MODELING AND SIMULATION OF COMPRESSION-IGNITION INTERNAL COMBUSTION ENGINES' EMISSIONS PRODUCED BY DIESEL AND BIODIESEL MIXTURES

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ABSTRACT

Biofuels have been identified as possible solutions to the problems caused by the usage of fossil fuels in energy production. Although they generally produce fewer emissions, there are indications that engines powered with biodiesel mixtures emit pollutants such as nitrogen oxides in greater quantities than when powered by fossil diesel. So, further investigation on the emissions produced by these two fuels is needed, with the goal of best knowing what kind of harm to the environment each one of those is causing. One of the best tools available for expanding any subject's comprehension, without spending lots of resources, are mathematical models. In order to better understand the relations between the fuel used to power a compression-ignition internal combustion engine (ICO) and the emissions produced as subproducts of the thermodynamic process, this paper aims at developing a mathematical model of the production of emissions according to the fuel mixture used. The main goal is to develop a simple model, from the point of view of chemical kinetics, but with the support of well-collected experimental data, and methods of mathematical model adjustments and validations, to make the model describe the reality of the phenomena with satisfactory precision. This Mathematical Model is completely implemented using FORTRAN® Language. There are 2 sorts of data: one used to calibrate and adjust the model's constants so the model can properly describe the reality of the events, and the other as the basis of comparison for the validation of the model after adjustments and calibrations. With this work, it is expected that the knowledge about how the use of these fuels impact global emissions, and how it is possible to optimize our energy production by using the best mixture of fuels at the optimal point between net power outtake and net emissions produced.

Keywords: compression-ignition; internal combustion engine; biofuels; emissions; mathematical modelling.

NOMENCLATURE

a	combustion reaction coefficient related to air
b	combustion reaction coefficient related to carbon
c	combustion reaction coefficient related to water
E	Element set composed by: O_2, CO, CO_2, N_2, NO_x
B11	Diesel fuel with 11% of Biodiesel
B25	Diesel fuel with 25% of Biodiesel
B50	Diesel fuel with 50% of Biodiesel
B75	Diesel fuel with 75% of Biodiesel
B100	Fuel with 100% of Biodiesel
W_j	Weight vector
$c_{exp,j}$	Experimental results
$c_{t,j}$	Theoretical results
k_i	Kinetic constants vector

Greek symbols

λ	excessive air ratio
δ	number of carbon atoms in biodiesel molecule
ζ	number of hydrogen atoms in biodiesel molecule.
ξ	number of oxygen atoms in biodiesel molecule
α	number of carbon atoms in diesel molecule
β	number of hydrogen atoms in diesel molecule

Subscripts

exp	experimental
t	theoretical
j	weight vector index
i	kinetic constant vector index

INTRODUCTION

Technological development is highly related to the increase in energy consumption. (Ritchie & Roser, 2014), showed through two sorts of data that this relation is likely to be truthful. The first, a historical series of the global primary energy consumption, starting in 1800, very close to the beginning of the Industrial Revolution shows that our energy consumption went from less than 10,000 TWh per year to more than 140,000 TWh per year, with the greatest increase on the growth happening around 1950s when the annual consumption was something near 30,000 TWh. In other words, the yearly consumption tripled in 150 years (1800 - 1950), and then, more than quadruplicated in the last 70 years (1950 – 2018), which gives us a yearly increase almost 12 times higher in the latter period (around 130 TWh/year from 1800 to 1950 vs 1500 TWh/year from 1950 to 2018).

Other valuable information made available in this study about energy is that the increase in energy use is mainly given by the increase of non-renewable and pollutant emissions producers' sources, like Oil, Coal, and Natural Gas. So, we are increasing our energy use, and the preference, in terms of energy source, seems to be the traditional sources against the renewables.

The second set of data tells us about the current energy consumption related to the GDP comparing countries considered well-developed with not so well-developed ones. Countries like Australia and Sweden, that the GDP per capita is around $45,000.00 have energy consumption at levels of 60.000kWh per capita. Other countries, like Chile and Turkey, that have a GDP near to $25,000.00 per capita, show an energy use of around 20,000kWh per capita. The majority of the high energy-consuming countries are located in Europe and almost all of the countries in the lower consumer section of the chart are sub-Saharan African countries.

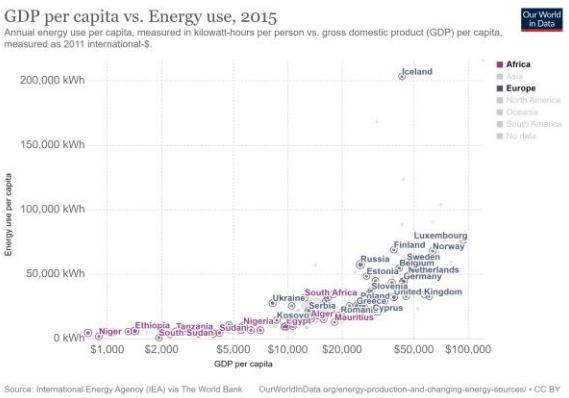


Figure 1: Comparison between GDP and energy consumption. In blue, the European countries are shown. In purple, the African . Source: (Our World In Data, 2020)

So, we can say that: energy consumption is and will keep growing as long as we keep developing ourselves into a better society, not only in technological ways.

However, the increase in energy usage does not only bring development with it. It is known that most of the energy production means have a bad counterpart attached. Almost all the energy sources commonly used by the human species have some kind of environmental impact in the process. Even the most environmentally friendly sources as wind and hydroelectric power are related to severe impacts as the death of animals by the wind turbine and the soil floods needed to build a hydroelectric power plant.

The main target of the researchers that aim to maintain the increase in energy production and consumption but in a sustainable way is fossil fuels as an energy source. They are being pointed as the greatest enemies of environmental health and stability, as they are correlated with the increase in atmospheric concentrations of gases that contribute to the increase in global temperature averages, or the greenhouse gases, as CO_2 and CO, CH_4 and nitrogen oxides or NO_x. As pointed by (Ritchie & Roser, 2017), electricity and heat productions are the main responsible for the production of greenhouse gases

With this set of information, it is possible to affirm that there is a need to further research in ways to keep increasing the energy production but ally with the reduction of the greenhouse gases emissions or the environmental impact that this particular energy source may cause. Thinking through these paths, the presented paper has the aspiration of studying the production of CO, CO_2 and NO_x in the process of production of energy in internal combustion engines driven by different diesel-biodiesel mixtures, so we have a better understanding of how the engine features and the fuel mixture influence on the amount of emissions produced, in order to be able to reduce these emissions in this specific process. The study is a mathematical model of the chemical reaction of the combustion process that happens in the interior of the engine, based only on the fuel mixture, and the engine load as inputs, resulting in the concentrations of the emissions previously mentioned produced by this process.

METHODOLOGY

Kinetical Model

To build the mathematical model of the emissions' production, a kinetic approach was chosen. It was decided to face the problem as a consumption–production situation. So, as we have a combustion process, and an extra process of

production of nitrogen oxides, the model consists of 7 equations:

1. An equation for the consumption of (D) diesel ($C_{12}H_{23}$);
2. An equation for the consumption of (BD) biodiesel ($C_{20}H_{36}O_2$);
3. An equation for the consumption of oxygen (O_2);
4. An equation for the consumption of nitrogen (N_2);
5. An equation for the production/consumption of carbon monoxide (CO);
6. An equation for the production of carbon dioxide (CO_2); and
7. An equation for the production of nitrogen oxides (NO_x) .

These 7 equations were written as:

$$\frac{d[D]}{dt} = -k_1[D][O_2] \quad (1)$$

$$\frac{d[BD]}{dt} = -k_2[BD][O_2] \quad (2)$$

$$\frac{d[O_2]}{dt} = -k_3[D][O_2] - k_4[BD][O_2] - k_5[CO][O_2] - k_6[N_2][O_2] \quad (3)$$

$$\frac{d[N_2]}{dt} = -k_7[N_2][O_2] \quad (4)$$

$$\frac{d[CO]}{dt} = k_8[D][O_2] + k_9[BD][O_2] - k_{10}[CO][O_2] \quad (5)$$

$$\frac{d[CO_2]}{dt} = k_{11}[D][O_2] + k_{12}[BD][O_2] + k_{13}[CO][O_2] \quad (6)$$

$$\frac{d[NO_x]}{dt} = k_{14}[N_2][O_2] + k_{15}[BD][O_2] \quad (7)$$

Where $[D]$ is the concentration of diesel in the system, $[BD]$ the concentration of biodiesel, $[E]$ are the concentration of the elements $E=\{O_2, CO, CO_2, N_2, NO_x\}$ and k_i, $i=\{1,2,3,4,5,6,7,8,9,10,11,12,13,14,15\}$ are the kinetics constants referent to that pair of elements' interactions. Like in eq. 4, k_7 is the kinetic constant linked to the interaction of N_2 and O_2 to consume, in this particular system, N_2. So, the constant will be an indicator of how intense these two compounds interact to consume N_2.

With these equations stated, the goal is to determine the values of the 15 kinetic constants presented on this simplified model. Five sets of data were chosen to serve as guidance for the adjustment of the model. These data were collected by (Matiolo et al., 2020) in an MWM D229 diesel engine. The chosen data were five different diesel-biodiesel mixtures all in one engine load, 24kW, which represents 55% of the engine maximum load capacity. The mixtures were 11% of biodiesel, 25%, 50%, 75%, and finally 100% of biodiesel. As the operational rotation of the referred diesel engine is known to be 1800 RPM, and the engine needs two cycles to complete a thermodynamic cycle, the fuel consumption was taken from kg/h to grams/cycle. In this way, the model will be set to estimate the mean emissions production per cycle of the engine thermodynamic process.

Numerical Method

To numerically solve the system, a Runge-Kutta-Fehlberg method ((Kincaid & Chaney, 2002)) was used. The initial conditions for the system are the main inputs of the model. Here, the measurement of fuel consumption in (Matiolo et al., 2020) was the source for the initial fuel quantities. For the nitrogen and oxygen availability, the stoichiometric proportion for the combustion reaction was used. The reaction was modeled by (Graciano et al., 2016) as

$$yC_\delta H_\zeta O_\xi + (1-y)C_\alpha H_\beta + \lambda a(O_2 + 3{,}76N_2) \rightarrow bCO_2 + cH_2O + 3{,}76\lambda aN_2 + (\lambda-1)aO_2 \quad (8)$$

where y represents the molar biodiesel fraction on the mixture, λ is the excessive air ratio (quotient between real and stoichiometric air-fuel ratios), δ, ζ and ξ are the numbers of carbon, hydrogen, and oxygen on the biodiesel molecule, respectively; α and β, the numbers of carbon and hydrogen on the diesel molecule; and a, b and c, the balanced coefficients in the combustion reaction. The excessive air ratio is where the engine load is taken into consideration and its values were measured in Matiolo et al. (2020) experiments. The composition of both biodiesel and diesel was simplified in the same manner as it was done in (Graciano et al., 2016), being $C_{20}H_{36}O_2$ and $C_{12}H_{23}$, respectively.

As in the combustion reaction equation, the molar fraction is used, and in (Matiolo et al., 2020) experiments, the fuel mixture is done relatively to fuel mass and the molecules of diesel and biodiesel have different molecular weights, a relation had to be

done, so the coefficient y truly represents the desired mixture. For a B11 mixture, for example, the molar fraction y that will give the 11% in mass of biodiesel is around 0.0628. All the molar fractions relative to the mixtures are listed in Table 1.

Table 1: Relation between biodiesel's mass percentage and molar fraction in fuel mixture

Fuel mixture in mass (%)	Biodiesel Molar Fraction (y)
B11	0.062821931
B25	0.153107465
B50	0.351648541
B75	0.619369708
B100	1.000000000

In order to evaluate precisely, all the conditions (except the excessive air ratio) were made dimensionless, relative to the fuel consumption per cycle of the engine. Here, it is possible to know the fuel consumption per cycle, the excessive air ratio (experimental), the molecular composition of the fuel, and the initial values of oxygen and nitrogen (theoretical), for all fuel mixtures. With this specific data, we are able to set the initial conditions for our model: the initial amount of fuel, and the composition of the mixture; and the initial amount of oxygen and nitrogen. The initial quantities of the emissions are set as null.

Constants Obtainment and Error Minimization

The next and greatest challenge is to determine the values of the 15 kinetic constants presented on the mathematical model. For this, a Nelder-Mead Simplex Method (Nelder & Mead, 1965)(Wright, 2012)(Luersen & Le Riche, 2004) was chosen to numerically minimize the error function between the theoretical value obtained by the model and the experimental data collected. The algorithm that was implemented in FORTRAN® was written by O'Neill, 1971. In other words, the Nelder-Mead Method minimizes the squared error function, while this is defined by:

$$\sum_{j=1}^{6} W_j (c_{exp,j} - c_{t,j})^2 \qquad (9)$$

in which c_t are the results of the kinetic model, and c_{exp} are the collected experimental data referent to the result j:

Table 2: Squared errors functions' Index

j	RESULT	j	RESULT
1	Produced CO	4	Consumed Diesel
2	Produced CO_2	5	Consumed Biodiesel
3	Produced NO_x	6	Mass Conservation of the system

and the expected results are: The experimental data collected by Matiolo et al., 2020, for the emissions productions (Eq. 9.1, 9.2, and 9.3); the Diesel and Biodiesel to be completely consumed (Eq. 9.4 and 9.5), and the sum of all masses at the beginning (Fuel mixture, Nitrogen, and Oxygen), to be the same as in the end (produced emissions, remaining oxygen, nitrogen, and residual fuel) (Eq. 9.6).

The vector is a weight vector so we can control the impact of each error function in the final error, giving us a tool to point the algorithm efforts into a better results direction.

The convergence point was determined by a fixed number of interactions. The best results were extracted after 20,000 interactions. After reaching the convergence point, the algorithm delivered the best kinetic constants available within the set of initial conditions.

Table 3: Example of weight vector used on squared error function.

j	W_i
1	1×10^{9}
2	1×10^{4}
3	1×10^{9}
4	1×10^{2}
5	1×10^{2}
6	1×10^{2}

RESULTS AND DISCUSSION

After several attempts to properly balance the weight vector in order to the model produce physically acceptable results, the best combination was found to be as shown in Table 4. This combination produced, after the previously set 20.000 interaction, the set of kinetic constants k_i exposed in Table 5.

Some observations of the constants. k_5 and k_{15}, in special, have values extremally small, in the order of 10^{-69} and 10^{-27} respectively. These constants are representing the consumption of O_2 in the interaction with CO to produce CO_2, and the influence of

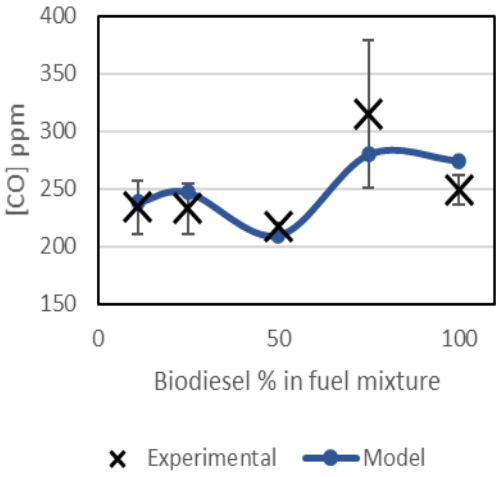
biodiesel (BD) in the production of NO_x. It is curious to notice that, especially the value of k_{15}, if we take into account that one of the main discussions around the environmental benefits in using biodiesel (BD) in ICO engines is about the possibility of the increase in NO_x emission levels, due to the presence of oxygen in biodiesel molecule, leading to increased availability of oxygen in the combustion chamber, acting in favor of NO_x formation. With the present experimental dataset, the influence of biodiesel content in fuel in nitrogen oxides emission levels is found as irrelevant.

With the constants determined, it was possible to solve numerically the chemical model proposed by Eq 1-7. The solution resulted in the concentration of each emission produced in every one of the five proposed scenarios, which were each one of the five fuel mixtures: B11, B25, B50, B75. All the results combined are exposed in Figure 2 and Figure 3.

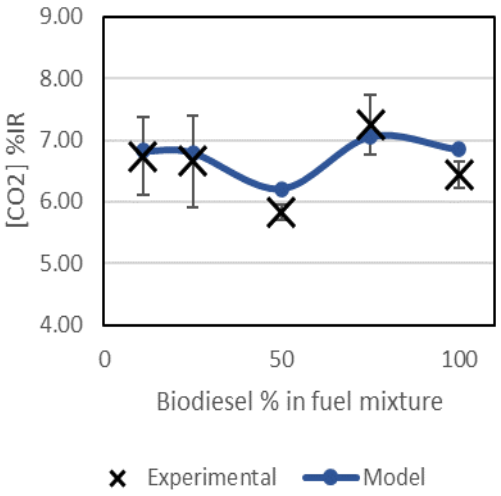
Table 4: Combination of weights that produced the best results after 20,000 interactions.

j	W_i
1	1×10^{9}
2	1×10^{4}
3	1×10^{9}
4	1×10^{2}
5	1×10^{2}
6	1×10^{4}

In Figure 2, the first graph "2.a" shows the comparison of the concentration of carbon monoxide ($[CO]$) in ppm measured by Matiolo et al., 2020 and the results obtained by the model proposed. The outline produced by the model's results seems to indicate a trend very close to the real concentrations. The greatest errors found for this particular emission were in B75 and B100, being 11.1% and 10,3%, only the second laying outside the measurement uncertainty. The second graph "2.b" is the comparison between the experimental and calculated data of the carbon dioxide ($[CO_2]$) concentration measured in %IR. These results show an excellent estimated profile calculated by the model, with only B50 and B100 having results outside the measurement uncertainty, with both presenting errors of 6.5% between the model result and the experimental measurement.



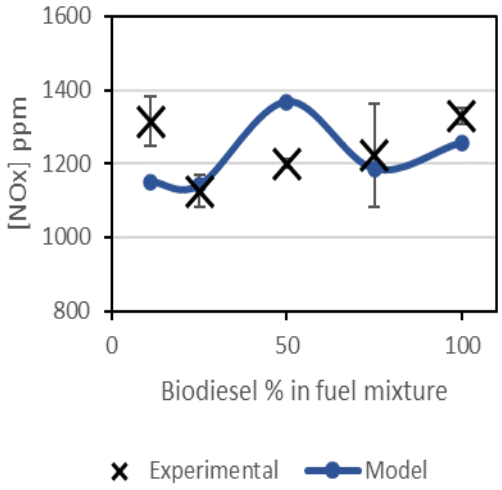
a)



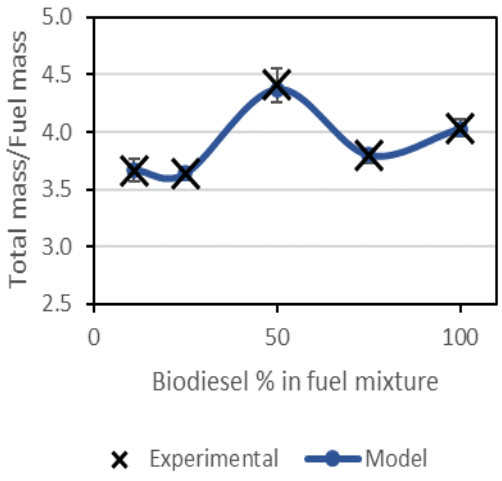
b)

Figure 2: Emissions produced by different fuel mixtures. Experimental and Modelled data comparison: a) CO (ppm) and b) CO2 (%IR).

In Figure 3 the graph "3.a" exposes the comparison between model results and experimental data of the nitrogen dioxides concentrations ($[NO_x]$). The most relevant errors are noted on B11 and B50, with modules of 12.5% and 14% respectively. These two, together with the B100 result, are the ones outside the measurement uncertainty, although the B100 error is significantly minor, being only 5.5%. The profile shows a slightly different behavior compared to experimental data, but the results are acceptable. Graph "3.b", shows the dimensionless mass (total mass and fuel mass quotient) conservation. These results demonstrated no error greater than 1%, bringing a physically strong argument in favor of the reliability of the model.



a)



b)

Figure 3: a) NOx produced by different fuel mixtures. Experimental and Modelled data comparison. b) Mass Conservation comparison. Experimental and Modelled data comparison.

The average error of the results was found to be 4.48%, including the mass conservation. The emissions average error was found as 5.89%, excluding the mass conservation.

Finally, the model, even with great simplifications, considering that combustion processes are one of the most complex kinds of reactions and that the model tangled the production and consumption of 7 species of compounds. Even with some punctual errors the global results are considered very promising, considering the complexity of the model's nature, depending on the numerical adjustment of fifteen chemical constants, and with a data set presenting a non-intuitive behavior.

Table 5: Set of kinetic constants found by the Nelder-Mead Simplex Algorithm (O'Neill, 1971)

i	$\mathbf{k_i}$
k_1	8.0449×10^{0} **s^{-1}**
k_2	9.5554×10^{0} **s^{-1}**
k_3	1.5242×10^{-1} **s^{-1}**
k_4	1.5205×10^{-1} **s^{-1}**
k_5	1.0324×10^{-69} **s^{-1}**
k_6	6.5670×10^{-2} **s^{-1}**
k_7	4.5025×10^{-6} **s^{-1}**
k_8	1.0112×10^{-1} **s^{-1}**
k_9	1.5205×10^{-1} **s^{-1}**
k_{10}	8.3924×10^{-1} **s^{-1}**
k_{11}	16.6129×10^{0} **s^{-1}**
k_{12}	19.1227×10^{0} **s^{-1}**
k_{13}	19.9936×10^{0} **s^{-1}**
k_{14}	2.0471×10^{-3} **s^{-1}**
k_{15}	1.6653×10^{-27} **s^{-1}**

REFERENCES

Graciano, V., Vargas, J. V. C., & Ordonez, J. C. (2016). Modeling and simulation of diesel, biodiesel and biogas mixtures driven compression ignition internal combustion engines, International Journal of Energy Research, 2. https://doi.org/10.1002/er.3286

Kincaid, D., & Chaney, W. (2002). Numerical Analysis: Mathematics of Scientific Computing - David Ronald Kincaid, Elliott Ward Cheney (3rd ed.).

Luersen, M. A., & Le Riche, R. (2004). Globali zed nelder-mead method for engineering optimization. Computers and Structures, 82(23–26), 2251-2260. https://doi.org/10.1016/j.compstruc.2004 .03.072

Matiolo, C. H., Vargas, J. V. C., Mariano, A. B., Martins, L., Oliveira, A., Jacob Furlan, B., Barbosa, J. P. W. & Kollross, E. C. (2020). Evaluation of Performance and Emissions of Genset with Diesel / Biodiesel. https://doi.org/10.26678/abcm.encit2020. cit20-0790

Nelder, J. A., & Mead, R. (1965). A Simplex Method for Function Minimization. The Computer Journal, 7(4), 308–313. https://doi.org/10.1093/comjnl/7.4.308

O'Neill, R. (1971). Algorithm AS 47: Function Minimization Using a Simplex Procedure. Applied Statistics, 20(3), 338. https://doi.org/10.2307/2346772

Our World In Data. (2020). GDP per capita vs. Energy use, 2015. https://ourworldindata.org/grapher/energy-use-per-capita-vs-gdp-per-capita?minPopulationFilter=1000000

Ritchie, H., & Roser, M. (2014). Energy - Our World in Data. OurWorldInData.Org. https://ourworldindata.org/energy#citation%0Ahttps://ourworldindata.org/energy

Ritchie, H., & Roser, M. (2017). CO_2 and Greenhouse Gas Emissions - Our World in Data. OurWorldInData.Org. https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions

Wright, M. H. (2012). Nelder, Mead, and the Other Simplex Method. Documenta Mathematica, I(Extra Volume: Optimization Stories), 271–276. http://math.uiuc.edu/documenta/vol-ismp/42_wright-margaret.pdf