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### DIESEL-BIODIESEL BLEND THERMO-OXIDATIVE STABILITY STUDY BY PRESSURIZED DIFFERENTIAL SCANNING CALORIMETRY

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#### ABSTRACT

To analyze the effect of the addition of biodiesel on the oxidative stability of its blends with diesel up to 20% of biodiesel, ASTM 6186 method was used at 290psi with pure oxygen and air using pressurized differential scanning calorimetry (PDSC), to see at different oxygen concentrations, the influence of the biodiesel content at high pressure levels on the auto-ignition temperature. As the PDSC heating chamber temperature increases, the thermal instability onset temperature ( $T_{\text{auto-ignition}}$ ) of the sample corresponds to its auto-ignition temperature followed by combustion, which is the basis of diesel engine operation at high pressures. PDSC analyses with pure oxygen were also carried out at 100 psi pressure, to see if at this lower initial pressure and oxygen concentration there would be different biodiesel content influence on the thermal oxidative stability. At these elevated pressures, it was verified that the pure diesel oil present the highest ignition temperature and in the blend samples, the higher is the biodiesel content, the lower is the thermo-oxidative stability temperature of the blend, decreasing respective ignition delay. The PDSC combustion peaks at 290 psi in air were wider than those in pure oxygen, indicating lower combustion rates due to the lower concentration of oxygen at same operating pressure. However, the thermo-oxidative stability temperatures as a function of the biodiesel content were very close in both cases. In pure oxygen, as the pressure increases from 100 to 290psi, the thermo-oxidative stability of the diesel/biodiesel blends increases due to the decreased volatility of the diesel component. The correlation that shows how the increase of biodiesel content decreases  $T_{\text{auto-ignition}}$ , changes from a linear to a polynomial function of 2nd order degree. Additionally, as more biodiesel is added to the diesel oil, the increase of the operating pressure increases the formation of carbonaceous residues, which explains the increased problems of residue formation in diesel cycle engines when using diesel / biodiesel blends.

**KEYWORDS:** diesel-biodiesel blends, thermo-oxidative stability, pressure and biodiesel content effects.

#### INTRODUCTION

Diesel oil, the principal fossil fuel originated from petroleum, is formed by several types of hydrocarbons with differentiated molecular weights. In a refinery, after passing the initial stages as desalination and preheating, the oil is submitted to subsequent distillation steps to separate its components in fractions of different molecular weights. In the initial atmospheric distillation step, fractions denominated light and heavy diesel oil, which are essential for the production of diesel oil, are separated, as well as other fractions such as naphtha, kerosene and light gas oil, depending on the global demand and the consumer market for oil products [1].

Diesel oil is used in internal combustion engines, where it is auto-ignited by simultaneous compression and heating in air. It is a complex mixture of paraffinic, naphthenic and aromatic hydrocarbons. The contents of these three different classes of hydrocarbons influence the properties of the final fuel. The present hetero atoms, such as sulfur, oxygen and nitrogen, even in small amounts in diesel, influence their physicochemical properties such as: density, viscosity and flash point [2, 3].

Ignition quality, volatility, vaporization, density, sulfur content and viscosity are critical properties for the diesel oil, which need to be examined and controlled to obtain an adequate diesel engine performance. These characteristic specifications are established according to each country.

The ignition quality, which is defined by the ignition delay time of the fuel in the engine, is the time elapsed between the moment fuel is injected in the combustion chamber and the beginning of its combustion by auto-ignition. This occurs at a specific temperature, attained at a specific pressure after being injected in the combustion chamber with air, where it is submitted to a fast increasing pressure process, which promotes a fast heating rate [4].

Another critical characteristic of important control is the volatility. Due to the lighter fractions of diesel oil, its control must be strict for safety reasons, such as the risk of flammability during handling, transport and storage. As a consequence, the most critical vaporization is that of the heavier fractions. When injection in the combustion chamber occurs, diesel components must be volatilized and burned completely in order to avoid carbonaceous residue formation, which affects the engine operating capacity.

Biodiesel is defined as a biofuel derived from renewable biomass for use in internal combustion engines, to be burnt after compression ignition or for the generation of other types of energy that can partially or totally replace fossil fuel in diesel engines [5].

In order to improve the quality of life of the population and to reduce pollution costs, metropolitan centers are investing in the production of biodiesel, to apply for international financing in the carbon credit market under facilitated condition, aiming the clean development mechanism under the Kyoto Protocol. As a consequence, the substitution of petroleum derivatives by biodiesel has been stimulated, to reduce the emission of pollutants causing the greenhouse effect. Thus, since the 80's, biodiesel has become the main alternative to partially substitute diesel oil, mainly due to successive oil supply crisis. Being a renewable source its production was streamlined and has grown in large scale, mainly in Brazil.

Having a different composition than diesel oil, biodiesel is an alkyl ester derived from respective vegetable oil fatty acids with linear chains, free of cyclic molecules frequent in fossil hydrocarbons. The presence of oxygen in alkyl esters, favors the combustion of the evolved gases, reducing the levels of carbon monoxide, as well as avoids SO<sub>2</sub> release during combustion, because biodiesel is a sulfur-free biofuel [6].

Biodiesel, when mixed with diesel oil, tends to improve some characteristics of this petroleum derivative by increasing its lubricity, which is very low in the currently low sulfur diesel oils, such as diesel S10, which has 10 mg.L<sup>-1</sup> of sulfur. The diesel engine injection system requires a fuel with a good lubrication property, because its components work under high stress, requiring the flowing liquid, to properly lubricate the moving parts of the engine, avoiding their premature wear [7].

Biodiesel fits perfectly into the current context of combating the causes of global warming and climate change, helping Brazil to maintain high levels of clean and renewable energy in its energy matrix. Nowadays, 45% of the energy produced and 18% of the fuels consumed are already obtained from renewable sources [8].

Due to its composition, biodiesel presents a highly reactive chemical structure, due to the possibility to form free radicals during its oxidation, which generate unpaired electrons, making the molecule highly reactive [9]. As a consequence, oxidized volatile and non-volatile compounds are generated, from the decomposition of the formed peroxides [10], the latter of which; remain in the liquid phase.

Due to the presence of double bonds in its fatty acid chains, in the presence of water and metals, biodiesel also becomes highly reactive in oxidative environment. Often there is formation of hydro-peroxides, which are unstable, easily reacting and forming heavy oxidized products in engines, which in turn, cause operational problems and/or failures, negatively affecting the performance of the diesel cycle engine [11, 12].

The chemical composition, which is the principal responsible of the oxidation stability, is one of the main critical parameters that ensure fuel quality, determining its physicochemical properties. Depending on the unsaturation degree of the chemical structure of a fuel, there are different levels of oxidation stability [13].

In Brazil, by law [14] diesel must be used in automotive engines mixed to an increasing minimum volume percent of biodiesel, which currently is 10% (B10), which in turn will be 20% in 2020.

To predict what may happen in the future years, when biodiesel content in diesel will be much higher, the present article shows the results of a study by PDSC, to know how the content of biodiesel affects the thermo-oxidative stability and auto-ignition temperatures of the blends at high pressures, with different biodiesel contents (B5 to B20) in pure oxygen atmosphere at 100psi and at 290 psi, in air as well.

To evaluate potential negative effects on the diesel engine performance and durability, the final combustion residues were quantified as a function of the biodiesel content in all pure oxygen analyses, to estimate the minimum non combusted residue formation.

## MATERIALS AND METHODS

### Sample preparation

Commercial diesel and biodiesel samples (named as B0 and B100) were used. Their specifications were all in accordance to the requirements of the respective limits determined by the Brazilian National Agency of Petroleum, Natural Gas and Biofuels (ANP). Therefore, the results of physicochemical tests of respective analytical reports were in accordance to the limits determined by normative entities such as ASTM, ABNT and ISO. The commercial sample of diesel oil S10-A (B0), contained 5.2 mg / kg of sulfur.

As determined by the ANP agency, the correct representation for biodiesel-diesel blend is given by "BXX", where "XX" denotes the volumetric percentage of biodiesel present in the blend. Mixtures B5, B10, B15 and B20 were prepared in the laboratory, which showed a perfect miscibility of biodiesel in diesel, at all these compositions.

### PDSC Analysis

All samples were analyzed in a TA Instruments, model Q200 PDSC equipment. After attaining the analysis pressure by filling the heating chamber with the proper gas and then, closing all gas entrances and exits, heating rate of 10°C.min<sup>-1</sup> was used from 25 to 300°C in static ambient mode. Samples of 5 mg were used in open aluminum crucibles. New crucibles were used for each analysis, to avoid that residues from a previous analysis did not interfere into the subsequent one. The admitted analysis gases, used to pressurize initially the heating chamber were oxygen and air, to simulate different oxidizing ambient. TA Instruments Universal Analysis software was used to obtain the PDSC curves and to treat the analysis data.

Operating pressures of 100 and 290psi were used to verify the effect of the biodiesel content on the different blend oxidative stabilities. The latter pressure and pure oxygen are indicated by ASTM 6186 method to test other fuels. However, at this pressure, pure air was also used, to see, at this pressure, the influence of an atmosphere equal to that of the combustion of the blends in diesel engines.

It must be noted that the initial 290psi pressure, was used according the ASTM method and also due to the maximum limited operating pressure of the analysis system. But this value is lower than the maximum pressure at which biodiesel/diesel mixtures are exposed in the compression chamber in the engine for their auto-ignition and burning.

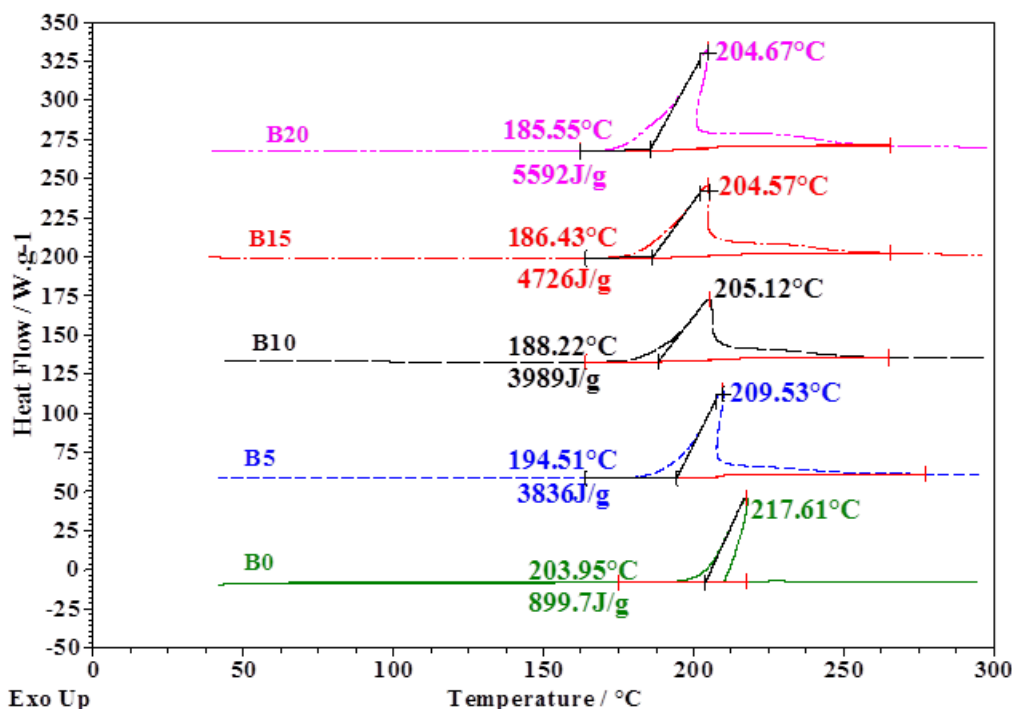
As the sample is heated in the PDSC chamber increasing its temperature, pressure increases. When the thermo-oxidative stability temperature ends, auto-ignition of the sample occurs, followed by its combustion. The auto-ignition temperature is determined by the extrapolated combustion PDSC peak onset temperature ( $T_{\text{auto-ignition}}$ ) of the sample, which corresponds to the ignition temperature under the chosen operating conditions of the study.

PDSC analyzes with pure oxygen at 100psi pressure were done to check if at this pressure, which is attained at the beginning of the analysis by a lower initial admitted oxygen concentration in the heating chamber of the PDSC, changes in the influence of the biodiesel content would occur on the thermo-oxidative stability of the studied blends.

## RESULTS AND DISCUSSION

### PDSC – 290psi in oxygen

The PDSC curves at 290psi in oxygen, for the diesel commercial sample B0 and blend samples B5, B10, B15 and B20 are shown in Fig. 1.



**Fig1** -PDSC curves of samples B0, B5, B10, B15 and B20 obtained in oxygen, at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$ , starting at 290 psi. (Curves were shifted for better visualization)

The results of Figure 1 at 290 psi show that pure diesel oil (sample B0) has the highest ignition temperature, being the most stable to those thermo-oxidative conditions. Similarly in samples B5, B10, B15 and B20 it is noticed that the higher is the biodiesel content, the lower is the oxidative stability temperature of the mixture, which is characterized by the respective auto-ignition temperature as indicated in respective PDSC peak in Figure 1.

The ignition has occurred in all cases at a very high rate, indicated by a very sharp exothermic peak formation. In the case of the blends, combustion occurs in two stages, since in these cases, the respective sharp PDSC peak is followed by a step with lower exothermic intensity and a much longer duration, characteristic of carbonaceous residue (char) burning, indicating that it was generated during the first combustion stage.

It must be noted that in the B0 diesel case, this second step did not happen, but instead, due to a much higher initial combustion rate, a temperature overrun has occurred, with respect to the programmed heating rate, at which, the controlling temperature system of the equipment stopped the heating process, causing a temperature decrease after the maximum of respective PDSC peak has been attained. This occurrence explains why the respective combustion enthalpy, which was calculated automatically by the software, as being apparently equal to  $899.7\text{ J}\cdot\text{g}^{-1}$ . This is a much lower value than the other blend cases at same operating conditions and also lower than the next measured combustion enthalpies for B0 ( $3062$  and  $2533\text{ J}\cdot\text{g}^{-1}$ ), for lower oxygen concentration cases.

#### **PDSC - 290 psi in air**

The PDSC curves of the commercial sample B0 and blend samples B5, B10, B15 and B20 subjected to an initial pressure of 290 psi in air, are shown in Figure 2, where the measured auto-ignition temperatures, heats of combustion per initial mass of sample and maximum heat generation temperatures of each case are indicated, as was done in Figure 1.

As air contains approximately 79 vol % of nitrogen, this time, the initial oxygen molar concentration was equal to 21% in the PDSC heating chamber, approximately five times less than in the previous case of pure oxygen at same total pressure. As can be seen from Fig. 2, the order of influence of the biodiesel content on the thermo-oxidative stability temperature, remained similar to the case of pure oxygen (Fig. 1), showing that higher

biodiesel contents promote higher acceleration of the oxidizing process, decreasing progressively the respective auto-ignition temperature.

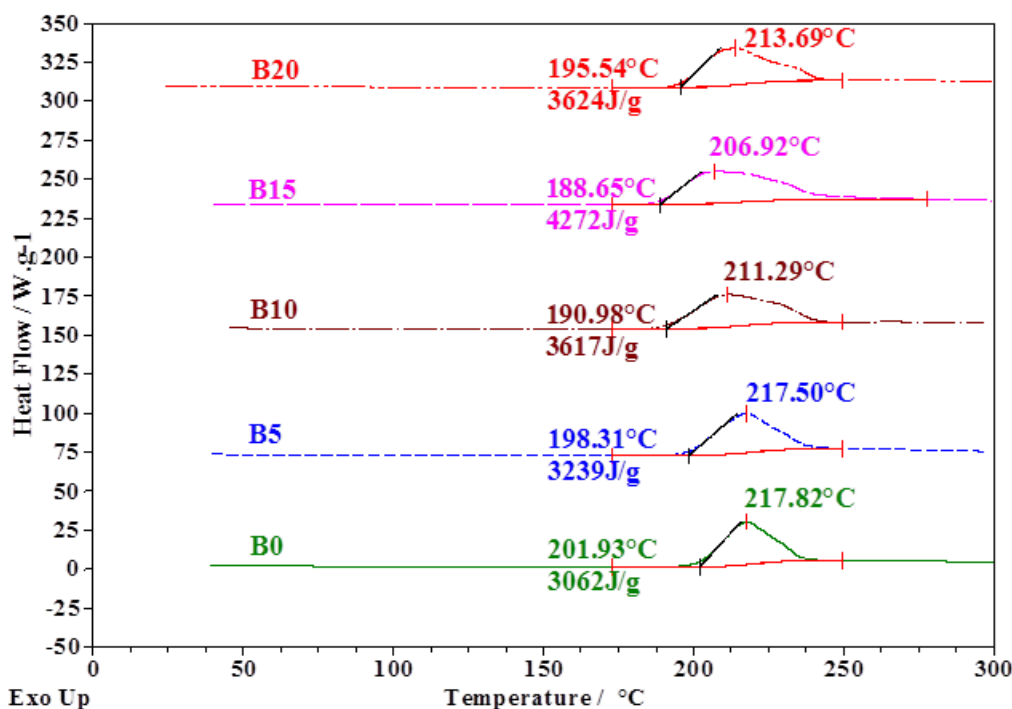


Fig.2 -PDSC curves of samples B0, B5, B10, B15 and B20 obtained in air at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  starting at 290 psi. (Curves were shifted for a better visualization)

The combustion peaks were broader than in the case of pure oxygen with lower heat generation peaks, indicating that lower combustion rates were occurring due to the lower concentration of oxygen than in case of pure oxygen at 290psi. However, the thermo-oxidative stability temperatures as a function of the biodiesel content were very close to those of the 290psi case with pure oxygen.

#### PDSC – 100psi in oxygen

Figure 3 shows the PDSC curves of the commercial sample B0 and the B5, B10, B15 and B20 blends in oxygen at 100psi. It should be noted that the environment of the PDSC heating chamber in these analyzes had an initial molar oxygen concentration equal to almost one-third (100/290) of that in the case of oxygen at 290 psi.

As the initial oxygen concentration in the PDSC chamber was between the two previous concentration cases, it caused the exothermic combustion peaks to be slightly more acute than the case with air at 290 psi, but less sharper than in the case of 290psi in oxygen, promoting intermediate combustion rates, when compared to the previous discussed cases. As a consequence, the order of influence of the biodiesel content in the thermo-oxidative stability temperature remained similar to the cases analyzed at 290 psi.

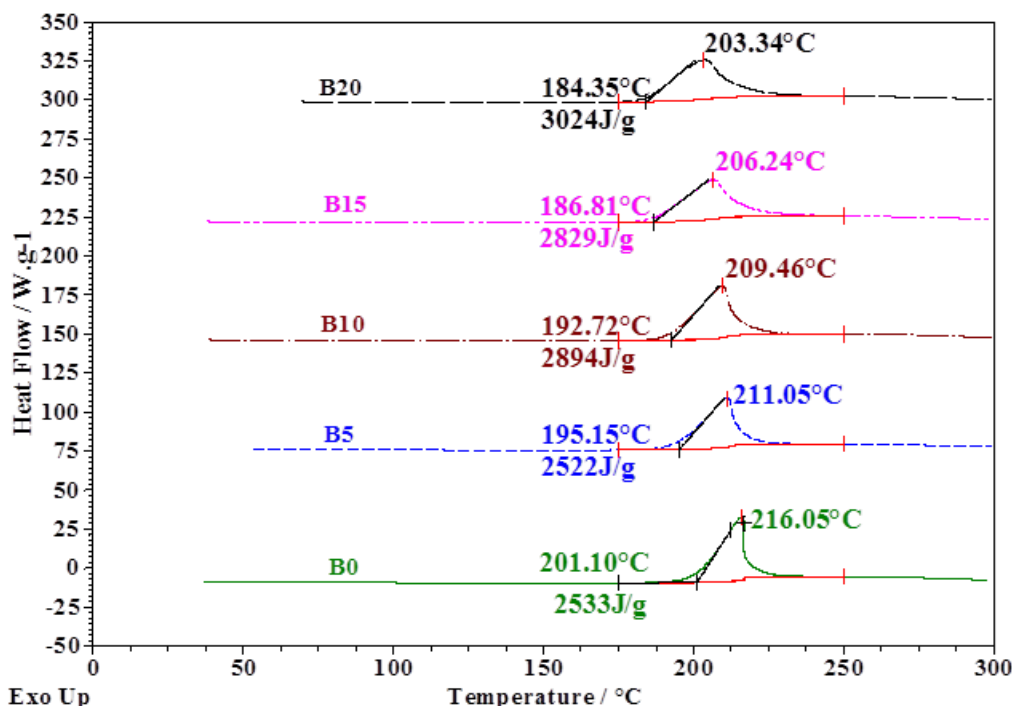


Fig. 3 - PDSC curves of samples B0, B5, B10, B15 and B20 in oxygen, at a heating rate of  $10^{\circ}\text{C}\cdot\text{min}^{-1}$  and initial pressure of 100 psi. (Curves were shifted for a better visualization)

#### Effect of biodiesel content on the auto-ignition temperature

To obtain quantitative correlations between the auto-ignition temperatures and the biodiesel content in each studied case, Figure 4 shows respective obtained functions, based on Table 1 data.

Table 1 Auto-ignition temperatures and heats of combustion of diesel and biodiesel/diesel blends measured during PDSC analyses at 290 psi in air and 290 and 100 psi, in  $\text{O}_2$

Sample	290psi in air		290psi in $\text{O}_2$		100psi in $\text{O}_2$	
	Tautoignition / $^{\circ}\text{C}$	$\Delta\text{H} / \text{J}\cdot\text{g}^{-1}$	Tautoignition / $^{\circ}\text{C}$	$\Delta\text{H} / \text{J}\cdot\text{g}^{-1}$	Tautoignition / $^{\circ}\text{C}$	$\Delta\text{H} / \text{J}\cdot\text{g}^{-1}$
B0	201.93	3062	203.95	899,7	201.10	2533
B5	198.31	3239	194.51	3836	195.20	2522
B10	190.98	3617	188.22	3989	192.70	2894
B15	188.65	4272	186.43	4726	186.20	2829
B20	195.54	3614	185.55	5592	184.40	3024

In the case of only diesel oil, when the pressure increases from 100 to 290 psi in oxygen, its auto-ignition temperature increases slightly, showing that a little higher temperature is needed to the vapor pressure of its lighter components be sufficient to overcome the higher ambient pressure and to vaporize, promoting its auto-ignition. At 290psi in air, because the mean molecular weight of air is little lighter than that of oxygen gas, a little lower increase in temperature is needed to begin diesel vaporization in the heating chamber to begin its auto-ignition. This results indicate that as in the case of diesel engines, the higher will be the operating pressure than 290psi, its auto-ignition, in the absence of biodiesel addition, will be higher than  $202^{\circ}\text{C}$ .

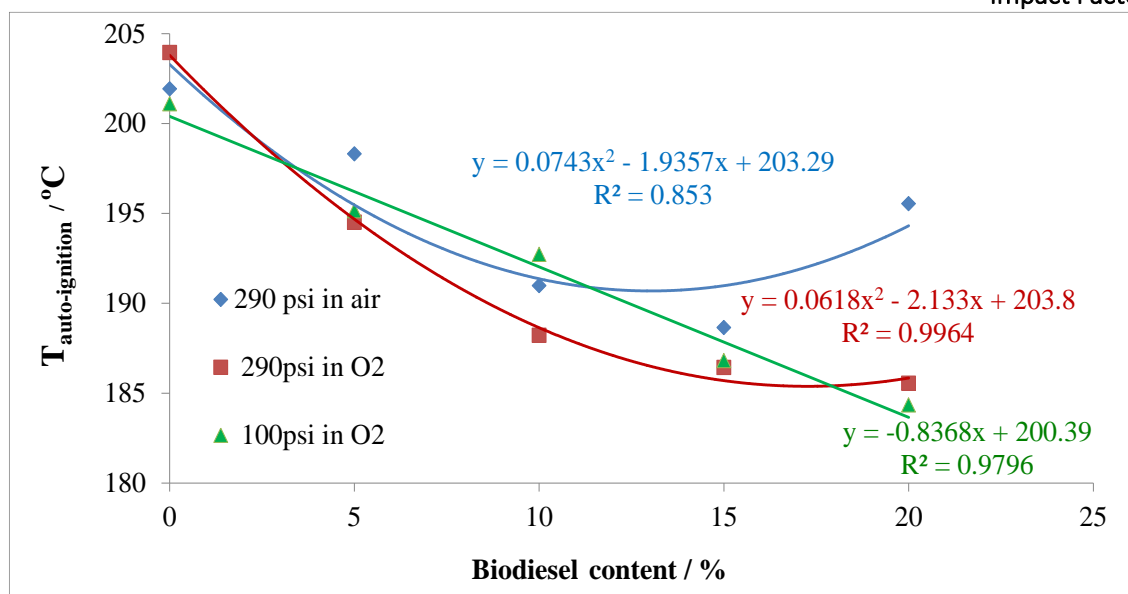


Fig.4 Auto-ignition temperatures as a function of biodiesel content for the three PDSC operating conditions: 100 psi in O<sub>2</sub> and 290 psi in O<sub>2</sub> and air

For the blends, in a general way, their  $T_{\text{auto-ignition}}$  decreases as biodiesel content increases, indicating that biodiesel addition decreases the ignition delay in diesel engines. In pure oxygen as the pressure is increased from 100 to 290 psi, the correlation changes from a linear to a polynomial function of the second degree, showing that the auto-ignition mechanism changes for higher contents of biodiesel. This effect is more evidenced in air at 290 psi, during which, at the highest tested content of biodiesel (20 vol%), the  $T_{\text{auto-ignition}}$  decreasing tendency noticed up to the 15 vol% case is reverted, very probably indicating a higher influence of the oxidative action of biodiesel on diesel components in liquid phase, indicating that higher additions of biodiesel will increase the ignition delay more than blends having up to 15% of biodiesel.

It is important to note that when biodiesel/diesel blend heating is done at atmospheric pressure, the higher is the biodiesel content, the higher is the auto-ignition temperature, because at this pressure, biodiesel is much less volatile than diesel [15], which may begin to volatilize at practically ambient temperature.

#### Quantification of the carbonaceous residues generated in the analyzes by PDSC

As was previously pointed out, one of the consequences of the use of biodiesel/diesel blends in diesel engines is that problems of carbonaceous residues affecting their performance and life time, have grown as the content of biodiesel in diesel has been increased. To have a quantitative evaluation of this problem, the mass of the used aluminum crucibles was measured before and after each PDSC analysis. Results are shown in Figure 5, for all the analyzed cases.

From Figure 5, it can be seen that, increasing the pressure from 100 psi to 290 psi, in the case of O<sub>2</sub>, the carbonaceous residue at the highest pressure is increased significantly, indicating that as at 290 psi, a lower mass of diesel components are volatilized than at 100 psi, which causes the oxidizing action of biodiesel to have more time to act, increasing the heavier oxidized components in liquid phase [16]. This causes a higher carbonaceous residue formation.

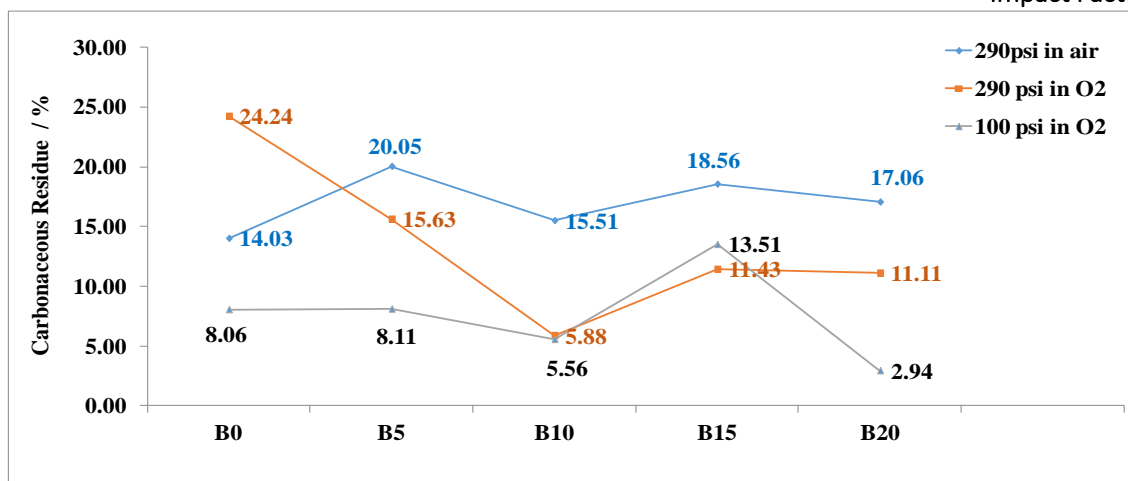


Fig.5 Carbonaceous residues formed during PDSC runs on initial sample mass percent basis

It is important to note that in air at 290psi, the mean residual carbonaceous mass of the blends is always higher than in only oxygen case at same pressure and biodiesel content, which is due to have less oxygen to promote a better combustion of the heavier present components, which only volatilize or decompose at higher temperatures during the PDSC runs.

Another important aspect is that, while at 290 psi in oxygen, there is a decreasing tendency to form residual carbonaceous as the biodiesel content is increased, the same does not happen in air at same pressure, during which, the formation of the carbonaceous residue is practically constant, indicating that, in these cases the lowest oxygen content of the ambient added to a high pressure condition, which avoids the pyrolysis and/or the thermal decomposition of the heavier present components promotes the maintenance of carbonaceous residues content.

## CONCLUSIONS

- In all analyzed cases of biodiesel/diesel blend heating at high pressure, the higher is the biodiesel content, the lower will be its auto-ignition temperature, showing that biodiesel presence accelerates the auto-ignition process.
- As a consequence, for diesel/biodiesel blends, in a general way, their  $T_{\text{auto-ignition}}$  decreases as biodiesel content increases, causing the decrease of the ignition delay in diesel engines.
- In pure oxygen, as the pressure is increased, the correlation between the auto-ignition temperature and biodiesel content changes from a linear to a polynomial function of second degree, showing that the oxidation and auto-ignition mechanisms are a function of pressure level and biodiesel content.
- The higher is the operating pressure, the lower will be the volatilization or pyrolysis of the heavier components, the lower will be the combustion efficiency and the higher will be the formation of combustion carbonation residues.
- Besides the increase on pressure level, decreasing the release of gaseous components to the heating chamber to be burnout after ignition, when compared to pure oxygen ambient at a same pressure, a lower concentration of oxygen, as occurs in air, leads to a lower combustion degree, which in turn promotes a higher formation of carbonaceous residues after combustion.

## REFERENCES

- [1] FISCHETTI, M. **Refinarias de Petróleo**. *Scientific American Brasil*, 49, 90-91 (2006).
- [2] CHEVRON. **Diesel Fuels Technical Review**. Chevron Products Company, 1998. Available at: [www.chevron.com.br](http://www.chevron.com.br) Accessed in August, 6, 2012.
- [3] ANP – **Agência Nacional do Petróleo e Biocombustíveis**. Available at: <[www.anp.gov.br](http://www.anp.gov.br)>. Accessed in August, 10 2017.
- [4] LEIVA C.R.M., CRNKOVIC P. M. e SANTOS A. M. **O emprego de termogravimetria para determinar a energia de ativação do processo de combustão de óleos combustíveis**. *Quim.Nova*, Vol.29, No.5, 940-946, 2006.



- [5] ANDRADE R.D.A. **Dissertação de Mestrado: Calor de Combustão de misturas do tipo Diesel/Biodiesel e Diesel/Bio-óleo.** Universidade de Brasília, Instituto de Química, November 2009.
- [6] LOBO I.P., FERREIRA S.L.C., CRUZ R.S. **Biodiesel: quality parameters and analytical methods.** Química Nova, vol.32 no.6 São Paulo, 2009.
- [7] PENTEADO, M.C.P.S. **Identificação de gargalos e estabelecimento de um plano de ação para o sucesso do programa brasileiro do biodiesel.** Ed.rev. São Paulo.2005.
- [8] MME – **Ministério de Minas e Energia.** Available at: <[www.mme.gov.br](http://www.mme.gov.br)>. Accessed in 15 jun. 2016.
- [9] LO, K.M., & CHEUNG, P.C.K. **Antioxidant Activity of Extracts from Fruiting Bodies of *Agrocybeaegerita* var. Alba.** Food Chemistry. V 89 (4) p.533-539.2005.
- [10] LIST, G.R., WANG, T. SHUKLA V.K.S. **Storage, Handling and Transport of Oils and Fats, in Bailey's Industrial Oil and Fat Products.** Sixth Edition. Edited by Fereidoon Shahidi.2005.
- [11] MONYEM, A. VAN GERPEN J.H. **The Effect of Biodiesel Oxidation on Engine Performance and Emissions / Biomass and Bioenergy.** v 20, 317-325. 2001.
- [12] KNOTHE G. **Review: some aspects of biodiesel oxidative stability.** Fuel Processing Technology, vol 88, 7, July 2007, 669-677.
- [13] KARAVALAKIS G., STOURNAS S., KARONIS D. **Evaluation of the oxidation stability of diesel/biodiesel blends.** Fuel 89 (2010), p. 2483–2489.
- [14] <http://www.anp.gov.br/noticias/4333-percentual-obrigatorio-de-biodiesel-passa-para-10>, Accessed in May 17, 2018
- [15] OLIVEIRA, T F, DWECK J, **Biodiesel Presence Effect on the Thermal and Thermo-Oxidative Stability of its Blends with Diesel Oil,** XXV Simpósio Internacional de Engenharia Automotiva, Blucher Engineering Proceedings, Vol 4,1, (2017) 712-723
- [16] OLIVEIRA, T.F., DWECK, J. **Liquid phase oxidation quantitative analysis of biodiesel/diesel blends by differential TG and DTAJ.** Therm Anal. Cal. 2018, online <https://doi.org/10.1007/s10973-018-7298-4>.