



RESEARCH ON BIODIESEL INCORPORATION AS A COMMERCIAL GASOLINE FUEL FOR OTTO CYCLE AUTOMOTIVE ENGINES

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Abstract. *This work represents a research on biofuels aimed at quality and emitted propulsion as well as the efficiency of this in relation to its greatest utility, automotive engine. It has a strong tendency to compare a mixture of gasoline and biodiesel with commercial gasoline, the emissions of carbon monoxide, carbon dioxide and low calorific value, for mixtures G3, G7 and G11 (percent by mass). Experimental tests were performed on an Otto cycle engine attached to the gas meter. Analyzed mixtures highlighted G3 which showed 0.8% (molar fraction of the available carbon in the fuel) at least in the production of carbon dioxide in the combustion gas, G11, extremely close to the values found in commercial gasoline. Also the outcome of G11 enthalpy of combustion, calculated theoretically by binding energy, showed an increase of 7%, which could be shown in preliminary experimental tests. This information opens an opportunity to do a research on a better income in terms of torque or a lower consumption for engines.*

Keywords: *Biofuel, Energy Efficiency, emissions*

1. INTRODUCTION

Until a few years ago the main limiting factor for energy development was the availability of renewable energy resources. One of the great challenges of this century is to find ways to meet the growing demand for fuel without causing changes in the global climate stability. Decentralization and increased production of oilseeds are stimulating factors for the biofuels development, since this important raw material is plentiful and easy to grow in Brazilian soils.

Thus oilseeds can be used as biofuel in automotive engines that requires an essential chemical process called esterification or transesterification. It refers to the reaction of a triglyceride (originated from plant or animal) with an alcohol in the presence or absence of catalyzer, which shows a mixture of oily acid esters known as biodiesel and the glycerol by-product, often envisioned as coproduct or same as the target product. According to Krause (2008) and Silva (2009), this process can be achieved through enzymatic reaction, catalytic and microwave radiation, which are indispensable fine adjustments of temperature, agitation and pressure.

Finally, Bueno (2007) states that this formed biodiesel has a similarity with the properties of diesel fuel as the parameters of the kinematic viscosity, density, cetane number and calorific value. These characteristics have led to the increase of this biofuel to diesel oil through the national biodiesel program created in 2004 and ratified through Law No. 11,097 of January 2005, which provides the addition of a minimum percentage of biodiesel to diesel fuel produced in any part of Brazil. In its first stage, the program provides a mixture of biodiesel at the rate of up to 2% (B2) with gasoline diesel at the rate of up to 5% (B5) eight years after the publication of the law. Based on the Monthly Bulletin of Biodiesel by the ANP in April 2013, the authorized production capacity of biodiesel is approximately 600 000 m³ per month while the demand is around 250 000 m³ per month. Thus, new incorporation opportunity would be welcomed by producers of biodiesel.

Takeshita's research (2006) shows that oil has a significant number of derivatives, however, the most important and the most used is gasoline, a clear flammable liquid with a reddish tone, which has a strong typical odor and insolubility in water. The common commercial gasoline consists of a mixture of light fractions of gasoline hydrocarbons, whose composition varies from C5 to C10 or C12, and still has additions of additives and octane regulators which may be other hydrocarbons derived from gasoline or ethanol as usually happens in Brazil.

Usually gasoline is marketed with a variable volume fraction 20-25% of anhydrous ethyl alcohol in its composition according to the authors Andrade (2009) and Fernandes et al. (2002) according to law No. 8723 from October, 1993. Taking into consideration a light fraction of oil, its input is widespread, enabling numerous applications, although usually it is supposed to be used in internal combustion engines of the Otto Cycle type. Its classification is given by the octane number, use and amount of anhydrous ethanol fuel, flammable limit, lower calorific value and several other properties as mentioned by Leonstsinis (1982).

The purpose of this research is based on comparing the viability of the mixture, gasoline and biodiesel, with commercial gasoline, as the emissions of carbon monoxide, carbon dioxide and lower calorific value, G3 for mixtures (97% gasoline and biodiesel 3 %) G7 (93% gasoline and biodiesel 7%) and G11 (89% gasoline and 11% biodiesel) - percentage by mass.

2. MATERIALS AND METHODS

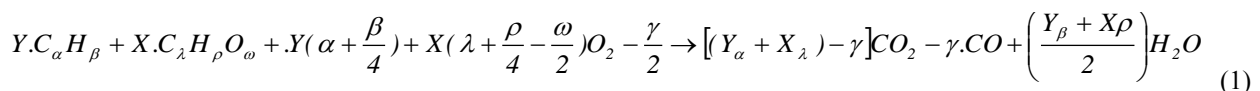
In this research the following equipment was used: Analytical Scale MARTE, model AL500C; Gas Meter TELEGAN for gas monitoring, Model TP20501; Otto Cycle Engine BRIGGS & STRATTON, specifications: single-cylinder 305 cc, 4 times, 10 hp, OHV, carbureted, Digital Thermometer INSTRUTEMP; Rotational Viscometer Brookfield, model RVT Braskem.

Commercial Gasoline of C type collected November 1, 2012; in Joinville, Brazil; Biodiesel (frying oil, ethanol, basic catalysts) – Derived from the studies conducted at the Institute Tupy. The following describes the test methods used to achieve this goal.

2.1 Calculation of Lower Calorific

With the engine in a steady mode - steady temperature - and properly connected to the gas meter, with a part of the fuel tank connected to the Otto cycle engine, a collection of gases from combustion occurs every four minutes. This procedure is repeated for mixture G3, G7 and G11.

According to Atkins (2004), standard enthalpy of reaction equals the enthalpy of combustion under standard conditions. Thus, knowing the LCV (lower calorific value) this equation of complete combustion and the enthalpy of reaction can be estimated by the average binding energy and we use this method to estimate the LCV of mixtures referred to in this work. The reaction of a generic organic fuel is expressed by Eq (1).



Where Y and X are the coefficients and $\alpha, \beta, \lambda, \rho, \omega, \gamma$ are the indices of the elements in organic compounds under analysis. The obtaining of the enthalpy for the average binding energy begins in Eq (2), where ΔH (enthalpy variation) is given by the sum of the difference in enthalpy of the reactants ($\Sigma H_{REAGENTS}$) for the products ($\Sigma H_{PRODUCTS}$).

$$\Delta H = \Sigma H_{REAGENTS} - \Sigma H_{PRODUCTS} \quad (2)$$

Using Eq (1) and making due consideration, it may be noted in Eq (3) and Eq (4) the enthalpy of the reactants and products changes respectively. Considering that {Type of connection} and values are referenced in Tab. 1. To achieve the LCV, which is ΔH of the complete combustion, use $\gamma = 0$.

$$\Sigma H_{REAGENTS} = [y(\alpha - 1) + x(\lambda - 1)]\{C - C\} + (Y_{\beta} + Y_{\rho})\{C - H\} + \left[Y\left(\alpha + \frac{\beta}{4}\right) + X\left(\lambda + \frac{\rho}{4} - \frac{\omega}{2} - \frac{\gamma}{2}\right) \right] \{O = O\} + \omega\{C - O\} + (\omega - 1)\{C = O\} \quad (3)$$

$$\Sigma H_{PRODUCTS} = (Y_{\alpha} + X_{\lambda} - \gamma)\{C = O + C = CO\} + \gamma\{C = O\} + \frac{Y_{\beta} + Y_{\rho}}{2} \{H - OH + O - H\} \quad (4)$$

Table 1 – Enthalpy of Connections Dissociation ΔH° (A-B)/(kJ.mol⁻¹) a 298 K

Diatomic Molecules									
H-H	436	F-F	155	Cl-Cl	242	Br-Br	193	I-I	151
O=O	497	C=O	1076	N≡N	945				
H-O	428	H-F	565	H-Cl	431	H-Br	366	H-I	299
Polyatomic Molecules									
H-CH ₃	435	H-NH ₂	460	H-OH	292	H-C ₆ H ₅	469		
H ₃ C-CH ₃	368	H ₂ C=CH ₂	720	HC≡CH	962				
HO-CH ₃	377	Cl-CH ₃	352	Br-CH ₃	293	I-CH ₃	237		
O=CO	531	HO-OH	213	O ₂ N-NO ₂	54				

2.2 Viscosity

The viscosity, which depends on the physico-chemical and temperature conditions of the material, measures the strength of the shear of a material in flow by means of friction or flow time. The developed practices the viscosity measuring proposed a comparative bond among the fuels: common commercial gasoline and compositions G3, G7 and G11.

The viscosity is very important because it is directly linked to the actions of the fuel in the fuel injection which directly influences the atomization of the fuel in the air and the effort required to provide the necessary volume for injection. The results are obtained by Brookfield rotational viscometer, model RVT Braskem, which consists in measuring the torque required to run a spindle immersed in the fuel and measuring is fulfilled by a calibrated spring which is interconnected to the pointer reproducing the measured value.

2.3 Flammability Limit

It represents the volume fraction of the minimum and maximum of the fuel in a mixture which when exposed to an ignition source generates a stable flame, the flammability limit, mentioned by Bui-pham et al. (1995), which is a very important in industry that requires this information in order to design and operate chemical plants as well as to transport the raw materials and products involved in the processes safely.

To make it clear, this concept states that an air-fuel mixture becomes flammable only when its composition, in terms of quantity of fuel, is within the range of flammability, whose extremes are defined by the lower limit (LL) and the superior limit (SL) of flammability of investigated fuel. These limits are determined by the equation of combustion, whereas atmospheric air - oxidant (O₂).

To receive the flammability extremes, we apply the flammability principles of Le Chatelier, which are used for the mixtures of flammable liquids, based on the data described in the experimental work of Vivas (2010), Carvalho & Mcquay (2007), who used the standards of ASTM E 681-01 method, which is shown in the Eq (5) and (6).

$$LL_{MIXTURE} = \frac{100}{C_1/LL_1 + C_2/LL_2 + \dots + C_n/LL_n} \quad (5)$$

$$SL_{MIXTURE} = \frac{100}{C_1/SL_1 + C_2/SL_2 + \dots + C_n/SL_n} \quad (6)$$

Where the volumetric % of each substance in the mixture is shown by the variable C. On the other side, the LL is not changed if only O₂ is used instead of air, while the SL increases with O₂ than with air only. Le Chatelier protects that if two compounds in LL are mixed, this new mixture will be also in the LL, and for SL the proportion is also true. These proportions are explained in the Fig 1.

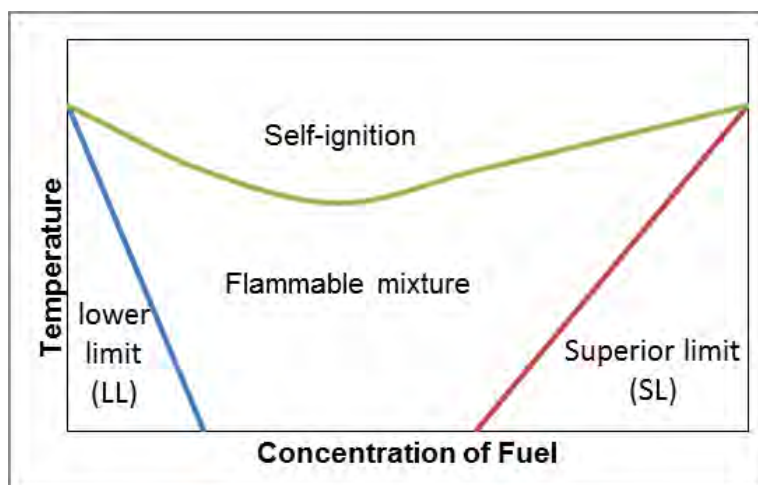
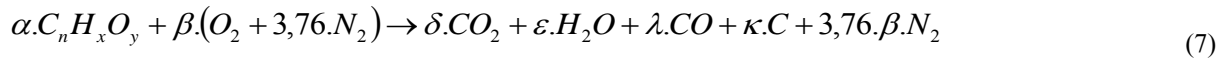


Figure 1 – LL Proportion - Temperature vs. Concentration

2.4 Parameters of Combustion

In order to get a successful combustion an organic compound as a fuel and air, comprising oxygen and nitrogen are commonly incompletely used. The following Eq (7) explains the generic reaction of combustion which confirms mentioned specifications.



You can find the values of the Eq (7), using the Eq (8) and (9), because the data of *Ratio* and X_{CO_2} are acquired for the reading of the gas meter, followed by equations of the indicated proportion.

$$Ratio = \left(\frac{X_{CO}}{X_{CO_2}} \right) \quad (8)$$

$$\%CO = \left(\frac{X_{CO}}{X_{CO} + X_{CO_2}} \right) \cdot 100 \quad (9)$$

To find the amount of the produced carbon dioxide, use the Eq (10) and (11) as described below:

$$\delta = \alpha.n - [(\%CO) \cdot \alpha.n] \quad (10)$$

$$\omega = \alpha.n \cdot (\%CO) \quad (11)$$

Finally, we use the Eq (12) and (13) where *m* and *n* indicate carbon of biodiesel and gasoline respectively.

$$\delta = x_{biodiesel} \cdot m + x_{gasoline} \cdot n - \omega \quad (12)$$

$$\omega = (x_{biodiesel} \cdot m + x_{gasoline} \cdot n) \cdot \%CO \quad (13)$$

3. EXPERIMENTAL DATA

Using the data of gases from combustion, as shown in Tab. 2, it was necessary to admit that:

- Gasoline is presented as iso-octane, despite being composed as a complex mixture of hydrocarbons that varies from four to twelve carbon atoms.
- The engine runs at a steady state and consequently there is no temperature variation in the block, gasoline, intake and exhaust;
- The biodiesel is presented as oleic ester;
- There was no emission of particulate elements;

Table 2. Received Data: Gasoline, G3, G7 and G11

Composition		Gasoline* ¹	G3		G7		G11	
Theories	Mass (g)	300	10	290	20	280	30	270
	N°. of moles(moles)	2,63158	0,03521	2,5439	0,07042	2,4561	0,1056	2,3684
	Mole fraction	1	0,0136	0,9864	0,02787	0,9721	0,0427	0,9573
Experiments	CO ₂ %	12,0667	11,9333		11,8333		11,7333	
	X _{co}	0,140	0,143		0,144		0,145	
	Ratio	0,1665	0,1675		0,1687		0,1694	
	O ₂ %	4,5667	4,8		4,9		5,1	

*1 referring to 80% of gasoline and 20% of alcohol by volume.

It is observed that the experimental data of the Tab. 2, received using the gas meter equipment in the act of combustion and the theory, are obtained through the mass of fuel.

Table 3 below shows the replace of the data of the Number of moles, Mole fraction, % CO₂, X_{co} and Ratio in the equations of incomplete combustion using Eq (4) and (9) and identifies the reactions for each mixture by combustion in Otto cycle engine.

Table 3 - Reaction of Incomplete Combustion

Gasoline	$C_8H_{18} + 11,9.O_2 \rightarrow 1,14.CO + 6,9.CO_2 + 9.H_2O$
G3	$0,99.C_8H_{18} + 0,012.C_{18}H_{36}O_2 + 13,74.O_2 \rightarrow 1,21.CO + 6,89.CO_2 + 9,12.H_2O$
G7	$0,97.C_8H_{18} + 0,03.C_{18}H_{36}O_2 + 13,93.O_2 \rightarrow 1,19.CO + 7,09.CO_2 + 9,25.H_2O$
G11	$0,96.C_8H_{18} + 0,04.C_{18}H_{36}O_2 + 12,46.O_2 \rightarrow 1,22.CO + 7,21.CO_2 + 9,38.H_2O$

Based on these equations, it has become possible to discover the actual value of enthalpy of the mixed fuel as set forth in Tab. 4.

Table 4 – Values of Enthalpy and Carbon Dioxide Fuel

Fuel	Enthalpy (kJ.mol ⁻¹)	Enthalpy (kJ/kg)	CO ₂
Gasoline	- 3521,83	-30893,21	85,82%
G3	-3475,19	-30301,65	85,06%
G7	-3466,72	-29863,73	85,63%
G11	-4412,65	-37780,66	85,53%

Figure 2 below shows the viscosity of the fuels mixtures measured at room temperature.

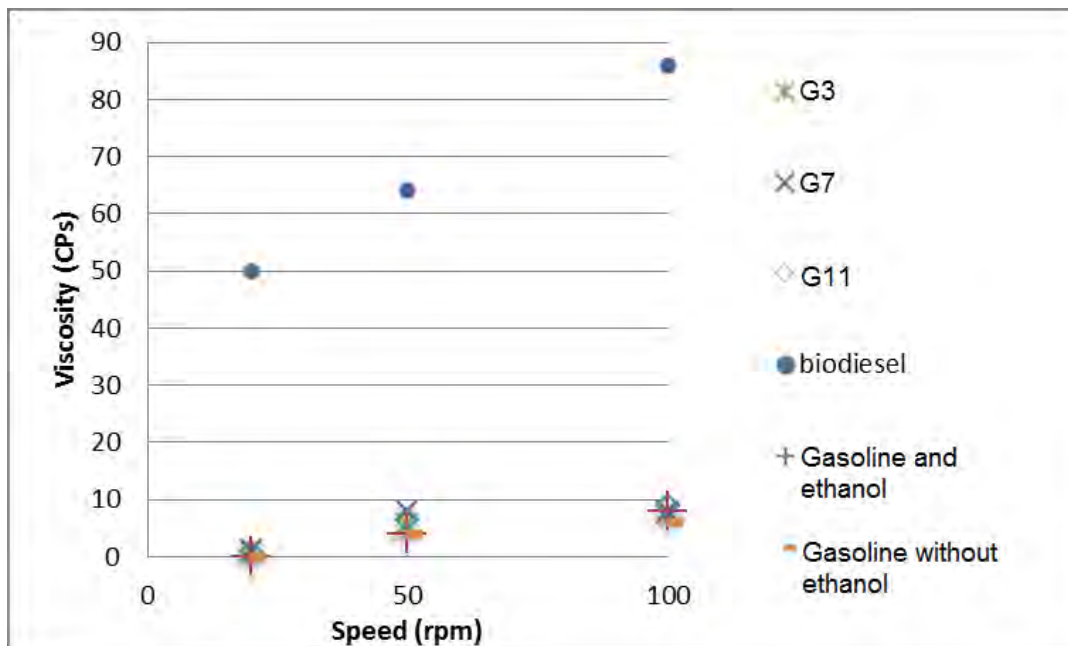


Figure 2. Representation of the Viscosity for mixtures

The Figure 3 shows the behavior of the biodiesel flammability limits calculated by Le Chatelier's principle, based on experimental data of the mixtures, with regard to the flammability limit measured for diesel and biodiesel mixtures mentioned in the work of Vivas (2010). There is a linear tendency in the relative volume fraction of the mixtures. Through the tendency analysis, we estimated the values for LL and SL of biodiesel, and these values were 0.0105 and 0.04 respectively.

Ferreira P., Bueno L.S.R. and Moura, L. M.

Research on Biodiesel Incorporation as a Commercial Gasoline Fuel for Otto Cycle Automotive Engines

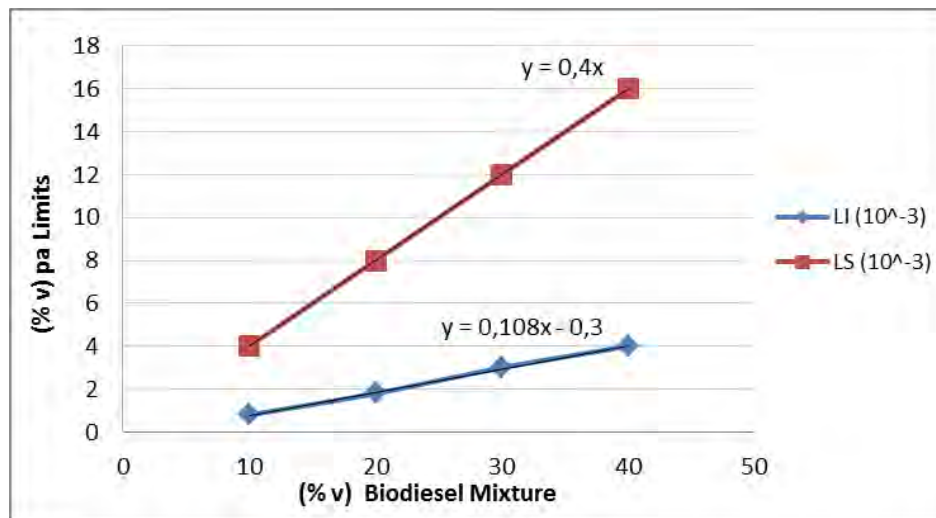


Figure 3. Calculated values for LL of biodiesel from mixtures

Another important variable is the vapor pressure, as this ensures the volatilization of the fuel entering the intake system of an engine, whether it is injected or carbureted. In preliminary studies with experimental apparatus some comparative values were received based on ASTM D6378 and ASTM 5191 methods for receiving the vapor pressure curve of the commercial gasoline (C), pure gasoline (P), ethanol and mixtures of gasoline with biodiesel. Observation of the values in the Figure 4 shows that the mixtures present the values of the vapor curve between the commercial gasoline and ethanol or pure one, which guarantees the possibility of these mixtures in the system with dual fuel engines.

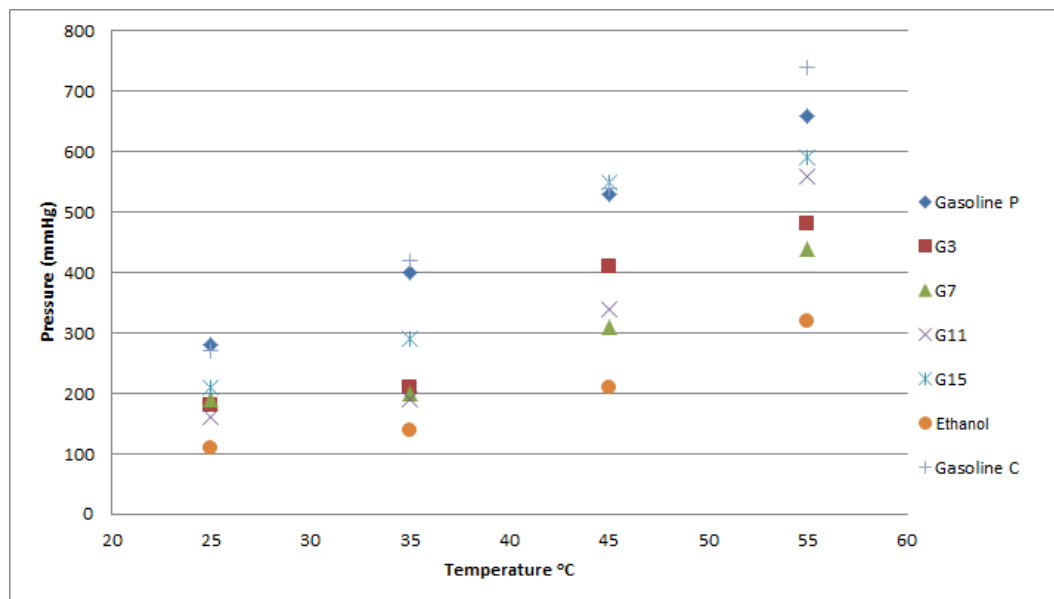


Figure 4. Curve Vapor Pressure

4. RESULTS AND DISCUSSIONS

Based on the viscosity, flammability limit and enthalpy, mixtures containing Biodiesel can be used in Otto cycle engines. These data allow the formulation of initial models for this specific purpose. The viability presented for these reasons shows that the generated enthalpy is close to that of gasoline, with higher values than gasoline has, from 10.5 to 11.1% by weight and a molar basis, respectively. As for the viscosity, the behavior shows similarity to the mixture, with the increase of the amounts due to the higher viscosity of biodiesel. These mixtures would require assessing their physical behavior during injection. The flammability limit for biodiesel, presented as a narrow stoichiometric band for combustion enabling, which would not be so serious due to better limits reported by gasoline. As the vapor pressure curve of the researched here mixtures have values between ethanol and gasoline, it enables its admission in the system of power engines.

5. CONCLUSION AND OUTLOOK

For the considerations and experimental equipment used in this research, the addition of biodiesel fuel - in proportions G3, G7 and G11 - provides a small increase in the release of carbon monoxide when combustion is performed in Otto cycle engine.

What about the emission of the generated gases, it was possible to measure carbon monoxide and carbon dioxide due to the limited capacity of the gas meter reading. Using the calculations of enthalpy originating from incomplete combustion equation of the mixture G11 showed 6887.45 (kJ / kg) of the energy more than the commercial pure gasoline available for combustion, this power can only be utilized if the engine is controlled with the test conditions.

The presented preliminary values of the vapor pressure curve of the researched mixture may be admitted to the research on the biofuel system engines referring to the engine intake system, proposing its volatilization as possible.

The addition of a fuel with a higher value of LCV would result in an increase in heat loss caused by the new features of this new fuel, a possible reduction of this loss could be given by an engine equipped with electronic fuel injection, suggesting it would be beyond the control based lambda probe, joining the amount of fuel injection to the working temperature of the engine. Consequently, it would keep the same power with less fuel consumption.

6. ACKNOWLEDGEMENTS

Capes for financial support.
The PUCPR and Catholic Santa Catarina by availability of equipment.

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