BIODIESEL CO_2 EMISSIONS, A COMPARISON WITH THE MAIN FUELS IN THE BRAZILIAN MARKET ACCORDING TO THE NATIONAL VEHICLES FLEETS IN THE LAST FOUR YEARS

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Abstract. *Biodiesel is gaining more and more interest as an attractive fuel due to the depleting fossil fuel resources and environmental degradation. Chemical biodiesel is composed of monoalkyl esters of long chain fatty acids derived from renewable feed stock like animal fats and vegetal oils. This paper presents the first results of an investigation carried out by the authors on the potentials of Biodiesel as an alternative fuel and main substitute of diesel fuel, comparing the CO_2 emissions of the main fuels in the Brazilian market with the biodiesel CO_2 emissions, in pure form or mixed in different proportions. (B2, B5, B20). The results of the study are shown in t CO_2 per m^3 fuel and in t CO_2 per year. The fuels are analyzed according to their chemical formula, stoichiometric combustion and fuel mean consumption for an automobile. The fuels studied were: gasoline, diesel, ethyl alcohol (anhydrous), biodiesel (frying oil) and biodiesel (soy bean oil). For the case of biodiesel, its complete life cycle was considered and, as consequence, the closed carbon cycle (photosynthesis). Using data provided by ANFAVEA (National Association Manufacturers of Automotive Vehicles - Brazil) the total emissions in t CO_2 of national vehicles fleets (2006) by type of fuel (gasoline, flex fuel, alcohol, diesel was obtained). On the other hand, with the data provided by DENATRAN (National Department of Transit), concerning the national diesel vehicles in the last four years in Brasil, the total CO_2 emissions and the percentage that it would decrease in the case of to use pure biodiesel (B100) or several mixtures, B2, B5 and B20,was calculated.*

Keywords*: biodiesel, emissions, alcohol, gasoline, diesel, combustion.*

1. INTRODUCTION

In the last three decades, the world has been confronted with some energy crises (1973, 1981 and 1992), due to the decrease of fossil resources and increase of environmental problems. This situation brought as consequence the search of the alternatives fuels, which would have to be not only sustainable, but also environmentally friendly and techno-economically competitive. The bio-fuels like ethyl alcohol, vegetable oil, biomass, biogas, synthetics fuels, biodiesel, etc, are starting to be of great interest to the developed countries. Some of these fuels could be used in a direct form; however, others need some type of modification for replace the conventional diesel fuel – gasification or digestion when one talks about biomass, and transesterification when one talks about biodiesel.

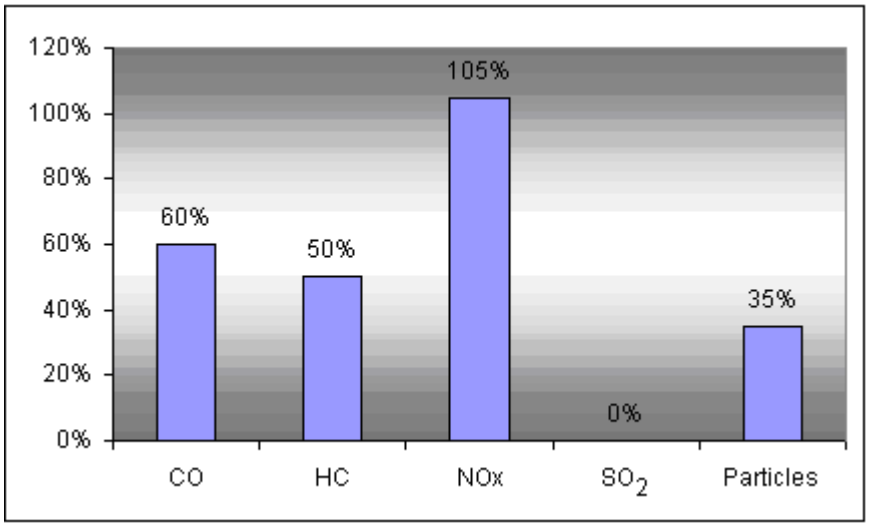
The influence of fossil resources in modern fuels has made whereupon the transport by road get to support, to a large extent, the growth in mobility demand, which is translated in an increase of greenhouse gas emissions, produced from fossil fuel combustion. During the last ten years, it was recognized that those gases, CO_2 in particular, represent a great threat for future generations, causing global warming and a worrisome climatic changes. The energy consumption of the road transport represented, in 1998, 28% of CO_2 emissions. According to the last estimates, if nothing is made to change the road traffic tendency, the CO_2 emissions will increase approximately 50% between 1990 and 2010, reaching 1113 million tons of CO_2 emissions, in comparison with the 739 million tons registered in 1990. Once again, the road transport is the main responsible for by this situation, since it represents 84% of the CO_2 emissions in comparison with the aerial transport, which represents 13% [Shaine, 2001].

This work represents the first study about biodiesel engine benefits. The fuel is one of the main alternative fuels to replace the conventional diesel fuel. A comparison in respect to CO_2 emissions is made with the main current Brazilian fuels in the market. The biodiesel emissions were considered for the fuel in pure form and blended in different proportions with the conventional diesel fuel. The results show a reduction in the CO_2 emissions levels in the atmosphere in case of replacing the conventional fuel by biodiesel. Data of ANFAVEA (National Association

Manufacturers of Automotive Vehicles – Brazil) and the DENATRAN (National Department of Transit) were collected, for the last four years in the case of the Brazilian road transportation system.

2. BIODIESEL EMISSIONS

The use of bio-fuels 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 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 an emission global decrease. Figure 1 shows the emissions of the main polluting agents. In the case of biodiesel combustion, the emissions are very low (with exception of NOx).



Source: Frances Institute of Petroleum

Fig. 1. Gaseous emissions of the biodiesel combustion in an internal combustion engine
The 100% is considered the emission level of the diesel engine

A 100% sulfur dioxide reduction is reasonable taking into account that biodiesel, by its vegetal origin, does not contain sulfur. The CO emissions for biodiesel combustion in diesel engines are 40 to 50% lower that the conventional diesel; this happens due to the presence of oxygen molecules, mainly in the methyl or ethyl ester (biodiesel), helping to obtain complete combustion. The particulate matter emissions (PM) are decreased to 35 to 45% in comparison with the diesel. [Biodiesel Board, 2006]. A decrease of unburned hydrocarbons due to complete combustion also takes place, because the chains of esters carbon-hydrogen and oxygen generate CO_2 and water in a complete way unlike the diesel fuel [Barnwal, 2005].

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. The CO_2 is released into atmosphere when the biodiesel is burned and is recycled by growing plants, which are later processed into fuel. Hence biodiesel also helps mitigate global warming [Sheehan, 1998]. Figure 2 shows the effect of biodiesel blend levels on CO_2 emissions.

The NOx emissions increase in 5%. It is evident that with biodiesel, due the improved combustion, the temperature in the combustion chamber can be expected to be higher and higher amounts of oxygen are also present, leading to formation of higher quantities of NOx in biodiesel-fueled engine. However, the biodiesel lower sulfur content allows the uses of NOx control technologies that cannot be otherwise used with conventional diesel. Hence biodiese fuel NOx emissions can be effectively managed and eliminated by engine optimization [Agarwal, 2007].

3. CO_2 EMISSIONS ACCORDING THE FUEL

The CO_2 amounts released to the atmosphere are beginning to constitute in an important parameter to be determined in the combustion processes, because this gas is the main responsible for the greenhouse effect [Carvalho e McQuay, 2007]. The European Union agreed in reducing its CO_2 emissions by 8% in the period 2008 –2012, in reference to the 1990 value [European Environment Agency, 1999]. The calculations of the emissions factors for the studied fuels are given in the following.

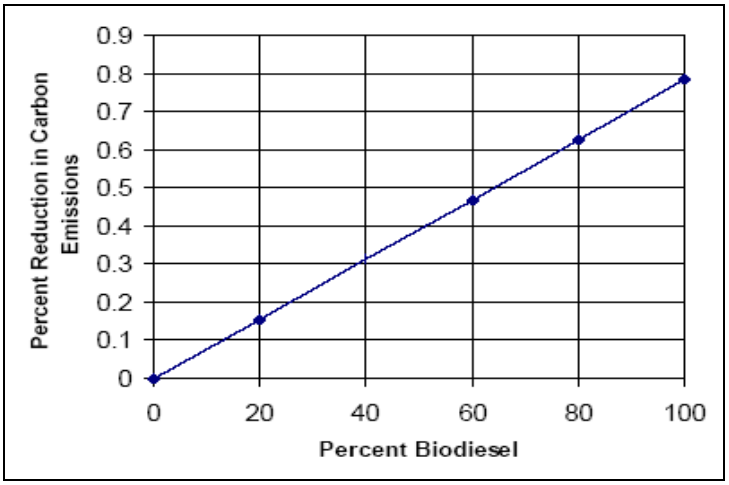


Fig.2. Effect of biodiesel blend level on CO_2 emissions [Sheehan, 1998]

3.1. Gasoline

The chemical formula of the gasoline is C_8H_{18} (octane) and its density is 0.75 t/m^3 [Perry e Chilton, 1973]. Observing its stoichiometric combustion reaction with air, the result is: 352 g of CO_2 by 114 g of gasoline. Taking into account the gasoline density, the result is: 352 t of CO_2 by 152 m^3 gasoline, to means, 2.316 t of CO_2 by m^3 gasoline.

3.2. Ethyl Alcohol

The chemical formula for ethyl alcohol is C_2H_5OH and its density is 0.79 t/m^3 [Russomano, 1987]. From its stoichiometric combustion reaction, the result is: 88 g of CO_2 by 46 g de alcohol, which, considering the alcohol density, gives: 88 t of CO_2 by 58.23 m^3 alcohol, to mean, 1.511 t of CO_2 by m^3 alcohol.

3.3. Diesel

The traditional chemical formula for the petroleum diesel is $C_{12}H_{26}$ and its density is 0.948 t/m^3 [Lacava, 2000], which result: 528 g of CO_2 by 170 of diesel. Taking into account the density of the diesel fuel, one obtains: 528 t of CO_2 by 179.32 m^3 diesel, i.e., 2.944 t of CO_2 by m^3 diesel.

3.4. Biodiesel (soybean)

The biodiesel density, made of soybean by the transesterification process with methanol, according to Handling and Use Guidelines (2006), is 0.9679 t/m^3. The average molecular weight of soybean oil methyl esters is 292.2 g/gmol. This was calculated using the average fatty acid distribution for soybean methyl esters below. Also below is the molecular weight and chemical formula for each of the component esters (Table 1).

From the stoichiometric combustion reaction with air, one has: 282.45 g of CO_2 in 100 g biodiesel. Taking into account the fuel density: 282.45 t de CO_2 by 103.32 m^3 of biodiesel, i.e., 2.734 t of CO_2 by m^3 soybean oil methyl esters (biodiesel).

3.5. Biodiesel (used-frying oils)

According to Mittelbach (1988), a biodiesel (used-frying oils) mass composition is: 77.4% C, 12% H, 11.2 % O, and 0.03 % S, which gives: 283.8 g of CO_2 by 100 g of biodiesel. Considering the biodiesel density, the result is: 283.8 t of CO_2 by 103.32 m^3 of biodiesel, i.e., 2.747 t of CO_2 by m^3 of biodiesel.

Biomass-derived fuels decrease the net atmospheric carbon in two ways: first, they participate in the relatively rapid biological cycling of carbon to the atmosphere (via engine tailpipe emissions) and from the atmosphere (via photosynthesis). Second, they substitute fossil fuels. Fossil fuel combustion releases (emits) carbon that took millions of years to be removed from the atmosphere; combustion of biomass fuels participates in a process that allows CO_2 to be rapidly recycled to fuel [Sheehan, 1998].

Table 1. Typical soybean oil methyl ester [National Biodiesel Foundation, 2006]

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	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)7CO_2CH_3$
Linolenic (E)	6	292.46	$CH_3(CH_2CH=CH)_3(CH_2)7\ CO_2CH_3$

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 mineral diesel [Sheehan, 1998]. Therefore, considering this aspect, in case of the use of B100 (biodiesel pure form) the result is: 0,635 t of CO_2 by m^3 biodiesel. Figure 3, shows a summary of the CO_2 emissions according the fuel used [Agarwal, 2007]

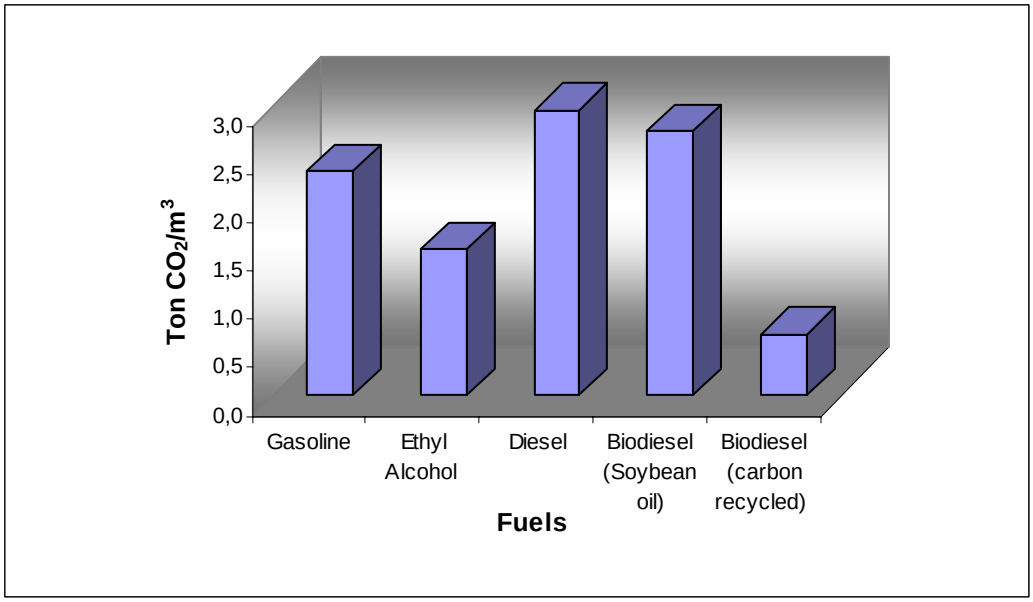


Fig. 3. CO_2 Emissions to respect the fuel used

4. VEHICLE CO_2 EMISSIONS

The biodiesel is the only renewable alternative fuel that can be used directly in any diesel engine without the need of making some type of modification. As its properties are similar to those of the diesel fuel derived from petroleum, both can be blended in any proportion without any inconvenience. The more common blend is 20% biodiesel with 80% diesel, called B20. On the other hand, in anhydrous form, the ethyl alcohol is miscible in gasoline. It is possible to use it in automobiles as an anti-detonation agent and also to decrease gasoline consumption. The percentage of alcohol in the Brazilian gasoline has varied throughout the years, between 20 a 25% in volumetric base [Carvalho and McQuay, 2007].

In order to obtain the vehicle emissions in tons (t) of CO_2 per year, the following case was considered: a vehicle that runs 15,000 km per year, use diesel fuel with 10 km per liter mean consumption. The vehicle will release 4.417 t CO_2 per year. Figure 4, shows the CO_2 emissions in t CO_2/year for the fuels analyzed above; for the gasoline it was considered a blend with alcohol, and for the biodiesel, was considered a reduction of 78.45 % in the CO_2 emissions (carbon recycled).

5. TON CO_2 EMISSIONS FOR THE LAST FOUR YEARS IN THE BRAZILIAN DIESEL FLEETS

According data of DENATRAN (National Department of Transit - Brazil), the national diesel fleets for the last four years are those given in Table 2.

Considering that the Brazilian diesel fleets run 20,000 km/year, using fuel diesel with 10 km/l mean consumption

for the last four years (dec/2002 – dec/2006), the CO_2 emissions would reach 9.25 Mt CO_2. On the other hand, if the fuel diesel were blended with biodiesel in different percentages (B2, B5, B20, B100), a decrease in the CO_2 emissions could be noticed clearly. Figure 5 compares the CO_2 emissions in tons, when 100% diesel fuel is used and when blends with biodiesel are used, for the last four years.

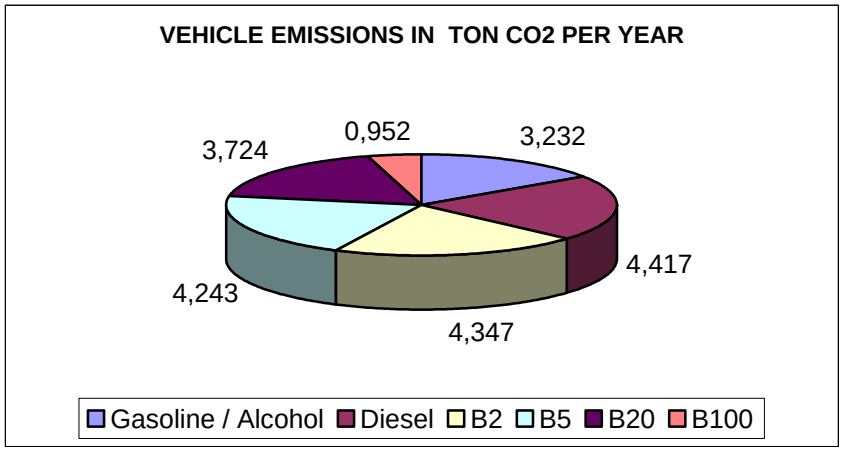


Fig. 4. Vehicle emissions per year.
Gasoline /alcohol (20% alcohol and 80% gasoline), B2 (2% biodiesel and 98% diesel)

Table. 2. Brazilian diesel fleets for the last four year.

TYPE OF VEHICLE	DEC/2002	DEC/2006	DIFERENCE
Truck	1 544,190	1 768,221	224,031
Truck tractor	211,603	280,037	68,434
Small bus	156,228	198,393	42,165
Bus	295,509	353,583	58,074
Total	**2 207,530**	**2 600,234**	**392,704**

Source: DENATRAN

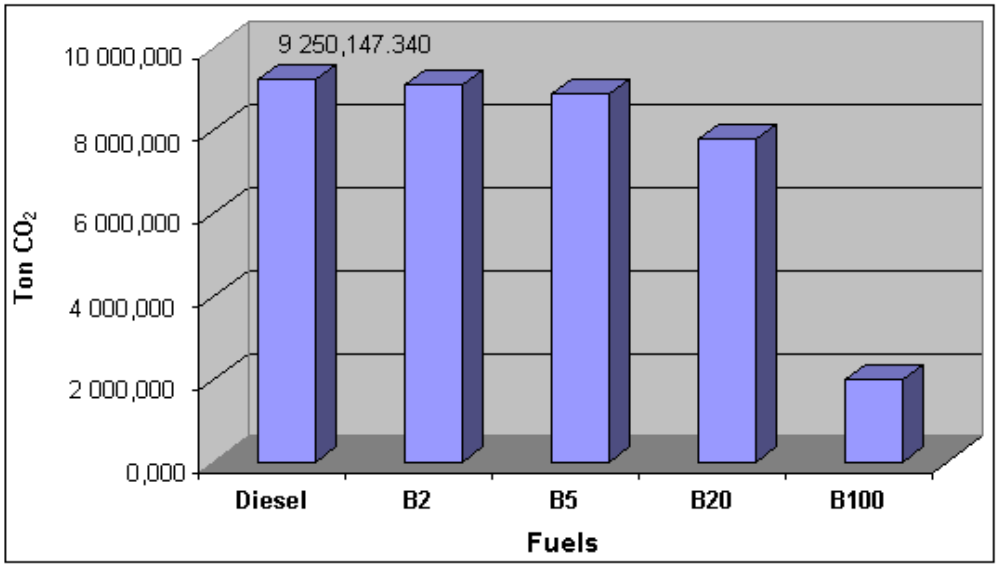


Fig. 5. CO_2 emissions by fuel type, for the last four years, for the Brazilian diesel fleet.

6. BIODIESEL USE BENEFITS IN THE BRAZILIAN FLEETS ACCORDING THE CO_2 EMISSIONS

The biodiesel presents an immense variety of advantages over conventional diesel fuel. For this reason, currently the

biodiesel appears like a serious competitor in the energetic market, taking into account the ecological benefits that its use represents:

- The biodiesel is the only renewable alternative fuel that can be used directly in any diesel engine, without the necessity to make some type of modification
- The biodiesel is biodegradable (98% in 21 days), no toxic and it has a flash point 150 °C approximately, to respect 64 °C of diesel fuel. This temperature causes that the biodiesel is safe to manipulate and to transport. [Biodiesel Handling, 2006].
- Due to near absence of sulfur in biodiesel, it helps reduce the problem acid rain due the transportation fuel. The lack of aromatic hydrocarbon (benzene, toluene etc) in biodiesel reduce unregulated emissions as well like ketone, benzene etc. [Agarwall, 2007]
- It has a high lubricating power that it protects to the engine. When added to regular diesel fuel in an amount equal to 1–2%, it can convert fuel with poor lubricating properties, such as modern ultra-low-sulfur diesel fuel, into an acceptable fuel. The wear of various vital parts reduced up to 30% because of additional lubricity properties of biodiesel. [Agarwall, 2007], [Van Gerpen, 2005]
- Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency. The cetane number measures how easily ignition occurs and the smoothness of combustion. [Meher, 2006].
- In view of environmental considerations, biodiesel is considered “carbon neutral” because all the carbon dioxide released during consumption had been sequestered from the atmosphere for the growth of vegetable oil crops. The oxygen presence in its molecular formula facilitates the combustion process into chamber combustions engine, it contributes to obtain a complete combustion with less polluting agents. [Sheehan, 1998].

The benefits that would happen with the insertion of the biodiesel fuel in the Brazilian fuel market, for the CO_2 emissions from the vehicles produced in Brazil in the last four years, is discussed in the following. The data (by fuel type) were provided by the ANFAVEA (National Association Manufacturers of Automotive Vehicles – Brazil), and they are shown in Table 3 and Figure 6.

Table. 3. Number of vehicles by type fuel - 2006 [ANFAVEA]

VEHICLES TO:	**JAN**	**APR**	**JUL**	**OCT**	**DEC**	**TOTAL**
Gasoline	77,418	85,785	88,607	84,369	62,383	**977,134**
Flex Fuel	100,301	97,496	113,215	123,623	112,596	**1 391,636**
Alcohol	31	49	17	151	98	**775**
Diesel	17,649	20,743	21,049	19,208	14,355	**241.489**
TOTAL	195,399	204,073	222,888	227,351	189,432	**2 611.034**

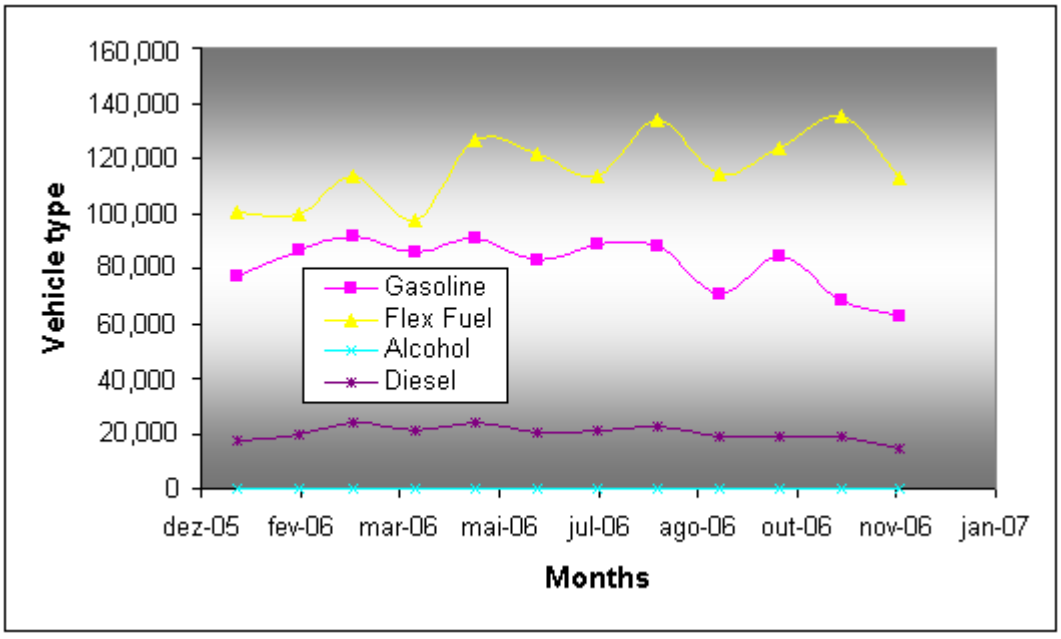


Fig. 6. Number of vehicles by type fuel - 2006 [ANFAVEA].

Working in the same way than in the previous cases, it is considered that all the vehicular fleet runs 15,000 km/year with 10 km/l mean consumption fuel. The CO_2 emissions for all Brazilian fleet of vehicles are shown in the Table 4 and Figure 7. In case of the implementation of a federal law obliging the blend of 2%, 5% and 20% of biodiesel in the diesel in the country, the total CO_2 emissions would be reduced as shown in Figure 8.

Table 4. CO_2 emissions of the national vehicular fleet that was produced in 2006 according the fuel type [ANFAVEA]

Vehicles to:	**N° of Vehicles**	**t CO_2/m^3 by vehicle**	**t CO_2 per year**
Gasoline	977,134	2.155	3 158,428.017
Flex Fuel *	1 391,636	2.155 / 1.511	4 095,200.695
Alcohol	775	1.511	1 756.891
Diesel	241,489	2.944	1 066,551.794
Total Vehicles	**2 611,034**		**8 321,937.397**

***** Considering that 70% of the times this vehicles use gasoline and, 30% of the time use alcohol.

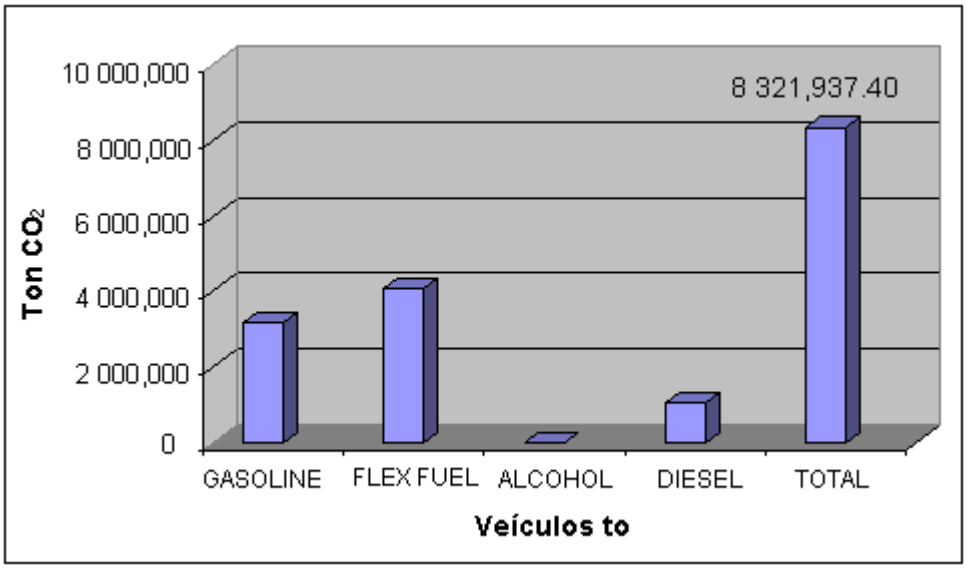


Fig 7. CO_2 Emissions according to fuel type.

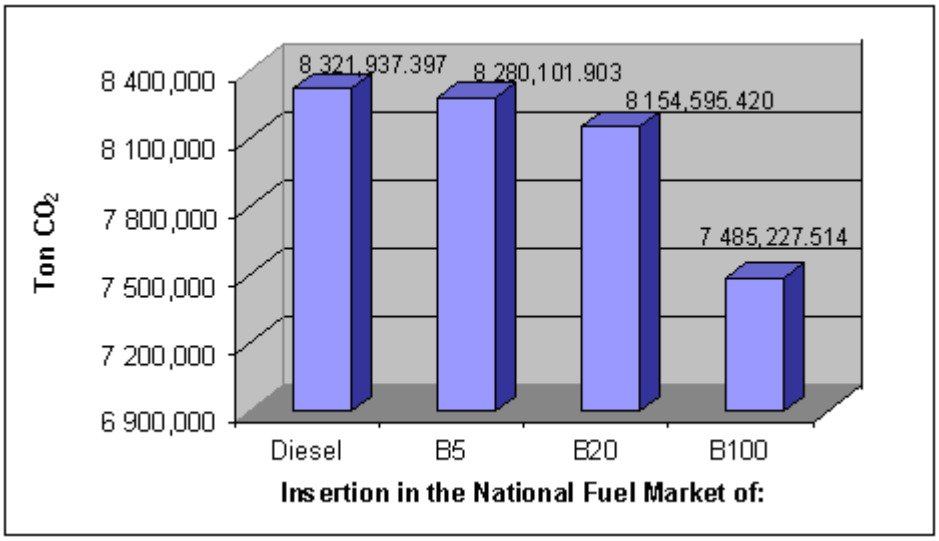


Fig. 8. Decrease of the CO_2 emissions for National vehicular fleet in 2006, if the diesel by biodiesel (B5, B20 e B100) were replaced in the energetic fuel matrix.

7. CONCLUSIONS

The use of alternative fuels is already a reality in several countries. A world production in billion liters of biodiesel was, in 2004, 2.5 billions of liters; in 2006, it was 8 billions liters, according to "Biodiesel", Brazilian magazine published on June 2006. The largest market in the world is Germany, that consumed in 2006, 2 billions liters of biodiesel. The countries that already use biodiesel are: Australia, Belgium, Canada, Spain, USA, Estonia, France, India, Malaysia, United Kingdom, Czech Republic, Thailand and Taiwan ["Exame" Brazilian Magazine, Feb 2007]. The interest of the developed countries happens as consequences of two factors: a) reduction of petroleum dependency, whose largest reserves are localized in politically complicated regions, b) the increase of environmental pressures: the world agreed to work for the fossil fuel substitution by renewable fuel (less polluting).

In reference to CO_2 emissions according to fuel type in t CO_2 by m^3, it was observed that the fuel that less releases CO_2 to the atmosphere is the ethyl alcohol; on the contrary, the fuel that releases most CO_2 to the atmosphere is the diesel. Due to the oxygenated nature of biodiesel where more oxygen is available for burning, this fuel decreases unburned hydrocarbon and CO emissions in the exhaust.

The main advantage is that CO_2 emissions to the atmosphere, in the case of biodiesel, can be considered as recyclable by growing plants. Therefore, the emission levels using this kind of bio-fuel are 78.45% lower in comparison with the diesel fuel. The parameter is 0.635 t of CO_2/m^3 of biodiesel (B100).

The Brazilian diesel vehicular fleet for the last four years (Dec 2002 to Dec 2006), including trucks, tractors trucks, small bus and busses increased by 392,704 vehicles, which released to the atmosphere 9.25 Mt of CO_2. If this vehicular fleet used 2% (B2) in the blend with diesel fuel, the CO_2 emissions would decrease in 1.8%. With 5% of blend (B5), the CO_2 emissions would reduce in 3.9%. With 20% of blend (B20), the CO_2 emissions would reduce in 15.7%.

The production of national vehicles by fuel type in 2006 totalizes 2 611,024 vehicles; being the "Flex Fuel" vehicles those that take place in greater amount, followed by the gasoline, diesel and alcohol vehicles. These vehicles released in 2006, 8.32 Mt of CO_2. If the Brazilian fuel energetic matrix would begin to use a blend with biodiesel, for example B20 for the diesel engine; the CO_2 emissions, considering the rest of vehicles (flex fuel, gasoline and alcohol), they would totalize 8.15 Mt of CO_2, that means 2.01% less of the total. This value must to that most of vehicles produced in Brazil are flex fuel and gasoline kind; both sum 2 368,770 vehicles in 2006. For these reason the interest of developed countries in to replace not only diesel by biodiesel fuel, but also to replace the gasoline by other bio-fuels. This explanation contrasts with the intention announced in January 2006 by the president of the United States in order to replace 20% of the consumed gasoline by bio-fuels too. ["Exame" Magazine, Feb 2007].

7. ACKNOWLEDGEMENTS

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