CORRELATION BETWEEN NOX AND CO EMISSIONS AND ACTIVATION ENERGY OF RENEWABLE FUELS.

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ABSTRACT

Biofuels have been widely used in conventional Diesel engines to replace, partially or totally, by fossil diesel. However, the use of an innovative fuel should be evaluated and an important feature to be considered is the ignition delay of the combustion process. Ignition delay can be correlated with activation energy (Ea) and greatly affects the performance of the engine, including pollutant emissions. This study presents the determination of activation energy of three pure fuels - farnesane, biodiesel and fossil fuel - and their blends. In addition, the correlation between Ea and NOx and CO emissions were established. Gases emissions were generated in the OM 926 LA CONAMA p7/EURO 5 diesel engine according to the European Stationary Cicle (ESC). Activation energies were determined by means of thermogravimetric experiments and the mathematic model free-kinetics. Our results indicate that when biodiesel is added to the blend with fossil Diesel, both activation energy values and NOx emission increase, but no direct correlation between Ea and CO emissions was observed. A contrary behavior was observed with farnesane in the blend, i.e., its addition in the fossil Diesel decreases both activation energy and NOx and CO emissions.

INTRODUCTION

The reduction of both the dependence on fossil fuels and global pollutant emissions has been a worldwide growing concern.

Diesel engine emits several pollutants due to thermal processes such as carbon monoxide (CO), carbon dioxide (CO_2), hydrocarbons (HC), nitrogen oxides (NOx) and particulate materials (MP). These pollutants can cause damage to both living beings and environment, which makes important to evaluate the performance and emissions when new fuels and new technologies are proposed.

The use of biofuels and their blends with fossil diesel without physical changes to the engine has been a trend [2]. Emissions are directly influenced by the fuel properties, namely cetane number, density, activation energy, surface tension etc. and factors related to the engine design: compression, injection time, bore, stroke, etc. [2] e [3].

Several studies have been developed to evaluate the emissions of the mixture of diesel and biofuels. [1] showed that the use of the diesel/biodiesel blend presented reduction of 28-46% of CO, but an increase between 6.95–17.62% of NOx compared to pure fossil diesel. [4] found that a binary mixture (30% Farnesane/70% fossil diesel) reduces CO emissions, but presents similar NOx emissions compared to the pure fossil diesel.

Other investigation presents the effect of the fuel properties in the pollutant emissions. [5], showed that high NOx emission is due to the oxygen in the chemical composition of the fuel.

[6] stated that physical properties of the fuel, such as volatility, density, surface tension and cetane number, have secondary impacts on the combustion process.

This study aims to determine activation energy for three different fuels (farnesane, biodiesel and fossil fuel) and their blends at five different percentages (25%, 50%, 70%, 80% and 90%) using thermogravimetric experiments and Model Free Kinetics. In addition, test were conducted in a diesel engine model OM 926 LA CONAMA P7/Euro 5 according to European Stationary Cycle (ESC) to determine CO and NOx emissions.

1 EXPERIMENTAL

1.1 MATERIALS AND METHODS.

Three different fuel samples, (1) commercial diesel S50 - according to ANP 42/09 [7] namely in this study by (D) sample, (2) renewable diesel from sugar cane named farnesane (F) sample and (3) biodiesel (B) sample were used in this study. Farnesane is a hydrocarbon ($C_{15}H_{32}$) was supplied by Amyris Brasil S.A. from a pilot plant located in Campinas – State of São Paulo (Brazil) and the soybean biodiesel was supplied by Brasil Ecodiesel from a plant located in Floriano – Piaui State (Brazil).

Properties of the pure samples are detailed in the Table 1. The elemental analyses were determined on the analyzer Leco CHN 1000 and the high heat value (HHV) was determined on IKA Werke C 2000. Cetane number was measured in an engine according standard ASTM D 613.

Table 1: Properties of the pure fuels

Analysis	Samples		
	Farnesane	Diesel	Biodiesel
Carbon (%)	84.67	85.54	76.5
Hydrogen (%)	15.33	14.46	12.74
Oxygen (%)	-	-	10.76
Nitrogen (%)	-	-	-
Sulfur (%)	0.001	0.003	0.001
Cetane Number	58	49	59
Cinematic Viscosity 40 ºC ($mm^2\ s^{-1}$)	2.95	3.11	4.42
Density a 20ºC ($g\ ml^{-1}$)	0.770	0.843	0.882
High heating value ($MJ\ kg^{-1}$)	46.9	45.3	39.7

Thermogravimetric experiments were performed in a TA Instrument Q50 balance and the analyses were carried out from room temperature up to 400 ºC at five heating rates: 5.0, 10.0, 15.0, 20.0 and 25.0 ° C min^{-1}. Sample mass of 3.6 ± 0.5 mg was used for each experiment, in addition, initial mass was kept lower than 4.0 mg in order to avoid effects such as mass and heat transfer during the decomposition of the materials.

Table 2: Specification of engine.

Engine make	Mercedes-Benz
Engine model	Engine OM926LA E5
Displacement volume	7.201 cm³
Number of cylinders	6 in line
Power	240 kW @ 2,200 min-1
Torque	1,300 Nm @ 1,200 to 1,600 min-1
Bore	106 mm
Stroke	136 mm
Compression ratio	17.5:1
Valves per cylinder	3, 1 intake and 2 exhaust
Fuel Injection System	UP Electronic, independent Unit Pumps + mechanical injectors nozzles
After treatment system	SCR (Selective Catalyst Reaction)

The atmosphere used was synthetic air with flow rate of 100 ml/min. Experiments were performed in triplicate and the average curve was used for the calculations.

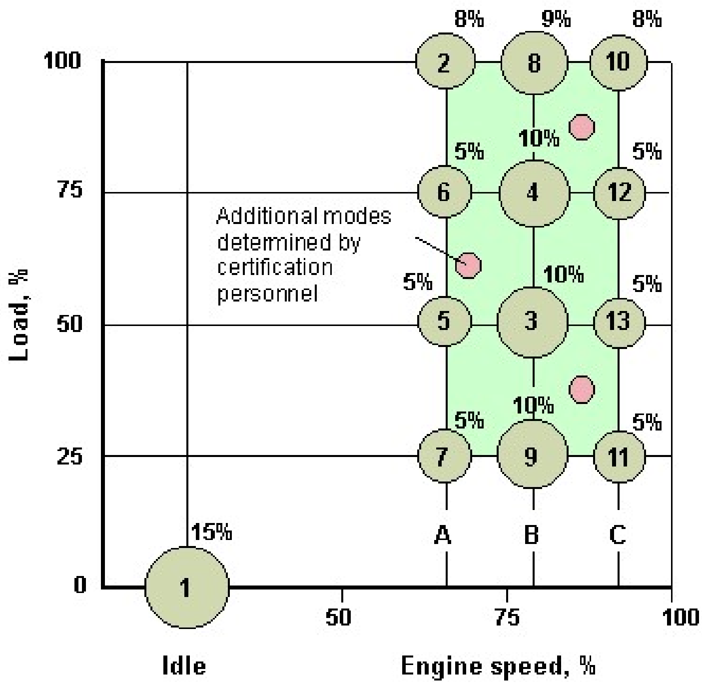

Figure 1 European Stationary Cycle (ESC) (De Jong *et al.*, 2012).

The European Stationary Cycle test (ESC) using a OM 926 LA CONAMA P7/EURO 5 diesel engine according Table 2, was applied to determine NO_x emission. “Figure 1” depicts the sequence of 13 measurement points concerning the combination of loads (25, 50 75 and 100 %) and speeds nA (1,340 rpm), nB (1,710 rpm) and nC (2,080 rpm) [8]. Tests have been performed by using blends of biodiesel/diesel and farnesane/diesel . The final value of NO_x for each pure fuel was determined considering the average of all experiments.

1.2 Mathematical model

Model-free kinetics was used for the determination of the activation energy, this model is based on isoconversional techniques to calculate the activation energy as a function of conversion (α) of the chemical reaction. Thus, this approach was used to follow all the conversions obtained from multiple experiments. This theory is based on "Equation (1)".

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

Where, t is the time, T the temperature, f (α) the model of the reaction and k (T) is the coefficient of Arrhenius reaction rate. After the necessary adjustments and considerations, as shown in several prior studies [9] e [10] the model Model-free kinetics is represented by "Equation (2)".

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R_\alpha}\frac{1}{T_\alpha} \tag{2}$$

Where β is the heating rate, g (α) to an integrated model of reaction and the subscript α represents the values related to a given conversion.

2 RESULTS

2.1 NOX EMISSION.

Table 3 shows NO_x emission and E_a activation energy for pure fossil diesel, farnesane and biodiesel and their blends at five different compositions. It can be noted that when farnesane is added to fossil diesel, NOX emission is reduced up to 11.22 % when compared with pure fossil diesel. However, when biodiesel is added to fossil diesel the NOx emission increases up to 21.29%.

According to [11] the majority of the reviewed studies in diesel engine showed that biodiesel and its mixture with diesel has an increasing trend in NO_x emission, in our study as the percentage of biodiesel increased in the blend, NOx emission increased from 0.32 until 21,29%. However, adding the farnesane to the fossil diesel a reduction of NO_x from 0,84 until 11.22%, was observed.

NO_x emissions are described in this study as normalized values considering 100% of NO_x emission for the fossil diesel.

In addition, it is interesting to note in the Table 3 that the lowest NO_x emission was obtained for pure farnesane, the highest NO_x emission for pure biodiesel and the intermediate values for the blends of both biofuels are added to the fossil diesel.

Table 3: E_a activation energy and NOx emission for diesel, farnesane, biodiesel and their blends

Samples	Diesel	Farnesane	Biodiesel	E_a (kJ/mol)	NO_x (%)
D	100	0	0	86.69 ± 8.68	100.000 ± 0.001
F10	90	10	0	86.25 ± 8.15	99.155 ± 0.005
F20	80	20	0	85.80 ± 7.63	96.006 ± 0.015
F30	70	30	0	85.36 ± 7.11	95.617 ± 0.007
F50	50	50	0	84.47 ± 6.06	95.003 ± 0.001
F75	25	75	0	83.36 ± 4.75	92.134 ± 0.004
F	0	100	0	82.24 ± 3.44	88.784 ± 0.004
B10	90	0	10	87.69 ± 8.19	100.316± 0.001
B20	80	0	20	88.68 ± 7.71	101.289± 0.003
B30	70	0	70	89.68 ± 7.23	103.745± 0.002
B50	50	0	50	91.67 ± 6.26	108.912± 0.002
B75	25	0	75	94.15 ± 5.05	118.407± 0.011
B	0	0	100	96.64 ± 3.85	121.289± 0.002

Figure 2 presents the correlation between E_a and NO_x emissions, in which is possible to observe that as activation energy increases, NO_x emission also increases. When biodiesel is added to the diesel, there is an increasing of both NO_x and activation energy, but when farnesane is added to diesel, a contrary behavior is observed, i.e, as the farnesane content increases in the blend, there is a lowering in both activation energy and NO_x emission.

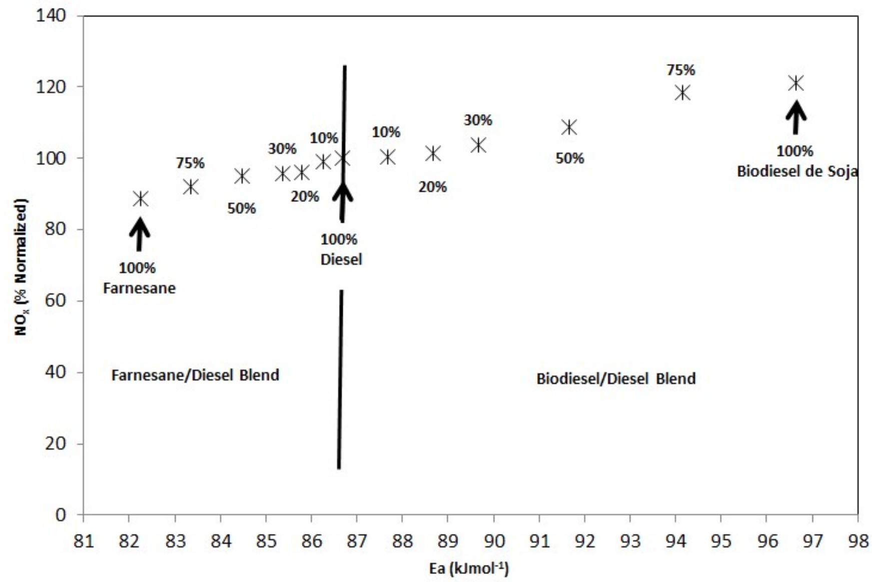

Figure 2. E_a Activation energy and NO_x emissions (Normalized as 100% of NO_x emission for the pure fossil diesel)

The entire correlation was obtained from the combination of all values considering farnesane/Diesel and biodiesel/Diesel. A linear correlation was obtained as presented in the Equation 3.

$$NO_x = 2.2526\,E_a - 96.41 \quad (3)$$

2.2 CO emission

CO emissions are described in this study as normalized values considering 100% of CO for pure fossil diesel. Table 4 shows CO emissions and Ea activation energy for pure fossil diesel, pure biodiesel, pure farnesane and their blends at five different compositions. It can be noted that the lowest value of CO emission was obtain for the diesel 25% /biodiesel 75% blend, for which CO emission reduced up to 36.4 %.

Table 4: E_a activation energy and NOx emission for diesel, farnesane and biodiesel and their blends

Samples	Diesel	Farnesane	Biodiesel	E_a (kJ/mol)	CO (%)
D	100	0	0	86.7 ± 8.70	100.000±0.020
F10	90	10	0	86.25 ± 8.15	95.861±0.010
F20	80	20	0	85.80 ± 7.63	91.391±0.011
F30	70	30	0	85.36 ± 7.11	86.424±0.011
F50	50	50	0	84.47 ± 6,06	90.894±0.022
F75	25	75	0	83.36 ± 4,75	79.967± 0.012
F	0	100	0	82.24 ± 3,44	84.934± 0.012
B10	90	0	10	87.69 ± 8,19	99.338± 0.010
B20	80	0	20	88.68 ± 7,71	89.404± 0.011
B30	70	0	70	89.68 ± 7.23	82.450± 0.036
B50	50	0	50	91.67 ± 6.26	69.536± 0.057
B75	25	0	75	94.15 ± 5.05	63.576± 0.016
B	0	0	100	96.64 ± 3.85	66.556± 0.030

CO emissions versus activation energy for all fuels are presented in the Figure 3, in which it is possible to observe that the highest emission was obtained for the pure diesel, but it is not correlated with the highest activation energy value. When farnesane is added to the fossil diesel, the activation energy decreases and CO emissions also decrease. However, when biodiesel is added to the fossil diesel, the activation energy increases and CO emissions decreases.

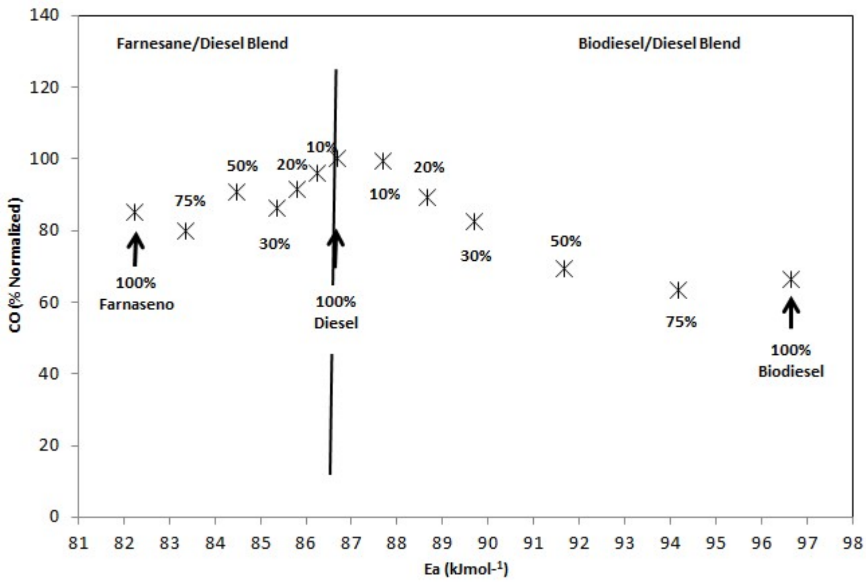

Figure 3. Ea Activation energies and CO emissions (Normalized as 100% of CO emission for the pure fossil diesel)

The entire correlation was obtained from the combination of all Ea and CO values considering farnesane/Diesel and biodiesel/Diesel. A polynomial correlation was obtained as presented in the Equation 4.

$$CO = 0.0709E_a^3 - 19.259E_a^2 + 1740.1E_a - 52213.2508 \quad (4)$$

2.3 Validation of both correlations: NOx versus Ea and CO versus Ea

An experimental validation was addressed to verify if the simulation of the NOx and CO emissions are consistent with experimental data. For this validation a single case of a tertiary mixture composed by 20% of farnesane, 70 % fossil diesel and 10% biodiesel was used in the OM 926 LA CONAMA P7/EURO 5 diesel engine and, from this experiment, NOx emission was102.09 %, i.e., 2.09% higher than for the pure fossil diesel and for CO, 86.4%.

For this tertiary mixture Ea was calculated considering the weighted average resulting in 86.80 kJ/mol, which was applied in the Equation 3 giving the NO_x value as 99.13 %. Equation 4 was used to predict CO emission and the value was 92,12%.

The difference between experimental and simulated results was calculated using Equation 5 and the values were 2.98% for NOx and 5.7% for CO.

$$difference = \frac{(experimental\ value - smulated\ value)}{experimental\ value}\ x\ 100\% \quad (5)$$

From the validation, as previously described, it is possible to predict NO_x and CO emissions for other blends (binary and tertiary mixtures) composed for farnesane, biodiesel and diesel.

Figure 4A and 4B are a ternary graph and present the prediction of NO_x and CO emissions, respectively, for different blends, which composition varies from 0.25% up to 80% of each fuel. In the inner part of the figures, there are calculated emissions values for the different proportions of fuels in the blend. The red arrows indicate the decreasing trend of the emission values.

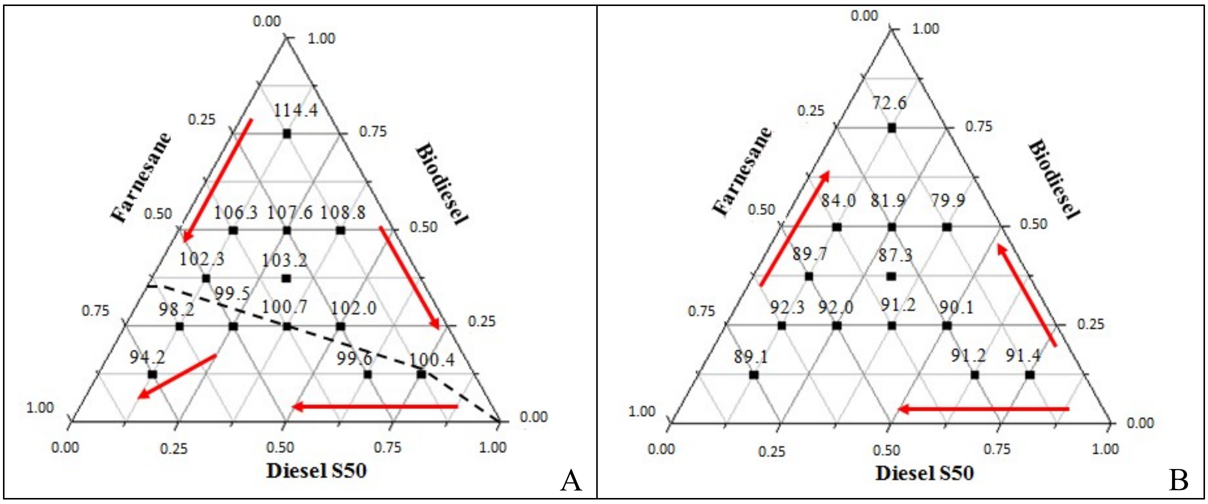

Figure 4. Ternary graph of NO_x (A) and CO (B) emissions for the tertiary mixture composed by different percentages of diesel, biodiesel and farnesane.

CONCLUSION.

Results of this study showed that there is a direct correlation between activation energy and NO_x emission for the biodiesel/diesel blend. When farnesane is added to diesel, there is a lowering in both activation energy and NO_x emission. The highest value of NO_x emission was obtained for pure biodiesel.

Related to CO emissions, results showed that the lowest value was obtained for biodiesel, followed by farnesane and the highest value, for pure fossil diesel.

According to the literature [12], [13] e [14], part of the NO_x formation is a due to the presence of oxygen in the composition of the fuel, which contributes to the high combustion efficiency leading to an increasing of the temperature and decreasing the CO emissions.

NO_x and CO emissions for the blends can be predicted from E_a values, which makes an interesting tool because Ea is determinate at a remarkably short time according methodology described in this study, i.e., using thermogravimetric analysis (TG) and a mathematic model (Model-Free Kinetics).

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