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Kinetic Study in the Production of Aeronautical FAME

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Kinetic parameters correlation is fundamental in biodiesel production, operation, and design. In this work, a MATLAB® application was developed to correlate kinetic parameters in the biodiesel production from palm kernel oil. The functions *fminsearc*h, *fmincon*, and *genetic algorithm* were employed to correlate energies, frequency factors, and reaction order. The tool was validated with experimental results reported in the literature. The correlated parameters with the genetic algorithm function show the most accurate result, it did not require initial estimation for the correlation process, and the convergence process did not stop a wrong local optimum, without losing the fundamental objective of this article, which is to facilitate the correlation of kinetic parameters.

1. Introduction

Since the beginning of industrialization, the average monthly concentration of atmospheric CO2 has increased from 336 ppm to 410 ppm between 1980 and 2019, and the main cause is the use of fossil fuels, coal, and natural gas (US Department of Commerce, 2020). Several countries have signed agreements, like the one in Paris in 2015, to promote the use of more sustainable technologies that keep the increase in global temperature below 2 °C and CO2 emissions below 450 ppm (Basha et al., 2009).
Biofuels are emerging as an alternative to reduce CO2 emissions and partially replace fossil fuels. Biofuels have been applied mainly in the automotive industry. Still, they can also be applied in the aeronautical industry, where it is forecast that the consumption of biofuels will be around 31 Mtoe (Million tons of oil equivalent) by the year 2030, according to the IEA (2020).
Commercial kerosene consumption (JET A1) is 200 Mtoe and is projected to increase 4.5% by 2050 in the aviation sector. The aviation industry is considered one of the most significant contributors of CO2 in the atmosphere, responsible for emitting 2% of gas emissions (IATA, 2013). Therefore, the airline associations together with the IATA seek to mitigate CO2 emissions by developing new technologies such as the mixtures between Jet A1 and fatty acid methyl esters (FAME) from short-chain vegetable oils, such as oil coconut, palm kernel, and babassu (Ranucci et al., 2018). Some authors have evaluated the partial replacement of Jet Fuel with FAME, where positives results have been obtained with mixtures up to 20% by volume of FAME, since at higher volumes the cold flow properties of the fuel, such as the cloud point and pour point, are outside the standards established by the ASTM D1655 (Lapuerta & Canoira, 2016).
Considering the future industrial-level production of palm kernel oil FAME, it is essential to know the kinetics of the transesterification reaction analyses, design, simulate, and control the reactor and the process, according to the conditions of temperature, catalyst concentration, and oil/methanol molar ratio (Bashiri & Pourbeiram, 2016). Several authors have studied the kinetics of transesterification with a homogeneous catalyst where two reaction mechanisms have been mainly analysed. The first mechanism is the global reaction in Eq. (1), in which

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one mole of triglycerides (TG) reacts with three moles of alcohol (A) to form one mole of glycerine (GL) and three moles of ester (E).

$$\mathrm{TG} + 3\mathrm{A} \underset{\mathrm{k_2}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{GL} + 3\mathrm{E} \tag{1}$$

The second mechanism studies the reaction in stages (Eq. 2 to 4), where one mole of TG reacts with one mole A and produces the intermediate products of diglycerides (DG) and monoglycerides that subsequently react with alcohol and form the final product E. Finally, the MG reacts with A and produces one mole of E and one mole of GL (Freedman et al., 1986).

$$\mathrm{TG} + \mathrm{A} \underset{\mathrm{k_2}}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{DG} + \mathrm{E} \tag{2}$$

$$\mathrm{DG} + \mathrm{A} \underset{\mathrm{k_4}}{\overset{\mathrm{k_3}}{\rightleftharpoons}} \mathrm{MG} + \mathrm{E} \tag{3}$$

$$\mathrm{MG} + \mathrm{A} \underset{\mathrm{k_6}}{\overset{\mathrm{k_5}}{\rightleftharpoons}} \mathrm{GL} + \mathrm{E} \tag{4}$$

In this work, an application was developed in MATLAB® R2019b to model the kinetics of the transesterification reaction for the mechanisms of the general reaction and reaction by elemental order stages, taking as experimental reference data from Issariyakul & Dalai (2012). It should be clarified that the fundamental objective of this article is to facilitate the correlation of kinetic parameters, beyond the theoretical discussions on the operation of the application.

2. Estimation of the kinetic parameters of the transesterification reaction

The kinetic parameters of transesterification are estimated by non-linear regression since the reaction rate expressions are composed of a system of non-linear equations, which must be integrated and adjusted to the experimental data. The solutions will not be the optimal parameters but reproduce the experimental information with an accurate fit (Green & Southard, 2019).

General reaction: It is modelled according to the elementary order reaction rate equation in Eq. (5) and the relationship of the consumption/formation rate of each component with the reaction stoichiometry in Eq. (6) (Hindryawati & Maniam, 2015).

$$r = -\frac{\mathrm{d\,C}_{TG}}{\mathrm{dt}} = k_1 \mathrm{C}_{TG} {\mathrm{C}_A}^3 - k_2 \mathrm{C}_{GL} {\mathrm{C}_E}^3 \tag{5}$$

$$\frac{r_{TG}}{-1} = \frac{\mathrm{r}_A}{-3} = \frac{r_{GL}}{1} = \frac{\mathrm{r}_E}{3} \tag{6}$$

Where. r is the reaction rate, k_i is the kinetic rate constants and C_i is the concentration of component i.

Reaction in stages: It is carried out according to the kinetic model proposed by Noureddini & Zhu, (1997), without taking into account the kinetic constants of the general reaction (Eq. 7 to 12) since these constants do not affect the reaction rate.

$$\frac{\mathrm{d\,C}_{TG}}{\mathrm{dt}} = -k_1 \mathrm{C}_{TG} \mathrm{C}_A + k_2 \mathrm{C}_{DG} \mathrm{C}_E \tag{7}$$

$$\frac{\mathrm{d\,C}_{DG}}{\mathrm{dt}} = k_1 \mathrm{C}_{TG} \mathrm{C}_A - k_2 \mathrm{C}_{DG} \mathrm{C}_E - k_3 \mathrm{C}_{DG} \mathrm{C}_A + k_4 \mathrm{C}_{MG} \mathrm{C}_E \tag{8}$$

$$\frac{\mathrm{d\,C}_{MG}}{\mathrm{dt}} = k_3 \mathrm{C}_{DG} \mathrm{C}_A - k_4 \mathrm{C}_{MG} \mathrm{C}_E - k_5 \mathrm{C}_{MG} \mathrm{C}_A + k_6 \mathrm{C}_{GL} \mathrm{C}_E \tag{9}$$

$$\frac{\mathrm{d\,C}_E}{\mathrm{dt}} = k_1 \mathrm{C}_{TG} \mathrm{C}_A - k_2 \mathrm{C}_{DG} \mathrm{C}_E + k_3 \mathrm{C}_{DG} \mathrm{C}_A - k_4 \mathrm{C}_{MG} \mathrm{C}_E + k_5 \mathrm{C}_{MG} \mathrm{C}_A - k_6 \mathrm{C}_{GL} \mathrm{C}_E \tag{10}$$

$$\frac{\mathrm{d\,C}_A}{\mathrm{dt}} = -\frac{\mathrm{d\,C}_E}{\mathrm{dt}} \tag{11}$$

$$\frac{\mathrm{d\,C}_{GL}}{\mathrm{dt}} = k_5 \mathrm{C}_{MG} \mathrm{C}_A - k_6 \mathrm{C}_{GL} \mathrm{C}_E \tag{12}$$

The expressions for the reaction speed of the transesterification show a system of non-linear equations; therefore, for the estimation of its kinetic parameters, a non-linear regression of the experimental data must be applied. A minimization is proposed for the sum of the squared errors (SSE) between the simulated and the experimental data (Eq. 13). The simulated data are obtained from integrating the speed equations by the fourth-order Runge-Kutta method.

$$SSE = \sum_{n:1}^{n} \sum_{i=1}^{i} (C_{i,Exp} - C_{i,cal})^2 \tag{13}$$

where, $C_{i,Exp}$ are the experimental concentrations of the component, $C_{i,cal}$ are the calculated concentrations, i is the number of reaction components and n is the number of samples in time. Three nonlinear optimization functions *fminsearch*, *fmincon*, and *genetic algorithm* were used to minimize SSE:

Fmincon function: This nonlinear optimization tool with constraints allows finding the local minimum of the objective function. Fmincon with the Active Set algorithm is a sequential quadratic programming method that performs a quasi-Newton estimation of the Hessian matrix to the Lagrangian based on the solution of the Karush-Kun-Tucker equations (The MathWorks, Inc, 2020).

Fminsearch function: This non-linear optimization tool allows minimization with the Nelder-Mead simplex algorithm. It is based on the simplex construction that achieves an approximation to the optimal point without the need to derive a function. This function, unlike fmincon, has no restrictions, so it is easier to use but it does not guarantee that the solution always converges to a local minimum.

Ga function (Genetic algorithm): It is a method that solves restricted and unrestricted optimization problems based on biological evolution and is considered a global minimum search engine. The algorithm starts from a random initial population, and searches for the optimal solution by crossing and mutation among the population members (Gestal et al., 2010).

2.1 Estimation of activation energy and Arrhenius pre-exponential factor

The estimation of the activation energy and the Arrhenius pre-exponential factor was performed by linearizing the Arrhenius equation (Eq. 14) with the help of the polifit function, which performs the curve fitting employing least squares.

$$k_i = A_0\, e^{-\frac{E}{RT}} \tag{14}$$

where, E: Activation energy [J mol^{-1}], A_0 : Pre-exponential factor [s^{-1}], T: Reaction temperature [K], R: Universal gas constant [8.3145 J mol^{-1} K^{-1}].

2.2 Application in MATLAB

An application was designed in the MATLAB® App Designer to create an interactive interface with the user. The experimental data of the concentrations of TG, DG, MG, E, GL, and A can be uploaded, as well as the rate constants of the transesterification reaction with the general reaction model and the stepwise reaction model. Also, the application allows calculating the activation energy and the Arrhenius pre-exponential constant, by linearizing the speed constants at different temperatures.

The application contains two similar tabs for calculating the constant reaction rates according to the reaction mechanism. Figure 1 shows the reaction tab in stages, in which the experimental data must be loaded from an Excel file, organized by columns as follows: time, TG, A, DG, MG, E, and GL. The minimization function is selected (fmincon, fminsearch, and genetic algorithm). The initial values of the constants are established, as well as the upper and lower limits for the functions fmincon and genetic algorithm. When the application calculates the speeds, a graph compares the calculated and the experimental data. The values of the speed constants and the correlation coefficient are displayed in the lower panel. The application allows saving the data obtained in a new Excel sheet.

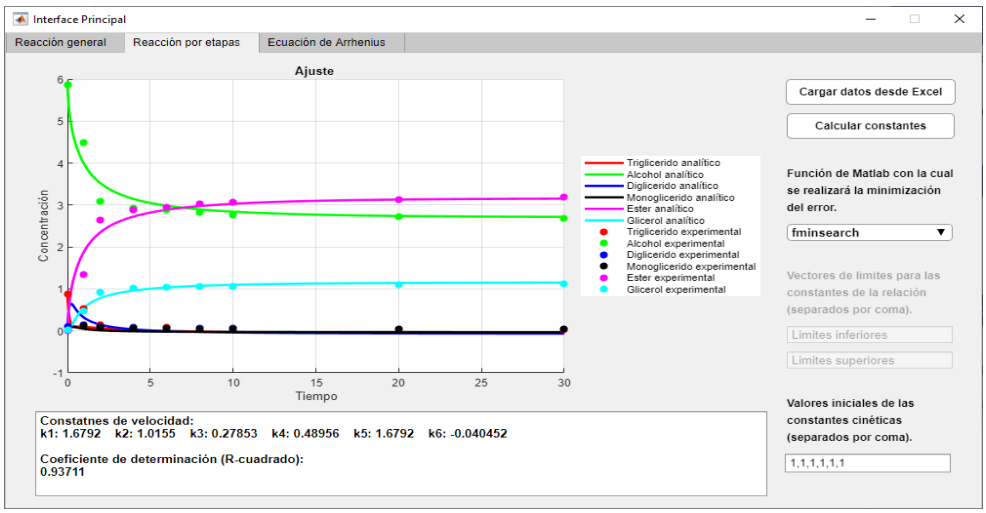

Figure 1: MATLAB® App Step Reaction Tab.

The application has a third tab called "Arrhenius equation" that determines the activation energy and the Arrhenius pre-exponential factor when linearizing the speed constants against the temperature (Figure 2).

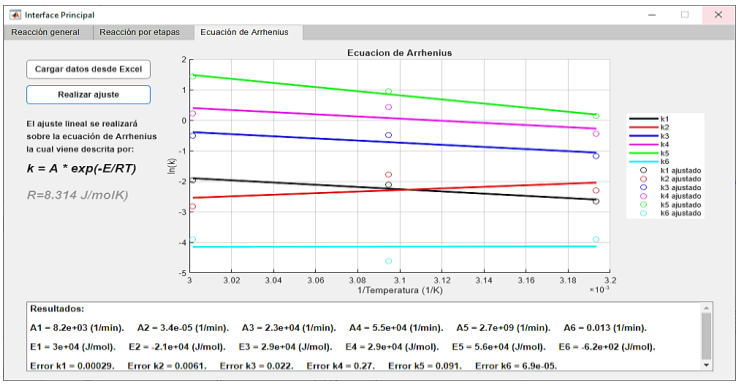

Figure 2: Arrhenius Equation Tab. MATLAB® App.

3. Case study

The kinetic parameters of the transesterification of palm oil at a temperature of 60 °C were modelled, taking as reference the experimental values of the concentrations of TG, DG, MG, A, E, and GL reported by Issariyakul and Dalai (2012). The fourth-order Runge-Kutta method was used to integrate the kinetic model. The functions fminsearch, fmincon, and genetic algorithm were tested to minimize the objective function SSE. The speed constants were limited between 0 and 5 for the functions fmincon and genetic algorithm, while the initial constants for fminsearch and fmincon were established as 1. Table 1 shows the calculated values of the speed constants for the general reaction case and the reaction in stages.

Table 1: Rate constants for transesterification of palm oil.

	Global Reaction		Reaction in stages			
	fmincon	fminsearch	fmincon	fminsearch	Genetic algorithm	(Issariyakul & Dalai, 2012)
	1.34E-2	1.35E-2	0.32	1.68	0.32	0.14
k_2	1.91E-11	-3.59E-4	0	1.02	1.13E-6	0.06
k_3			0.42	0.28	0.42	0.6
k_4			0	0.49	2.44E-6	1.24
k_5			4.97	1.68	0.62	4.18
k_6			0	-0.41	9.28E-8	0.02
R^2	0.83	0.88	0.94	0.94	0.94	-

In the case of the general reaction, the fminsearch function obtains the best fit to the experimental data since its coefficient of determination is 0.88 However, a negative value is obtained in the rate constant k_2, which indicates that the mass balance is not fulfilled since the function assumes that the TG concentration is negative after 5 minutes of reaction (Figure 3a). The fmincon function shows a coefficient of determination of 0.83, where k_1 is greater than k_2, which indicates that the forward reaction speed is greater than the reversible reaction speed (Figure 3b).

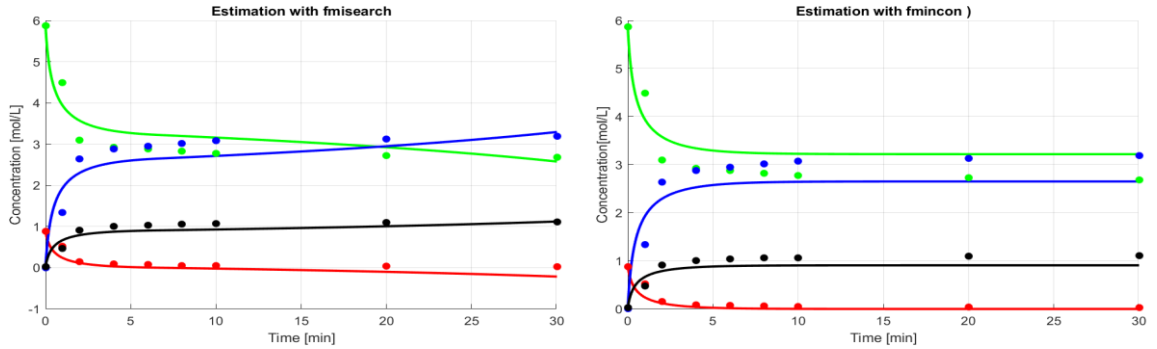

Figure 3: Experimental data and calculated data for triglycerides (●, —), alcohol (●, —), ester (●, —), and glycerin (●, —): (a) fmincom and (b) fminsearch.

The coefficient of determination for the stepwise reaction with the different minimization functions are above 0.93, which indicates a good fit to the experimental data. However, the rate constants of the reversible reactions, k_2, k_4, and k_6 obtained with the function fmincon adopt the value of the lower limit, since the function neglects the effect of the reversible constants within the objective function (SSE). When fminsearch is used, a negative value is obtained at the constant k_6 because the function allows no restrictions on the variables and calculates some negative concentrations. The genetic algorithm function has an advantage over the other functions since it is a global minimum search tool, while fmincon and fminsearch are local minimum search. Therefore, the solution obtained is close to the optimal global points. Figure 4 shows the comparative results between the minimized functions (fmincon, fminsearch, and genetic algorithm) and the experimental data.

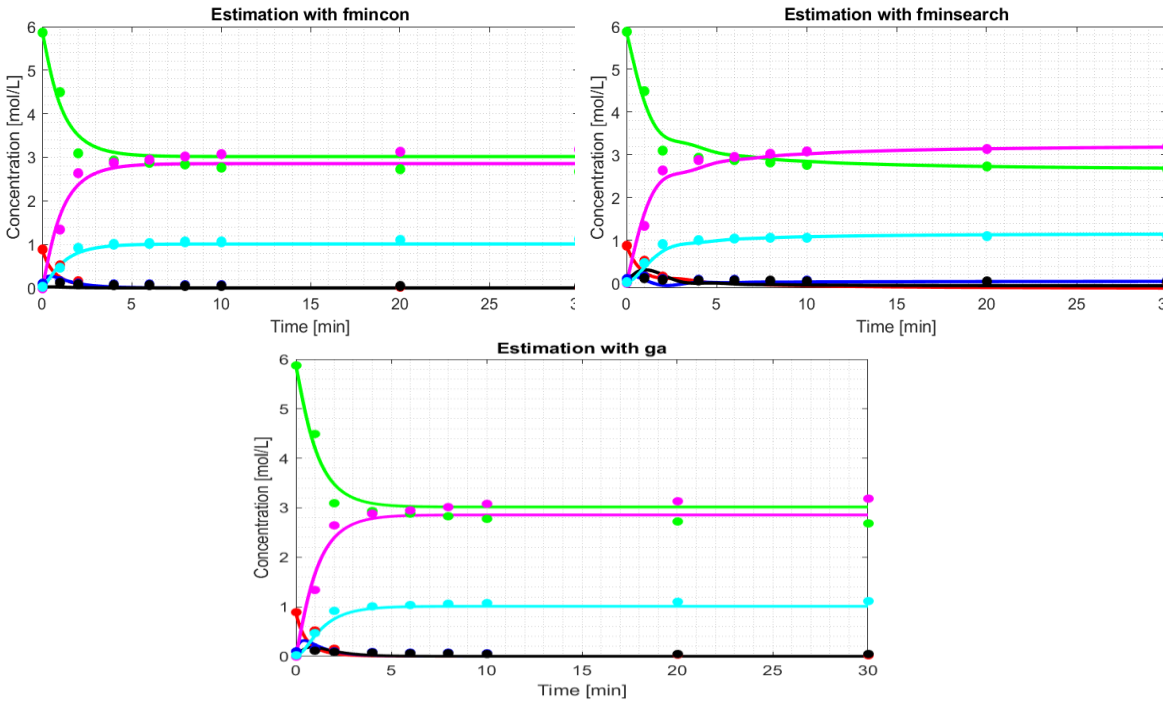

Figure 4: Experimental data and calculated data for triglycerides (●, —), diglycerides (●, —), monoglycerides (●, —), alcohol (●, —), ester (●, —) and glycerin (●, —): (a) fmincom, (b) fminsearch and (c) genetic algorithm (ga).

Finally, the activation energy and the pre-exponential factor were determined by linearizing the Arrhenius Equation of the velocity constants obtained at temperatures of 40 °C, 50 °C, and 60 °C by Issariyakul & Dalai (2012) (Table 2). Activation energy values are between the range of 27.3 and 61.5 kJ mol^{-1}, as reported by various authors (Darnoko & Cheryan, 2000; Jansri et al., 2011).

Table 2: Linearization results of the Arrhenius equation.

Parameter	k_1	k_2	k_3	k_4	k_5	k_6
A (min^{-1})	8.2E+03	3.4E-05	2.3E+04	5.5E+04	2.7E+09	1.3E+2
E (kJ mol^{-1})	30.22	-21.44	28.94	29.15	56.09	-0.62

4. Conclusions

The step reaction model shows a better fit than the global reaction approximation. Parameters correlated with the genetic algorithm function show the most accurate result (coefficient of determination greater than 0.94). In addition, the genetic algorithm function overcomes the limitations of fminsearch and fmincon, it did not require an initial estimate for the correlation process, and the convergence process did not stop at an incorrect local optimum, indicating that metaheuristic methods for error minimization, and convergence, without the need for rigorous initial or frontier values, are the most appropriate, as well as being mathematical-computational tools applicable to the kinetics of other biodiesels. The application developed in MATLAB® allows us to correlate the kinetic parameters with a precise adjustment of the experimental results, allowing the evaluation of the reaction mechanisms and the analysis of the reaction time and temperature.

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