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The Blend Ethanol/Gasoline and Emission of Gases

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1. Introduction

By simulation, the sparkling ignition internal combustion engine, mechanic Otto cycle, four strokes, can be approximated to a thermodynamic cycle made of four different phases such as intake, compression (combustion), expansion and exhaustion.

According to Heywood (1988), the combustion reactions from those engines are characterized by a very rapid detonation, with the following characteristics: high pressure, due to the compression phase; a reaction zone extremely thin; the lack of chemical balance because of a very short residence time; a drop in temperature next to the gas valves outlets, due to expansion in the exhaust and then to the environment.

In a stoichiometry, the relative amount of the resulting products to the atmosphere depends on the chemical composition of the fuel, engine design, conditions of operation, the intermediate species that are formed during the process and the presence of a catalyst in the exhaust.

The blended ethanol gasoline has major effects on reducing emissions of greenhouse gases, while the engine design, as well as the operation conditions, and the presence of a catalyst in the exhaust, decrease pollutants and greenhouse gases.

The preliminary combustion processes are explained by reactions mechanisms and chemical kinetics, and are important to show how these gases are formed and to determine the emission levels.

The engine has a decisive role in the efficient burning; in this case, the physical and chemical properties of the fuel must be specified in accordance with the requirements of your project.

On the other hand, in Otto cycle engines, adding ethanol to gasoline, it reduces emissions of greenhouse gases like carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), and pollutants like carbon monoxide (CO), volatile organic compounds (VOC). Though, there is an increase in nitrogen oxides (NOx), and aldehydes (RCHO).

The purpose of this study is to compare the emissions of pollutant and greenhouse gases, when using the blend gasoline/ethanol or hydrated ethanol; understanding the differences between the combustion of two types of vehicles, and reviewing mechanisms that allow the increments and reduction of pollutant and the greenhouse gases.

2. Combustion in Otto cycle engines

The amount of the fuel components oxidation depends on temperature, oxygen concentration and how they mix with the gases. For these conditions occur, it is necessary that: the air/fuel ratio to obey stoichiometry; fuel spray be made and, the devices that perform this operation, the carburetor (older system) and electronic fuel injection, are in perfect conditions of operation.

The air / fuel ratio should be closer to stoichiometric. Inadequate concentration of oxygen promotes the partial oxidation of hydrocarbons during the preliminary process of combustion, the expansion and the exhaustion, with the CO, VOC and particulates.

The unfinished spray of fuel provides the accumulation of fuel in the cylinder walls. This occurs either from non calibrated equipments or at the start moment, when the engine is cold. In both cases, the fuel not burned, or partially burned, can form a thin layer on the wall. There is flame extinction and, as a result, we get an incomplete combustion and CO, VOC and particulates emissions. This problem is avoided by the adoption of multipoint injection system, because it is more efficient than the previous one.

Incomplete combustion can occur during startup when the engine is cold, or the spark timing in relation to air / fuel mixture cannot be adequately controlled. In both cases, there may have misfire or partial burning.

The formation of gaps between the cylinder and piston engines, as they get older, allows its filling, due to the flame at the entrance slit, and the mixture escapes from the preliminary process of combustion. The gas coming out of these cracks during the expansion process is a source of CO, VOC and particulates.

The engine oil can form a thin film on the cylinder wall, piston and cylinder head. The layers of oil can absorb hydrocarbons during the compression process and, during the expansion, it could release these substances to the gases formed. This mechanism allows a fraction of the fuel to exhaust of the preliminary process of combustion.

2.1 Mechanisms of chemical reactions in the engines

The detailed chemical mechanisms of pollutant formation and kinetics of these processes is important to determine the emission levels. The breakdown of molecules (pyrolysis) predominates during the preliminary process of combustion while the oxidation of hydrocarbons (which escape the process) occurs during the expansion and exhaust.

For nitrogen oxides, the formation and destruction of intermediate chemical species are not part of the combustion process; but the reactions that produce them occur in this environment.

The combustion reaction mechanisms of several hydrocarbons, including heptane and iso-octane were studied by Curran et al (1997-98) and the pure ethanol by Marinov (1998), both at Lawrence Livermore National laboratory in California.

Westbrook et al (1999) studied in the chemical kinetics model, the number of chemical species involved in combustion reactions. (Table 1)

Fuel	H_2	CH_4	C_3H_8	C_6H_{14}	$C_{16}H_{34}$
Species number	7	30	100	450	1200
Reactions Number	25	200	400	1500	7000

Table 1. Chemical species formed in combustion.

The flue gas analysis carried out shows that many organic compounds found in the exhaust are not originally in the fuel, indicating that significant changes occur during the process.

The observations made in these studies concluded that the reactions of decomposition (pyrolysis) are predominant at high temperatures, above 900K, and the reactions at low temperatures, below 900 K, dominate the oxygen addition reactions.

In a stoichiometric reaction, the relative amount of the resulting products into the atmosphere depends on the chemical composition of fuel, engine design, conditions of operation, the intermediate species that formed during the process and the presence of a catalyst in the exhaust.

The surveys reveal that at high temperatures occur decomposition on fuel molecules, extraction of hydrogen atoms, oxidation, isomerization and addition to double bond.

At this stage, there is a predominance of decomposition reactions and extraction of hydrogen which, according to Curran et al, responds for 50% of fuel consumption, as the example below:

$$RH + O_2 \rightarrow R_1H + OH^{\cdot} \quad (1)$$

$$RH + O \rightarrow R_1H + OH^{\cdot} \quad (2)$$

At temperatures below 900 C occur the following reactions keys: extraction of the H atom of alkanes, cyclic ether, aldehyde or ketone, addition of radicals to oxygen, split hemolytic CC and OO and decomposition of several radicals, radical reaction of the peroxide alkyl with HO_2 and H_2O_2 isomerization of the radical peroxide and hydroperoxide alkyl, scission of hydroperoxy alkyl radical, alkyl hydroperoxide radical oxidation and formation of cyclic ether hydroperoxido alkyl radical and hydroperoxide radical. Many reactions have the product OH and HO_2.

$$RO_2^{\cdot} + H_2O_2 \rightarrow ROOH + HO_2^{\cdot} \quad (3)$$

$$ROOH^{\cdot} \rightarrow alceno + HO_2^{\cdot} \quad (4)$$

$$ROOH^{\cdot} \rightarrow RO^{\cdot} + HO_2^{\cdot} \quad (5)$$

Marinov (1998), citing Borison and Norton and Dryer et al, modeling studies shows that the pyrolysis of ethanol forms the three major isomers radicals.

$$C_2H_5OH + X \rightarrow CH_2CH_2OH + XH \quad (6)$$

$$C_2H_5OH + X \rightarrow CH_3CHOH + XH \quad (7)$$

$$C_2H_5OH + X \rightarrow CH_3CH_2O + XH \quad (8)$$

X are OH, OH_2, CH_3 radicals or O and H atoms.

The addition of ethanol to gasoline increases the concentration of HO and OH_2 throughout the course of combustion and consequent increases the concentration of oxygenated compounds. The presence of theses radicals at high temperatures reduces emissions of HC (equations 1 and 2) and CO, as the following reaction:

$$CO + OH^{\cdot} \rightarrow CO_2 + H^{\cdot} \quad (9)$$

California Environmental Protection Agency (1999) in the article "Air Quality Impacts of the Use of Ethanol in California Reformulated Gasoline", citing a study by Koshland et al (1988), shows that mixing gasoline and ethanol 10% by volume (3.7% oxygen by weight) significantly reduces CO (13%), VOC (6%), benzene (11%), and increases NOx (5%), acetaldehyde (159%) as well as evaporative emissions.

Heywood (1988) estimated the emissions for gasoline without catalytic converted on the following values: NOx, from 500 to 1000 ppm; CO, 1 to 2% and unburned hydrocarbons (expressed as methane) at 3000 ppm.

2.2 Formation of carbon compounds

2.2.1 Carbon Monoxide

According to Muharam (2005), the formation of CO to 1250 K starts from the thermal decomposition of formyl and acetyl radicals, as follows:

$$CHO \rightarrow CO + H \quad (10)$$

$$CH_3CO \rightarrow CO + H \quad (11)$$

At low temperatures, around 600 K, the chain reaction for the formation begins with the decomposition of three isomers of carbonyl radicals and, after the formation of several intermediates, CO is produced through the decomposition and oxidation of small amounts of light cetyl radicals, as follows:

$$CH_3CO \rightarrow CH_3 + CO \quad (12)$$

$$C_2H_5CO \rightarrow C_2H_5 + CO \quad (13)$$

$$CHO + O_2 \rightarrow CO + HO_2^{\cdot} \quad (14)$$

$$C_3H_7CO \rightarrow CO + nC_3H_7 \quad (15)$$

2.2.2 Carbon dioxide

Formation occurs by the reaction of carbon monoxide with the radicals hydroxyl (OH) and hydroperoxide (HO_2); both at high and low temperature, according to the equations:

$$CO + HO_2^{\cdot} \rightarrow CO_2 + OH^{\cdot} \quad (16)$$

$$CO + OH^{\cdot} \leftrightarrow CO_2 + H^{\cdot} \quad (17)$$

Nevertheless, there is an increase of CO_2 emissions. However, this is the best option from environmental point of view, because the removal of CO from the atmosphere is made trough the mentioned reaction, which is preferred, because it is more reactive. This alternative, however, reduces the levels of OH, which is the route for the removal of methane. Consequence, there is an increased concentration of this gas in the atmosphere.

At temperatures of 600 and 700 K, it begins with the decomposition of carbonyl radicals to form the cetyl radical, after the formation of intermediate compounds. The formation of CO_2 also occurs through the reaction between OH radicals and ketones:

$$OH^{\cdot} + CH_2CO \rightarrow CO_2 + CH_3^{\cdot} \quad (18)$$

2.2.3 Methane

In conformity to Muharan (2005), the formation of methane occurs primarily through decomposition of cetyl radicals, with the addition of the oxygen atom to ethylene and decomposition of n-propyl radical which forms an intermediate, the methyl radical. This one reacts with the formaldehyde, ethylene and hydrogen atoms to form methane:

$$CH_2O + CH_3^{\cdot} \rightarrow CH_4 + CHO \quad (19)$$

$$C_2H_4 + CH_3^{\cdot} \rightarrow CH_4 + CHO \quad (20)$$

$$CH_3^{\cdot} + H \rightarrow CH_4 \quad (21)$$

The mechanisms of destruction of the formed methane are shown below:

$$CH_4 + O \rightarrow CH_3^{\cdot} + OH^{\cdot} \quad (22)$$

$$CH_4 + H^{\cdot} \rightarrow CH_3^{\cdot} + H_2 \quad (23)$$

$$CH_4 + OH^{\cdot} \rightarrow CH_3^{\cdot} + H_2O \quad (24)$$

It should be noticed that the formation of methane occurs in conjunction with the emissions of methane occurs in conjunction with hydrocarbons (HC). Heywood (1988) described the formation of these emissions and concluded that the contribution of the occurred processes in the gas cylinder is small.

2.3 Nitrogen compounds

The nitrogen that forms nitric oxide in the combustion, which will route for the formation of nitrous oxide comes from two sources: atmosphere nitrogen (N_2) and organic (in the fuel). The N_2 from the air is the most important source in the reactions that occur in internal combustion engines. Heywood (1988) estimated that if the fuel contains a significant amount of organic nitrogen – over 1% in weight (an example is biomass), the final NO emission can increase between 10 and 30%. In light petroleum distillates (gasoline, for example), this is low, around 0,07 – in this case, the organic nitrogen slightly affects the concentration of NO in the flue gas.

The processes of formation of nitrogen oxides have a different mechanism. It should be noticed, however, that the combustion reactions produce an increase in temperature that

allows the formation of NO which is a NO_2 and N_2O precursor; the interactions with compounds from combustion processes explain their processes of destruction. Thus, the two processes are linked.

There are four proposed mechanisms to explain the formation of NO: the Zeldovich, or thermal NO, Fenimore, or "prompt", NO, from the formation of N_2O, and the decomposition, of organic compounds of nitrogen.

In internal combustion engines, using gasoline, the typical temperatures lie around 2000 K. In this case, the prompt Zeldovich mechanism explains the formation of approximately 95% NO. The contribution due to the prompt NO is estimated in less than 5% and the rest are very small.

Breaking the triple bond of nitrogen from the air requires an extremely hugh activation energy, around 220 Kcal/mol. An oxygen molecule (O_2) is not able to direct reaction between molecular nitrogen and molecular oxygen is too slow. To explain the formation of NO, Zeldovich proposed the following mechanism:

$$O + N_2 \rightarrow NO + N \tag{25}$$

$$O_2 + N \rightarrow NO + O \tag{26}$$

Later, another reaction was added:

$$OH^{\cdot} + N \rightarrow NO + H^{\cdot} \tag{27}$$

This proposed mechanism consisted of three reactions mentioned above is known as the extended Zeldovich mechanism. NO concentrations correspond to equilibrium at temperature conditions at the exit of the cylinders.

Due to the characteristics of combustion reactions, the formation of NO does not reach chemical equilibrium. As the temperature of exhaust gases falls during the course of expansion, the reactions that involve NO stuck and its concentration remains at levels that correspond to equilibrium under conditions of exhaustion.

The combustion reactions under the conditions prevailing in the cylinder at adiabatic flame temperature, in an internal combustion engine, are decisive in the formation of NO and by extension of NOx and N_2O.

The NO formation rate, according to the Zeldovich mechanism, is strongly accelerated above 2000 K and negligible if the temperature is below 1700 K. It is concluded that the exhaust gases to the atmosphere there is no more formation of NO, only reactions with the other gases.

Another factor that may increase the concentration of NO is the contribution from the pyrolysis of ethanol to the concentration of OH and HO_2 radicals. Preferably they react with CO, reducing its emissions, but an increase in concentration should also contribute to the increase of NO (Zeldovich equation of 3).

The residence time of combustion gases in the engine is another variable to be observed. Below 10 seconds, the formation of NO is small; above this value, it is accelerated.

According to Heywood, in the conditions prevailing in the exhaust, the following secondary reactions occur:

$$N_2O \xrightarrow{+O} NO \tag{28}$$

$$N_2O \xleftarrow{+H,+OH,+O,+M} N_2 \tag{29}$$

It is observed that an increase in the concentration of OH, due to addition of anhydrous ethanol, reduces the concentration of CO (equation 13) and prevents that:

$$CO + NO \rightarrow N_2O + CO_2 \tag{30}$$

In this case, there is an increase in emissions of NOx and N_2O reduction.

Due to a certain amount of NO formed at high temperature, it can be concluded that at low temperatures the concentrations of N_2O in the output gas into the atmosphere are in an inverse relation with the NOx formed (equation 30).

3. Main variants in the formations of greenhouse gases

Reducing emissions of greenhouse gases and pollutants gases is closely correlated to fuel consumption, so that the vehicle efficiency is reflected in the amount of emitted gases.

The efficiencies and emissions measured in laboratory depend on two factors only: characteristics of manufactured vehicles and used fuel. On the other hand, when the vehicle is in use, the actual emissions vary depending on a number of factors, including the driving cycle, maintenance, age and environmental conditions (temperature, humidity).

Good conditions of public roads, no traffic jams in the city, and conscious motorists improve the driving cycle and then reduce vehicle gases emissions. In addition to these, regular maintenance and old vehicles removing is necessary. These actions depend on investments to keep roads in good conditions, also depend on public policies to encourage the exchange of old cars and supervise drivers.

The lower emissions can be achieved by using low pollution potential fuels. The engine design must be compatible with the physicochemical properties of the fuel, so that the performance can be improved by reducing consumption and mechanical maintenance.

3.1 Characteristics of manufactured vehicles

The characteristics of manufactures vehicles depend on consumer preference for one type of vehicle and automotive technology applied.

In developed countries, like United States, during the economic boom time, consumers prefer bigger and more powerful engines, increasing fuel consumption and emission of greenhouse gases. On countries with less power of purchase, such as Brazil, they have a fleet of more compact vehicles and powerless engines. Thus, they don't pollute that much.

Considering, however, the average age of fleet vehicles in countries with higher power of purchase, they have lower emissions, due to their lower age (older vehicle emit more pollutants than newer ones).

De Cicco and Ross (1993) apud Azuaga (2000) bring together the technical approaches in the manufacture of the vehicle in order to increase the efficiency of vehicles, in three parts: the engine, transmission and load (vehicle weight, size and aerodynamics). In addition, one can cite the final control systems.

The use of advanced technologies in motor improves combustion efficiency, because the incomplete reactions are related to the emissions of some greenhouse gases. Three aspects are discussed: improving the fuel air mixture, for a better dispersion of fuel in the air; the closer this ratio to the stoichiometric equations provided in the reaction, and a shorter residence time of gases in the cylinder.

The most notable improvements regarding to this were the exchange of electronic carburetors by fuel injection, electronic ignition mapped and the adopting of more than one valve per cylinder. The first two technologies, as observed by DeCicco and Ross (1993) apud Azuaga (2000), improved the dosage to be introduced into the combustion chamber through load sensors, speed, temperature and pressure, and the third dispersion of fuel in the air that feeds the engine.

Important to note that improvements have been made to the engine to reduce friction between parts, with the introduction of variable valve timing, a mechanism that allows control of the position according to the vehicle operating conditions and thus, efficiently manage the processes of induction and exhaust (De Cicco and Ross 1993 cited in IPCC 1999).

Combustion gases leaving the exhaust of a vehicle, despite the technological efforts, contain certain amount of greenhouse gases. To eliminate them the auto industry has implemented a converter in the exhaust in order to promote a catalytic chemical reaction between them.

To reduce the loss of the mechanical efficiency of the transmission, which occurs when there is no efficient synchrony between it and the engine, new technologies have been produced, including front-wheel drive, automatic transmission and variable torque control.

This control allows the engine to operate at a lower speed under a given load condition and increases the speed when more power is required, as noticed by De Cicco and Ross (1993), cited Azuaga (2000).

The adoption of front wheel drive cars eliminates the heavy steering shaft providing energy savings by reducing the vehicle weight although it is not suitable for most models of light commercial vehicles.

The load reducing, by reducing the size of the compartments (truck, rear seats etc.) and components weight (through a careful redesign of its parts), and the use of new materials such as plastic, aluminum and mild steel, permit lighter vehicles been manufactured and then, there is a decrease in fuel consumption.

A technologically advanced aerodynamics reduces the consumption because it allows less air resistance. This is possible with the elimination of acute angles in the side panels, between the hood and windshield.

The use of this technology, however, is restricted to passenger cars. It does not apply to light commercial vehicles, which requires open and load spaces, and specific height from the ground to run off the road.

3.2 Characteristics of fuels and emissions

There are limitations in efforts to completely eliminate emissions gases from oil products responsible for global warm. The existence of fossil carbon in its chemical composition will necessarily have compounds like HC, CO_2, CH_4 and CO, reducing of emissions can be done by the use of biofuels and catalysts in the exhaust.

3.2.1 Gasoline

Gasoline, without the addition of ethanol, is primarily made of branched and unbranched aliphatics, cyclic (naphthenic), and aromatics, besides substances that contain atoms of sulfur, nitrogen, metals and oxygen. Table 7 shows the origin and properties of the main substances and blends used in the formulation of gasoline and the processes to obtain it, site Petrobras (2011).

Currently, the refinery gasoline is made of carefully balanced mixtures of hydrocarbons, to meet the performance requirements on engines, and to avoid the emissions of pollutants.

The gasoline chemical composition control is made from their physicochemical properties, such as: ASTM distillation; octane index; volatility; calorific value; and Reid vapor pressure. When analyzing the properties of gasoline manufactured in Brazil, one has to consider that it currently contains 25% of anhydrous ethanol (according to applicable law it may vary between 18 and 25).

The ASTM distillation of petroleum products at atmospheric pressure is one of the tests that evaluate the range and boiling oil and its derivatives to ensure the correct specification of the final product and the refining processes control.

	Process	Boiler point range (°C)	Motor octane number.
Butane. Isopentane	Crude oil distillation and transformation processes	Zero 27	101 75
Alkylate	Alkylation	40 - 150	90 – 100
Light naphtha	Crude oil distillation.	30 - 120	50 – 65
Heavy naptha	Crude oil distillation.	90 - 220	40 – 50
Hydrocracking naphtha	Hydrocracking Process Technology	40 - 220	80 – 85
Cracker naphtha	Fluid catalytic cracking process.	40 - 220	78 – 80
Naphtha polymer	Olefin polymerization.	60 - 220	80 – 100
Coker naphtha	Delayed Coking Process Technology.	30 - 150	70 – 76
Naphtha reform	Catalytic reforming	40 - 220	80 – 85

Table 2. Gasoline.

In Brazil, the application of ASTM distillation (in gasoline) gets ranges from 30 to 215 ° C. The content of 10% gasoline evaporated in the ASTM distillation is related to the minimum amount required for initial ignition to occur; the 50% of the distillate is related to the heating

and engine performance, while the remaining 90% is intended to minimize deposits formation, which is a source of emissions.

Volatility is the fuel agility to turn from liquid to vapor and this property is related to the 10% evaporated ASTM distillation. A fuel with high volatility promotes HC emissions, both in cold start and in the tank.

Currently there is a strong trend in reducing the volatility parameters, without compromising the ignition of the fuel. The way we can reduce this property is decreasing the amount of butane in gasoline in Brazil (see Table 1).

The Reid vapor pressure is the absolute pressure practiced by a mixture at 37.8 ° C with a rate of vapor/liquid of 4 to 1. The parameter is often used to characterize the volatility of gasoline and crude oils.

This test is mainly used to indicate the requirements that must be met for the products transportation and storage, including vehicles, preventing accidents and minimizing the losses.

It is observed that the higher the temperature, the greater is the evaporative emissions, and then the need to specify the volatility according to the region where it will be used and the season of the year.

A fuel with a low heat of vaporization and vapor pressure allows more complete combustion; the opposite can cause incomplete vaporization and a lack of control in the air/fuel relation making the burning process very difficult.

The aromatics have a high heat of vaporization and boiling point, then the difficulty of evaporation. These properties limit their use because they difficult the formation of homogeneous mixture air/fuel. As a result, there is a partial burning with the formation of CO and VOCs, especially during cold start.

Anhydrous ethanol also has a high heat of vaporization, but this property is compensated by its low boiling temperature, 10 ° C. In this case there is no difficulty of forming an air / fuel mixture as occurs with the aromatic.

The octane index measures the ability of a chemical compound to withstand high pressures without detonating. In the event of this fact, there will be a partial burning of fuel.

Engine designers take the octane into account to determine compression ratio, ignition advance curves and injection time.

The linear hydrocarbons have little resistance to compression and, for this reason, its concentration in gasoline should be controlled; the n-heptane, for example, has an octane rating of zero.

Branched hydrocarbons resist high pressures inside the cylinders, without detonation and consequent win of power; iso-octane, for example, has an octane rating of 100.

Hydrocarbons containing double bonds are desirable because they generally have high octane, but there are some restrictions on its use in engines, because they can easily bond with hydrogen to form paraffin. Besides, it is revealed that the decrease of its content decreases the formation of volatile organic compounds.

The aromatics (benzene and toluene are the most used) have the advantage of being chemically more stable than other unsaturated compounds; thus they are more resistant to auto ignition than iso-octane, during compression stroke. Benzene, for example, that has an index equal to 120 octanes, can be used as an agent to raise this ratio in fuels.

Ethanol has high octane without problems enthalpy and the boiling point presented by the aromatics compounds. You can reduce the volume of aromatics, replacing the oxygen, without prejudice to the octane number of gasoline without increasing emissions.

The hydrocarbons have the advantage of having a high calorific value by reducing fuel consumption due to energy availability increase.

Ethanol has a low calorific value compared to hydrocarbons. Consequently, the mixture ethanol/gasoline has a lower calorific value than pure gasoline.

A fuel of higher calorific value, however, has the disadvantage of forming NO, NO_2 and N_2O by extension, due to a higher adiabatic flame temperature.

3.2.2 Ethanol hydrated

The carbon removed from the atmosphere by photosynthesis, and stored in biomass will serve as row material for bioethanol production, which will be burned in engines that emit CO_2 engines.

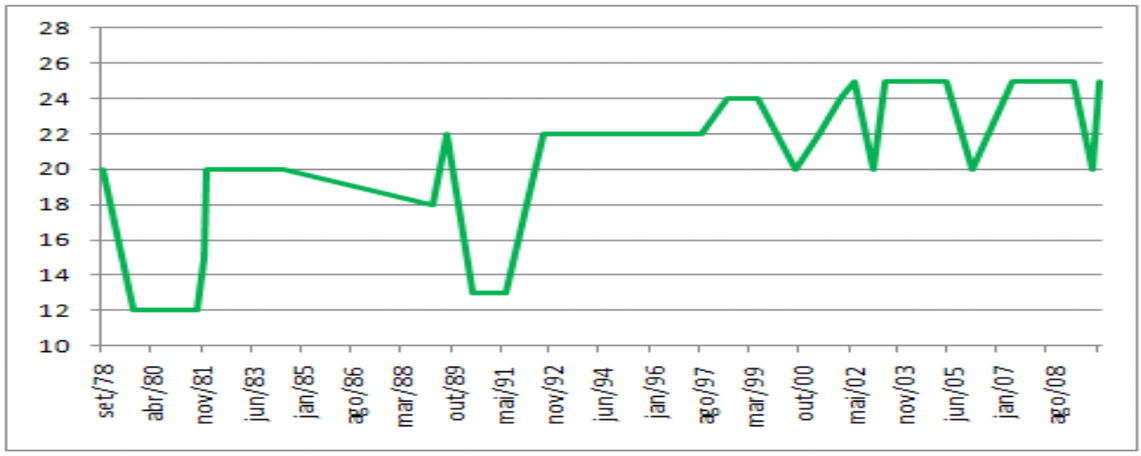
The process is closed, which net income is zero in terms of CO_2 emissions, while fossil fuel burning releases into the atmosphere carbon stored over millions of years. The addition of ethanol brings the following advantages and disadvantages:

- The fact of having 11% oxygen by mass results in better combustion, reducing emissions of gases such as CO, CH_4 and HC.
- The ethanol carbon is produced by photosynthesis; so it does not contributes to the global warming.
- The presence of oxygen increases compounds like NOx and RCHO. The combination of these agents leads to an increased formation of 'photochemical smog' and tropospheric ozone.
- The calorific value of ethanol is about 30% lower than gasoline.
- The ethanol has high octane index, which allows a higher compression ratio and more powerful engine.

4. Emissions of gases

The reasons why emissions of internal combustion engines varied in the period 1980-2002 were described in “Main variants in the formations of greenhouse gases”.

The emissions, in kg/vehicle, depend on the variables: the fleet, driving cycle, maintenance, fleet age, environmental conditions and traffic. The emission factors depend more on the technology used to improve the characteristics of manufactured vehicles and fuels. The engines did not have significant technological developments in 1980-1985. During this period, the increase in the percentage of ethanol in gasoline and the production of hydrated ethanol engines were responsible for the variations.



Note: the percentage increase data of ethanol in gasoline were obtained from the ordinances of Ministério de Agriculture, Pecuária e Abastecimento.

Fig. 1. Percentage of Ethanol in Gasoline 1978-2009.

The fall in oil prices and the ethanol supply crisis in 1986 completely changed the automotive scenery in Brazil. Gasoline vehicles, which in the past have had their production reduced, increased its share of the fleet and dominated the market at the expense of hydrated ethanol.

With a fleet reduction of hydrous ethanol in 1987, initially there was an increase in greenhouse gas emissions. They, however, began to decline because of the incentives given by the government for the manufacture of vehicles of 1.000 cc; the conversion of engines to use natural gas; and the use of ethanol vehicles for taxis. After 1992, to accomplish CONAMA Resolution Nº 010/1989, the companies have been introducing new technologies in vehicle manufacturing and fuels formulas (Main variants in the formations of greenhouse gases). These applications allow the reduction of emissions.

In this decade, there has been a considerable increase in metropolis fleet, generating large traffic congestion. In these conditions, there is an increase of emissions.

4.1 Emission factors

The determination of emission factors of Brazilian vehicles must be adapted to the characteristics of the fuels used in Brazil, hydrated ethanol and the blend gasoline/anhydrous ethanol.

The Conselho Nacional de Meio Ambiente (CONAMA) does not require the measurement of CH_4 and N_2O, but includes (HC) and RCHO a corresponding part of the volatile organic compound without methane. Both are not included in international data.

The emission factors of CO, HC, NOx and RCHO for the period 1980 to 2009, used in this work, are from Motor Vehicle Air Pollution Control Program (PROCONVE), while CO_2 and CH_4 are from the First National Atmospheric Emissions Inventory for Road Motor Vehicles of the Ministério do Meio Ambiente.

N_2O emissions will not be calculated due to the lack of emission factors for blend gasoline/ethanol and hydrated ethanol. Some authors use the emission factors of pure

gasoline, but the final figures may be overestimated. For this reason it is not possible to evaluate the effect of the blend.

To understand the role of ethanol in reducing the emission factor of CO, see equations 16 and 17, HC and CH_4 according to equations 1 and 2. For NOx, see equations 25, 26, 27 and 30. RCHO has the precursor products in equations 6 e 7.

CO, NOx emissions factors (left axis of the graphs) and HC (right axis) of the blend ethanol/gasoline are higher than hydrous ethanol in the period between 1980-1985 (Figures 2 and 3).

The ethanol emissions factors of CO, HC, considering the reaction mechanisms, are lower than gasoline and RCHO (right axis of the graphs) higher. However, the lowest values for NOx, can only be understood assuming that the engine of ethanol has better technology than that of gasoline in the period studied (Figures 2 and 3).

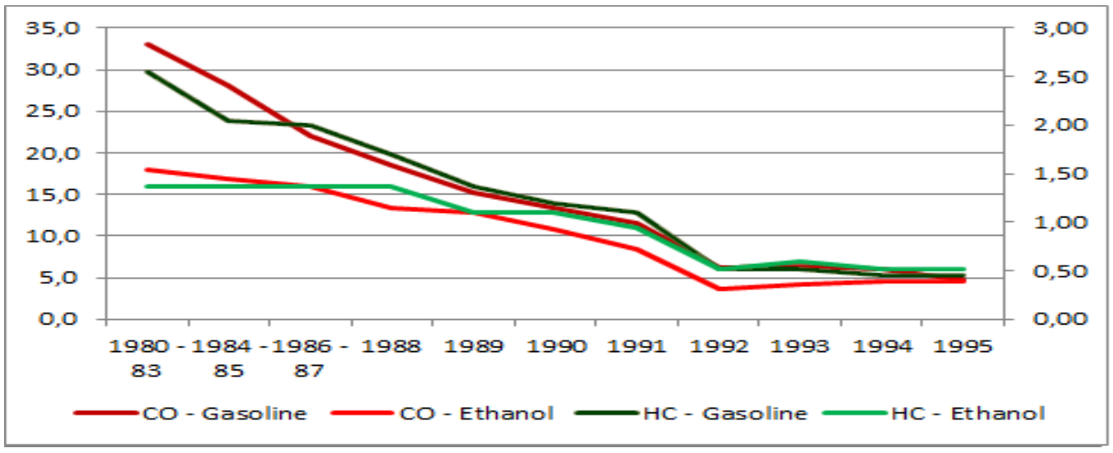


Fig. 2. Emission factors of CO and HC 1980-1995.

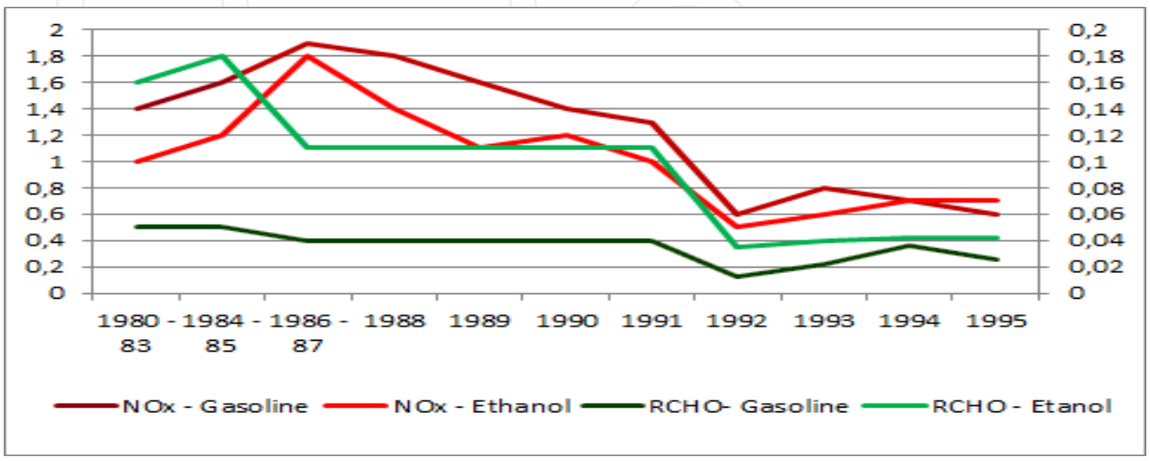


Fig. 3. Emission factors of NOx and RCHO 1980-1995.

The gasoline forms a smaller amount of oxygen. For this reason, their emissions of aldehydes (right axis) are smaller than ethanol (Figure 3), as expected in the mechanisms of combustion reactions.

After 1992, to meet the Resolution CONAMA 010/1989, Automakers and Refineries have introduced new technologies in engines that use a blend of ethanol/gasoline, and formulate new kinds of fuels (see Main variants in the formations of greenhouse gases).

Encouraged by the government, the of 1.000 cc engines manufacturers have participated with 71% of sales in 2001 (dropping to 52,7% in 2009) also contributed to the emissions reducing.

For ethanol engines, the reductions are much smaller, due to their manufacture gradual reduction, as in this case, there were no new technologies incorporated.

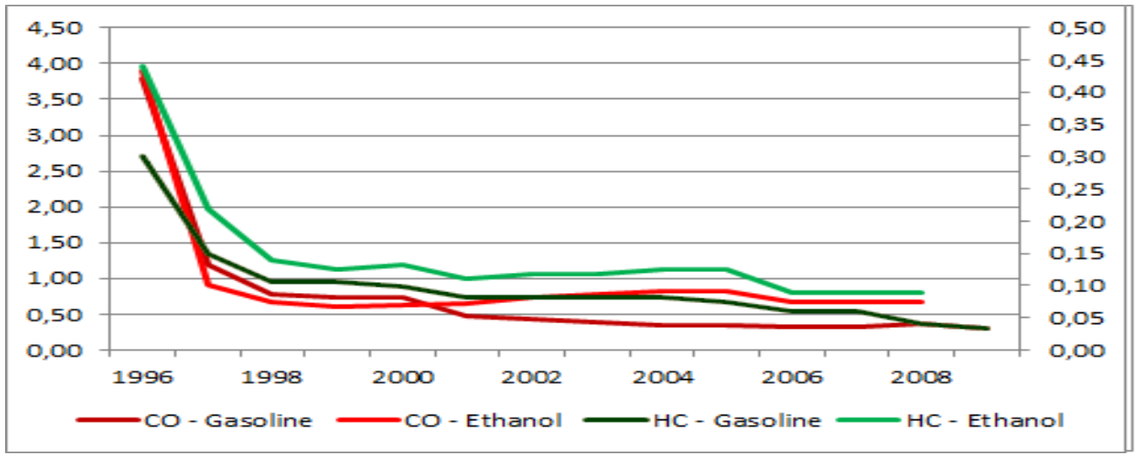


Fig. 4. Emission factors of CO and HC 1996-2009.

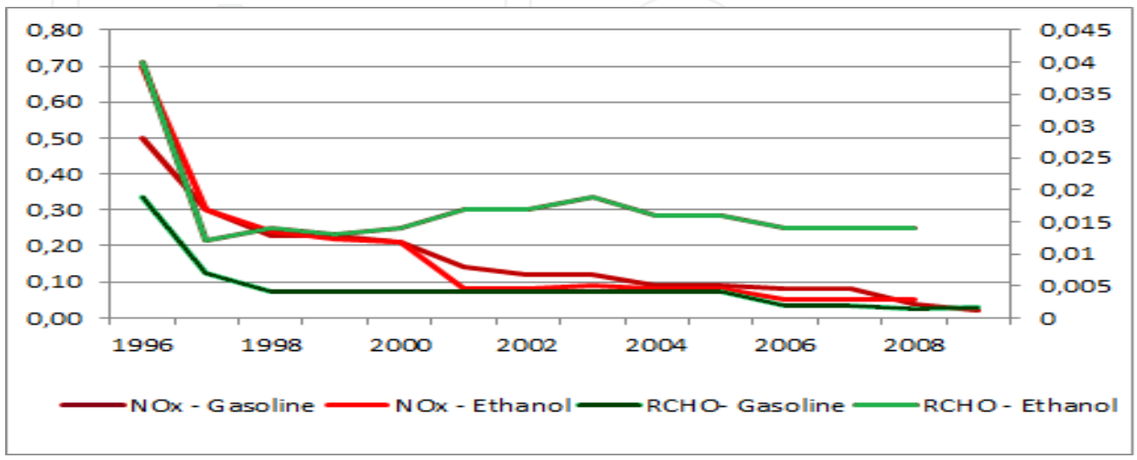


Fig. 5. Emission factors of NOx and RCHO 1996-2009.

The manufacture of flex-fuel engines since 2003 has changed the pattern of emissions of the Brazilian fleet. The engine flex-fuel interrupted the downward trend of emission factors.

For CO and HC there is a wide variation (figure 6). Then, you cannot establish a pattern of behavior.

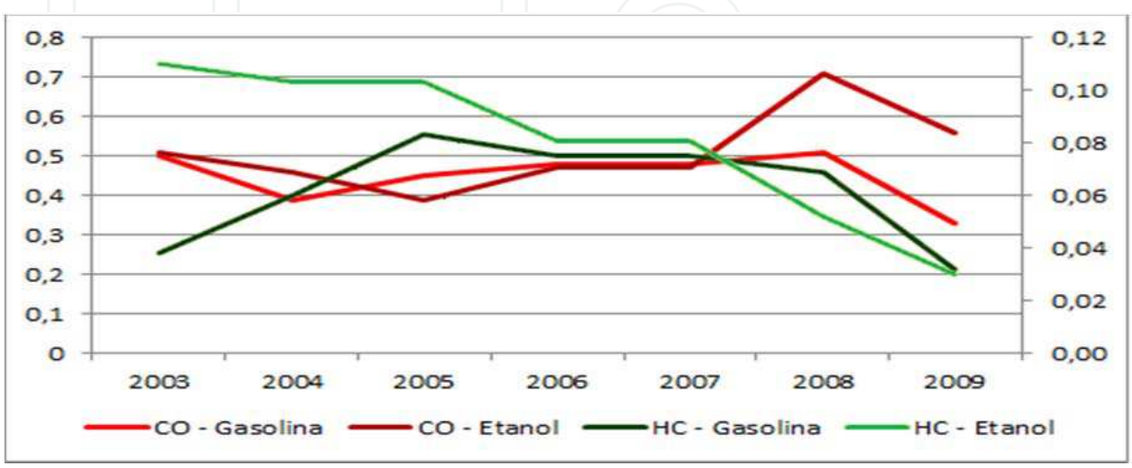


Fig. 6. Emission factors of CO and HC for fuel-flex.

You can see, however, that NOx and RCHO ethanol is higher than gasoline, as expected in the mechanisms of combustion reactions (Figure 7).

The problem with the new technology is the compression ratio, which is not adjusted for the octane best value of both fuels.

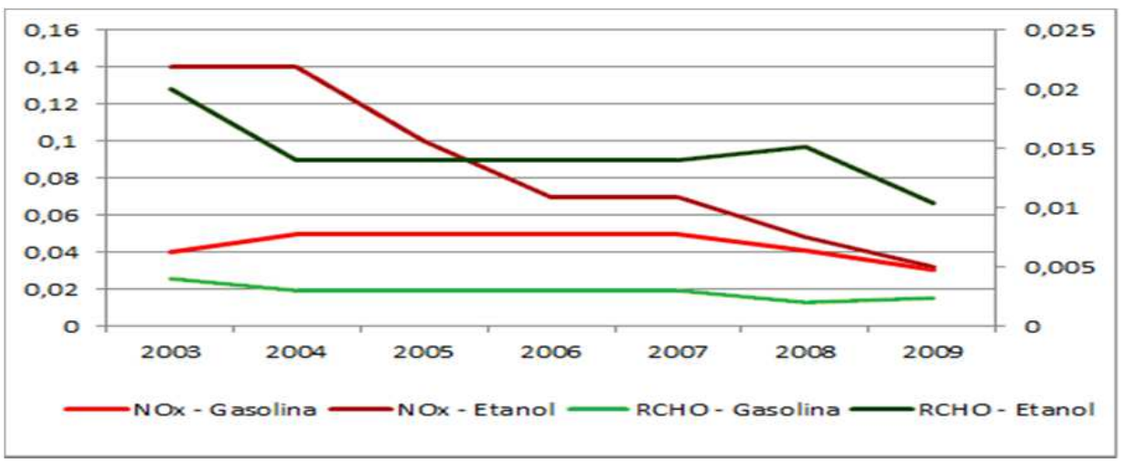


Fig. 7. Emission factors of NOx and RCHO for fuel-flex.

4.2 Gases emissions by Otto cycle vehicles

The variables that influence the emissions of pollutant and greenhouse gases were analyzed in Chapter 3.To analyze the impact of these action variables, first were used data from the National Atmospheric Emissions Inventory for Road Motor Vehicles of the Ministério do Meio Ambiente.

4.2.1 Pollutant gases emissions by Otto cycle vehicles

During the period of 1980-1995, gasoline engines have their emissions of CO, NOx (left axis), and HC, RCHO (right axis), influenced by the reduction of the fleet and the emission factors. Unlike the factors, the emissions follow the expected by the mechanisms of combustion reactions, ie, CO and HC are higher for gasoline, while NOx and RCHO are higher for ethanol.

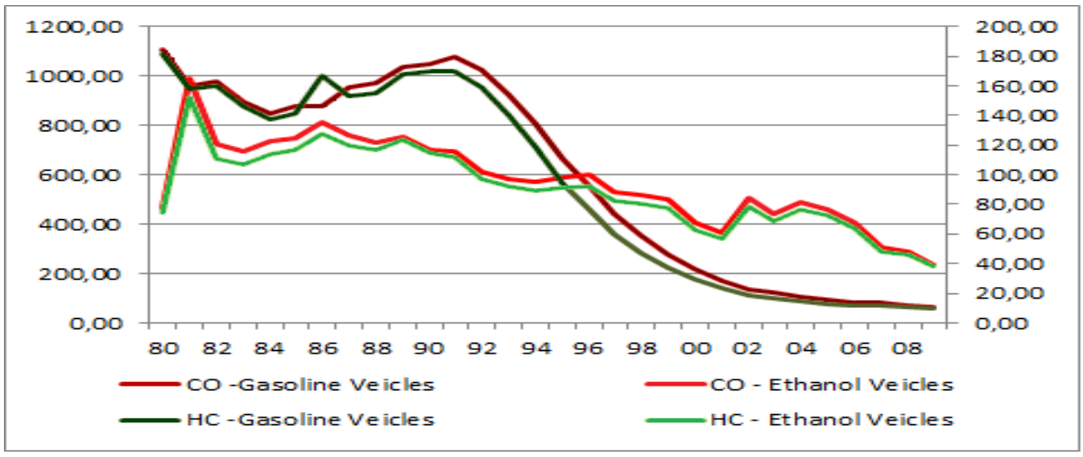


Fig. 8. Emission of CO and HC.

After this period, the fleet reduction of ethanol, and the technological developments of the engines, driven by the demands of Resolution CONAMA 010/1989, started making a difference. Emissions of CO and HC are also higher for ethanol.

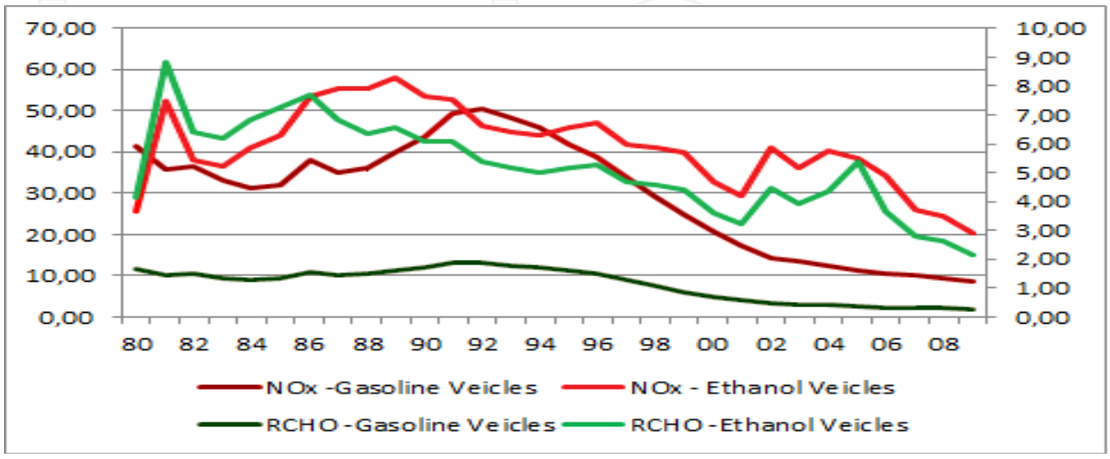


Fig. 9. Emission of NOx and RCHO.

In 2003, a new technology was introduced in Brazil, the engine "flex-fuel", becoming a best-seller. For this reason, hydrated ethanol and gasoline cars gradually ceased to be manufactured in the country and they had to start being imported.

The manufacture of flex-fuel engine has changed the pattern of emissions in the country. The gasoline engines have smaller greenhouse gases emissions, CO, HC and NOx RCHO, compared with ethanol. The reason is the compression ratio, which is not adjusted for the best value of the fuel octane.

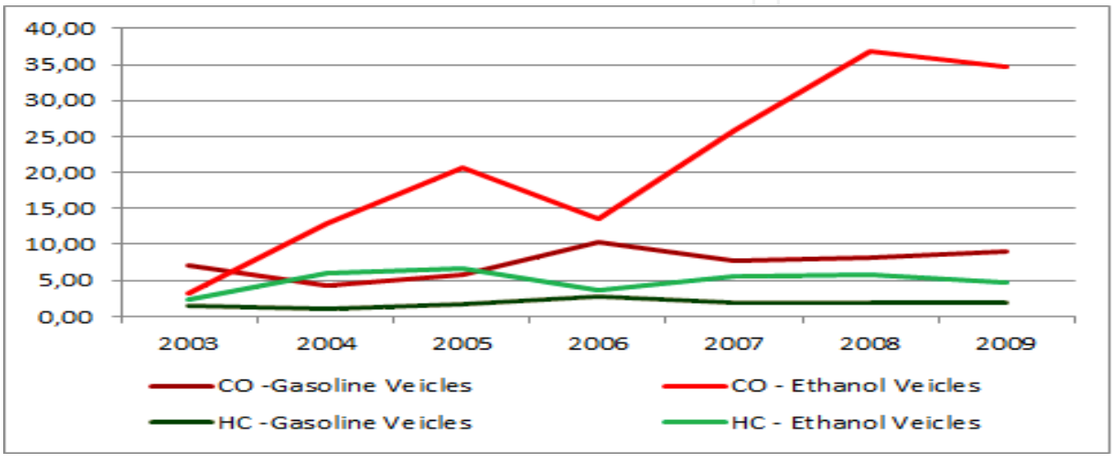


Fig. 10. Emission of CO and HC for fuel-flex.

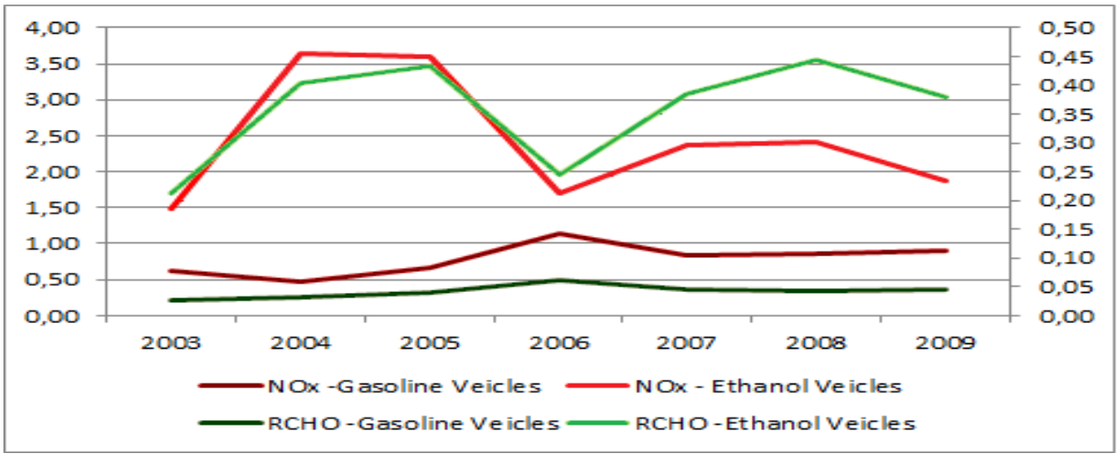


Fig. 11. Emission of NOx and RCHO for fuel-flex.

4.2.2 Greenhouse gas emissions vehicle Otto cycle

Ethanol consumption by the national fleet allows emissions of greenhouse gases in the transportation sector are substantially below those that could be achieved if the only fuel used was pure gasoline.

In the period 1980/87 the decline in fossil CO_2 emissions was due to the use of ethanol, while the increase occurred between 1988/97 was due to the reduction of its use. The decline from 1998/07 is due in part to a fleet of predominantly motor 1000 cc, the technological evolution of engines and from 2003, with the price drop and a greater supply, the market returned to using ethanol, figure 12.

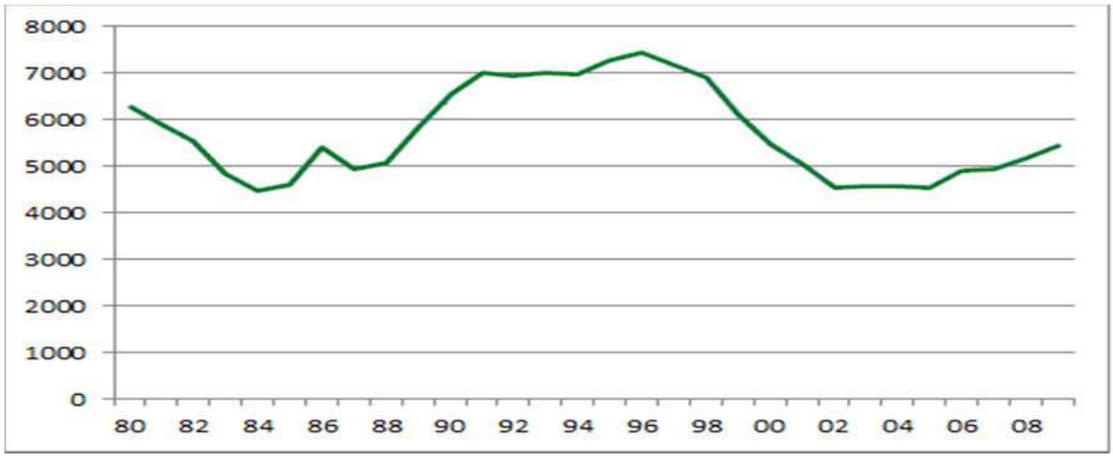


Fig. 12. Emissions of CO_2.

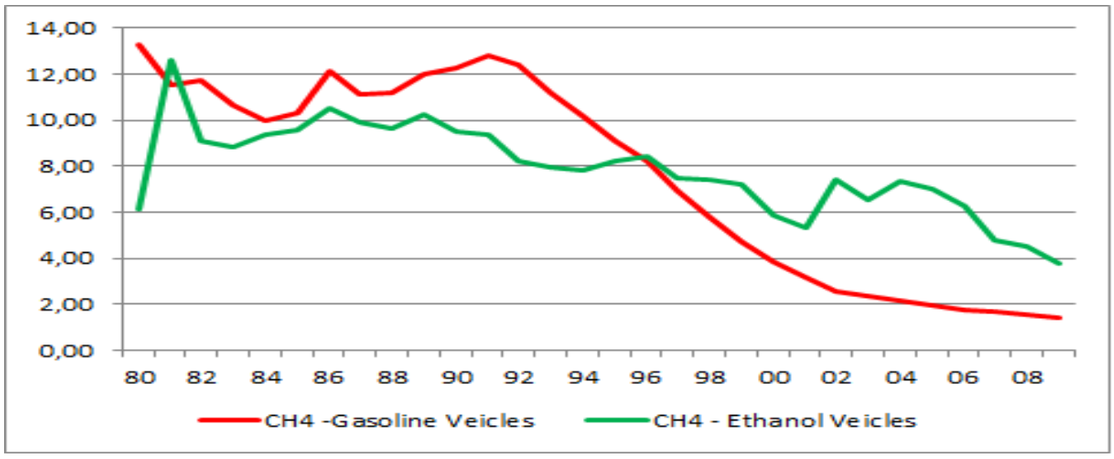


Fig. 13. Emissions of CH_4.

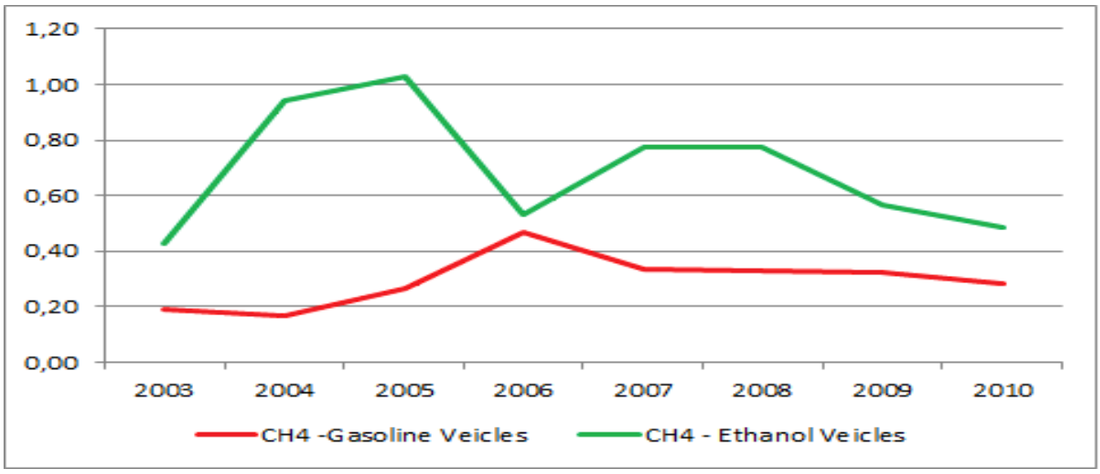


Fig. 14. Emissions of CH4 for fuel-flex

It should be noted that the CO_2 from burning of hydrous ethanol, is not counted in the emissions of greenhouse gases. The carbon removed from the atmosphere through photosynthesis and stored in biomass will serve as a feedstock for biofuel production, which in turn will be burned in engines. The process is closed, whose net income is zero in terms of CO_2 emissions, without considering the contributions of land use disputes whose values are not resolved.

Dedicated gasoline engines, in the period 1980-1995, have its emission of CH_4 affected by the reduction of the fleet and the emission factor. After this period, the fleet reduction of ethanol, the technological developments of the engines, driven by the demands of Resolution CONAMA 010/1989, start making a difference.

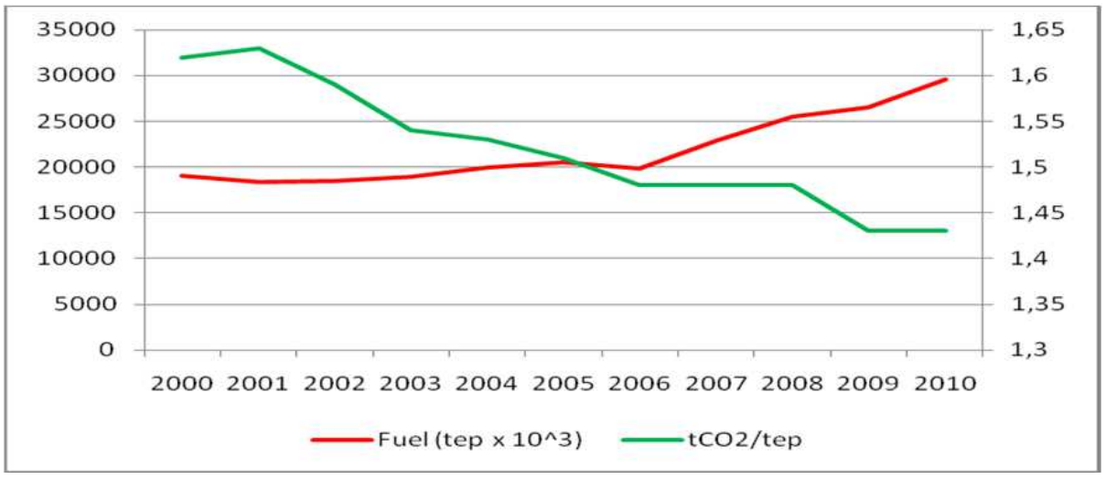


Fig. 15. Avoided Emissions.

4.2.3 Avoided emissions

The replacement of fossil carbon by the one that comes from biofuels reduces CO_2 emissions. We can estimate the difference between those from a hypothetical situation where the fleet of vehicles consumes only pure gasoline and the related to a real situation, where the fleet consists of vehicles that consume a mixture of gasoline/anhydrous ethanol and vehicles that require ethanol hydrated.

The Energy Research Company has estimated the avoided emissions (tCO_2/toe) in the period of 2000 to 2010. For comparison the same figure plotted in fuel consumption (gasoline more ethanol), in the period.

5. Conclusions

The changing profile of the Brazilian fleet allows you to compare the factors that contributed to the amount of emissions of pollutant and greenhouse gases, establishing a connection between the mechanisms of chemical reactions, the fuel composition, the evolution in technology of the vehicle and composition of gases coming out from the exhaust.

The values of the factors and emissions of CO, HC and NOx blend gasoline/ethanol and ethanol are influenced: by the presence of OH, HO_2 radicals and the introduction of new technologies in vehicles manufacturing and fuel formulation.

The addition of ethanol, increasing the OH and HO_2 concentrations, can be noted between 1980 and 1990, when vehicles did not have more advanced technologies. In this case, there was a reduction of the factors and emissions of CO and HC, while the factors for NOx decreased, and the emissions increased.

To meet the CONAMA Resolution No. 010/1989, which was enforced in 1992, vehicles manufacturers have introduced new technologies, including: more efficient engines with less power; catalyzers in the exhaust, reduction in fuel consumption due to an improved aerodynamics, reduction in vehicles weight and the petroleum refiners introduced new formulations.

After 1996, this set of measures began to influence, reducing the factors and the emissions of all gases. The hydrated ethanol vehicle had lower earnings due to lower technology incorporation and to a reduction in manufacturing.

The RCHO factors and emissions are much higher for hydrated ethanol than gasoline / ethanol mix throughout the entire period, including “flex-fuel" engines, showing that the formation of oxygenated hydrocarbons is strongly influenced by the OH and HO_2 radicals.

With the success of "flex-fuel" sales, hydrated ethanol vehicles are no longer manufactured and gasoline is focusing on more power and deluxe segment.

Due to a unique compression ratio for fuels with different octane ratings, "flex-fuel" engines, using blend ethanol and ethanol/gasoline, had a reduction in efficiency and thus higher emissions.

The values of CO and NOx emissions for blend gasoline/ethanol and hydrous ethanol reveal the need of an evolution in technology of the engines "flex-fuel".

The advantage of adding ethanol to gasoline and the manufacturing of engines that use hydrated ethanol are in the emission of greenhouse gases.

Looking at CO_2 emissions of a car that runs on a blend ethanol and gasoline compared to pure gasoline, there is a 22% reduction on average. This decrease reaches 100% when it comes to cars that use ethanol only, without considering the life cycle analysis.

Further studies are needed to understand the influence of adding ethanol to gasoline and the use of hydrous ethanol, such as "Determination of emission factor of N_2O", "Emissions of N_2O by mixing gasoline / ethanol and hydrous ethanol", and "Comparison emissions between pure gasoline and blend gasoline/ethanol".

Considering that in the next year cellulosic ethanol could be a reality, these studies provide a basis for developing policies and technologies that reduce environmental impact.

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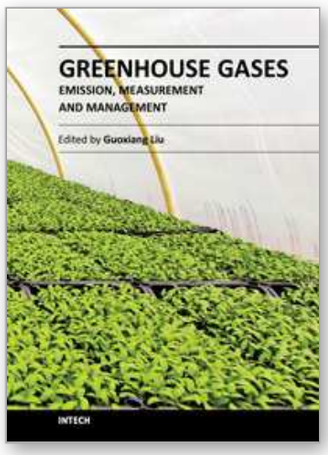
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Understanding greenhouse gas sources, emissions, measurements, and management is essential for capture, utilization, reduction, and storage of greenhouse gas, which plays a crucial role in issues such as global warming and climate change. Taking advantage of the authors' experience in greenhouse gases, this book discusses an overview of recently developed techniques, methods, and strategies: - A comprehensive source investigation of greenhouse gases that are emitted from hydrocarbon reservoirs, vehicle transportation, agricultural landscapes, farms, non-cattle confined buildings, and so on. - Recently developed detection and measurement techniques and methods such as photoacoustic spectroscopy, landfill-based carbon dioxide and methane measurement, and miniaturized mass spectrometer.

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