ECOLOGICAL EFFICIENCY IN INTERNAL COMBUSTION ENGINES: A GASOLINE, ALCOHOL, DIESEL AND BIODIESEL ANALISYS

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Abstract. This paper evaluates and quantifies the environmental impact of the use of some renewable fuels and fossils fuels in internal combustion engines. The following fuels are evaluated: gasoline blended with alcohol, conventional diesel fuel, biodiesel in pure form and blended with diesel fuel, and natural gas. The ecological efficiency concept depends on the environmental impact caused by CO_2 , SO_2 , NO_x and particulate material (PM) emissions. The exhaust gases from internal combustion engines, in the case of the gasoline (blended with alcohol), biodiesel and biodiesel blended with conventional diesel, are the less polluting; on the other hand, the most polluting are those related to conventional diesel. They can cause serious problems to the environment for their dangerous components for the human, animal and vegetable life. The resultant pollution of each one of the mentioned fuels are analyzed, considering separately CO_2 , SO_2 , NO_x and particulate material (PM) emissions in internal combustion engines, which are mostly used in urban transport. Biodiesel in pure form (B100) and blended with conventional diesel as fuel for engines are better than conventional diesel fuel. The ecological efficiency for pure biodiesel (B100) of 87.6 %; for biodiesel blended with conventional diesel, when used in engines, is 78.7 %; for gasoline, it is 82.4 %, and for natural gas, it is 91.3 %. All these figures considered a thermal efficiency of 30% for the internal combustion engine.

Keywords: Ecological efficiency, engine, biodiesel, vehicular fuels

1. INTRODUCTION

The environmental protection is one of the most frequent problems; nowadays, the reduction of the pollutant indicators of toxic substances in the environment, produced by the industrial and the automotive transportation sectors, is one of the most important targets that are being taken in account in the majority of the industrialized countries. It is necessary that both sectors adopt future strategies for the reduction of pollutants emissions to the atmosphere, with the purpose of reducing the dangerous concentrations in the air.

In the last three decades, the world has been confronted with energy crises due to the decrease of fossil resources with the increase of environmental problems and the prices of the derivates. This situation brought as consequence the search of alternatives and renewable fuels, which would have to be not only sustainable, but also friendly in respect to environment and techno-economically competitive. The biofuels like ethanol, vegetable oil, biomass, biogas, synthetics fuel, biodiesel, etc, are starting to be of high interest to the developed countries. Some of these fuels could be used in a direct form; however, others need some kind of modification to replace the conventional diesel fuel – gasification or digestion when the subject is biomass, and transesterification when it is biodiesel.

About 700 million tons of carbon monoxide, 150 million tons of nitrogen oxides, 200 million tons of solid particles, and 200 million tons of sulphur dioxides are released in the atmosphere. The majority of these substances are produced by the transport sector. Currently, the internal combustion engines (ICE) produce about 85% of energy that is consumed in the planet, for which the vehicles engines constitute a large portion. The exhaust gases that contain toxic substances represent the most dangerous risks related to the environment pollution [1]. The methodology proposed in this paper analyzes the efficiency in internal combustion engines from the ecological point of view, for the separate concentrations of pollutants (CO₂, SO₂, NO_x, PM). The ecological efficiency parameter (ϵ) was considered for steam cycles that use coal [2]; it was extended for combined cycle plants that use natural gas, internal combustion engines and advanced cycles that use biomass as fuel [3]. The ecological efficiency evaluates the environmental impact caused by the emissions in ICE's, considering the combustion of 1 kg of fuel and not the amount of released gases in the generation of a power unit.

2. THE EQUIVALENT CARBON DIOXIDE

The coefficient for the equivalent carbon dioxide $(CO_2)_e$, a hypothetical pollutant concentrations factor, in other words, it would come to be the average sum of main polluting gases, in order to obtain a same value of comparison of fuel emissions, is determined by Eq.(1) [2, 4]. For the calculation of this coefficient, the maximum allowed value for the CO_2 concentration is divided by the corresponding air quality standard for NO_x , SO_2 and PM in one hour. The expression for $(CO_2)_e$ is:

$$(CO_2)_e = (CO_2) + 80 (SO_2) + 50 (NO_X) + 67 (PM)$$
(1)

In Eq. (1), $(SO_2)_e = 80(SO_2)$ is the sulphuric dioxide equivalent in (CO_2) , $(NO_x)_e = 50(NO_x)$ is the nitrogen dioxide equivalent in (CO_2) and the particular matter equivalent in (CO_2) is $(PM)_e = 67$ (PM). The best fuel from the ecological standpoint is that which presents a minimum amount of $(CO_2)_e$ obtained from its burning. In order to quantify this environmental impact, the "pollutant indicator" (Πg) is defined by Eq. (2).

$$\Pi_g = \frac{(CO_2)_e}{Q_i} \tag{2}$$

with $(CO_2)_e$ is taken in kg/kg (kg per kg of fuel), Q_i is the fuel low heating value, expressed in MJ/kg, and $\prod g$ is expressed in kg/MJ.

3. ECOLOGICAL EFFICIENCY

The ecological efficiency is defined as an indicator which allows the evaluation of thermoelectric power plant performance in respect to pollutants emissions, by comparing the hypothetically integrated pollutant emissions (CO_2 equivalent emissions) to the existing air quality standards. The conversion efficiency is also considered a determining factor on the specific emissions, expressed by a fraction number. Eq. (3) can be used for the determination of ecological efficiency [2, 4, 5 and 6]:

$$\varepsilon = \left[\frac{0,204 \, n}{n + \prod_g} Ln \left(135 - \prod_g\right)\right]^{0.5} \tag{3}$$

where ε comprises, in a single coefficient, the aspects that define the thermoelectric unit environment impact intensity, fuel composition, combustion technology, pollutant indicator and thermodynamic efficiency. " ε " is directly proportional to thermoelectric power plant efficiency (η), inversely proportional to \prod_g , the pollutant indicator value, and also is located between 0 and 1, similar to the thermoelectric efficiency. The situation is considered unsatisfactory from the ecological point of view when $\varepsilon = 0$; however, $\varepsilon = 1$ indicates an ideal situation from the point of view of energetic efficiency. According to the fuel classification, pure hydrogen would have 0% of impact in the environment, while sulphur would cause 100% of impact; see Table (1) for details

Table 1 – Fuel virtual characteristics [6].

Fuel	S %	CO ₂ (kg/kg fuel)	Qi (MJ/kgf)	∏g (kg/MJ)	3
Hydrogen	-	0	10,742	0	1
Sulphur	100	1,400	10,450	134	0

4. METHODOLOGY

Ecological efficiency values for internal combustion engines for the case of urban transport are calculated for different fuels: diesel fuel, gasoline (blended with alcohol), biodiesel (B100 and B20) and natural gas. The chemical composition of reactants and products will be used to analyze the fuels. It will considered a excess air ratio of 100% for the diesel fuel and biodiesel, 50% for the natural gas and gasoline, finally 30% for alcool. In spite of being a toxic gas, CO doesn't contribute in great amount to the greenhouse effect, as much that to calculate the ecological efficiency parameter, wasn't taken in account, therefore for this work its calculation is not relevant. On the other hand, the NOx emitted during the combustion depends on the fuel composition, the way of operation and the project of the burners and combustion chamber. Therefore, in section five of this paper are showed the emission factors for different analyzed fuels always considering MCI technologies.

4.1. Diesel

In Brazil, diesel fuel consumption is attributed to the transport sector, which represents 80% in the energy matrix. From this total, 94% are destined for the road transport system. The Brazilian oil diesel compared with the American and European, presents a high sulphur level. Since January 1998, the national diesel fuel has 0.5% of sulphur content at the most [7]. The main pollutants when diesel fuel is used are: carbon dioxide, sulphur oxides and particulate material.

The traditional chemical formula for the petroleum diesel is $C_{12}H_{26}$ and its density is 0.948 ton/m³ [8]. The combustion reaction for normalized air excess α follows:

$$1C_{12}H_{26} + 18.5 \alpha O_2 + 69.56 \alpha N_2 \rightarrow 12 CO_2 + 13 H_2O + 69.56 \alpha N_2 + 18.5(\alpha - 1)O_2$$
(4)

Adopting diesel burning with 100% air excess, after the stoichiometric balance, a percentage in mass of each compound resulting from this reaction is: 10.06% CO₂, 4.46% H₂O, 74.21% N₂ and 11.28% O₂ (Tab 2). On the other hand, from its combustion reaction, the result is: 528 CO₂ g for 170 g diesel oil. Taking into account the diesel density, the result is: 528 ton of CO₂ for 179.32 m³ of oil diesel, or: 2.944 ton of CO₂ for m³ of oil diesel. [9].

Applying the percentage in mass of each compound, it is possible to compose an equation for the specific heat (Cp) of the exhaustion gases, in the case of diesel combustion [10].

$$Cp_D = 1.0039562 + \frac{3.39987 \cdot T}{10^5} + \frac{3.02996 \cdot T^2}{10^7} - \frac{1.3168 \cdot T^3}{10^{10}}$$
(5)

4.2. Gasoline

Gasoline is a fuel constituted basically of hydrocarbons and a small portion of oxygenized compounds. These hydrocarbons are, in general, less heavy fuels than those that compose diesel fuel, because they are formed by molecules of small carbonic chains (normally has 4 the 12 carbon atoms). Beyond the hydrocarbons and the oxygenized compounds, gasoline contains sulphur, nitrogen and metallic compounds, all these with low concentrations [7].

Blending of alcohol in gasoline is obligatory by Brazilian federal law. Currently, it is in vigor the Resolution n°35 ANP (Petroleum National Agency), of February 06, which determines that from March 2006, the percentage of anhydrous alcohol blended in gasoline, should not exceed 20%. This resolution applies for all gasoline types (common gasoline, *supra* gasoline, podium gasoline and premium gasoline).

The chemical formula of gasoline is C_8H_{18} (octane) and its density is 0.75 ton/m³ [11]. The combustion reaction for normalized air excess α follows:

$$C_{8}H_{18} + 12.5 \alpha O_{2} + 47 \alpha N_{2} \rightarrow 8 CO_{2} + 9 H_{2}O + 47 \alpha N_{2} + 12.5 (\alpha - 1) O_{2}$$
(6)

Considering gasoline burning with 100% of air excess, the percentages in mass of each compound resulting from the reaction is: 9.93% CO₂, 4.57% H₂O, 74.22% N₂ and 11.28% O₂. See Table 2 for detail. On the other hand, the CO₂ emission for this fuel is 352 g of CO₂ by 114g of gasoline. Taking into account the gasoline density, the result is: 352 ton of CO₂ for 152 m³ of gasoline, which means: 2.316 ton of CO₂ by m³ of gasoline [9].

Applying the percentage of each component mass the compound gasoline Cp equation is obtained [10].

$$Cp_{Gasoline} = 1.0056085 + \frac{3.18652 \cdot T}{10^5} + \frac{3.05263 \cdot T^2}{10^7} - \frac{1.32317 \cdot T^3}{10^{10}}$$
(7)

Anhydrous ethanol is miscible in gasoline, which allows its use as a blend in automobiles, reducing gasoline consumption and discarding the use of specific antiknock agents. The percentage of anhydrous ethanol in gasoline has varied along the years between 20 and 25% in volumetric basis [12]. The chemical formula for ethanol is C_2H_5OH and its density is 0.79 t/m³ [13]. The emission of CO₂ for this fuel is: 88g CO₂ by 46g alcohol; in consequence: 1.511 ton of CO₂ by m³ of alcohol (see the reaction below).

$$1C_2H_5OH + 3\alpha O_2 + 11.28\alpha N_2 \rightarrow 2CO_2 + 3H_2O + 11.28\alpha N_2 + 3(\alpha - 1)O_2$$
(8)

Considering 100% of air excess during burning, the percentages in mass of each compound resulting from this reaction are: 10.12% CO₂, 6.21% H₂O, 72.63% N₂ and 11.04% O₂ (see Table (2)). Similar to gasoline, the equation for the Cp of the exhaust gases in the case of the alcohol combustion is obtained. Eq. (9) shows the formula for Cp o ethanol as function of temperature [9].

$$Cp_{\acute{Alcohol}} = 1.018719 + \frac{3.41881 \cdot T}{10^5} + \frac{3.09569 \cdot T^2}{10^7} - \frac{1.33244 \cdot T^3}{10^{10}}$$
(9)

4.3. Biodiesel

Chemically, biodiesel is composed of monoalkyl esters of long chains and fatty acids derived from renewable feed stock like vegetable oils and animal fats. It is produced by transesterification, in which oil or fat is reacted with a monohydric alcohol in presence of a catalyst. The biodiesel is used in compression ignition engines (diesel engines) or

heating boilers. The biodiesel fuel has in general, the same or similar properties of the conventional diesel fuel and can be blended in any percentage with diesel fuel.

Biodiesel presents a slightly lower heating value (LHV) in comparison with the diesel fuel (117.093 Btu/gal, instead of 131.295 Btu/gal). Its kinematics viscosity, in general, varies between 1.9 and 6 cSt; this parameter does not differ much from the values corresponding to diesel fuel (1,3 and 4,1 cSt). Its density is approximately 0.9679 ton/m³ at 15°C and its flash point is above 150 °C, which is higher than the value for diesel fuel, whose flash point varies between 60 and 80 °C. The flash point makes biodiesel safer to manipulate and to transport [14]. Biodiesel has a Cetane Number slightly higher than diesel fuel. It has a high lubricating power, which protects the engine. When added to regular diesel fuel, in amounts of 1-2%, it can convert fuels with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel. [15].

Biodiesel shows a wide variety of advantages on its fossil origin partner (diesel fuel). Nowadays, biodiesel is growing as a serious competitor in the energy market, which also takes into account the ecological benefits that its use represents. Biodiesel is composed of a wide variety of fatty acid. Its main acids, with their molecular weights and chemical formulae, are shown in Table 3. Its combustion reaction for normalized air excess α follows:

$$0.04437 \text{ A} + 0.01675 \text{ B} + 0.08432 \text{ C} + 0.1765 \text{ D} + 0.02052 \text{ E} + 9.037 \alpha \text{ O}_2 + 33.979 \alpha \text{ N}_2 \rightarrow 6.419 \text{ CO}_2 + 5.92 \text{ H}_2\text{O} + 33.979 \alpha \text{ N}_2 + 9.037 (\alpha-1)\text{O}_2$$
(10)

Again, considering combustion with 100% air excess, the percentages in mass of each compound resulting from this reaction is: 10.943 % CO₂, 4.13% H₂O, 73.72% N₂ and 11.20% O₂ (see Table 2). The CO₂ emission for the fuel is 282.45g CO₂ per ton. Taking into account its density, the result is: 282.45 ton of CO₂ by 103.32 m³ of biodiesel, which means 2.734 ton of CO₂ by m³ of biodiesel [9]. As in the previous cases, it is possible to obtain an equation for the Cp of the biodiesel exhaust gases.

$$Cp_{Biodiesel} = 0.996432 + \frac{4.81565 \cdot T}{10^5} + \frac{2.89509 \cdot T^2}{10^7} - \frac{1.27827 \cdot T^3}{10^{10}}$$
(11)

One of the blend most common in the market of biodiesel sale is the B20 (80% diesel and 20% biodiesel), the combustion products (mass percentages) for this blend is: 10.235 % CO₂, 4.392% H₂O, 73.11% N₂ and 11.263% O₂ (see Table 2)

4.4. Natural Gas

According to COMGAS (Gas Supplying Company for the State of São Paulo), the natural gas volumetric composition is: CH₄ (methane) 89.3%; C₂H₆ (ethane) 8%; C₃H₈ (propane) 0.8%["]; C₄H₁₀ and C₅H₁₂ (butane and pentane) 0.1%; CO₂ (carbon dioxide) 0.5% and N₂ (nitrogen) 1.3%. With this composition, its molecular mass is 17.689 g.gmol⁻¹ and, consequently, its density is 789.68 kg/Nm³. The following equation for normalized gas excess is utilized.

$$0.893CH_4 + 0.08C_2H_6 + 0.008C_3H_8 + 0.0005C_4H_{10} + 0.0005C_5H_{12} + 0.005CO_2 + 0.013 N_2 + 2.118 \alpha O_2 + 7.965\alpha N_2 \rightarrow 1.087CO_2 + 2.064H_2O + 7.965\alpha N_2 + 2.118(\alpha - 1)O_2$$
(12)

Again, considering combustion with 100% of air excess, the percentages in mass of each compound resulting from this reaction are: 7.99% CO₂, 6.20% H₂O, 74.49% N₂ and 11.32 O₂ (see Table 2) [9]. The equation for Cp of natural gas is:

$$Cp_{NaturalGas} = 1.0299756 + \frac{4.36102 \cdot T}{10^7} + \frac{3.38685 \cdot T^2}{10^7} - \frac{1.41704 \cdot T^3}{10^{10}}.$$
(13)

5. TOXICITY IN INTERNAL COMBUSTION ENGINES

The main toxic compounds in the exhaust gases of the internal combustion engines are carbon monoxide and nitrogen oxides. Carbon monoxide appears in the exhaustion gases as result of fuel incomplete combustion; the reason is insufficient oxygen in the combustion chamber or fuel particles that are not burned properly. Table 4 shows the main emissions of an internal combustion engine.

The substances that compose the exhaust gases can be classified in several groups. Nitrogen, oxygen, hydrogen, steam and carbon dioxide belong to not toxic group substances. The toxic group of substances includes carbon monoxide (CO), nitrogen oxides (NO_x) , hydrocarbons (C_xH_y) , aldehydes (R_xCHO) , soot, sulphur dioxides (SO_2) , sulphydric acid and solid particles. The polyaromatic hydrocarbons (PAH) are carcinogenic substance and form a special group [17].

A small vehicle releases to the atmosphere in average between 0.6 to 1.7 kg/h of CO; a truck releases between 1.5 and 2.8 kg/h CO. In general, when 1 kg of diesel fuel is burnt, it release between 80 and 100g toxic compounds, specifically: 20 to 30g of CO, 20 to 40g of NOx, 4 to 10g of HC (hydrocarbons), 10 to 30g of SO_x, 0.8 to 1g of aldehydes, 3 to 5 g of soot, etc. When 1 kg of gasoline is burned, it releases between 300 and 310 toxic compounds, specifically: 225 g of CO, 55 g of NO_x, 20 g of HC, 1.5 to 2 g of SOx, 0.8 to 1 g of aldehydes, 1 to 1.5 g of soot [1]. PM emissions of diesel fuel for automotives vehicles is 13.2 kg/m³[18]; in the case of gasoline for automotives vehicles, the PM emission is 1.44 kg/m³. On the other hand, an internal combustion engine burning gas, without any emissions control equipment in the tailpipe (i.e. catalyst), releases to the atmosphere: 13.61 g/MWh of PM-10; 0.26 g/GJ of SO₂ and 94.58 g/GJ of NOx. [19].

PRODUCTS	Alcohol	Diesel	Gasoline *	Nat. Gas	B20 **	B100
CO ₂ (%)	15.136	10.058	13.503	10.549	10.235	10.943
H ₂ O (%)	9.288	4.458	6.679	8.194	4.392	4.129
N ₂ (%)	70.622	74.206	72.874	73.783	74.110	73.724
$O_2(\%)$	4.954	11.278	6.943	7.474	11.263	11.204

Table 2 – Combustion products (mass percentage)

* Gasoline with 20% of alcohol ** 80% diesel and 20% biodiesel

Fatty Acid	Weight (%)	Mol. Wt. (g)	Formula
Palmitic (A)	12	270.46	$C_{15}H_{31}CO_2CH_3$
Stearic (B)	5	298.52	$C_{17}H_{35}CO_2CH_3$
Oleic (C)	25	296.5	$C_{17}H_{33}CO_2CH_3$
Linoleic (D)	52	294.48	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂)7CO ₂ CH ₃
Linolenic (E)	6	292.46	CH ₃ (CH ₂ CH=CH) ₃ (CH ₂)7 CO ₂ CH ₃

Table 3 – Typical soybean oil methyl ester [21].

Table 4 – Exhaust gases in internal combustion engines (volume percentage) [1].

COMPONENTS	MAXIMUM CONT	OBSERVATION	
	GASOLINE	DIESEL	
Nitrogen	74 - 77	76 - 78	Non toxic
Oxygen	0.3 - 0.8	2.0 - 18.0	Non toxic
Steam	3.0 - 5.5	0.5 - 4.0	Non toxic
Carbon dioxide	5.0 - 12.0	1.0 - 10.0	Non toxic
Carbon monoxide	0.1 - 10.0	0.01 - 0.5	Toxic
Nitrogen oxide	0.1 - 0.5	0.001 - 0.4	Toxic
Hydrocarbons	0.2 - 3.0	0.009 - 0.5	Toxic
Aldehyde	0 - 0.2	0.001 - 0.009	Toxic
Sulphur dioxide	0 - 0.002	0-0.03	Toxic
Soot (g/m^3)	0 - 0.04	0.01 - 1.1	Toxic

6. THE CASE OF CARBON IN THE BIODIESEL

The use of biomass (vegetal oils) for energy generation also will release CO_2 . However, this biomass is derived from plants that consumed, during their growth, the same amount of the gas that will be returned to the atmosphere after its final use. The main target for the use of bio-fuels is to decrease the emissions of gaseous pollutants to the atmosphere, mainly CO_2 emissions, with the purpose of reaching the targets of the Kioto Protocol. As already indicated, the use of biodiesel takes with itself a global emission decrease. A 1998 biodiesel life cycle study, jointly sponsored by the US Department of Energy and the US Department of Agriculture, concluded that biodiesel decreases net CO_2 emissions by 78.45% compared to conventional diesel. Therefore, considering this aspect, in the case of the use of B100 (biodiesel pure form) the result is 0.635 ton of CO_2 by m³ biodiesel [16].

The use of biofuels in ignition compression engines can play a vital role in helping the developed and developing countries to reduce the environmental impact of fossil fuels. The main target for the use of biofuels is to decrease the emissions of gaseous pollutants to the atmosphere, mainly CO_2 emissions, with the purpose of reaching the targets of the Kioto Protocol. As already indicated, the use of biodiesel takes with itself an emission global decrease. Fig. 1 shows

the emissions of the main polluting agents. In the case of biodiesel combustion, the emissions are very low (with exception of NOx). The 100% reduction in the sulphur dioxide emissions is reasonable, because its vegetal origin (vegetal oils and animals fats) that does not contain sulphur. The carbon monoxide emissions in the biodiesel combustion for engines diesel are 40 to 50% lower than conventional diesel fuel; this is consequence mainly by the presence of oxygen in the chemical formula of methyl esters or ethyl ester (biodiesel) getting a more complete combustion. The PM emissions will reduce between 35 to 45% in comparison with diesel fuel [21]. A reduction of the hydrocarbons is produced due to a more complete combustion; obtaining that the carbon-hydrogen and oxygen chains of esters, to generate CO_2 and H_2O in a complete process to difference to the diesel fuel [17].



Figure 1 – Pollutants emissions of the biodiesel combustion in an internal combustion engine. The 100% is considered the emission level of the diesel engine [20]

The CO_2 case is different in respect other polluting agents. The emissions generated by biodiesel during the combustion in engines or boilers are "recyclable" through the vegetables photosynthesis. Fossil fuel combustion releases carbon that took millions of years to be removed from the atmosphere; combustion of biofuels participates in a process that allows CO_2 to be rapidly recycled to fuel [21, 22]. The NO_X emissions increase in 5%. The increment is originated by the temperature reduction in the tailpipe engine, this bring about the reduction of the delay ignition, and, as consequence, an injection point advance. This, together to higher amounts of oxygen makes possible the NO_X emissions increase [23].

7. ECOLOGICAL EFFICIENT CALCULATION

The Tab (5) shows a comparison between the fuels analyzed: natural gas, gasoline (alcohol), diesel and biodiesel in internal combustion engines with reference to his emissions. In the Fig. 2 are shown the ecological efficient values for the four fuels analyzed: diesel, gasoline, biodiesel (B100 and B20), and finally the Fig. 3 shows the ecological efficient values in function of internal combustion engines efficiency.

8. CONCLUSIONS

This work shows that is possible to evaluate the environmental impact by internal combustion engines using the ecological efficiency parameters; therefore, it can be concluded:

The use of pure biodiesel (B100) or blended with diesel (B20) in internal combustion engines, especially in compression ignition engine; it represents an excellent option on the ecological point of view. Obviously this is observed according to the figure 3, that the efficiency for the B20 blend is less than the one of gasoline, must to that the mixture even owns 80% of diesel and the gasoline counts with 20% of alcohol. the natural gas appears like the best due the few particles emissions and null emissions of SO₂.

With respect to the CO_2 emissions, according the fuel type in ton of CO_2 for m³. It is observed that the fuel with less CO_2 emissions to the atmosphere is the natural gas and the one that it release is the Diesel fuel. Biodiesel presents a similar situation to respect diesel fuel. In fact, biodiesel emit larger quantities of CO_2 than conventional fuel, but as most of this is from renewable carbon stocks, that fraction is not counted towards the greenhouse gas emissions from the fuel; on the other hand, biodiesel has more oxygen molecules with respect to diesel fuel, therefore, the combustion process is more complete and, as consequence, to reduction in the CO emissions. The CO_2 released by petroleum diesel was fixed from the atmosphere during the formative years of the earth, whereas the CO_2 released by biodiesel gets continuously fixed by plant and may be recycled by the next generation crops. Therefore, the main advantage of the

biodiesel is that CO_2 emissions can be considered as recyclable by the growing plants. Then, the emission levels using this kind of bio-fuel are 78.45% lower in comparison with the diesel fuel. The calculated parameter is 0.635 ton of CO_2/m^3 of biodiesel (B100). The quantity of emission for internal combustion engines using pure biodiesel (B100) is: 0.6561 kg/kg of fuel for CO_2 , 0.042 kg/kg of fuel for NO_x and 0.009931 kg/kg of fuel of particulate material (PM). In the case to use 20% of biodiesel mixed with 80% diesel (B20) the emission levels are: 2.5986 kg/kg of fuel for CO_2 , 0.024 kg/kg of fuel for NO_x and 0.01421 kg/kg of fuel of particulate material (PM).

Table 5 – Comparison of results of pollutant emissions between the fuels analyzed in internal combustion engines.

Pollutant Emission kg/kg of fuel	Nat. Gas	Diesel	Gasoline *	Biodiesel B20	Biodiesel B100	Diesel / B100
CO _{2e}	2.975	8.529	5.905	7.491	2.974	2.9
MP	$0.205 \cdot 10^{-3}$	$15.27 \cdot 10^{-3}$	$2.116 \cdot 10^{-3}$	$14.21 \cdot 10^{-3}$	9.931 ·10 ⁻³	1.5
NOx	$0.513 \cdot 10^{-2}$	4 .10-2	5.5 ·10 ⁻²	4.04 .10-2	$4.2 \cdot 10^{-2}$	0.9
SO ₂	1.411 [.] 10 ⁻⁵	3 ·10 ⁻²	$0.2 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$	-	-
CO_2	2.704	3.106	2.853	2.599	0.656	4.7
Total (kg/kg of fuel.)	2.709	3.161	2.912	2.677	0.708	4.5
Ecological Efficiency (%)	91.31	78.79	82.05	78,97	87.59	

* Gasoline with 20% of alcohol.



Figure 2 - Diesel, gasoline, biodiesel (B20 and B100) and natural gas ecological efficiency



Figure 3 – Ecological efficiency variation in function of internal combustion engines efficiency. Gasoline with 20% anhydrous alcohol

The total emissions for diesel in comparison with the biodiesel (B100) are 4.5 times more, based in the kg/kg of fuel relation. In terms about ecological efficiencies, according to the analyzed fuels; natural gas, gasoline, diesel, biodiesel B100 and biodiesel B20 are respectively 91.31 %, 82.05 %, 78.79 %, 87.59 % and 78.97 %. The studies show that the biodiesel use as alternative fuel, from an ecological point of view, is better that diesel fuel, showing the highest values of ecological efficiency.

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