



## ACTIVATION ENERGY, NO<sub>x</sub> AND CO EMISSIONS OF RENEWABLE FUELS AND THEIR BLENDS WITH FOSSIL DIESEL.

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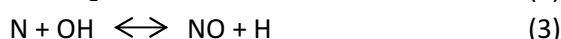
**Abstract.** Biofuels have become an alternative to replace fossil diesel in engines. However, their use needs fundamental studies related to several aspects, such as pollutant emissions, performance and physical-chemistry characteristics of the fuel. This study aims to evaluate two renewable fuels: biodiesel and farnesane and their blends with fossil diesel at five different percentages (25%, 50%, 70%, 80% and 90%). Biodiesel is a product from transesterification of soybean oil and farnesane, a renewable diesel from sugar cane. Experiments and results have performed at two stages. The first is related to the NO<sub>x</sub> and CO emissions formed in European Stationary Cycle (ESC) in a diesel engine OM 926 LA Euro 5, and the second, the determination of activation energy using thermogravimetry and the Model Free Kinetics. Results showed that activation energy and emissions are largely dependent on the fuel composition. Pure biodiesel presented the highest value of activation energy (96,64 kJ/mol), pure farnesane, the lowest (82,24 kJ/mol) and the pure fossil diesel an intermediate value of 86,68 kJ/mol. As the percentage of biodiesel increases in the blend, NO<sub>x</sub> emission increased (0,32 - 21,29%) and CO decrease (33,44 - 0,66%). However, blending the farnesane with fossil diesel reduced both NO<sub>x</sub> (11,22 - 0,84%) and CO (15,09 - 4,14%) yields. The emissions trends were interpreted on the basis of normalized values.

**Keywords:** farnesane, biodiesel, NO<sub>x</sub> and CO emissions, activation energy.

### 1. INTRODUCTION

The reduction dependence on fossil fuels and global emissions has been a worldwide growing interest the use of biofuels and their use in diesel engines without changing the characteristics of the engine (Henein, 1976; Conconi e Crnkovic, 2013). The combustion in diesel engines is one of the processes responsible for the formation of NO<sub>x</sub> and CO, which production is influenced by the property of the fuel (cetane number, density, activation energy, etc.) and the characteristics of the engine (compression, injection time, bore, stroke, etc.) (Chigier, 1981).

Nitrogen oxides (NO<sub>x</sub>) consist of nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O), formed in combustion processes and can be described by chemical mechanism also known as thermal Zeldovich mechanism. An important characteristic of the NO<sub>x</sub> is that they are mainly formed from the oxidation of air nitrogen at high temperatures. The three reactions that produce thermal NO<sub>x</sub> proposed by Zeldovich are:



The Fenimore or prompt NO<sub>x</sub> mechanism is directly related to chemical characteristic of the fuel, in which the the burning of hydrocarbon in the flame zone allows the immediate NO production from the air (Hill and Douglas Smoot, 2000; Saravanan, Nagarajan *et al.*, 2012). In total NO formation in this mechanism is less important than the thermal mechanism, the reactions involved in this mechanism are:





Carbon monoxide (CO) is an intermediate product of the hydrocarbons combustion. Due to the temperature and the residence time of the reaction combustion, an incomplete combustion reaction occurs and consequently promoting the formation of carbon monoxide. In rich mixtures usually there are high CO emissions, and the main parameter that affects the formation of CO is the high fuel/ air ratio.

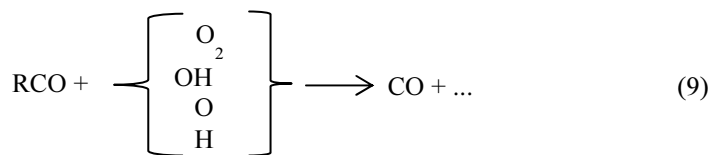
The mechanism of CO formation can be summarized in the reaction 7 (Bowman, 1975):



The reaction to produce CO radical RCO can occur by thermal decomposition, (reaction 8)



Or may occur via thermal decomposition :



Where RCO is the radical to produce CO. This reaction indicates that several radicals present in the combustion process influence the formation of CO (Bowman, 1975)

Combustion conditions interferes directly in the engine performance and considerable attention should be given to the ignition, which is a complex phenomenon involving many physical - chemical processes. One of the most important parameters in the study of combustion is the ignition delay, which prediction is of particular interest for both fuel combustion characteristics and emissions.

Ignition delay in diesel engine is measured by cetane number and is related to both fuel properties and fuel ignition quality. Ignition delay is composed by physical and chemical delays and the last one is considered to be the rate-controlling process for the formation of intermediate species, responsible for the propagation of the flame in the combustion (Chigier, 1981). The rate formation of such species can be given by Arrhenius-type equation where the activation energy is a kinetic parameter of the combustion process and it is characteristic of each used fuel.

Activation energy is related to the ignition delay by the "Equation (1)" proposed by Wolfer in 1938 (Henein, 1976; Chigier, 1981; Heywood, 1988).

$$\tau = Ap^{-n}e^{\left(\frac{E_a}{RT}\right)} \quad (1)$$

The  $\tau$  is the ignition delay,  $p$  is pressure,  $T$  the temperature,  $R$  is the gas constant universal,  $E_a$  the activation energy,  $n$  the kinetic coefficient and  $A$  the frequency factor.

Based on direct relation between ignition delay and the activation energy, one can qualify different fuels by their activation energy.

Since ignition delay is relative the activation energy ( $E_a$ ), this study aims to determine activation energy and correlated it with  $NO_x$  emission. For this purpose, three different pure fuels (fossil diesel, renewable diesel and biodiesel) and their blends have been studied.

This study aims to evaluate two renewable fuels: biodiesel and farnesane and its blends with fossil diesel in five different percentages (25%, 50%, 70%, 80% and 90%) Testes have been conducted in a diesel engine : OM 926 LA CONAMA P7/Euro 5 European EURO test Stationary Cycle (ESC). In those experiments  $NO_x$  and CO emissions have been determined and their correlations with activation energy have been established.

## 2. MATERIALS AND METHODS.

### 2.1 Samples.

Three different fuel samples, (1) commercial diesel S50 - according to ANP 42/09 (Petroleo, 2009) (Petroleo, 2009) namely in this study by sample (D) (2) renewable diesel from sugar cane named farnesane sample (F) and (3) biodiesel sample (B) according to ANP 07/08 (Crnkovic, Leiva *et al.*, 2007; Petroleo, 2008) were used in this study. Farnesane 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 – Piauí 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 °C (mm <sup>2</sup> s <sup>-1</sup> )	2,95	3,11	4,42
Density a 20°C (g ml <sup>-1</sup> )	0,770	0,843	0,882
High heating value (MJ kg <sup>-1</sup> )	46,9	45,3	39,7

## 2.2 Thermogravimetric experiments

Thermogravimetric experiments were performed in a TA Instrument Q50 balance and the analyses were carried out from room temperature up to 400°C at five heating rates: 5.0, 10.0, 15.0, 20.0 and 25.0 ° C min<sup>-1</sup>. 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.

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.

## 2.3 Model-free kinetics

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 ( $\alpha$ ) of the chemical reaction. Thus, this approach was used to follow all the conversions obtained from multiple experiments. This theory is based on “Equation (2)”.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

Where,  $t$  is the time,  $T$  the temperature,  $f(\alpha)$  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 (Vyazovkin and Wight, 1999; Crnkovic, Leiva *et al.*, 2007) the model Model-free kinetics is represented by “Equation (3)”.

$$\ln \frac{\beta}{T_\alpha^2} = \ln \left[ \frac{RA}{E_\alpha g(\alpha)} \right] - \frac{E_\alpha}{R_\alpha T_\alpha} \quad (3)$$

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

## 2.4 Tests on diesel engine

An European Stationary Cycle test (ESC) using a OM 926 LA CONAMA P7/EURO 5 diesel engine. was applied to determine  $\text{NO}_x$  emission. “Figure 1” depicts the sequence of 13 measurement points concerning to the combination of loads (25, 50 75 and 100 %) and speeds  $n_A$  (1340 rpm),  $n_B$  (1710 rpm) and  $n_C$  (2080 rpm) (De Jong, Vijlbrief *et al.*, 2012). Tests have been performed by using blends of biodiesel/diesel and farnesane/diesel . The final value of  $\text{NO}_x$  for each pure fuel was determined considering the average of all experiments.

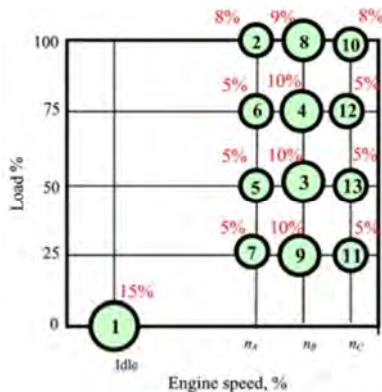


Figure 1 European Stationary Cycle (ESC).

## 3. RESULTS

### 3.1 $\text{NO}_x$ emission.

$\text{NO}_x$  emissions are described in this study as normalized values considering 100% for  $\text{NO}_x$  emission from fossil diesel. Table 2 and 3 show  $\text{NO}_x$  emission for pure fossil diesel, biodiesel, farnesane and their blends at five different compositions respectively. It can be noted that when farnesane is added to fossil diesel,  $\text{NO}_x$  emission is reduced to 11,22% compared with pure fossil diesel and when biodiesel is added to fossil diesel the emission increased up to 21,29%.

Table 2:  $\text{NO}_x$  emission for pure fossil diesel, pure farnesane and their blends

Diesel (%)	Farnesane (%)	$\text{NO}_x$ (% Normalized)
100	0	100,0
90	10	99,16
80	20	96,01
70	30	95,62
50	50	95,0
25	75	92,13
0	100	88,78



Table 3: NO<sub>x</sub> emission for pure fossil diesel, pure biodiesel and their blends

Diesel (%)	Biodiesel (%)	NO <sub>x</sub> (% Normalized)
100	0	100,0
90	10	100,32
80	20	101,29
70	30	103,74
50	50	108,91
25	75	118,41
0	100	121,29

In addition, it is interesting to note that the lowest NO<sub>x</sub> emission was obtained for pure farnesane, the highest NO<sub>x</sub> emission for pure biodiesel and the intermediate values when blends of both biofuels are added to the fossil diesel.

Tables 4 and 5 show the E<sub>a</sub> for pure diesel, pure farnesane and their blends.

Table 4: Activation Energy (E<sub>a</sub>) for pure fossil diesel, pure farnesane and their blends

Diesel	Farnesane	E <sub>a</sub> (kJ/mol <sup>-1</sup> )
100	0	86,69
90	10	86,25
80	20	85,80
70	30	85,36
50	50	84,47
25	75	83,36
0	100	82,24

Table 5: Activation Energy (E<sub>a</sub>) for pure fossil diesel, pure biodiesel and their blends

Diesel	Biodiesel	E <sub>a</sub> (kJ/mol <sup>-1</sup> )
100	0	86,69
90	10	87,69
80	20	88,68
70	30	89,68
50	50	91,67
25	75	94,15
0	100	96,64

By establishing the correlation between E<sub>a</sub> and NO<sub>x</sub> emissions, it can be noted in the Figure 2 that activation energy increases and NO<sub>x</sub> emission also increases. When biodiesel is added to the diesel, there is an increasing of both NO<sub>x</sub> 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<sub>x</sub> emission.

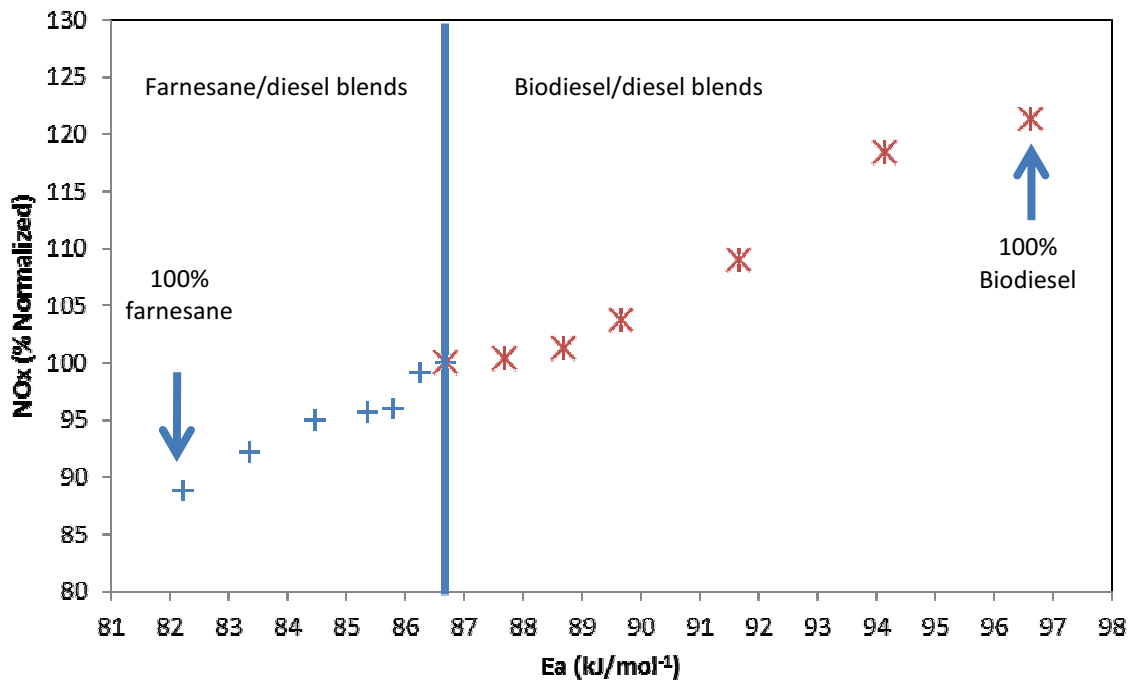


Figure 2. Activation energies (Ea) and CO emissions (% Normalized) for the fuels

### 3.2. CO emission

CO emissions are described in this study as normalized values considering 100% of CO for pure fossil diesel. Tables 6 and 7 show CO emissions 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 diesel blend and when biodiesel is added to fossil diesel the emission reduced up to 33,44 %. The lowest value was obtained for pure biodiesel (Table 7). CO emission is reduced to 15,09% for the 25% farnesane/75% fossil

Table 6: CO emissions for pure fossil diesel, pure farnesane and their blends

Diesel (%)	Farnesane (%)	CO (% Normalized)
100	0	100,0
90	10	95,86
80	20	91,39
70	30	86,42
50	50	90,89
25	75	79,97
0	100	84,91



Table 7: CO emissions for pure fossil diesel, pure biodiesel and their blends

Diesel (%)	Biodiesel (%)	CO (% Normalized)
100	0	100,0
90	10	99,34
80	20	89,40
70	30	82,45
50	50	69,54
25	75	63,58
0	100	66,56

Tables 8 and 9 show  $E_a$  for pure fossil diesel, pure farnesane, pure biodiesel and their blends farnesane/fossil diesel blend. It can be noted in figure 3 that when farnesane is added to the fossil diesel, the activation energy increases and CO emission also increases, however when biodiesel is added in fossil diesel the activation energy decreases and CO emission also decreases.

Table 8: Activation Energy ( $E_a$ ) for pure fossil diesel, pure farnesane and their blends

Diesel	Farnesane	$E_a$ (kJ/mol <sup>-1</sup> )
100	0	86,69
90	10	86,25
80	20	85,80
70	30	85,36
50	50	84,47
25	75	83,36
0	100	82,24

Table 9: Activation Energy ( $E_a$ ) for pure fossil diesel, pure farnesane and their blends

Diesel	Biodiesel	$E_a$ (kJ/mol <sup>-1</sup> )
100	0	86,69
90	10	87,69
80	20	88,68
70	30	89,68
50	50	91,67
25	75	94,15
0	100	96,64

In order to facilitate the understanding of the correlation between CO emission and activation energy, Figure 3 shows the results CO emissions *versus* activation energy for all fuels, in which it is possible to observe that the highest emission was obtained for pure diesel, but it is not correlated with high activation energy value. In addition, the lowest emission values were obtained for pure renewable fuels.

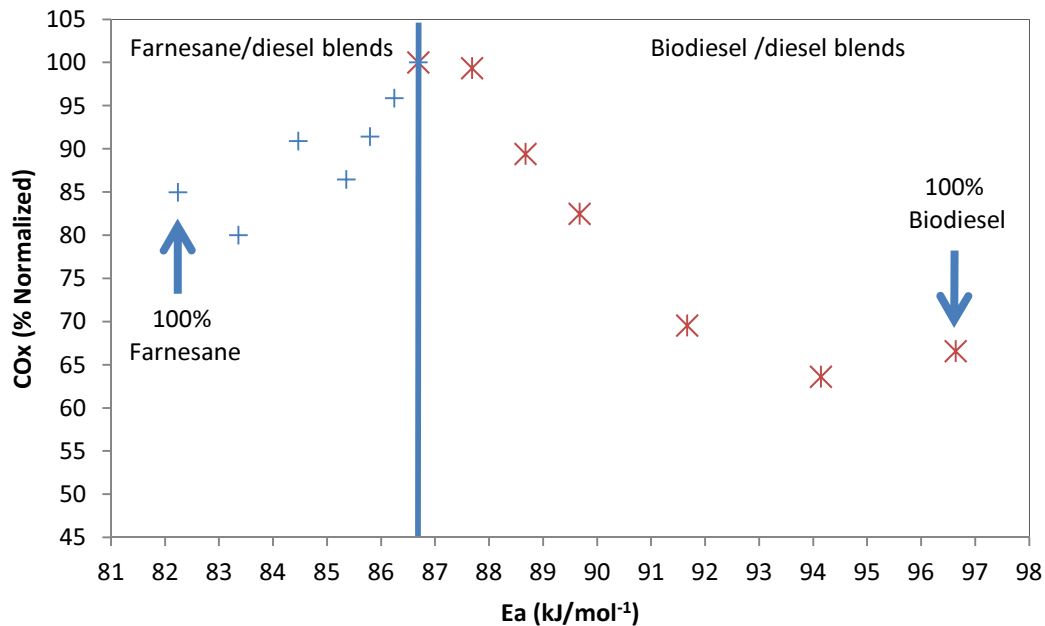


Figure 3. Activation energies (Ea) and CO emissions (% Normalized) for the fuels

#### 4. CONCLUSION

In this study, two renewable fuels (Farnesane and biodiesel), a fossil fuel and their blends have been evaluated. The evaluation consisted of emissions ( $\text{NO}_x$  and CO), activation energy determination for the combustion process and the correlation between emissions and activation energy. Experiments have been conducted in an European Stationary Cycle test (ESC) using a OM 926 LA CONAMA P7/EURO 5, in which the pollutant was formed.

Results showed that there is a direct correlation between activation energy and  $\text{NO}_x$  emission for the biodiesel/diesel blend. However, when farnesane is added to diesel, a contrary behavior is observed, i.e., as the farnesane content increases, there is a lowering in both activation energy and  $\text{NO}_x$  emission.

The highest values for both  $\text{NO}_x$  and activation energy are obtained for pure biodiesel and the lowest values, for pure farnesane. According to the literature (Lin e Lin, 2007; Qi, Chen *et al.*, 2010; Varatharajan and Cheralathan, 2012) and CO decrease (Lin e Lin, 2007; Varatharajan and Cheralathan, 2012), the higher oxygen content in the molecular composition of the fuel, the higher combustion efficiency. This behavior leads an increasing of the temperature and, consequently, promoting  $\text{NO}_x$  formation.

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

In this case the difference among fuels is the presence of oxygen, on one hand biodiesel is an ester with oxygen in its molecular composition and on the other, farnesane and diesel are hydrocarbons without oxygen in their molecular composition. The presence of oxygen favors the complete combustion and, consequently, decreasing the CO formation.

#### 5. ACKNOWLEDGEMENTS

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