Kinetic study and simulation of the biodiesel production process using a mixture of palm and rapeseed oils

Estudio cinético y simulación del proceso de producción de biodiésel a partir de una mezcla de aceites de palma y colza

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ABSTRACT

This study focuses on demonstrating the changes that occur in the transesterification reaction of methanol and African palm oil (Elaeis guineensis) when mixed with rapeseed oil. All changes were analyzed both at the kinetic level and in terms of the technical feasibility of large-scale production in a basic medium, catalyzed by sodium hydroxide. The best reagent concentration conditions were determined statistically in each case and then used to obtain the reaction kinetics through chromatographic analysis at regular time intervals. The quality of the product obtained was compared with the specifications of the ASTM D6751 standard, demonstrating compliance with these standards. Once the necessary data had been obtained, the production process for this biofuel was simulated using the SuperPro Designer® simulator. The results obtained show that modifying the fatty acid content by adding rapeseed oil to palm oil favorably changes its reaction kinetics, improving its energy produced to energy consumed ratio.

Keywords: biodiesel, kinetics, simulation, transesterification

RESUMEN

This study focuses on demonstrating the changes that occur in the transesterification reaction of methanol and African palm oil (Elaeis guineensis) when mixed with rapeseed oil. All changes were analyzed both at the kinetic level and in terms of the technical feasibility of large-scale production in a basic medium, catalyzed by sodium hydroxide. The best reagent concentration conditions were determined statistically in each case and then used to obtain the reaction kinetics through chromatographic analysis at regular time intervals. The quality of the product obtained was compared with the specifications of the ASTM D6751 standard, demonstrating compliance

with these standards. Once the necessary data had been obtained, the production process for this biofuel was simulated using the SuperPro Designer® simulator. The results obtained show that modifying the fatty acid content by adding rapeseed oil to palm oil favorably changes its reaction kinetics, improving its energy produced to energy consumed ratio.

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INTRODUCTION

Biodiesel is currently understood to be a mixture of fatty acid alkyl esters obtained from oils and fats through chemical reaction processes, mainly transesterification with short-chain alcohols such as methanol or ethanol (Avhad & Marchetti, 2015; Mandari & Devarai, 2022). Its main boom has occurred in recent years thanks to its renewable and biodegradable nature and the reduction in greenhouse gas emissions when used in place of fossil diesel (Kivevele et al., 2024).

At the industrial level, the production process for this biofuel encompasses stages of raw material pretreatment (oil extraction), catalytic reaction, biodiesel–glycerol phase separation, product purification, and alcohol recovery, all of which significantly modify the energy and economic efficiency of the process (Pasha et al., 2021; Trirahayu et al., 2022). The quality of the oil used as raw material, particularly its free fatty acid and water content, is used as a guideline to determine the viability of different catalytic route options, as well as the degree of complexity in the separation processes used in the purification of the final product (Gebremariam & Marchetti, 2021).

Basic homogeneous catalysis, carried out using alkali hydroxides or alkoxides, is the most widely used technology on an industrial scale due to the high reaction rates obtained, as well as the high conversions achieved under moderate conditions (Avhad & Marchetti, 2015). However, this catalysis option is overshadowed by its high sensitivity to free fatty acids, which leads to the formation of soaps and hinders the separation of the final product (Mandari & Devarai, 2022).

On the other hand, homogeneous acid catalysis allows the processing of raw materials with high free fatty acid content through esterification reactions, but requires longer reaction times and more severe conditions, which leads to increased operating costs and corrosion problems (Khodadadi et al., 2020).

Similarly, heterogeneous catalysts have been extensively studied as a sustainable alternative, as they allow for easier separation, catalyst recirculation, and a reduction in effluents (Hossain et al., 2019; Zhang et al., 2022). Some metal oxides such as CaO, supported materials, zeolites, and nanostructured catalysts have shown encouraging results, although they still face challenges related to deactivation, leaching, and limitations in diffusion systems (Kibar et al., 2023).

As an alternative to the above catalysts, the use of enzymes such as free or immobilized lipases offers certain advantages, such as improved operating conditions and high selectivity, making them an attractive alternative for waste oils. However, their high cost limits their industrial application (Mandari & Devarai, 2022). Similarly, non-catalytic routes such as transesterification under supercritical conditions have been studied for their tolerance to impurities, but they require high pressures and temperatures, which reduces their economic

viability (Gebremariam & Marchetti, 2021).

Computer simulation is a key tool in the comprehensive analysis of biodiesel production, as it allows for the evaluation of mass flows obtained during the process, as well as its energy assessment. It also allows for the optimization of operating conditions and the estimation of technical, economic, and environmental variables (Pasha et al., 2021). Some previous studies report stoichiometric and kinetic models used in simulators such as Aspen Plus and Aspen HYSYS, which allow for the analysis of continuous and batch processes in different operating scenarios (Liu et al., 2021; García et al., 2010).

The optimization of the different production processes for this biofuel usually focuses on variables such as the alcohol- oil ratio, the catalytic load, the reaction temperature, and the alcohol separation and recovery processes, using multi- objective approaches that simultaneously evaluate economic and environmental criteria (Ahmed et al., 2022; Woinaroschy et al., 2014).

The SuperPro Designer simulator has been widely used as a robust tool for industrial process simulation and techno- economic analysis of biodiesel plants, especially when detailed equipment sizing and rigorous cost estimation are required (Gebremariam & Marchetti, 2021; Bansod et al., 2025). Its use allows for the evaluation of different process configurations, analysis of their sensitivity in production costs with respect to important variables, and comparison of alternative production and purification technologies (Kivevele et al., 2024).

In several studies, SuperPro Designer has been used as a complement to other simulators, integrating advanced thermodynamic models and cost analyses to provide a comprehensive view of the technical and economic performance of the production process (Trirahayu et al., 2022).

METHODOLOGY

Experimental

An experimental laboratory-scale study was conducted, complemented by process simulation, to evaluate biodiesel production through transesterification and its technical and energy feasibility. Refined vegetable oils were used as raw material and were previously characterized for their fatty acid composition by gas chromatography.

Laboratory-scale transesterification reactions were done using 50 g of oil per batch. Sodium hydroxide was used as a homogeneous catalyst to allow the oil's reaction with methanol. Catalyst and methanol-to-oil molar ratio were varied, while reaction time was established at 30 minutes. Once the reaction time was reached, the biodiesel-rich phase has been purified using silica (Trysil®) to remove soaps and subsequently dried to determine yield.

Statistical analysis of the experimental results was performed using ANOVA to identify the most influential operating parameters. Kinetic studies were then completed under optimal conditions by measuring each component concentration at different reaction times. Quality

parameters of the final product, including density, viscosity, oxidation stability, water content, acidity, and iodine value, were performed following AOCS standard methods (Mehlenbacher, 1997).

Once kinetic data of the reactions were obtained, simulation of the biodiesel production process was performed using the simulator Superpro Designer 8.5 © (SPD). Data used for process simulations were taken from the experiments and located in each separation process. Selection of the best separation conditions were achieved by sensitivity analysis. Finally, the process was energetically evaluated by experimental calorimetric determination of the obtained product and by simulations report. A global view of the followed method to achieve the results of the simulations is shown in figure 1.

Figure 1
Process flow diagram for biodiesel production. Adapted from Alvarez&Bello (In press, 2026), Iberociencias
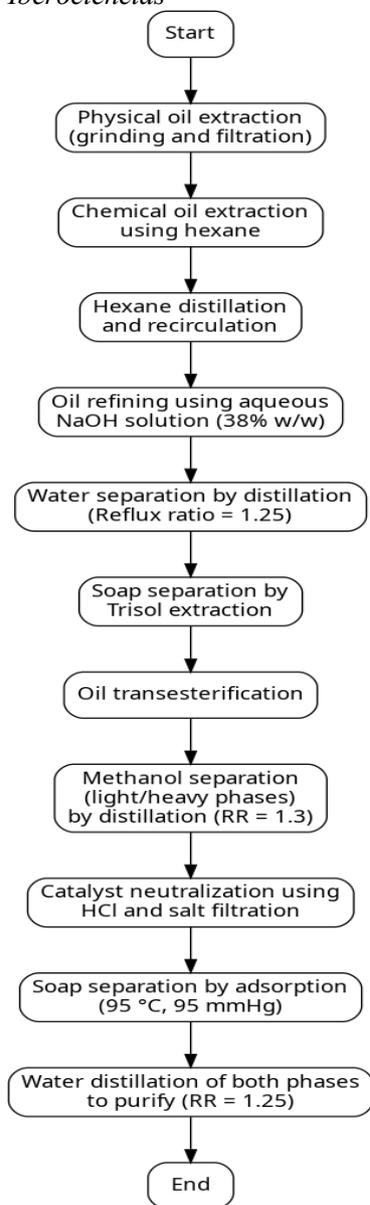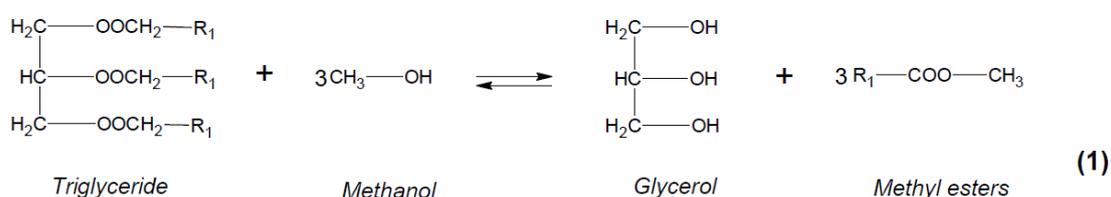
RESULTS

Optimal transesterification conditions for refined African palm oil using sodium hydroxide were reported by Alvarez et al (2021) at concentrations of 0.6% w/w and methanol-to-oil molar ratio of 5:1. For the palm oil–rapeseed oil mixture, optimal conditions were reached with 1.0% w/w of catalyst and an alcohol/oil molar ratio of 7 to 1. These results highlight the influence of oils composition (Table 1) on reaction behavior.

Kinetic analysis shows that the addition of rapeseed oil increases reaction rates (Figura 2-3), which can be assigned to the changes in fatty acid composition, specifically the higher oleic and linoleic acids content. Saponification reactions were unavoidable; however, their impact was reduced by the best conditions obtained during experimentation. The kinetic model showed excellent agreement with experimental data (Table 2). In addition, the quality values of the product satisfy the ASTM D6751 norm (Table 3).

Table 1

Fatty acids composition in the studied oils

Fatty acid	African Palm Oil	Rapeseed Oil
Lauric	0.44	0
Myrístic	2.33	1.8
Palmític	41.53	4.84
Stearic	4.74	0.93
Oleic	38.22	61.52
Linoleic	12.79	23.18
Linolenic	0.15	7.73

$$\text{Triglyceride} + 3\,CH_3{-}OH \rightleftharpoons \text{Glycerol} + 3\,R_1{-}COO{-}CH_3 \tag{1}$$

$$R_1\text{-}COO\text{-}CH + NaOH \longleftrightarrow R_1\text{.}COONa + H_2O \tag{2}$$

Free Fatty Acid + Sodium Hydroxide → Sodium ester + Water

Figure 2

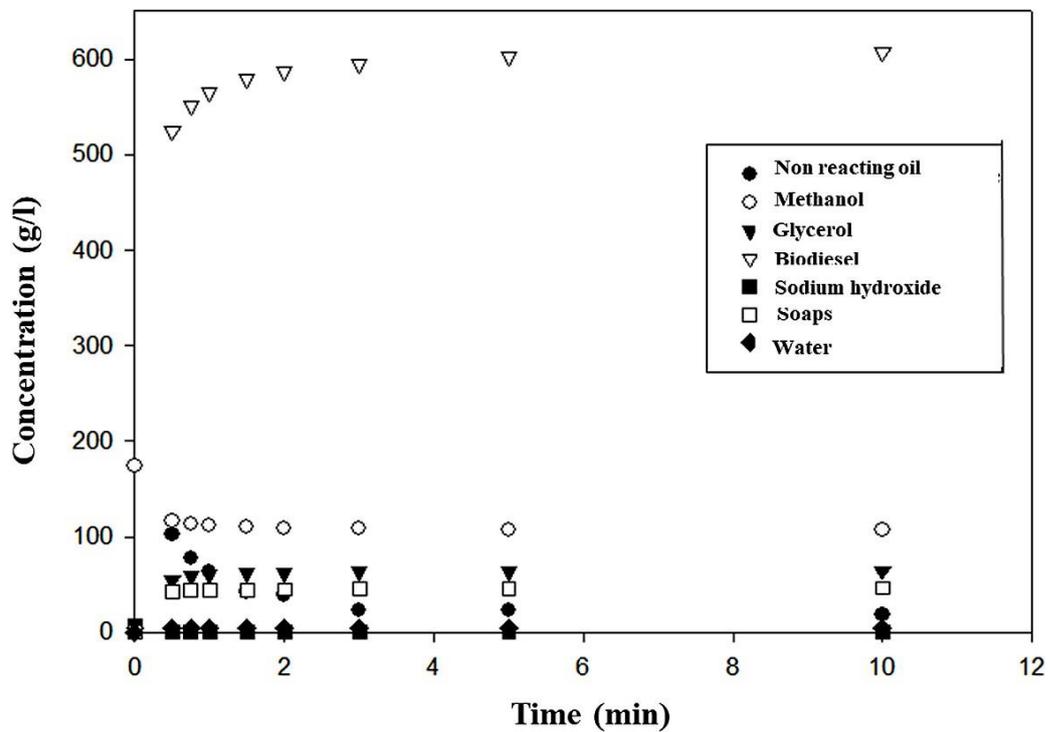*Obtained concentrations for transesterification and saponification reactions of an African palm oil-rapeseed oil mixture at 40ºC*
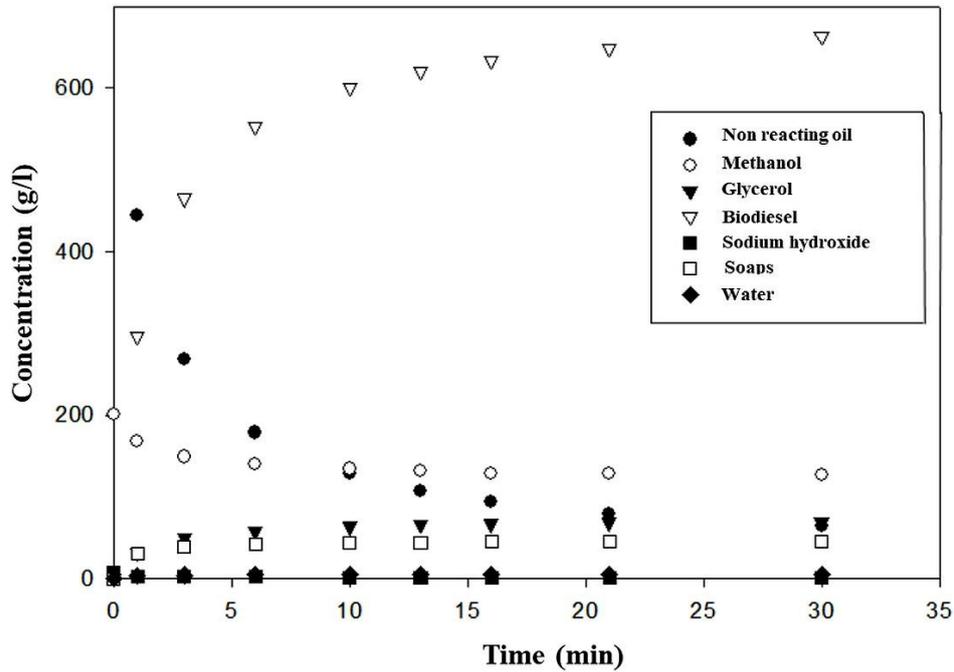
Figure 3

Obtained concentrations for transesterification and saponification reactions of an African palm oil-rapeseed oil mixture at 50ºC

Table 2

Activation energies and pre-exponential factors corresponding to the kinetic constants found for transesterification of an african palm/rapeseed oils blend

Constant	Palm and rapeseed oils blend	
	Activation energy [=] KJ/mol	exponential factor
K$_1$	255.70	1.04 E 40
K$_2$	212.30	9.65 E 31
K$_3$	312.27	1.62 E 50
K$_4$	150.40	6.61 E 21

Where:

   K$_1$ = Direct kinetic constant for reaction from vegetable oil to biodiesel. K$_2$ = Reverse kinetic constant for reaction from vegetable oil to biodiesel.

   K$_3$ = Direct kinetic constant for reaction from free fatty acids contained in the vegetable oil to soaps. K$_4$ = Reverse kinetic constant for reaction from free fatty acids contained in the vegetable oil to soaps.

Table 3

Quality parameters of the produced biodiesel from African palm/rapeseed oils blend

Standard	ASTM D6751 Norm m and rapeseed oils mixture	Lower limit	Upper limit
▢ at 15 º C [=] Kg / m^3	869.35	….	….
▢ at 40 º C [=] mm^2 / s	4.6247	1.9	6
Oxidation Stability [=] h	5.38	3	….
Water content [=] mg/Kg	236.8	….	500
Acidity [=] mg KOH/g	0.15	….	0.5
Iodine Value	76.99	….	….

   The flowsheets of biodiesel production process simulated for the analyzed blend are shown in figures 6 and 7 and correspond to the extraction and refining of oils, and their transformation to biodiesel, respectively.

Figure 4

Extraction and refining flow sheet for vegetable oils in the biodiesel production. Reproduced from Álvarez et al. (In press, 2026), Iberociencias

Figure 5

Oils transesterification flowsheet and sub products separation for biodiesel production. Reproduced from Álvarez et al. (In press, 2026), Iberociencias

Separation processes needing heat as distillation were designed using firstly shortcut methods and then refined by rigorous methods with a $R / R_{min} = 1.25$. Thermodynamical properties of fatty acids and their methyl esters were taken from literature (Osmont & Catoire (2007), Vatani & Merphooya (2007), Drapcho et al (2008)). Based on the presented diagrams, energetic services evaluation for the analyzed process using this blend is shown in table 4.

Table 4

Energetic requirements of biodiesel production process using a palm oil/rapeseed oil mixture

Service	Consumed energy in Kcal/h
	African palm- rapeseed oils mixture
Cooling and Heating	1,535,703.85
Equipment power	1,121,332.72
Total	2,657,036.57

Total energy was calculated based on the combustion heat, obtained from a calorimeter and the biofuel stream of the simulated processes, getting a heat flow of 22,573,627.09 Kcal/h for the analyzed blend, so the produced energy / consumed energy rate is 7.15. This can ensure the energetic feasibility of the process and is higher than the reported rate (5.81) for African palm alone (Alvarez & Bello. In press, 2026).

CONCLUSIONS

Results obtained from this research show that it is possible to produce biodiesel using a mixture of palm and rapeseed oils, obtaining a positive energy balance, which guarantees its technical feasibility of production.

Similarly, adding an extra oil to the process, such as rapeseed oil, has a positive effect on the transesterification kinetics, allowing for shorter reaction times and thus a reduction in the energy required for the process.

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