lungs [75]; in which these studies are generally 1-2 hr at approximately 100-300 μg/m^3 with healthy adults. In these same exposures, several soluble substances which mediate inflammation, e.g., interleukin-8 (IL-8) were shown to be increased by use of lung lavage or inducing sputum production to recover airways secretions. PM from diesel exhaust induced an adjutancy effect using nasal instillations of 300 μg particles in allergic subjects as common biomarkers of allergy (e.g., increased IgE production and histamine release) increased in nasal secretions [76]. Neutrophil influx into the lungs of healthy volunteers exposed to nearly 500 μg/m^3 wood smoke for 2 hr was observed [77] suggesting a common outcome from different combusted fuel sources.

Epidemiologic evidence has shown gasoline fuel emissions as a potential lung cancer cause as well [78]. Studies have shown that the gasoline exhaust increased DNA single strand break, promoted lipid peroxidation andoxidative protein damage and decreased activities of superoxide dismutase in lungs and brains. Though, it decreased the activities of glutathione peroxidase in lungs but not in the brain. The present data suggested that gasoline exhaust exposure could cause oxidative damage to lungs and brains of rats. That is to say that gasoline is a toxin to brains of mammals, not only to lungs [79].

However, lung cancer studies on biofuels emissions are limited. In general the findings are for fossil fuels that showed an elevated risk for the development of lung cancers in those with greater exposure compared to workers with lower exposure.

5.2.2. Mutagenicity and genotoxicity assessments

Mutagenicity assays in general can detect the genotoxicity effect of either single chemical and physical agents or heterogeneous mixtures. The Ames mutagenicity test is a short-term *in vitro* assay that has frequently been used to establish mutagenicity [80]. *Salmonella ryphimurium/mammalian* microsome test [81] detects mutagenic proprieties of a wide spectrum of chemicals by reverse mutation of a series of *Salmonella ryphimurim* tester strains. In general, the bacterial stains used to detect frameshift mutagens and base pair substitutions are TA98 and TA 100, respectively [64]. The Ames test is the most frequently used test system worldwide to investigate mutagenicity of complex mixtures like combustion products [82].

Studies about the mutagenicity of biofuel report a wide range of results. Studies about PM exhaust from burning of ethanol or methanol in gasoline blends submitted to the mutagenicity Ames test report that in all the ethanol blended fuel tests, the mass of PM associated to emitted organic compounds from the exhaust was lower than that observed during the control tests using pure gasoline. In the same way, others studies report that in most cases, estimates of the emission of mutagenic combustion products from the exhaust were lower using alcohol blend [83]. However, studies about the influence of ethanol–diesel blended fuels on mutagenic and genotoxic activities of particulate extracts showed higher mutagenicity for E20 (diesel with 20% v.v. of ethanol) compared to E15, E10 and DF (Diesel fuel). Additionally it was found that DF and E20 had a higher genotoxic potential than the other fuel blends [63].

In terms of biodiesel use, studies indicate that biodiesel exhaust is significantly less mutagenic in comparison with diesel fuel [82,84-88]. On the other hand, some studies reported no difference between diesel and biodiesel exhaust or nearly the same mutagenic effects [89, 90]. Moreover, some studies reported increase in the mutagenic effects with the use of biodiesel added to diesel [91-94]. It is important to highlight that the studies found high mutagenicity considering that the biodiesel mutagenicity was generally high or similar compared to diesel and in some other studies were comparing biodiesel to low sulfur diesel.

5.2.3. Oxidative stress assessments

The exposure to air pollutants promotes an event called oxidative stress. It can be defined as a disturbance in the prooxidant-antioxidant balance in favor of the former, leading to potential damage. The hypothesis is that many of the adverse health effects promoted by air pollutants may derivate from oxidative stress, initiated by the formation of reactive oxygen species (ROS) within affected cells [95]. In its simplest form then, oxidative stress is a potentially harmful process that occurs when there is an excess of free radicals, a decrease in antioxidant defenses, or a combination of these events [96].

After inhalation, PM deposited in the lung may stimulate the formation of ROS, such as hydroxyl and superoxide anion radicals. These ROS can be either directly derived from PM or endogenously produced by chemical components of PM, such as transition metals and quinone structures that undergo redox cycling. Furthermore, enhanced ROS formation in the lungs is likely involved in the activation of transcription factors and the induction of cytokines and chemotactic factors. Via these mechanisms, continuous exposure of the lungs to PM-induced ROS formation can cause pulmonary inflammation and eventually cause and/or aggravate impairment of lung development and lung diseases like chronic obstructive pulmonary disease, cystic fibrosis and asthma [80].

The assessment of radical generating capacity has been studied by many methods. Oxygen radicals cannot be detected directly because of their short half-lives, and therefore several alternative methods have been developed. In one method, a molecular probe reacts with the radical species and forms a stable product that can be analyzed with analytical methods, e.g. spectrophotometric analysis of thiobarbituric-acid reactive substances or the dithiothreitol (DTT) assay. Another method is based on biological indicators to assess the formation of ROS by PM, such as the induction of strand breaks in fX174 RF plasmid DNA or the formation of oxidized DNA-bases like 8- oxo-7,8-dihydro-20-deoxyguanosine (8-oxodG). A third method is based on the detection of free radicals by electron spin/paramagnetic resonance (ESR/ EPR) spectroscopy in combination with spin trapping compounds [80].

Studies carried out using Biodiesel and pure plant oil indicated significant reductions of the oxidative potential measured via DTT assay, about 95%, compared to diesel fuel [93]. However, studies measuring oxidative potential of ethanol exhaust are limited.

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5.2.4. Cytotoxicity assessments

Cytotoxicity assessment is currently essential to evaluate the potential human and environmental health risks associated with chemical exposure, and to limit animal experimentation whenever possible. Several different methods have been used to establish the citotoxicity of air pollutants. Air pollutants have a high potential to damage cells in a concentration- and a time-dependent manner in which the reactive oxygen species play an important role inducing cytotoxicity to the cells [97]. The most important distinctions between these sets are the use of various cell types (lungs cells, macrophages cells, embryonic cells, endothelial cells, fibroclast cell, and others, in which it can be from human or animals) and the time of incubation, varying from 4 to 72h. Also, different fractions and extraction procedures have been used. These differences and variables should be taken into account when results from different studies are compared [80].

Fossil fuels have been studied for many years and a range of researches have shown that the air pollutants promote toxicity and in some case apoptosis (cell death) to animals and human cells [98]. The studies found that biofuel presents a variable cytotoxicity compared to fossil fuels. In general, biodiesel presents an increase in cytotoxicity effects when compared to diesel fuel [82, 93, 99] or no significant differences in cytotoxicity between biodiesel and diesel exhaust [84, 88]. A study carried out using ethanol added to gasoline fuel demonstrated a strong decrease of ethanol exhaust cytotoxicity potential compared to gasoline exhaust [100].

6. Conclusions

Biofuels are promoted in many parts of the world and concern of environmental and social problems have grown due to increased production of this fuels. Production of biofuels promises substantial improvement in air quality through reducing emission from burning of the fuel used in vehicle engines. Some of the developing countries have started biofuel production and utilization as transport fuel in local market. Thus, below are described some important conclusions that we can be done about the use of biofuels by vehicle engines.

Compared to fossil diesel, the emission of regulated and non-regulated compounds from biofuels burning are generally equal or lower. An exception is NOx emission, which is generally higher with use of the biofuels, more specifically of the biodiesel use. The amount of compounds emitted depends considerably of the type engine, its configuration, the load condition and the use of a catalyzer. In most cases, reducing the emission of unwanted compounds requires modification in the standard engines for the use of biodiesel and/or raw vegetable oil and ethanol.

The recent literature demonstrates an increase in research activities on biofuels, especially within recent years. Even with the massive amount of data available, it is still difficult to accurately assess the environmental and health effects of the use of biofuels such as ethanol, biodiesel or raw vegetable oils in vehicle engines. At present, is difficult to conclude what will change with biofuels in terms of toxicity. There are few research activities with the aim to study the toxicological effectiveness of biofuels or their emissions, even though this topic is of great relevance. Furthermore, the results of the available studies could fluctuate widely. Several findings on acute and mechanism-specific toxicity indicate less or comparable effects induced by biofuels in comparison to fossil fuels. However, indications for negative impacts that are induced both by the biofuels themselves and their emissions have been reported. Based on the data available, human health risks associated with spills or the use of biofuels currently cannot be ruled out. Therefore, additional experimental studies are necessary to provide a more comprehensive dataset for the identification of new alternative fuels which could have lower issue impacts for the environment.

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