Brazilian Journal of Development

Emissions simulation by coupling chemical equilibrium and reduced kinetics for gasoline/ethanol mixture in IC engines

Simulação de emissões acoplando equilíbrio químico e cinética reduzida para mistura de gasolina / etanol em motores CI

DOI:10.34117/bjdv6n10-208

Recebimento dos originais: 05/09/2020
Aceitação para publicação: 09/10/2020

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ABSTRACT

The analysis of the combustion engine is one on which fails the thermodynamic equilibrium hypotheses since the variables and the system constants are fast changing with time therefore you need a special treatment for this situation. The chemical equilibrium thermodynamics indicates start and end of the process but doesn't reveal the time that the phenomenon occurs. The chemical kinetics has information on the time. The methodology of chemical equilibrium calculations was based on mass balances and equilibrium relations generating a nonlinear system with twenty-two incognita and twenty-two algebraic equations. To solve the nonlinear system, it was chosen an iterative method by Newton-Raphson associated with a new methodology for the determination of the initial estimative of the system avoiding the non-convergence of the system. It was possible to calculate the concentrations of twenty-one chemical species generated in the combustion of various fuels. It was made a comparison between the results from other softwares, finding compatible results for concentrations of emissions generated. After the validation of the chemical equilibrium routine, it was developed the chemical kinetics routine with six chemical equations for the prediction of species concentrations (NO and CO). A simulation of an IC engine was developed using the coupling of the methodology of chemical equilibrium and kinetics. In the engine simulation model developed, as the crank angle increases, it was done the integration of species chemical compositions with coupling chemical equilibrium and kinetics by derivatives addition. The resulting non-linear system with twenty-one differential equations was integrated by a fourth order Runge-Kutta method. Made some experiments on a Flex-Fuel engine with mixtures gasoline/ethanol: E25 (25% anhydrous ethanol), H30 (30% hydrous ethanol), H50 (50% hydrous ethanol), H80 (80% hydrous ethanol) and H100 (100% hydrous ethanol). The results obtained in the computer simulation of the engine were compatible with these experimental data.

Keywords: Mathematical modeling, emissions, ICE, chemical equilibrium, chemical kinetics.

RESUMO

A análise do motor de combustão é uma falha nas hipóteses de equilíbrio termodinâmico, uma vez que as variáveis e as constantes do sistema estão mudando rapidamente com o tempo, portanto, necessita-se um tratamento especial para esta situação. A termodinâmica do equilíbrio químico indica o início e o fim do processo, mas não revela o tempo em que o fenômeno ocorre. A cinética química informa sobre o tempo. A metodologia dos cálculos de equilíbrio químico baseou em balanços de massa e relações de equilíbrio, gerando um sistema não linear com 22 equações incógnitas e algébricas. Para resolver o sistema não linear, foi escolhido um método iterativo de Newton-Raphson associado a uma nova metodologia para a determinação da estimativa inicial do sistema, evitando a não convergência do sistema. Calculou as concentrações de 21 espécies químicas geradas na combustão de vários combustíveis. Realizou uma comparação entre os resultados de outros softwares, encontrando resultados compatíveis para as concentrações de emissões geradas. Após a validação da rotina de equilíbrio químico, foi desenvolvida a rotina de cinética química com seis equações químicas para a previsão das concentrações das espécies (NO e CO). A simulação do motor CI desenvolvido usou o acoplamento da metodologia de equilíbrio químico e cinética, à medida que o ângulo de manivela aumenta, realiza a integração das composições químicas das espécies com o acoplamento do equilíbrio químico e cinético por adição de derivadas. O sistema não linear resultante com 21 equações diferenciais foi integrado por um método de Runge-Kutta de quarta ordem. Foi feito alguns experimentos em um motor Flex-Fuel com misturas gasolina / etanol: E25 (25% etanol anidro), H30 (30% etanol hidratado), H50 (50% etanol hidratado), H80 (80% etanol hidratado) e H100 (100 % etanol hidratado). Os resultados obtidos na simulação computacional do mecanismo foram compatíveis com esses dados experimentais.

Palavras-chave: Modelagem matemática, emissões, CI, equilíbrio químico, cinética química.

1 INTRODUCTION

Currently one of the biggest challenges in modeling IC engine is the simulation of pollutant emissions. Despite the methodologies for chemical equilibrium calculations Ishkakova and Spilimbergo (2002) and Gordon and Mcbride (1971) and chemical kinetics Westbrook and collaborators (2008), there isn’t a computer code able to calculate with precision and robustness the emissions of internal combustion engines. In order to solve the system with several chemical reactions, more than three hundred, leads to some difficulties with the conventional numerical methods. Although there are several methods to solve the problem today, it is necessary to associate several of these to get not so good results. In this work, it was proposed a methodology of coupling in order to increase the level of accuracy with less computational effort as possible.

The approach only by chemical kinetics is complex and still there isn’t a representative kinetic mechanisms for commercial fuels such as gasoline, which can have more than 400 components (WESTBROOK *et. al*, 2002). The calculation only through the methodology of chemical kinetics (MIET *et. al*, 2009) system generates a greater number of reactions, which, without the support of chemical equilibrium, is very expensive computationally. Often in this case the use of super computers is necessary and there is the Stiffness instability that may occur in the solution of differential equations. The chemical equilibrium methodology employs the equilibrium constants of reactions chosen and mass balances for system modeling (FERGUSON, 2001) (MELO, MAGNANI, 2020). Another method consists in minimizing the Gibbs free energy of the species considered Gordon and Mcbride (1971), using the method of Lagrange multipliers for the numerical solution of the system. This methodology is used by software as CEA (NASA-SP-273) and GASEQ (MORELY, 2004). The western part of the world uses mainly this methodology and the eastern part uses the methodology of chemical equilibrium constants. As an example, the BOOST code allows the simulation of pollutant emissions in engine and uses chemical equilibrium model with decoupled chemical kinetics for prediction of pollutants. The computer program (BOOST, 2020) represents the state of the art in the simulation of emissions in internal combustion engines.

2 METHODOLOGY

This work consists of the development of computational routines to predict emissions in internal combustion engines based on the methodology of chemical equilibrium associated with a chemical kinetics. The mathematical modeling of chemical equilibrium was based on mass balances and equilibrium relations generating a nonlinear system with twenty-two incognita and twenty-two equations. To solve the nonlinear system it was chosen an iterative method by Newton-Raphson associated with a new methodology for the determination of the initial estimates of the system, avoiding the non-convergence of the system. The chemical reaction equation for a fuel of molar composition $C_\alpha H_\beta O_\Upsilon N_\delta$ with air and the equivalence ratio ϕ. The symbol ε represents the stoichiometric relation for the combustion reaction of ε moles of fuel for a mole of air (FERGUSON, 2001).

Table 1 shows the system non-linear equations obtained by chemical equilibrium methodology.

Table 1: System of non-linear equations of chemical equilibrium and mass balance relations.

Equations description	**Equations**
General combustion equation	$\varepsilon\phi C_\alpha H_\beta O_\Upsilon N_\delta+0{,}21O_2+0{,}79N_2 \rightarrow \eta_1 CO_2+\eta_2 H_20+\eta_3 N_2+\eta_4 O_2+\eta_5 CO+\eta_6 H_2+\eta_7 H+\eta_8 O+\eta_9 OH+\eta_{10} NO+\eta_{12} CH_4+\eta_{13} NH_3+\eta_{14} HCN+\eta_{15} CH_20+\eta_{16} N_20+\eta_{17} NO_2+\eta_{18} HO_2+\eta_{19} N+\eta_{20} NH_2+\eta_{21} HCO+\eta_{22} CN$
Molar fraction relaction	$\eta i = yi \,.\, Nmoles$
Carbon mass balance	$\varepsilon\phi\ \alpha = \sum_{nc=1}^{nc}(nC\ y_{nC}).Nmoles$
Hydrogen mass balance	$\varepsilon\phi\ \beta=\sum_{nH=1}^{nH}(nH\ y_{nH}).Nmoles$
Oxygen mass balance	$\varepsilon\ \phi\ \Upsilon+0.42 = \sum_{nO=1}^{nO}(nO\ y_{nO}).Nmoles$
Nitrogen mass balance	$\varepsilon\ \phi\ \delta + 1{,}58 = \sum_{nN=1}^{nN}(nN\ y_{nN}.).Nmoles$
$H_2 \leftrightarrows 2\,H$	$K_1{}^2 = \frac{y_7^2\ P}{y_6}$
$O_2 \leftrightarrows 2\,O$	$K_2^2 = \frac{y_8^2 P}{y4}$
$H_2+O_2 \leftrightarrows 2\,OH$	$K_3^2 = \frac{y_9^2}{y_4\ y_6}$
$O_2 + N_2 \leftrightarrows 2\,NO$	$K_4^2 = \frac{y_{10}^2}{y4\ y3}$
$H_2 + O_2 \leftrightarrows 2\,H_2O$	$K_5^2 = \frac{y_2^2}{y_6^2\, y4\, P}$

$2CO+O_2 \leftrightarrows 2\,CO_2$	$K_6^2 = \frac{y_1^2}{P\,y_5^2\,y_4}$
$CO+3H_2 \leftrightarrows CH_4+H_2O$	$K_7 = \frac{y_{12}\;y_2}{y_5\;y_6^3\,P^2}$
$N_2\;+3\,H_2 \leftrightarrows\;2\,NH_3$	$K_8^2 = \frac{y_{13}^2}{P^2\;y_3\;y_6^3}$
$NH_3+CH_4 \leftrightarrows HCN+3\,H_2$	$K_9 = \frac{P^2\,y_{14}\;y_6^3}{y_{13}\;y_{12}}$
$N_2O + OH \leftrightarrows N_2 + HO_2$	$K_{12} = \frac{y_{18}\;y_3}{y_{16}\;\;y_9}$
$HO_2 + NO \leftrightarrows NO_2 + OH$	$K_{13} = \frac{y_{17}\;\;y_9}{y_{18}\;\;y_{10}}$
$O + HO_2\;\leftrightarrows OH + O_2$	$K_{14} = \frac{y_4\;\;y_9}{y_8\;\;y_{18}}$
$N + NO\;\leftrightarrows N_2 + O$	$K_{15} = \frac{y_3\;\;y_8}{y_{19}\;\;y_{10}}$
$HCN+OH\;\leftrightarrows NH_2 + CO$	$K_{16} = \frac{y_{20}\;\;y_5}{y_{14}\;\;y_9}$
$CN + H_2O \leftrightarrows HCN + OH$	$K_{18} = \frac{y_{14}\;y_9}{y_{22}\;\;y_2}$
$H_2\;\leftrightarrows 2\,H$	${K_1}^2 = \frac{y_7^2\;P}{y_6}$

Source: (THE AUTHORS, 2020)

To solve the nonlinear system it was chosen an iterative method by Newton-Raphson. It was possible to calculate the concentrations of twenty-one chemical species generated by the combustion of various fuels as ethanol and gasoline, for a given pressure, temperature and fuel/air equivalence ratio. Other similar softwares performed the calculations by minimizing the Gibbs free energy, using the technique of Lagrange multipliers to avoid the initial value instabilities. In this new methodology the initial estimative was generated at a fixed fuel/air equivalence ratio (0.6), for a specified temperature (1500 K) and pressure (101325 Pa), and then, chemical equilibrium solutions were found at several increments of fuel/air equivalence ratios until one reaches the desired value of mixture ratio. After that, the temperature and pressure were changed until the desired values. This initialization procedure proved to be more robust and the extra computational costs were low related to Lagrange multipliers based methods.

After validation of chemical equilibrium routine it was developed the chemical kinetics routine, with six equations for the prediction of species concentrations (NO and CO).

Table 2 shows the velocity constants of chemical reactions for combustion species generations. These six equations were based in Zeldovich's mechanism and in the kinetics data found in literature (GRIMECH, 2010). The nitrogen monoxide (NO) and carbon monoxide (CO) species have slow velocity of conversion and it is not right to make calculations by chemical equilibrium methodology.

Table 2 - Velocity constants of chemical reactions of some combustion species generations.

Reactions	**Velocity constants of direct reactions ($cm^3/mol.s$)**	**Temperature range (K)**
$O + N_2 \leftrightarrows NO + N$	$7.6x10^{13}\ e^{-38000/T}$	300-5000
$N + O_2 \leftrightarrows NO + O$	$6.4x10^{9}\ e^{-3150/T}$	300-3000
$N + OH \leftrightarrows NO + H$	$4.1x10^{13}$	300-2500
$0NO_2 + O \leftrightarrows NO + O_2$	$3.9x10^{12}\ e^{240/RT}$	300-3000
$N + CO_2 \leftrightarrows NO + CO$	$3x10^{12}\ e^{-11300/RT}$	300-3000
$OH + CO \leftrightarrows H + CO_2$	$3x10^{12}\ e^{-11300/RT}$	300-3000

Source: (GRIMECH, 2010)

Methodology of coupling developed in this work used the theory of non-equilibrium chemical or chemical imbalance. For the analysis of the combustion engine, it is one on which the thermodynamic equilibrium hypotheses fails since the variables and the system constants are fast changing with time. Therefore, you need a special treatment for this situation. The chemical equilibrium thermodynamics indicates the start and the end of the process, but it does not reveal the time that the phenomenon occurs. The chemical kinetics has information on the time (SODRÉ, MORAIS, JUSTINO, 2011). It was reasoning to make the coupling between these two methodologies. In each small step of the engine, crankshaft angle has a new state of pressure, temperature and equivalence ratio which indicates the chemical equilibrium state. The chemical equilibrium would respond for each specific state of crank angle, but the phenomenon occurs rapidly and the species having slow kinetics, as nitrogen and carbon monoxide, are delayed to respond to an indication of the equilibrium. This is an accumulation or a consumption of these species generating a phase delay which is indicated by the chemical kinetics. Hence it is the coupling between the equilibrium chemical balance and chemical kinetics given by a differential equation representing the overall contribution of each model. Equation 5 was used to connect the chemical equilibrium and the kinetics chemical. Considering a single chemical reaction (Eq. 1), as example,

$$\mathrm{A} \quad \underset{k2}{\overset{k1}{\leftrightarrows}} \quad \mathrm{B} \tag{1}$$

$$\frac{d[A\ ]}{dt} = -(k1)\,.\,[A] + k2\,.\,[B] \tag{2}$$

In equilibrium,

$$\frac{d[A\ ]}{dt} = 0 \tag{3}$$

$$(k1)\,.\,[A] + k2\,.\,[B] = 0 \tag{4}$$

$$Keq = \frac{k1}{k2} = \frac{[B]}{[A]} \quad or \quad k1 = Keq\,.\,k2 \tag{5}$$

Differentiating (eq.5) is obta/ined (eq.6),

$$\frac{dk1}{dt} = (k2)\,.\,\frac{dKeq}{dt} \quad + \quad (Keq)\,\frac{dk2}{dt} \tag{6}$$

The differential equation proposed for the modeling of emissions used in this work is described by equations (7) and (8).

$$\frac{d[A]}{dt} = \frac{d[A]}{dt}\Big|_{equilibrium} + \frac{d[A]}{dt}\Big|_{kinetics} \tag{7}$$

$$\frac{dyi}{dt} = \frac{dyi}{dt}\Big|_{equilibrium} + \frac{dyi}{dt}\Big|_{kinetics} \tag{8}$$

The way to demonstrate the equations (7) and (8) would assume that they are analogous to equation (6). Therefore, each term of the equations eq. (6), eq. (7) and eq. (8) should be similar eq. (9,10,11).

$$\frac{dk1}{dt} = \frac{d[A]}{dt} \tag{9}$$

$$(k2)\,.\,\frac{dKeq}{dt} = \frac{d[A]|_{equilibrium}}{dt} \tag{10}$$

$$(Keq)\,\frac{dk2}{dt} = \frac{d[A]|_{kinetics}}{dt} \tag{11}$$

Substituting (eq.2) to (eq.11) leads to equations 12 and 13,

$$(Keq).\,\frac{dk2}{dt} = -\,(k1)\,.\,[A] + \,k2\,.\,[B] \tag{12}$$

$$\frac{dk2}{dt} = \frac{-\,(k1)\,.\,[A] + \,k2\,.\,[B]}{Keq} \tag{13}$$

Substituting eq. (2) to (11) into equations 12 and 13, gives equation 10 and leads to equations 14 and 15.

$$(k2)\,.\,\frac{dKeq}{dt} = \frac{d[A]|_{equilibrium}}{dt} \tag{10}$$

$$(k2)\,.\,\frac{dKeq}{dt} = \frac{[A_1\,] - [A_0\,]}{[t_1\,] - [t_0\,]}\,\Big|_{\substack{\text{derivative numerical}\\ \text{chemical equilibrium}}} \tag{14}$$

$$\frac{dKeq}{dt} = \frac{\frac{[A_{1(P,T,Ø)}\,] - [A_{0(P,T,Ø)}\,]}{[t_1\,] - [t_0\,]}}{k2} \tag{15}$$

Substituting (eq.13) to (eq.15) into equations 6, 12 and 13.

$$\frac{d[A]}{dt} = \frac{d[A]}{dt}\Big|_{equilibrium} + \frac{d[A]}{dt}\Big|_{kinetics} \tag{7}$$

Through a series of conversions by constant, equation 7 becomes the equation 8, ending the deduction.

$$\frac{dyi}{dt} = \frac{dyi}{dt}\Big|_{equilibrium} + \frac{dyi}{dt}\Big|_{kinetics} \qquad (8)$$

By analogy, the IC engine can be compared to an AC electrical power system that feeds a resistor and a capacitor. The analogy of the electrical system is interesting because of having a sinusoidal voltage source (AC) which is similar to movement of the piston in the cylinder. It is observed that the capacitor charges and it takes time to unload and a resistor controls the current flow. The phase delay is inevitable in this case, as it occurs in internal combustion engines on the distribution of species in the transient regime. In the case of the electrical system, modeling is done by the use of phasors to describe the phase delay and amplitude.

Chemical equilibrium would be analogous to the capacitor and the chemical kinetics analogous to resistor that controls the current flow.

Using the Kirchhoff's second rule for electrical systems AC power that feeds a resistor and a capacitor, was obtained equation 16 which is analogous to equation 8.

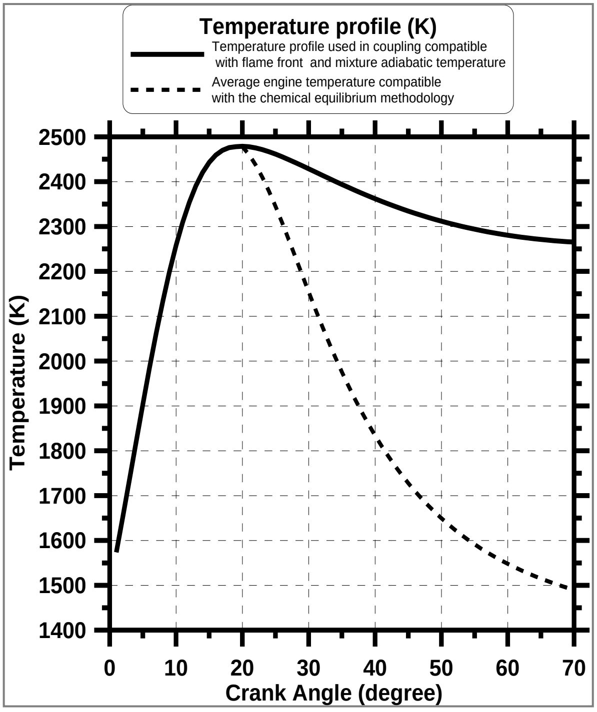
$$\frac{dV(t)}{dt} = \frac{dV}{dt}\Big|_{resistor} + \frac{dV}{dt}\Big|_{capacitor} \qquad (16)$$

$$\frac{dyi}{dt} = \frac{dyi}{dt}\Big|_{equilibrium} + \frac{dyi}{dt}\Big|_{kinetics} \qquad (8)$$

An IC engine simulation was developed from the coupling chemical equilibrium methodology with a kinetics. It is necessary that the user provides the curves relating to the operation of the engine: curve of pressure, temperature and equivalence ratio versus the crank angle described as least square fittings. The curve of pressure (FAN, LI, 2012), temperature (DRYER,2008) and equivalence ratio versus the crank angle using the least square fittings.

For this methodology of coupling it is used the temperature profile flame front compatible with the methodology of chemical kinetics in accordance with Figure 1.

Figure 1: Profile temperature used in IC engine simulation.



Source: (THE AUTHORS, 2020)

In the engine simulation developed, the crank angle increases in small steps. In which one, there is the calculation of species compositions with coupling chemical equilibrium and kinetics, by derivatives calculations that leads to a non-linear system with twenty-one differential equations (eq.8). These equations were integrated by a fourth order Runge-Kutta method.

$$\frac{dyi}{dt} = \frac{dyi}{dt}|_{equilibrium} + \frac{dyi}{dt}|_{kinetics} \qquad (8)$$

The derivative of chemical equilibrium are numerically calculated in small steps in function of the crankshaft angle, according to the equations 16 e 17.

$$\frac{dyi}{dt}|_{equilibrium} = \frac{[y_{1(P,T,\emptyset)}] - [y_{0(P,T,\emptyset)}]}{[t_1] - [t_0]} \qquad (16)$$

$$\frac{d[yi]}{dt} = \frac{d[yi]}{d\Theta} \cdot \frac{d\Theta}{dt} \quad or \quad \frac{d[yi]}{d\Theta} = \frac{\frac{d[yi]}{dt}}{\frac{d\Theta}{dt}} \qquad (17)$$

The kinetic derivatives were calculated according to the equations through of table 2.

$$\frac{d[NO]}{dt} = -(\text{k1f} + \text{k2f} + \text{k3f} + \text{k4f} + \text{k5f} - \text{k1r} - \text{k2r} - \text{k3r} - \text{k4r} - \text{k5r}) \qquad (18)$$

$$\frac{d[N]}{dt} - (\text{k1f} - \text{k2f} - \text{k3f} - \text{k1r} + \text{k2r} + \text{k3r} - \text{k5f} + \text{k5r}) \qquad (19)$$

$$\frac{d[N2]}{dt} = \ -(-\text{k1f} + \text{k1r}) \qquad (20)$$

$$\frac{d[O]}{dt} = \ -(\text{k1f} - \text{k4f} + \text{k1r} + \text{k2f} - \text{k2r}\ ) \qquad (21)$$

$$\frac{d[OH]}{dt} = -\ (\ \text{k3f} + \text{k3r} - \text{k6f} + \text{k6r}) \qquad (22)$$

$$\frac{d[O2]}{dt} = -\ (-\text{k2f} + \text{k4f} + \text{k2r} - \text{k4r}) \qquad (23)$$

$$\frac{d[H]}{dt} = -\ (\text{k3f} - \text{k3r} + \text{k6f} - \text{k6r}) \qquad (24)$$

$$\frac{d[NO2]}{dt} = -\ (-\text{k4f} + \text{k4r}) \qquad (25)$$

$$\frac{d[CO2]}{dt} = (-\text{k5f} + \text{k5r} + \text{k6f} - \text{k6r}) \qquad (26)$$

These kinetics constants in equations 18 at 26 are showed in equations 27 at 38.

$k1f = k1\ .\ [O]\ .\ [N_2]$ (27)

$k2f = k2\ .\ [N]\ .\ [O_2]\ )$ (28)

$k3f = k3\ .[N]\ \ .\ [OH]$ (29)

$k4f=\ \ k4\ \ .[NO_2).\ [O]$ (30)

$k5f=\ \ k5\ .\ [N]\ .\ [CO_2]$ (31)

$k6f=\ \ k6\ .\ [OH].\ [CO]$ (32)

$$k1r = (k1f / kp1) \cdot [N] \cdot [NO] \quad (33)$$

$$k2r = (k2f / kp2) \cdot [O] [NO] \quad (34)$$

$$k3r = (k3f / kp3) \cdot [H] \cdot [NO] \quad (35)$$

$$k4r = (k4f / kp4) \cdot [NO] [O] \quad (36)$$

$$k5r = (k5f / kp5) \cdot [NO] \cdot [CO] \quad (37)$$

2.1 EXPERIMENTAL

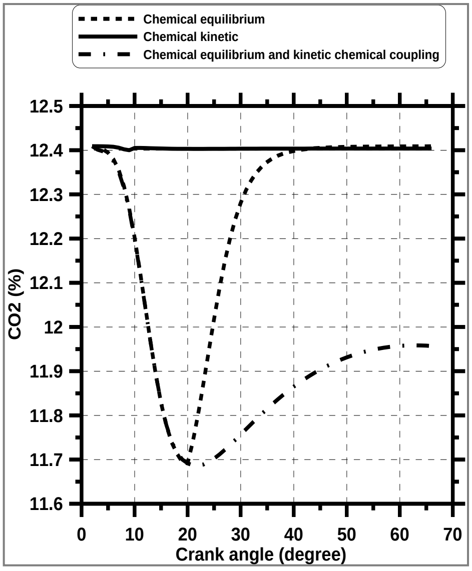
Melo (2010) made some experiments on a Flex-Fuel engine with mixtures of gasoline/ethanol, E25 (25% of anhydrous ethanol), H30 (30% of hydrous ethanol), H50 (50% of hydrous ethanol), H80 (80% of hydrous ethanol) and H100 (100% of hydrous ethanol).

A total of 3 different operational conditions were chosen based on the TETRA-FUEL FIAT FIRE engine, 1.4 L. Two intermediate speeds (2250 and 3875 rpm) and one low speed (1500 rpm) were chosen with a 60 Nm torque partial load stoichiometric condition. Before doing the experimental tests, it was necessary to adjust the MOTEC ECU for each different fuel to run with equivalence ratio equal to 1, similar to the original engine map. Brazilian Flex-Fuel vehicles work with equivalence ratio equal to 1 on most partial load operation to maximize the 3-way catalyst efficiency in order to reduce pollutant emissions. During the experiments ECU MOTEC was configured to work on a closed loop with constancy. For full charge, the setpoint for mixture was 1.11 to improve power generation. Previous tests were done to optimize spark timing for the Maximum Brake Torque (MBT) without knocking presence. MOTEC software has a screen for spark timing (°BTDC) versus torque (Nm) visualization. This feature allows spark timing optimization either visually or by calculating the angle for maximum torque, by using zero derivative of the parabola generated by fitting the torque and spark timing data. This procedure was repeated for each fuel at each different engine operating point. The emission data was measured by FTIR, without the catalyst bed, continuously for at least 120 s and the average data was calculated by the automation system. For other variables (fuel consumption, speed, torque, temperatures, etc.), 60 seconds data acquisition was done, at least 2 minutes after stabilization at the operating condition. Average values of each variable were saved by the automation system. Each fuel was tested four times on each operating point. Before changing fuels, a careful procedure was used to clean the fuel lines and other fuel devices (MELO,2010).

3 RESULTS AND DISCUSSION

The simulation previsions of species concentrations by chemical equilibrium methodology and equilibrium and kinetics coupling were showed in figures 2, 3 and 4.

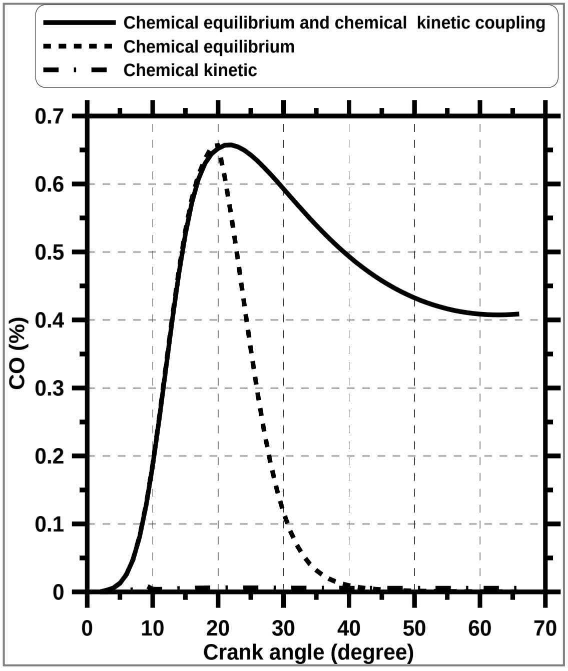
Figure 2: Results of simulation for carbon dioxide by chemical equilibrium, chemical kinetics and coupling.



Source: (THE AUTHORS, 2020)

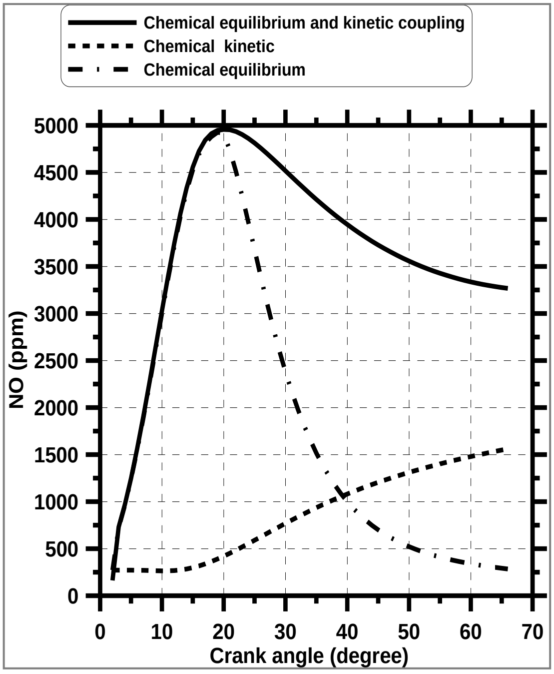
The engine simulation (Fig.2, 3,4) shows a considerable change in the prediction of species after the coupling of the methodology of chemical equilibrium with the chemical kinetics, with the coupling having a more realistic result.

Figure 3: Results of simulation for carbon monoxide by chemical equilibrium, chemical kinetics and coupling.



Source: (THE AUTHORS, 2020)

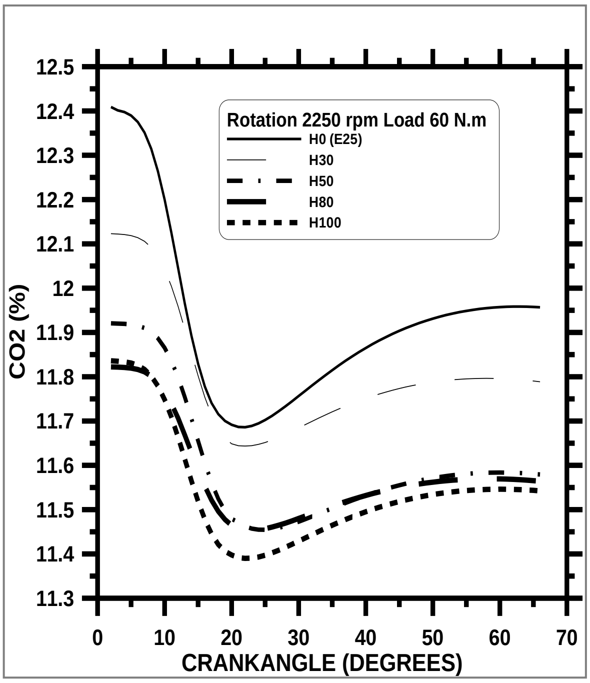
Figure 4: Results of simulation for nitrogen monoxide by chemical equilibrium, chemical kinetics and coupling.



Source: (THE AUTHORS, 2020)

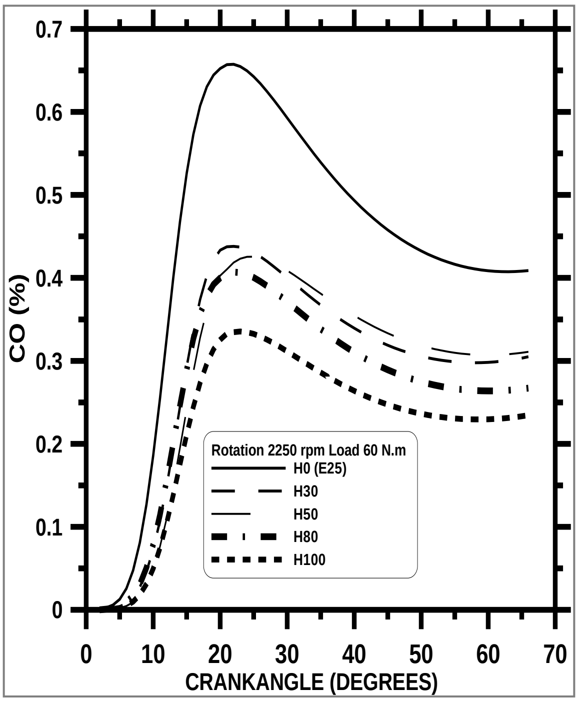
Figures 5, 6 and 7 show the results obtained by computational simulations for partial load engine 2250 rpm and load 60 N.m., for mixtures of gasoline/ethanol in transient regime.

Figure 5: Results of computational simulations for 2250 rpm, load 60 N.m, for carbon dioxide emission in transient regime.



Source: (THE AUTHORS, 2020)

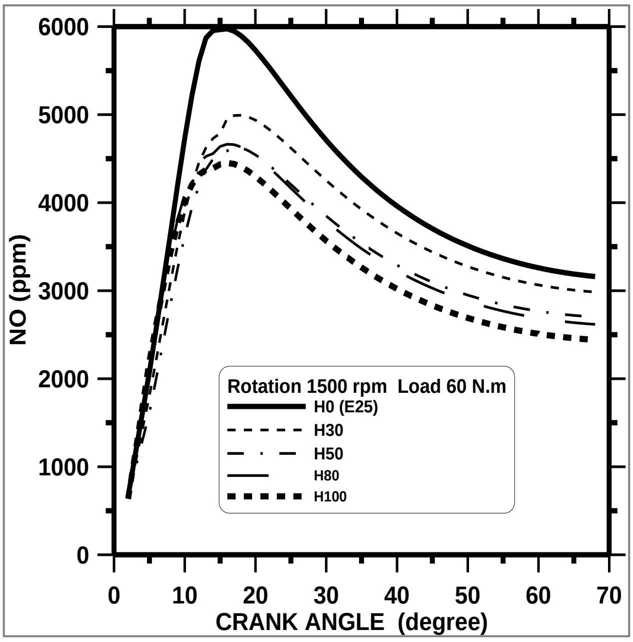
Figure 6: Results of computational simulations for 2250 rpm, load 60 N.m, for carbon monoxide emission in transient regime.



Source: (THE AUTHORS, 2020)

The figure 6 shows results nitrogen monooxide (NO*)* obtained by computational simulations of partial load engine conditions, 1500 rpm and load of 60 N.m., for mixtures of gasoline/ethanol in transient regime.

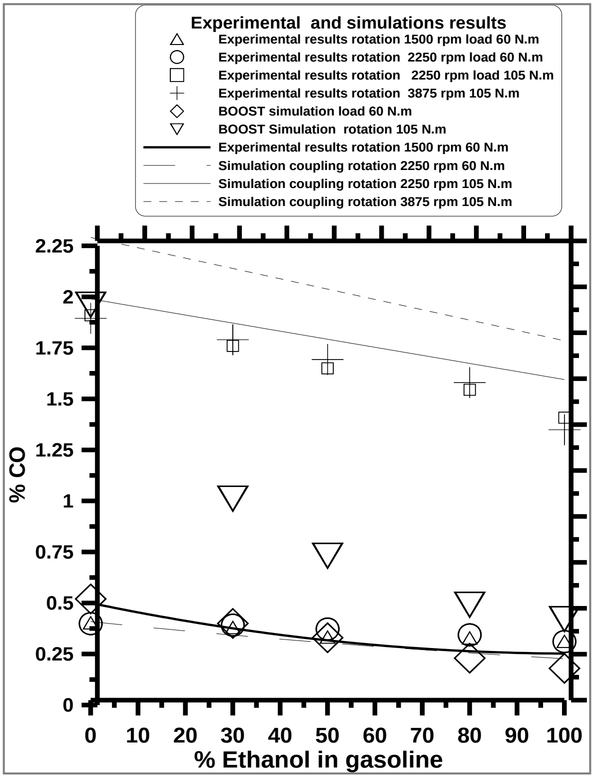
Figure 7: Results of computational simulations for 1500 rpm, load 60 N.m, for nitrogen oxides emissions in transient regime.



Source: (THE AUTHORS, 2020)

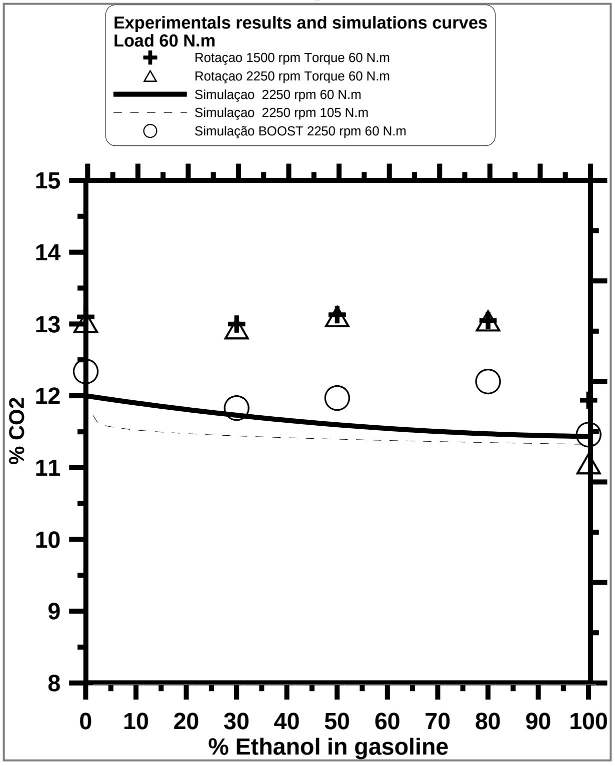
The figures 8, 9 and 10 shows experimental results (MELO, MACHADO, BELCHIOR, 2012) against simulations curves.

Figure 8: Simulations curves versus experimental results for carbon monoxide .



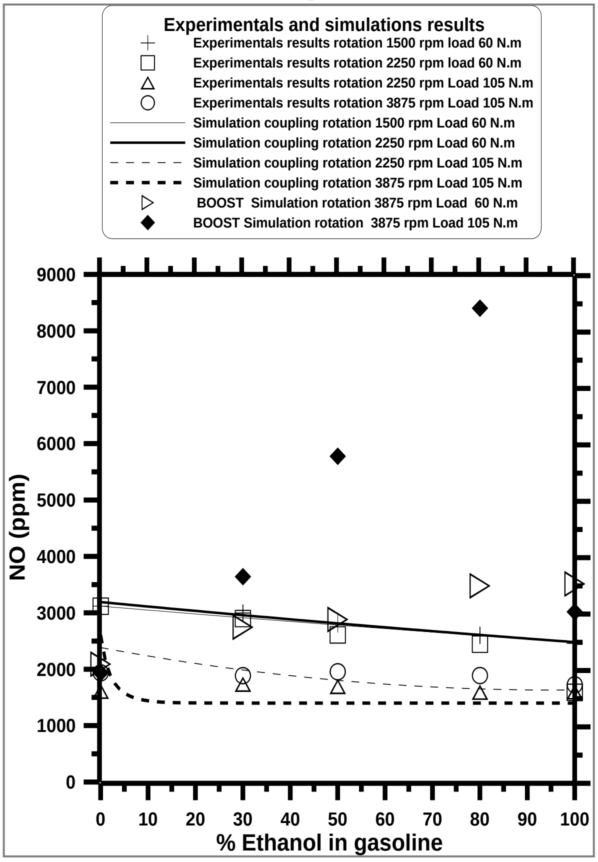
Source: (MELO, MACHADO, BELCHIOR, 2012)

Figure 9: Simulations curves versus experimental results for carbon dioxide .



Source: (MELO, MACHADO, BELCHIOR, 2012)

Figure 10: Simulation curves versus experimental results for nitrogen oxides.



Source: (MELO, MACHADO, BELCHIOR, 2012)

The routines development for prevision of species concentrations by chemical equilibrium coupling with kinetics has a more realistic result. The pollutants emissions decrease with the addition of ethanol. It was noted better settings for the simulation program developed in comparison with the experimental data than the simulations in software BOOST. The results obtained in the simulation were consistent with the values found in the literature that validates the computer model, despite the small differences (one percent). The analysis of the experimental results (MELO, MACHADO, BELCHIOR, 2012) of the compared simulations revealed good adjustments. The differences in results found can be explained by oscillations of equivalence ratio in transient regime, which can produce changes in the result of emissions and the retention of fuel in the gaps of the combustion chamber)(crevice) and the absorption of the fuel by the lubricant oil.

The emission of hydrocarbons cannot be predicted by the methodology of chemical equilibrium or chemical kinetic, requiring a third model which assesses the retention of fuel into the gaps of the combustion chamber (crevices) and the absorption of the fuel by the lubricant oil film (MELO, MACHADO, BELCHIOR, 2012).

4 CONCLUSIONS

The present work aimed to develop computational routines for the prediction of emissions in internal combustion engines through the coupling of the methodology of chemical equilibrium with the chemical kinetics and comparison of simulations obtained with the experimental results measured by ours research group (MELO, MACHADO, BELCHIOR, 2012).

The routine developed for prediction of species by the method of chemical equilibrium and compatible solutions presented in the same order of magnitude compared with the results of the literature. In the simulation engine in transient obtained a considerable change in the prediction of species after the coupling of chemical equilibrium with the chemical kinetics. The coupling has a more realistic result in accordance with the experimental data. According to the simulations and the experimental data obtained, it was revealed that the addition of ethanol in the gasoline reduces the emission of carbon monoxide and nitrogen compounds. The emission of carbon dioxide increased with addition of ethanol because there is a reduction in the emission of carbon monoxide. It was noted better settings for the simulation program developed in comparison with the experimental data than the simulations in software BOOST. The results obtained in the simulation were consistent with the values found in the literature that validates the computer model, despite the small differences found (one percent). The differences between the computer simulations and the experimental results as a whole can be explained by the variation in the fuel/air equivalence ratio in the transient regime. The engine simulation program developed with the methodology of chemical equilibrium coupled with reduced chemical kinetic model has the advantage of reducing /the simulation time compared to simulations that work with the full chemical kinetics model, calculating emissions with precision and robustness.

For future studies it might be suggested the coupling of routines developed into a complete engine simulation, with the inclusion of a routine for crevice and to the catalyst.

ACKNOWLEDGEMENTS

This work is a part of the research project PETROBRAS / UFMG No. 0050.0036569.07.4

REFERENCES

[1] BRAMLETTE, R. DEPCIK, C. “Review of propane-air chemical kinetic mechanisms for a unique jet propulsion application”. *Journal of the Energy Institute*, 2019. https://doi.org/10.1016/j.joei.2019.07.010

[2] BISWAL, A.; KALE, R.; TEJA, G.; BANERJEE, S.; KOLHE, P.; BALUSAMY, S. An experimental and kinetic modeling study of gasoline/lemon peel oil blends for PFI engine. *FUEL Elsevier*, 267, 2020. https://doi.org/10.1016/j.fuel.2020.117189

[3] CHANG.M, *et. Al*, "Effects of ambient temperature on firing behavior and unregulated emissions of spark-ignition methanol and liquefied petroleum gas/methanol engines during cold start", *FUEL Elsevier*,2012. https://doi.org/10.1016/j.fuel.2010.08.012

[4] CHEOLWOONG P, *et. al*, "Performance and exhaust mission characteristics of a spark ignition engine using ethanol and ethanol-reformed gas". *FUEL Elsevier,* 89 (2118–2125) Elsevier (2010) pp. 2118-2125. https://doi.org/10.1016/j.fuel.2010.03.018

[5] CHENG, C.S. *et. al*, "Diesel engine gaseous and particle Emissions fueled with diesel – oxygenate blends ", *FUEL Elsevier* 94 (317–323), 2012. https://doi.org/10.1016/j.fuel.2011.09.016

[6] CHU, H.; XIANG, L.; NIE, X.; YA, Y.; GU, M.; JIAQUIANG, E. "Laminar burning velocity and pollutant emissions of the gasoline components and its surrogate fuels: A review". *FUEL Elsevier*, 269, 2020. https://doi.org/10.1016/j.fuel.2020.117451

[7] DRYER, F. "Ignition of syngas/air and hydrogen/air mixtures at low temperatures and high pressures: Experimental data interpretation and kinetic modeling implications", *Combustion and Flame Elsevier* 152 (293–299) (2008). DOI: https://doi.org/10.1016/j.combustflame.2007.08.005

[8] TAN, PI. Q. HU, Z. Y. LOU, DI. M. "Regulated and unregulated emissions from a light-duty diesel engine with different sulfur content fuels", *FUEL Elsevier*, 1086–1091 (2009). https://doi.org/10.1016/j.fuel.2008.11.031

[9] DE-GANG LI, H. *et. al*, "Physico - chemical properties of ethanol–diesel blend fuel and its effect on performance and emissions of diesel engines" *Renewable Energy* 30 (967–976), 2005. https://doi.org/10.1016/j.renene.2004.07.010

[10] FAN.Q, LI. L, "Study on first-cycle combustion and emissions during cold start in a TSDI gasoline engine". *FUEL Elsevier*, 2012. https://doi.org/10.1016/j.fuel.2012.07.025

[11] FERGUSON C. "Internal combustion engines". Applied thermo sciences. New York: McGraw-Hill, 2001.

[12] KORRES, D. M. *et al.*, "Aviation fuel JP-5 and biodiesel on a diesel Engine", *FUEL Journal* 87 (70–78), Elsevier 2008. https://doi.org/10.1016/j.fuel.2007.04.004

[13] GARCIA, S. G. et. al. "Life cycle assessment of flax shives derived second generation ethanol fueled automobiles in Spain". *Renewable and Sustainable Energy Reviews*, 13 (2009) 1922–1933. https://doi.org/10.1016/j.rser.2009.02.003

[14] GORDON, S. and McBRIDE B. J. “NASA Computer Program for Calculation of Complex Chemical Equilibrium Composition, Rocket Perfomance , Incident and Reflected Shocks”, Jouguet Detonations NASA Lewis Research Center, 1971.

[15] GRIMECH; “ Thermodinamic data”, http://www.me.berkeley.edu/gri-mech, 2010.

[16] HEYWOOD, J. B.” Internal Combustion Fundamentals, Mc Graw-Hill , 1986.

[17] KANG, D. *et. al*, “Auto-ignition study of FACE gasoline and its surrogates at advanced IC engine conditions”. *Proceedings of the Combustion Institute*, v. 0, p. 1-9, 2018. https://doi.org/10.1016/j.proci.2018.08.053

[18] MIET, K., *et. al*, “Heterogeneous reactivity of pyrene and 1- nitropyrene with NO2: Kinetics, product yields and mechanism”. *Atmospheric Environment* 43 837–843 Elsevier 2009. https://doi.org/10.1016/j.atmosenv.2008.10.041

[19] ISHKAKOVA. R, SPILIMBERGO, A. P. “Modelagem computacional de processos em equilíbrio químico FORTRAN 90”. IX Congresso Brasileiro de engenharia e ciências térmicas, 2002.

[20] MELO, T.C.C. “Experimental investigation of different hydrous ethanol-gasoline blends on a flex fuel Engine”, *SAE International Technical Papers*, 2010. https://doi.org/10.4271/2010-36-0469

[21] MELO, T.C.C., MACHADO, G. B., BELCHIOR, “Hydrous Ethanol-Gasoline Blends: Combustion and Emission Investigations on a Flex-Fuel”, *FUEL Elsevier*, 2012. http://dx.doi.org/10.1016/j.fuel.2012.03.018

[22] MELO, R. A. P. de., MAGNANI, F. S., “Modelo cinético para estimativa de poluentes do ar em motores de combustão interna”, *Brazilian Journal of Development*, 2020, v. 6, n.5, p.27982-28005. https://doi.org/10.34117/bjdv6n5-300

[23] MORELY.C., “Chemical Equilibrium Package for Windows”. Measurements of Exhaust Hydrocarbons from a SI Engine, *SAE Technical Paper* 1997- 971016, 2004. http://www.gaseq.co.uk/

[24] MUSTAFA, K., et. al. “The effects of ethanol–unleaded gasoline blends on engine performance and exhaust emissions in a spark-ignition engine”, *Renewable Energy*, 34 (2101–2106), 2009. https://doi.org/10.1016/j.renene.2009.01.018

[25] SOFTWARE BOOST AVL “Advanced Simulations Technologies”. https://www.avl.com/boost

[26] SODRÉ, J. R., 2000, “Modelling NOx emissions from spark-ignition engines”, Proceedings of the Institution of Mechanical Engineers; 214, 8; *Proquest Science Journals*; pp. 929, 2000. https://doi.org/10.1177/095440700021400811

[27] SODRÉ, J. R., MORAIS, A. M., JUSTINO, A. M. A., 2011, “Simulação numérica de um motor diesel operando com hidrogênio como combustível”, *SAE Technical Paper* 2011-36-0053, 2011.

[28] SODRÉ, J.R., YATES D.A, "Species and Time Resolved Measurements of Exhaust Hydrocarbons from a SI Engine", *SAE Technical Paper,* 1997- 971016, 1997.

[29] USLU, S.; BAHATTIN, M.; CELIK, B. "Performance and Exhaust Emission Prediction of a SI Engine Fueled with Iamyl Alcohol-Gasoline Blends: An ANN Coupled RSM Based Optimization.". *FUEL Elsevier*, 265, 2020. https://doi.org/10.1016/j.fuel.2019.116922

[30] WESTBROOK C.K., *et. al*, "A comprehensive modeling study of iso-octane oxidation", *Combustion and Flame* 129:253–280, 2002. https://doi.org/10.1016/S0010-2180(01)00373-X

[31] WESTBROOK C.K, *et. al*, "Detailed chemical kinetic oxidation mechanism for a biodiesel urrogate",Combustion and Flame 154, 507–528, 2008. https://doi.org/10.1016/j.combustflame.2009.10.013

[32] ZHUKOV,V P., SECHENOV, V. A., STARIKOVSKII , A. Y. "Autoignition of n-decane at high pressure", Combustion and Flame 153 (2008) 130–136. https://doi.org/10.1016/j.combustflame.2007.09.006