

Techno-economic evaluation of biodiesel production using by-product as raw material and hydrotalcite-hydroxyapatite as catalyst

Avaliação tecno-econômica da produção de biodiesel utilizando subproduto como matéria-prima e hidrotalcita-hidroxiapatita como catalisador

Evaluación tecno-económica de la producción de biodiesel utilizando subproducto como materia prima e hidrotalcita-hidroxiapatita como catalizador

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Abstract

Biodiesel is one of the main sources of renewable energy that can be obtained from oils and fats by transesterification. However, biodiesel produced from vegetable oils as a raw material is expensive. Thus, an alternative and inexpensive raw material such as vegetable oil deodorizing distillate (VODD) can be used as a raw material for the production of biodiesel. In this study, technical-economic analyzes were carried out in the biodiesel production process using VODD as raw material and hydrotalcite-hydroxyapatite as heterogeneous catalyst. Four different scenarios were considered for the economic technical evaluation of the biodiesel production process: heterogeneous catalysis, homogeneous catalysis, reduced ethanol flow in the process input stream, and different proportions of the biodiesel:diesel mixture. Biodiesel production presented a positive internal rate of return (IRR), and in comparison, with the minimum attractiveness rate (MAR), it was economically viable based on the sales prices of the revenues practiced. In the sensitivity analyses, it was observed that the catalyst acquisition price was the most critical factor in the economic analysis of the simulated plant. Using different catalysts, a comparative study showed that the heterogeneous catalyst makes the process less expensive with the purification steps. Thus, it can be confirmed that the results obtained from this study can open paths for new developments in the biodiesel process in relation to the use of residual raw material and new materials to be used as catalysts.

Keywords: Biodiesel; Capital investment costs; Economic evaluation; Heterogeneous catalysis; Transesterification.

Resumo

O biodiesel é uma das principais fontes de energia renovável que podem ser obtidas a partir de óleos e gorduras por transesterificação. No entanto, o biodiesel obtido a partir de óleos vegetais como matéria-prima é caro. Assim, uma matéria-prima alternativa e barata, como destilado de desodorização de óleos vegetais (DDOV) pode ser usado como matéria-prima para a produção de biodiesel. Neste estudo, análises técnico-econômicas foram realizadas no processo de produção de biodiesel usando DDOV como matéria-prima e hidrotalcita-hidroxiapatita como catalisador heterogêneo. Foram considerados quatro diferentes cenários para a avaliação técnica econômica do processo de produção de biodiesel: catálise heterogênea, catálise homogênea, redução do fluxo de etanol na corrente de entrada no processo e diferentes proporções da mistura biodiesel:diesel. A produção de biodiesel apresentou uma taxa interna de retorno (TIR) positiva, e em comparação com a taxa mínima de atratividade (TMA), apresentou-se viável economicamente a partir dos preços de venda das receitas praticadas. Nas análises de sensibilidade, observou-se que o preço de aquisição do catalisador foi o fator mais crítico na análise econômica da planta simulada. Utilizando diferentes catalisadores, um estudo comparativo mostrou que o catalisador heterogêneo torna o processo menos caro com as etapas de purificação. Desta forma, pode-se concluir que os resultados obtidos a partir deste estudo podem abrir caminhos para novos desenvolvimentos no processo de biodiesel em relação ao uso de matéria-prima residual e novos materiais para ser usados como catalisador.

Palavras-chave: Biodiesel; Custos de investimento de capital; Avaliação econômica; Catálise heterogênea; Transesterificação.

Resumen

El biodiesel es una de las principales fuentes de energía renovable que se puede obtener a partir de aceites y grasas por transesterificación. Sin embargo, el biodiésel obtenido a partir de aceites vegetales como materia prima es caro. Por lo tanto, una materia prima alternativa y de bajo costo, como el destilado desodorante de aceite vegetal (DDOV), se puede utilizar como materia prima para la producción de biodiesel. En este estudio se realizaron análisis técnico-económicos al proceso de producción de biodiesel utilizando DDOV como materia prima e hidrotalcita-hidroxiapatita como catalizador heterogéneo. Para la evaluación técnica y económica del proceso de producción de biodiesel se consideraron cuatro escenarios diferentes: catálisis heterogénea, catálisis homogénea, reducción del flujo de etanol en la corriente de entrada al proceso y diferentes proporciones de la mezcla biodiesel:diesel. La producción de biodiesel presentó una tasa interna de retorno (TIR) positiva, y en comparación con la tasa mínima de atractivo (TMA), fue económicamente viable a partir de los precios de venta de los ingresos practicados. En los análisis de sensibilidad se observó que el precio de adquisición del catalizador fue el factor más crítico en el análisis económico de la planta simulada. Usando diferentes catalizadores, un estudio comparativo mostró que el catalizador heterogéneo hace que el proceso sea menos costoso con los pasos de purificación. Por lo tanto, se puede concluir que los resultados obtenidos de este estudio pueden abrir caminos para nuevos desarrollos en el proceso de biodiesel en relación con el uso de materia prima residual y nuevos materiales para ser utilizados como catalizador.

Palabras clave: Biodiesel; Costos de inversión de capital; Evaluación económica; Catálisis heterogénea; Transesterificación.

1. Introduction

The continued increase in energy demand is the main objective all the world, independent of the concept of petroleum depletion. Furthermore, inherent particles emitted by the conventional fossil fuel combustion process have contributed to environmental pollution. Therefore, renewable energy sources are necessary to satisfy the energy demand, and to prospect the future. In this sense, biodiesel is considered a viable alternative fuel, because it is non-toxic and biodegradable and can be used together with conventional petroleum-based fuels to create blends (Singh et al., 2020; Karmee et al., 2015).

Transesterification and esterification reactions are currently the most used (Ambat et al., 2018; Rincón et al., 2014) for the biodiesel production. Regarding the transesterification reaction, it occurs between the biomass feedstock using an alcohol as solvent in a presence of a catalyst. As result, the biodiesel is composed of fatty esters and the main byproduct as glycerol. The lipid raw material can be vegetable oil or animal fat. The oils normally used are soybean oil, sunflower oil, rapeseed oil, and palm oil as lipid raw materials. Since these raw materials are also used as food, their abundant use to produce biofuel (energy) can lead to food shortages (Sajid et al., 2016). To avoid this conflict between energy and food demand, in recent years, researches have been directed towards the production of biodiesel from non-edible raw materials (Mishra & Goswami, 2018; Atabani et al., 2013; Ashrafui et al., 2014). Among the non-edible raw materials, including vegetable oils, there are residues that can be utilized. One of them is the vegetable oil deodorizing distillate (VODD), a potential residual raw material for the production of biodiesel (Almeida et al., 2021; Vilas Bôas et al., 2020).

Vegetable oil deodorization distillate (VODD) is a byproduct originated from the processing steps of vegetable oils, and has been recognized as a potential raw material for the biodiesel production, as it is relatively cheaper than edible oils (Aboelazayem et al., 2018; Zhang et al., 2003). Moreover, it represents approximately 0.3–0.5% of the raw material, and contains tocopherols (3–12%), triglycerides (45–55%), free fatty acids (FFA, 25–35%), sterols (7–8%), hydrocarbons, and other unsaponifiable in small amounts. Free fatty acid (FFA) and triglycerides account for 80% of VODD, and can be transformed into biodiesel (Vilas Bôas et al., 2020; Yin et al., 2016; Wang et al., 2006).

Industrial biodiesel production uses homogeneous basic catalysts (NaOH, KOH, or CH₃ONa) for different substrates (Tran et al., 2013). Despite the low cost of the process and easy handling, such catalysts are sensitive to water, and free fatty acids due to the eminent by-products of soap formation, which results in a considerable amount of wastewater generation (De Lima et al., 2016; Lotero et al., 2005). In contrast, homogeneous acid catalysts are efficient and often used as substitutes for base catalysts. However, they also require neutralization steps, which can cause the formation of stable soaps and emulsions

(Su; Guo, 2014). Therefore, to avoid these disadvantages of both homogeneous systems, heterogeneous catalysts have been proposed and are being investigated and applied (Pinto et al., 2019). Moreover, heterogeneous catalysts are recyclable, non-corrosive, and can simplify separation and purification steps (Yin et al., 2016).

In this perspective, the high stability, low cost, and easy synthesis of the hydrotalcite-hydroxyapatite material meet the requirements previously stated (Vilas Bôas et al., 2020). However, hydrotalcite ($Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$) is commonly used in catalytic reactions due to its high basicity and surface area, and accentuated basic characteristic (Nowicki et al., 2016). The hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) has an amphoteric character, ion exchange capacity, adsorption capacity, and thermal stability and is normally applied in the biomedical area, due to its biocompatibility and osteointegration characteristics (Essamlali et al., 2017; Lugovskoy et al., 2016). Recently, the synthesis of a material composed of hydrotalcite and hydroxyapatite (HT-HAp) phases was proposed, and its performance was evaluated in soybean oil transesterification and water treatment (Rodrigues et al., 2018). Several studies have investigated the conditions of synthesis and composition of hydrotalcite and hydroxyapatite in the catalytic performance in the production of biodiesel (Vilas Bôas et al., 2020; Coral et al., 2019; Navajas et al., 2018; Brasil et al., 2017; Essamlali et al., 2017).

According to Dabdoub and Bronzel (2009), due to the large number of variables that can affect the production yield of a biodiesel plant, such as the alcohol/oil molar ratio, catalyst type, operating temperature, among other factors, it is important as well the economic analysis of the process to determine the viability of a plant. Based on these considerations, the main objective of this study was to carry out an economic and technical evaluation of the biodiesel production process from the by-product of vegetable oil deodorization distillate (VODD) using hydrotalcite-hydroxyapatite (HT-HAp) as catalyst and ethanol as solvent. Four different scenarios for the economic technical evaluation biodiesel production process were considered: heterogeneous catalysis, homogeneous catalysis, reduction in the flow of ethanol in the process, and different proportions of biodiesel:diesel mixture. Though, it was possible to identify the main variables that are necessary to determine the ideal conditions to make the process viable. Furthermore, the results obtained from this study may open paths for new developments in the biodiesel process with the use of residual raw material and new materials to be used as a catalyst.

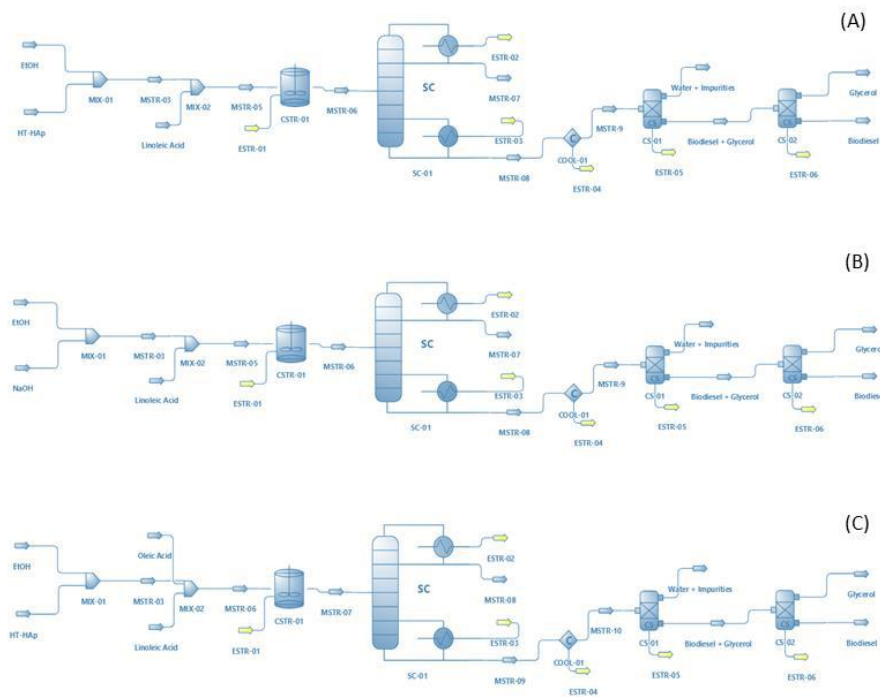
2. Methodology

In previous works developed by Almeida et al. (2021), simulations of the biodiesel production process (FAME) were carried out using vegetable oil deodorization distillate (VODD), a residue originating from the processing step of vegetable oils, as residual raw material and hydrotalcite-hydroxyapatite (HT-HAp) as heterogeneous catalyst. The simulations were performed using a DWSIM Version 6.3 open interface software. In the study, the lipid raw material, ethanol, and the catalyst were fed together to a CSTR-01 conversion reactor (Figure 1). The thermodynamic model used to represent the liquid phase was the NRTL (Non-Random Two-Liquids). The process flowchart consisted of the reaction step (oil transesterification), the separation of the ethyl esters produced, and the steps of separating excess ethanol and purifying the biodiesel.

Different scenarios were simulated aiming the production of biodiesel on an industrial scale and different production strategies were chosen for evaluation. The first strategy used VODD and commercial soybean oil as lipid raw materials. Meanwhile, the second strategy investigated the use of different types of catalysts, such as hydrotalcite-hydroxyapatite (HT-HAp) as a heterogeneous catalyst and sodium hydroxide (NaOH) as the homogeneous catalyst. There was also the third strategy, which investigated the use of different molar ratios of 1:6, 1:12, and 1:45 oil/alcohol. Subsequently, each strategy was analyzed with the conversion of triglycerides into ethyl esters (biodiesel). The results obtained confirmed the suitability of VODD as potential raw material to produce biodiesel (conversion $\geq 95\%$), as it is relatively cheaper than edible oils and contributes to the use of waste. Thus, it was confirmed that the chemical catalyst was able to form the main fatty acid esters even using a residual raw material.

Considering that in the three different scenarios biodiesel was obtained with the necessary specifications, an economic analysis was carried out for the process using the following conditions: 1:9 molar ratio of VODD/ethanol, using HT-HAp as a catalyst (5 %wt.), and 101 kPa in the CSTR-01 reactor. The temperatures of the reactor inlet and outlet currents were equal to 70 °C (Almeida et al., 2021). Sensitivity analyzes were also performed comparing different input variables in order to maximize the economic feasibility of producing this biofuel.

Figure 1. Process flow diagram of the biodiesel production processes with: (a) VODD as a lipid raw material and HT-HAp as a catalyst; (b) VODD as a lipid raw material and NaOH as a catalyst; (c) commercial soy oil as a lipid raw material and HT-HAp as a catalyst.



Source: Authors.

2.1 Techno-economic evaluation

The economic viability of a process is one of the most crucial steps in the development of a project. Thus, an economic study aligned with a technical analysis are two fundamental parameters to be studied in an industrial process (Peters et al., 2003; Perry & Green, 1999). However, once the technical feasibility of a production plant is confirmed, it is important to study its economic potential. About the production of biodiesel through the chemical route, this assessment helps to identify obstacles related to the use of new materials as catalysts for transesterification on an industrial scale.

Few works reported in the literature involve the economic analysis of biodiesel synthesis using HT-HAp as a catalyst and, furthermore, no economic feasibility study of a production plant for this biofuel obtained from vegetable oil deodorization distillate was found (VODD) and ethanol through this technological route. Therefore, the results of the simulations presented by Almeida et al. (2021) were used for the economic study of the process with the intention of determining its feasibility and the differences caused using different catalysts in the process.

The economic viability of a biodiesel plant is associated with the elaboration of a well-organized structure for the production and distribution of biofuel. Therefore, some economic criteria were considered to carry out the economic evaluation, such as: The fixed investment capital was estimated based on the cost of setting up the system, that is, it involved

the mobilization of resources for a period. The working capital, necessary to operate the system initially, was calculated based on the estimate of covering the costs of purchasing raw materials and utilities in the initial 30 days of the system. The operating cost was divided and classified according to those that alter with the production rate and those that do not. In this system, for variable costs, costs with raw materials (including ethanol and catalyst), operators, and utilities (electricity and cooling water) were considered. Fixed costs were related to expenses with the supervisor and facilities (upkeep and depreciation of equipment, general expenses).

Otherwise, project revenues were obtained through the sale of biodiesel, the main product, and the sale of the by-product of the transesterification reaction, crude glycerol. Meanwhile, the main economic indicators considered in the system were the internal rate of return (IRR), based on a minimum attractiveness rate (TMA) of 25%; and the payback time. The IRR was calculated based on the cash flow after deducting income tax (Receita Federal, 2021). The IRR calculation method was based on Perry and Green (1999), Peters et al., (2003).

The economic evaluation performed in this study can be classified as study estimate. Thus, terrain layout information, process instrumentation, and tubing were not considered. Although they are required in the design of chemical plants, replacement pumps were not considered either. It was considered a factory operating 14 hours a day for 330 days a year, totaling 4620 h/year. The f.o.b (Free On Board) prices of all raw materials, catalysts, and products used in this work were taken from the literature.

3. Results and Discussion

The biodiesel production process was simulated using vegetable oil deodorization distillate (VODD) as lipid raw materials and hydroxylapatite (HT-HAp) and sodium hydroxide (NaOH). The operational conditions of the simulations were chosen according to previously published works of the research group (Almeida et al., 2021; Vilas Bôas et al., 2020). From this simulation, an economic analysis was carried out applying all the raw materials, products, and utilities presented in Table 1, as well as the prices of each one considered in the simulations.

The yield of methyl esters was considered the same obtained experimentally on a laboratory scale (88.5%) since the operating conditions used were also the same. The glycerol obtained from the purification column, obtained as a by-product of the transesterification reaction, was considered as by-product for later sale containing 99% of glycerin, according to the simulation performed. Based on the data fed into the simulator, on the predetermined operating conditions, and the equations on the economic analysis presented in the methodology, Table 2 illustrates the technical aspects obtained previously in the simulation.

The production of biodiesel and glycerol, by batch, obtained was equivalent to 245.18 kg and 0.2775 kg, respectively. For this, 45.14 kg of VODD, 406.32 kg of ethanol, and 33.98 kg of catalyst (HT-HAp/NaOH) were used. The total time of each batch was 7 h, totaling 660 batches per year. Under these conditions, the amount of biodiesel produced during the 330 days of plant operation corresponded to 161.82 tons/year. The main economic aspects will be discussed in detail in the next topics.

Table 1. Prices of inputs and utilities used in economic evaluation.

Inputs and Utilities	Specification	Price
<i>Raw materials</i>		
Vegetable oil deodorizing distillate ¹	donation	-
Ethanol ²	99.8% PA	US\$ 0.35/kg
Catalyst ³	Hydrotalcite-hydroxyapatite*	US\$ 19.00/kg
	NaOH**	US\$ 0.35/kg
<i>Products</i>		
Biodiesel ⁴	98% in ester mass	US\$ 1.450/kg
Glycerol ⁵	99% in mass	US\$ 0.141/kg
<i>Utilities</i>		
Cooling water ⁶	400 kPa; 32.2 °C	US\$ 706.09 ano
Electricity ⁷	-	US\$ 22,730 ano

¹Donation by Bunge Alimentos located in Gaspar – SC; ²Hexis Cientifica (2021); ^{3*}Haihang Industry (2021); ^{3**}Hexis Cientifica (2021); ⁴ANP (2021); ⁵Biomercado (2021); ⁶CEDAE (2021); ⁷Light Energia (2021). Source: Authors.

Table 2. Technical aspects of the simulation of biodiesel production (Almeida et al., 2021).

Technical aspects	
Project lifetime (years)	10
Plant capacity (ton/year)	320.39
<i>Input currents (kg/batch)</i>	
Deodorization distillate	45.14
Ethanol	406.32
Hydrotalcite-hydroxyapatite	33.98
NaOH	33.98
<i>Output currents (kg/batch)</i>	
Glycerol	0.2775
Biodiesel	245.18
Batch time (h)	7
Total batches per year (h)	4620

Source: Authors.

It was considered that the hydrotalcite-hydroxyapatite catalyst used in the process was reused in five reaction cycles. Because hydrotalcite-hydroxyapatite is a solid catalyst, it is possible to reuse up to five reaction cycles without significant loss of its catalytic activity, after separation from the reaction medium (Xie et al., 2017). According to Ramos et al. (2016), the heterogeneous catalysis route can be more economic because of the easily separation and purification of the biofuel, allowing the possibility of reusing the catalyst in new reactions.

Xie et al. (2017) investigated solid catalyst reuse by performing subsequent cycles of transesterification reaction under optimized reaction conditions (25:1 methanol/oil molar ratio, 1.3% wt. hydroxyapatite catalyst encapsulated with γ -Fe₂O₃ nanoparticles and a reaction temperature of 65 °C). After completion of the transesterification, the solid catalyst was separated from the reaction mixture, washed with n-hexane and methanol, dried at 80 °C in an oven, and then reused in the next transesterification reaction. The results showed that the solid catalyst can be reused five times with no significant loss in catalytic activity. The decrease in catalytic activity occurred about 10% in the decrease in conversion after the five cycles, probably due to organic or carbonaceous substrates having been deposited on the surface of the recycled catalyst, leading to blockage of the catalyst's active sites. Therefore, the authors concluded that the solid base catalyst has good stability and reuse in the process.

3.1 Total investment

The total investment is attributed to the amount required to cover expenses related to the purchase of equipment, manufactures, facilities, as well as the expenses involved in the operation of the plant as a whole. The method used to calculate

the fixed investment capital was based on the purchase price of the equipment (factor method) (Perry and Green, 1999). This amount was equivalent to US\$921,102.88, updated for the year 2021. Table 3 illustrates in details the direct and indirect costs.

Table 3. Fixed investment capital of the simulated biodiesel plant.

A. Direct cost of the plant	
1. Equipments	\$ 921,102.88
2. Electricity	\$ 4282.26
3. Cooling water	\$ 706.09
B. Indirect cost of the plant	
3. Chemical engineer	\$ 15189.43
4. Technical	\$ 13924.28
C. Total cost of the plant (C = A + B)	\$ 955,205.75
D. Contractor fees and Contingencies	
5. Rates	\$ 46055.14
6. Contingencies	\$ 92110.29
E. Fixed capital of the project (E = C + D)	\$ 1093370.4

Source: Authors.

The estimated working capital was US\$17,999.49 needed to cover expenses for purchasing raw materials, operators, and utilities during the first 30 days of production. Thus, the total investment of this project was equivalent to the sum of the fixed investment capital and the working capital, totaling US\$1111369.89.

3.2 Operational cost (OC)

Table 4 details the operational costs classified as variable and fixed costs. The cost involving the purchase of materials corresponds only on the acquisition of ethanol and the hydrotalcite-hydroxyapatite catalyst since the vegetable oil deodorization distillate was donated by Bunge Alimentos, located in Gaspar-SC. The donation of the raw material reduces considerably the operational costs, which varied from 70-85% when refined oils were used (Haas et al., 2006). The estimation of the total cost of materials is calculated based on the mass balance carried out to produce biodiesel (Equations 1, 2, and 3).

$$(input\ ethanol/kg)/batch * 2\ batches/day * (330\ days) * ethanol\ cost \quad (1)$$

$$(input\ HT-HAp/kg)/batch * 2\ batches/day * (330\ days) * HT-HAp\ cost = catalyst\ reuse/5 \quad (2)$$

$$Material\ cost = ethanol + HT-HAp\ catalyst \quad (3)$$

Table 4. Operating costs to produce biodiesel in the simulated plant.

Variable costs	\$/ year
Material (ethanol + HT-HAp)	\$ 179081.76
Operator	\$ 13924.28
Utilities	\$ 4988.35
Fixed costs	
Supervisor	\$ 15189.43
Facilities	\$ 111136.99
Total cost	\$ 324320.81

Source: Authors.

The annual operating time of the pilot plant was considered 4620 hours per year. Thus, an operator working per shift was required, totaling 2 shifts per day. The salary of each operator was considered \$326.40/month, based on the salary of a chemistry technician in Brazil (Sindquim, 2020).

As the utilities-related costs consist of expenses with heat transfer agents – cooling water – and the energy cost required by the process, these values were estimated based on the energy balance calculated by the simulator. The annual consumption of electricity and cooling water was, respectively, 22730.0 kWh and 451.897 kg.

Fixed costs were determined from the expenses related to the supervisor and the facilities. The supervisor, being the Chemical Engineer, technically responsible for production, had his working hours fixed in an 8-hour daily shift, corresponding to \$1,265.82/month, based on the salary of a chemical engineer in Brazil (Sengerj, 2020).

The facilities costs were associated to equipment maintenance, depreciation, and diversity, such as insurance, local taxes, and plant overheads. The maintenance cost was estimated from 5% of the direct fixed capital cost (CFD). Depreciation was calculated using the factor methods based on the individual cost of each piece of equipment. Expenses related to insurance, local taxes, and general expenses were estimated at 1%, 2%, and 5% of CFD, respectively.

3.3 Economic indicators: Internal rate of return and time of return

The main economic indicators that were used in this work to evaluate the profitability of the process were the internal rate of return (IRR) and the return time. The IRR will be compared to a minimum attractiveness rate (MAR) of 25%, to analyze the project's feasibility or not.

Using the data in Table 1, the preliminary economic analysis showed an IRR equivalent to 25%, equivalent to the estimated MAR, and a payback time of 2.7 years. The unit cost of biodiesel, calculated based on the ratio between the annual operating cost and the production rate per year, was \$4.60/kg. This general scenario was obtained considering the price of hydrotalcite-hydroxyapatite (HT-HAp) catalyst.

In this context, the production of biodiesel presented a positive IRR, and in comparison, with the TMA, it was economically viable based on the sales prices of the revenues, still requiring a more detailed study to make the biodiesel process more profitable.

According to the results illustrated in Table 5, they revealed that considering the current price of the HT-HAp catalyst, the simulated biodiesel plant is economically viable. However, the cost of the catalyst is a critical factor for the economic analysis of this process. Due to that, an analysis of the sensitivity of the revenue as a function of the variation in biodiesel prices was also studied.

Table 5. Economic aspects of the simulation of biodiesel production in the simulated plant.

Economic Aspects	
Total investment (\$/year)	1111369.89
Annual operating cost (\$/year)	324320.81
Total revenue (\$/year)	420728.88
Biodiesel unit price (\$/kg)	4.60
Internal rate of return (IRR)	25%
Return time (years)	2.70
Minimum Attractiveness Rate (MAR)	25%

Source: Authors.

3.4 Sensitivity analysis

The sensitivity analysis aims to assess the risk level of the project and identify the most critical aspects for the success or failure of the production plant. The analysis was performed fixing all the variables to verify how sensitive the internal rate of return (IRR) estimation is according to this variation, with the exception of one of them. The critical parameters are those that, although they varied not so much, cause a great disturbance in the results of the economic evaluation. Thus, the present work considered four different scenarios for the economic analysis: (I) analysis of the sale price of biodiesel using the HT-HAp catalyst in the process; (II) analysis of the sale price of biodiesel using the NaOH catalyst in the process; (III) analysis of reduction of ethanol flow in the process input stream using the HT-HAp catalyst; and (IV) analysis of the sale price of

biodiesel using different proportions of biodiesel:diesel. The sensitivity analysis, therefore, will indicate which variables are critical for the project's economic viability.

3.4.1 Biodiesel sales price analysis using HT-HAp catalyst

This sensitivity analysis was conducted to assess the influence of using the HT-HAp catalyst on the final profitability of the process. To evaluate the influence of the price of biodiesel on economic indicators, simulations were carried out with the sale price of biodiesel varying between \$2.60/kg and \$6.50/kg, to reach the minimum attractiveness rate (MAR) 25% at least, making the process economically viable based on biodiesel sales prices. All other variables, including the sale price of raw glycerol, remained constant. Table 6 and Figure 2 illustrate the behavior of the IRR and the payback time, according to the variables.

Table 6. Influence of biodiesel price on IRR and turnaround time.

Biodiesel price (\$/kg)	IRR (%)	Return time (years)
2.60	0.72	11.5
3.50	11.08	4.6
4.60	25.00	2.7
5.50	34.08	1.9
6.50	45.59	1.5

Source: Authors.

As can be seen in Figure 2, the IRR and the payback time are inversely proportional. The IRR increases with the increase in the price of biodiesel, while the payback time decreases, but in different functions.

Biodiesel sales prices below \$2.60/kg did not show significant IRR and payback time values, as these results were outside the analysis range. By varying the price from \$2.6/kg to \$6.50/kg, there was an increase from 0.72% to 45.59% in the IRR, corresponding to an increase of 98.4%. This value highlights the great influence of the biodiesel price on economic viability.

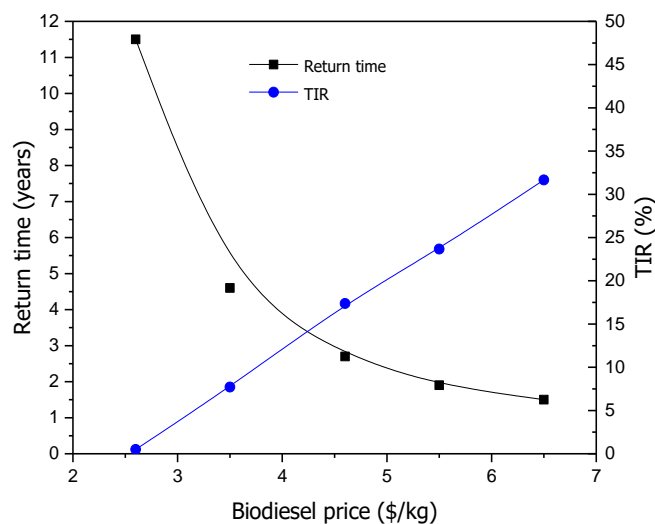
Through this analysis, it was also possible to determine the minimum price that biodiesel should be offered to make the project economically sustainable, that is so that the IRR is at least equal to the MAR. This amount was equivalent to \$4.60/kg, \$2 more than the amount initially determined.

This scenario proved to be more viable from an economic point of view, because the use of a heterogeneous catalyst in the process makes a reduction in the number of steps for the separation of the catalyst at the end of the reaction. In addition, the raw material (vegetable oil deodorization distillate - VODD) used in the process has a lower value because it is a by-product, which reduced the variable costs. Therefore, the main factors that proved to be more sensitive in relation to the final economic return of the project were the price of the HT-HAp catalyst and the price of biodiesel.

Zhang et al. (2003) simulated, with the support of HYSYS[®] software, the production cost of a plant with a production capacity of 8000 ton/year of biodiesel following four different production routes: two routes from alkaline transesterification, one using oil from refined soybeans (Case I) and another from residual soybean oil from the frying process (Case II). The other two routes were through acidic transesterification using residual oil: via acid catalysis (Case III) and by acid catalysis using hexane extraction (Case IV). Conversion rates of 97% and 95% were observed for basic and acid transesterifications, respectively. The result of the internal rate of return obtained for the proposed scenarios was -85.27%, -51.18%, -15.63%, and -21.48% for processes I, II, III, and IV, respectively. According to the authors, the alkaline transesterification of refined soybean oil (Case I) generated a higher operating expense, due to the high cost of acquiring refined oils and treating wastewater. However, cases III and IV proved to be more viable from an economic point of view, due to the use of lower value

raw materials, reducing variable costs. In addition to data, the main factors that proved to be sensitive in relation to the final economic return of the project were the price of residual oil and the price of biodiesel.

Figure 2. Influence of biodiesel price on IRR and return time.



Source: Authors.

Similar work was realized by West et al. (2008) for the methanolysis of canola oil considering the presence of 5% m/m of free fatty acids. Among the four processes studied (basic catalysis, acid homogeneous, heterogeneous, and supercritical conditions), the one with the lowest and highest total production cost was the process catalyzed by solids (\$4.45 million) and via basic catalysis (\$5.78 million), respectively. The internal rates of return for these processes were -22.2%, -8.71%, 58.76% and -0.9%. As can be observed, the production of biodiesel from heterogeneous catalysis was the only technological route to show liquid profits and, therefore, a positive IRR. According to the authors, this reflects the high operating costs required by other processes. In case I, there was a higher cost in the treatment for glycerol purification and catalyst cost, while in cases II and IV, excessive consumption of methanol was observed.

3.4.2 Analysis of the sale price of biodiesel using NaOH as a catalyst

In this scenario, the use of sodium hydroxide (NaOH) as a catalyst was chosen to compare the operating cost of the simulated plant with the use of HT-HAp catalyst in the process. Therefore, aiming to emphasize the importance of using this low-cost catalyst, a comparative scenario with the cost of hydroxalcite-hydroxyapatite (HT-HAp) as it is a heterogeneous catalyst currently not used in industrial plants was carried out.

Table 7 and Figure 3 illustrates the behavior of the IRR and payback time according to the economic indicators. To evaluate the influence of the price of biodiesel, simulations were carried out with the price of biodiesel ranging between \$2.60 and \$6.50/kg, to reach at least the minimum attractiveness rate (MAR) of 25%, ensuring an economically viable process.

Table 7. Influence of biodiesel price on IRR and return time.

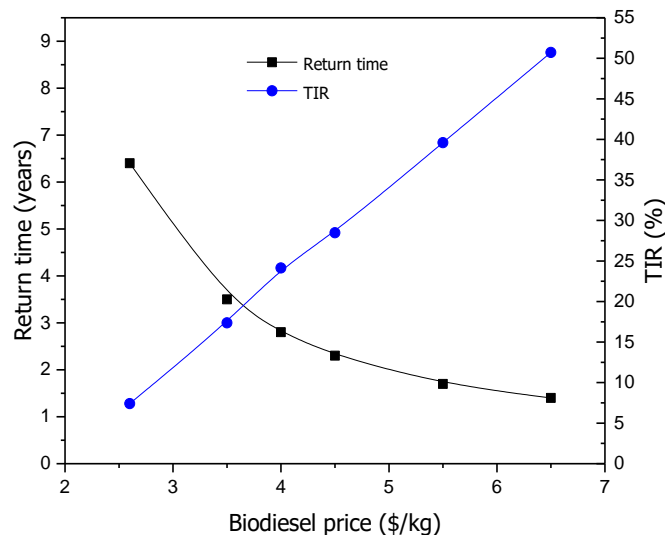
Biodiesel price (\$/kg)	IRR (%)	Return time (years)
2.60	7.69	6.4
3.50	18.04	3.5
4.00	25.00	2.8
4.50	29.54	2.3
5.50	41.04	1.7
6.50	52.55	1.4

Source: Authors.

As can be observed in Figure 3, the IRR and the payback time are also inversely proportional. The IRR increases with the increase in the price of biodiesel, while the payback time decreases. The variation of the price from \$2.60/kg to \$6.50/kg caused an increase from 7.69% to 52.55% in the IRR, corresponding to an increase of 85.37%. This value also highlighted the great influence of the biodiesel price on economic viability.

Through this analysis, it was possible to determine the minimum price that biodiesel should be offered using NaOH as a homogeneous catalyst, comparing the results with the other ones that used HT-HAp as a heterogeneous catalyst (Table 6). This amount was equivalent to \$4.00/kg, \$1.4 more than the initially determined amount. In other words, the process that used the NaOH catalyst obtained the minimum price of biodiesel that must be offered (\$4.00), while the process that used the HT-HAp catalyst obtained the minimum price of \$4.60. This difference in value was equivalent to only \$0.60 less than the process using the HT-HAp catalyst.

Figure 3. Influence of biodiesel price on IRR and payback time.



Source: Authors.

The homogeneous alkaline technology is currently the most used method for biodiesel production, mainly due to the higher reaction yield. As a disadvantage, the purification methods used in this case make the project more expensive comparing to the use of heterogeneous catalysts. Moreover, it is necessary to treat a large volume of basic wastewater and high energy consumption. However, the process has many limitations mainly on the amount of energy required for product purification and catalyst removal, and furthermore, these catalysts are not reusable (Mansir et al., 2017). Therefore, due to the small difference in the price of biodiesel being equivalent to only \$0.60 less than the process that used the HT-HAp catalyst demonstrates that the use of the HT-HAp catalyst would make the process less expensive mainly because of the purification

steps. This is caused by the easily separation of the catalyst at the end of the process, and the possibility of reusage of the catalyst.

According to West et al. (2008) the solid catalyzed process for biodiesel production is more efficient than alkaline catalysis and supercritical processes. The study emphasized the lowest capital investment with a higher IRR through a technically simple process. Thus, different types of solid catalysts have already been developed to overcome the disadvantages of homogeneous catalysts currently used in industries.

Santana et al. (2010) simulated, with the HYSYS® software, a continuous production plant with a capacity of 1000 kg/h of biodiesel using as raw material castor oil, ethanol in the oil/alcohol ratio 1:12, and alkaline catalyst, obtaining 100% conversion. The researchers studied three different scenarios for the economic analysis: (I) considering the price of castor oil in Brazil equal to \$1.15/kg, considering the glycerol purification step; (II) castor oil price equal to \$1.15/kg, without the glycerol purification step and (III) considering the oil price equal to \$0.526/kg. The results of production costs for each analyzed scenario were, respectively, \$1.56/L, \$1.52/L, and \$0.92/L. Comparing the cases I and II, the glycerin purification steps proved to be expensive, making the process not economically attractive. The increase in operating cost was mainly attributed to the high energy consumption of this purification step, about 82% of the energy of the entire plant. Scenario III, optimistic about the low purchase price of castor oil, showed the influence of the raw material purchase price, reflecting on the project profitability through a more affordable oil price.

3.4.3 Analysis of reduction of ethanol inlet flow in the process input stream using the HT-HAp catalyst

The reduction in raw material costs is a major factor in the cost of production, considering that for the two previous scenarios it represented most of the expenses. Therefore, a sensitivity analysis was carried out for the reduction of ethanol flow in the biodiesel production process using VOED as a residual raw material and HT-HAp as catalyst. Consequently, this analysis will indicate that the ethanol flow is a critical variable for the economic feasibility of the project.

In this scenario, an analysis was carried out considering 10% of the flow of ethanol, to reduce the cost of this raw material and assess the influence that the price of biodiesel would have on economic indicators. Simulations were carried out with the sale price of biodiesel ranging between \$2.60/kg and \$6.50/kg, to reach the minimum attractiveness rate (MAR) of 25%, to make the process economically viable to from the sale prices of biodiesel. Table 8 and Figure 3 illustrate the behavior of the IRR and the return time, according to variables.

Table 8. Influence of biodiesel price on IRR and return time.

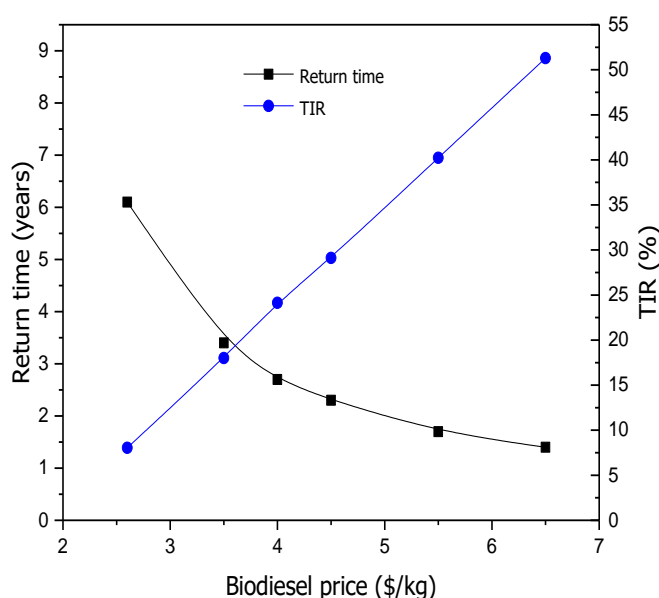
Biodiesel price (\$/kg)	IRR (%)	Return time (years)
2.60	8.33	6.1
3.50	18.68	3.4
4.00	25.00	2.7
4.50	30.18	2.3
5.50	41.68	1.7
6.50	53.19	1.4

Source: Authors.

As can be observed in Figure 4, the IRR and the return time are inversely proportional. The IRR increases linearly with the increase in the price of biodiesel, while the return time decreases, but in different functions. While, in Table 8, when the price varied from \$2.6/kg to \$6.50/kg, there was an increase from 8.33% to 53.19% in the IRR, corresponding to an increase of 84.34%.

Through this analysis, it was also possible to determine the minimum price that biodiesel should be offered to make the project economically sustainable, that is so that the IRR is at least equal to the MAR. This amount was equivalent to \$4.00/kg, which represented \$0.60 less in the sales price with the reduction of the ethanol flow in the process input stream.

Figure 4. Influence of biodiesel price on IRR and return time.



Source: Authors.

The results obtained proved that, in fact, the reduction in the flow of ethanol in the process is not the preponderant factor for the reduction of the biodiesel production cost. A 13% reduction in the sale price of biodiesel showed only a small variation in the total costs of the process. In other words, this variation to 10% of the ethanol input flow did not impact the total costs of the process but considering only the variable cost. This is because the size of the operating plant had a negative influence on the composition of costs, which can be seen mainly due to the high cost of facilities. Facilities costs correspond to costs associated with equipment maintenance, depreciation, and diversity, such as insurance, local taxes, and general expenses of the plant, making it the plant with the highest operating cost.

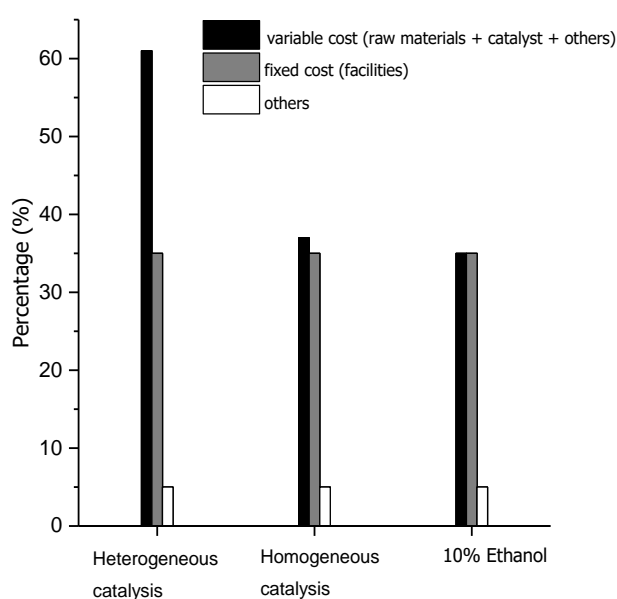
When observing the values obtained for the three different scenarios, for each process, the plant that operated with heterogeneous catalyst (HT-HAp), or homogeneous catalyst (NaOH) or reduction in the flow of ethanol, did not present sales prices of biodiesel equivalent to biodiesel with a commercial price of \$1.45, that is, a value remarkably lower than obtained by the three different scenarios, thus, the presence of government subsidies would be necessary so that the process could reach this sale price and become competitive in the market.

Figure 5 illustrates the composition of the biodiesel production cost for each scenario discussed. The variable cost (raw materials + catalyst + others) contributes to 61% of the total costs for the heterogeneous catalyst, 37% for the homogeneous catalyst, and 35% for the reduction of ethanol input flow. The residual raw material, VODD, contributes to the reduction of raw material costs as it is a low-value by-product. Meanwhile, the fixed cost (facilities) contributes about 35% of the total costs for all cases. This indicates that even the heterogeneous catalyst has a higher cost compared to other cases, there was not a large increase in the sale price of biodiesel. In the scenario that analyzed the reduction in the flow of ethanol, the

variable cost and the fixed cost contribute the same amount, both contributing 35%. This explains why the variation to 10% of the ethanol input flow has not impacted the total costs of the process.

According to Cao et al. (2020), the authors investigated three chemical processes to produce biodiesel based on the economic evaluation through the COMFAR III software. The following cases were: process catalyzed by alkaline catalyst using virgin vegetable oil (process I), a process catalyzed by acid catalyst using residual cooking oil (process II), and process using supercritical using residual cooking oil (process III). In which, it can verify that in the sensitivity analysis operating costs significantly impacted the sale price of biodiesel, this analysis was more tangible in process III.

Figure 5. Breakdown of biodiesel production cost for each scenario.



Source: Authors.

While Cruz et al. (2017) studied the simulation of three biodiesel production plants via ethylic transesterification, using macauba oil as a source of triglycerides, all simulated in the Aspen HYSYS 8.8 software. The plants were designed to operate with a flow of 1000 kg h^{-1} of oil and the routes used were Acid Homogeneous Catalysis, Basic Homogeneous Catalysis, and Transesterification in Supercritical Medium. An economic feasibility analysis was also carried out for the simulated plants, estimating, from them, the biodiesel production cost. Finally, a sensitivity analysis was performed to observe the effect of oil price and flow variation on biodiesel production costs. In which the authors can observe, in relation to the distribution of annual operating costs for the three processes, that Acid Catalysis had the lowest annual operating cost, totaling US\$ 11,889,100.00 while Basic Catalysis and the Supercritical presented US\$ 13,354,670.00 and US\$ 12,587,100.00 respectively. It can be concluded that the size of the plant operating by basic catalysis had a negative influence on the composition of costs, this can be seen mainly by the high cost of labor and plant support, making it the plant with the highest operating cost.

3.4.4 Analysis of the sale price of biodiesel using different proportions of biodiesel:diesel

The revenue generated by each case studied was related to the sale of biodiesel, and to the sale of glycerol, which was produced with mass purity above 87%, enabling its commercialization with minimum glycerol mass purity of 83%. Therefore,

according to a preliminary economic analysis, the unit cost of biodiesel produced with HT-HAp as catalyst was \$4.60/kg, what makes the process profitable.

However, a sensitivity analysis of the proportion of the mixture biodiesel:diesel was carried out. The analysis was done considering the most updated value of diesel on the market (\$0.90/kg) (ANP, 2021). Table 9 shows the price of pure biodiesel and the price of biodiesel obtained by the process that used HT-HAp mixed with diesel in different proportions.

Table 9. Influence of the sale price of biodiesel using different proportions of the biodiesel:diesel mixture.

Mix ratio biodiesel:diesel	Biodiesel price (kg)
Pure biodiesel	\$4.60
B15 (15% of biodiesel mixed with diesel)	\$1.59
B10 (10% of biodiesel mixed with diesel)	\$1.36
B8 (8% of biodiesel mixed with diesel)	\$1.27
B6 (6% of biodiesel mixed with diesel)	\$1.18
B4 (4% of biodiesel mixed with diesel)	\$1.08
B2 (2% of biodiesel mixed with diesel)	\$0.99

Source: Authors.

In relation to the cases studied, the price of pure biodiesel with the highest diesel blend (B15) decreased from \$4.60 to \$1.59, representing a decrease of \$3.01 in the sale price. Therefore, the introduction of diesel proved to be efficient to reduce the sale price of biodiesel for the commercial market. Thus, among the 6 cases analyzed with the different proportions of biodiesel:diesel, the lowest price of fuel was found with B2 (2% of biodiesel), representing a decrease in the biodiesel price of \$3.61. This fact indicated that the addition of small proportions of biodiesel to diesel represented a great impact compared to the price of pure biodiesel, making the biodiesel sales price more competitive to the biodiesel price in the commercial market (\$1.45).

According to Guarieiro et al. (2008), an alternative fuel needs to be technically competitive, easily accessible and compatible with environmental protection needs. All the results above mentioned showed the profitability of the introduction of biodiesel in the energy matrix, increasing the process revenue, without altering the equipment and utilities costs. Another advantage of the mixture biodiesel:diesel is the reduction of the volume imported by Brazil, due to the fact that the Brazilian product does not attend the internal demand. According to ANP, 5% of biodiesel mixed with diesel fuel consumed in the country represents savings of 380 million dollars/year.

3.5 Breaking Point

The breaking point is determined as the minimum production rate in order to generate sufficient revenue to be equal to the total cost. This point is calculated varying the production levels that will directly influence the project cash flow. For this calculation, a biodiesel sale price of \$4.60/kg was adopted, corresponding to the minimum price that makes the process economically viable.

Table 10 and Figure 6 represents the costs and revenues obtained as a function of the biodiesel production rate. Variable costs are those that vary as a function of the production rate, while fixed costs remained unchanged.

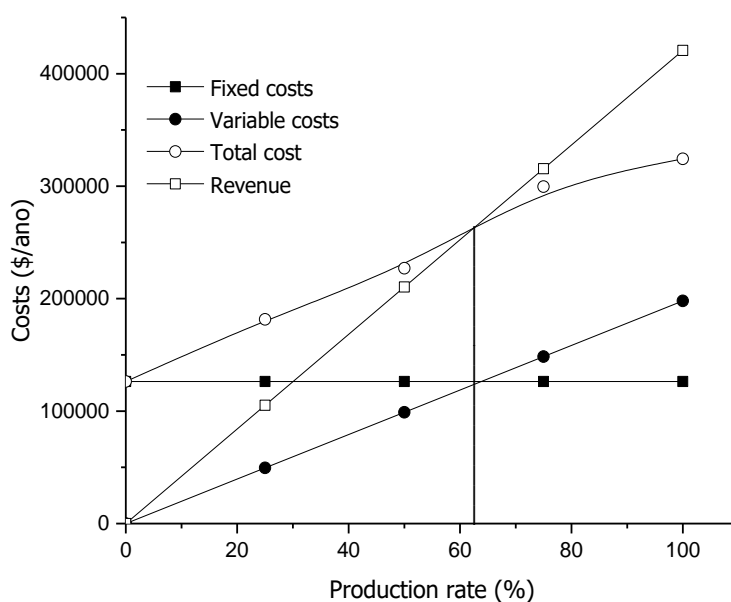
In Figure 6 is possible to observe that the minimum required production rate is 64%. This implies stating that if the plant operates below this value, the production costs will be greater than the total revenue obtained from the sale of biodiesel and glycerol and, therefore, the cash flow will remain negative, thus harming the plant profitability.

Table 10. Cash flow analysis as a function of biodiesel production rate.

Production rate (%)	Fixed cost (\$/year)	Variable cost (\$/year)	Total cost (\$/year)	Revenue (\$/year)
0	126326.42	0	126326.42	0
25	126326.42	49498.60	181619.65	105182.22
50	126326.42	98997.19	227024.57	210364.44
75	126326.42	148495.79	299672.69	315546.66
100	126326.42	197994.39	324320.81	420728.88

Source: Authors.

Figure 6. Leveling point: revenues and costs as a function of the production rate.



Source: Authors.

4. Conclusion

In this study, it was possible to conclude that the plant becomes viable, from an economic point of view, with the biodiesel cost of \$4.60. The breaking point pointed out a minimum production rate of 64%. Regarding the sensitivity study, it was observed that the catalyst acquisition price was the most critical factor in the economic analysis of the simulated plant. Using different catalysts, a comparative study showed that the heterogeneous catalyst makes the process less expensive with the purification steps. Meanwhile, in the sensitivity analysis of the reduction of ethanol flow in the process input stream, it was not a major factor in reducing the cost of producing biodiesel. In the other side, the sensitivity analysis varying the proportions of biodiesel:diesel mixture indicated that the addition of small proportions of biodiesel to diesel represented a large impact compared to the price of pure biodiesel. In view of the results obtained, we future suggest the study of other sources of triglycerides, in order to compare, both from a technical and economic point of view, the efficiency of the biodiesel production process. Animal fat residues (beef and chicken) are potential alternatives, especially in the southeastern region of the country.

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