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Simulation and Optimization ff Biojet Fuel Production through Single-Step Route and Residual Raw Material

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The use of biokerosene stands out for its potential to reduce environmental impacts on aviation's use. One of the most promising and advanced routes for industrial use is the hydroprocessing of fatty acid esters (HEFA), and, although the biokerosene production is still more expensive than the conventional kerosene, many studies are focusing on process improvement and the development of catalysts with higher efficiencies. One possible approach to cost reduction of this route is the use of residual raw materials and one reactor, which can replace commonly used vegetable oils and reduce hydrogen consumption. In order to find better yields at lower costs, this work aims to simulate, optimize and verify the economic viability of the production of biojet fuel by HEFA route through a single-step process with reduction in hydrogen consumption, and using soybean acid oil as a residual raw material. The base simulation was developed using the Aspen Plus V10 software®, with literature data. Subsequently, different reactor conditions were tested, varying the hydrogen/oil ratio, pressure and temperature in the reactor to determine the optimal operating conditions to produce a high-quality biofuel. In addition, an energy integration analysis was carried out to reduce energy and utilities consumption, as well as CO_2 emission analysis to verify environmental impacts for this route compared to fossil aviation kerosene. Finally, a preliminary economic analysis was performed, and an estimate of the investment required for the installation of a manufacturing unit was calculated.

1. Introduction

The aviation sector is becoming increasingly accessible for the transportation of products and people. According to Wei et al. (2019), forecasts indicate that the number of air transport users will double in the next 20 years, indicating that the use of aviation fuel will grow accordingly. Therefore, the impact of the aviation industry on atmospheric emissions also increases, which indicates the importance of studies involving bio-aviation fuel (BAF), since its use could make the carbon cycle more sustainable. When applied in the aviation sector, biofuels have the potential to reduce carbon dioxide emissions by up to 80 % throughout its life cycle (IATA, 2017).
One of the most promising production routes is the hydroprocessing of fatty acid esters (HEFA), due to the potential of a quality biofuel production. Different triglyceride feedstock can be used to produce biojet fuel by this route, such as vegetable oil, waste oil and animal fats (Gutiérrez-Antonio et al., 2018). However, the HEFA route still brings the challenge of producing biokerosene with a competitive price, compared to fossil kerosene or aviation turbine fuel (ATF). The route involves high operating costs, the need of two reactors to promote the hydroprocessing of fatty acids, in addition to high consumption of hydrogen gas. Therefore, studies on the route aim to reduce costs and make it economically viable by changing catalyst types and reaction conditions, for example, with some works showing promising results. Zhao et al. (2015) and Choi et al. (2015) converted fatty acids into hydrocarbons without the use of hydrogen using sunflower oil and stearic acid. Scaldaferri and Pasa (2019) also produced biojet fuel without H_2, using an unusual niobium phosphate catalyst in one-step process. Zhang and Zhao (2015) proposed the use of limonene as a second raw material to provide hydrogen for the hydroprocessing of palm oil. Verma et al. (2011) proposed a single-step process using a sulfide catalyst (Ni-Mo with ZSM-5 zeolite support), using algae and jatropha oil.

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Regardless of which strategy is used, the studies still present challenges to be overcome, especially with the quality of the biokerosene and costs involving large-scale production. In order to find better yields at lower costs, this work aims to simulate the production of aviation biokerosene from HEFA route reducing the number of steps, hydrogen consumption and using soybean acid oil, a residual raw material. The objective is to evaluate the possibility of large-scale biojet production adopting these reducing costs strategies with optimized reactor conditions, evaluating its economic viability, besides the energy and environmental impacts involved.

2. Methodology

The process was simulated with the software Aspen Plus V10®, using conversion and kinetics data obtained in the literature. The flowsheet was designed considering two stages for biokerosene production: the hydrolysis of soybean acid oil (R-01) and the hydroprocessing of fatty acids (R-02). The hydroprocessing was carried out in only one reactor for the hydrodeoxygenation, hydrocracking and hydroisomerization reactions, originally carried in two reactors in the traditional route. Hydrolysis aims to transform the triglycerides present in the initial raw material into fatty acids, to facilitate their further treatment and reduce the amount of hydrogen needed. The developed flowsheet can be seen in Figure 1.

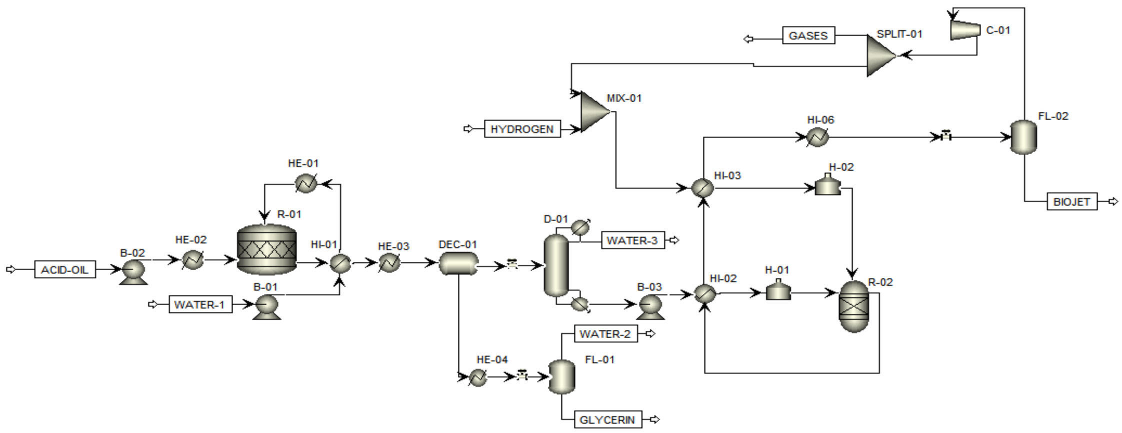

Figure 1: Biojet production unit by single-step route

The thermodynamic model adopted throughout the simulation was the PSRK (Predictive Soave-Redlich-Kwong) since it is suitable for mixtures of polar compounds, nonpolar and light gases, using high temperatures and pressures. With the simulation developed, preliminary tests were made using a 2^3 factorial planning to evaluate the reaction behavior in the hydroprocessing reactor and to search optimal operating conditions varying temperature, pressure, and hydrogen/oil ratio. Also, an energy analysis was made using the tools of Aspen Plus V10® and Aspen Energy Analyzer V10® for application of cost-effective energy integration exchangers in simulation. An economic analysis was developed based on parameters of operating costs, initial capital, costs with raw materials, equipment, utilities, and payback period. Finally, an environmental analysis was developed by greenhouse mass balance in a cradle-to-gate cycle, considering extraction and processing of natural resources, intermediate products, and the manufacture of the main product, using CO_2 emission data from the literature.

3. Results and Discussion

3.1 Parametric Analysis

From the 2^3 factorial planning in R-02 reactor, it was possible to compare the composition of the final product for each operating condition, focusing on selectivity, yield, and isomers and linear hydrocarbons ratio (i/n). The evaluated conditions and results are shown in Table 1.

Parametric conditions tested were based on work published by Cheng et al (2014) and Zhang et al. (2017). For all experimental conditions, the simulation presented good biokerosene yield values. An important parameter to be analyzed to define the quality of biokerosene is the isomers and linear hydrocarbons ratio (i/n). The literature shows that a high quality biokerosene presents values of i/n>4.5, for better combustion quality and freezing properties (Sousa, 2018). It is also possible to observe that good values of this parameter were obtained for the analyzed conditions. The lowest i/n values are observed for the simulations performed at higher temperatures, presenting low variation with changes in pressure and amount of hydrogen. For simulations at the lowest temperatures, there was an increase in i/n ratio for all pressures and hydrogen/oil ratios applied.

Table 1: Results of parametric analysis

Test	Temperature (ºC)	Pressure (bar)	Hydrogen/oil ratio	Linear Selectivity (%)	Isomer Selectivity (%)	Aromatics Selectivity (%)	i/n	Yield
000	390	40	1000	13.5	73.98	-	5.48	68.16
+++	500	50	1500	15.44	70.14	1.85	4.54	69.55
++-	500	50	500	15.42	70.08	1.92	4.54	69.20
+-+	500	30	1500	8.49	38.42	39.97	4.52	77.85
+--	500	30	500	8.35	37.77	40.74	4.52	83.16
-++	300	50	1500	11.10	76.38	-	6.88	77.38
-+-	300	50	500	11.10	76.38	-	6.88	86.25
--+	300	30	1500	11.15	76.33	-	6.84	77.38
---	300	30	500	11.15	76.33	-	6.84	73.49

Besides, it is possible to analyze the influence of temperature and pressure on the number of aromatics, in which the highest temperature implying larger amounts of aromatics, being unfavorable to combustion characteristics. The increase in pressure contributes to reduce the number of aromatics, and the use of temperatures lower than 500 ºC favors the formation of a higher quality biokerosene, besides allowing greater energy savings. For process yield, higher values were obtained for the simulation with temperature of 500 ºC, pressure of 30 bar and 500 hydrogen/oil molar ratio, and for the simulation using temperature of 300 ºC, pressure of 50 bar and 500 molar ratio. However, as the experiment with higher temperature is discarded by the number of aromatics formed, the most advantageous process conditions in terms of yield and process economy is the one with higher pressure. Therefore, the best operating point is 300 ºC, 50 bar and 500 hydrogen/oil molar ratio.

3.2 Energy Analysis

For the energy analysis, using Aspen Energy Analyzer V10®, the simulator pointed to 89.4 % of possible energy savings with the use of energy integration exchangers. Therefore, some exchanger scenarios were simulated to analyze which combination would present the greatest energy savings. In addition to the exchangers proposed by the simulator, an energy integration exchanger was used to heat the inlet oil stream in the R-02 reactor with the outlet stream of the reactor itself, since the outlet stream leaves the equipment at high temperatures and the input stream needs to be heated before entering the equipment. The information about the tested scenarios is presented in Table 2.

Table 2: Scenarios of energy integration exchangers proposed by simulator

Scenario	1	2	3	4	5
Number of Exchangers	4	2	3	4	3
Energy Savings (%)	81.4	85.7	79.1	78.1	75

Scenario 2 was chosen for presenting the highest energy savings, with the use of two energy integration exchangers to heat the inlet hydrogen stream in reactor R-02 and the inlet water stream in reactor R-01, with the respective output streams of each reactor. With this scenario, there was an 86 % energy savings, close to the savings stipulated by the software.

3.3 Economic Analysis

After the inclusion of energy integration exchangers, it was possible to develop the economic analysis using the prices of raw materials and products presented in the literature. Table 3 shows all the values used in the simulation.

Table 3: Raw material and product prices used in simulation

Component	Price (USD/kg)
Biokerosene	0.93
Crude Glycerin (Landress, 2019)	0.21
Hydrogen (Dagdougui et. Al., 2018)	1.25 to 3.5
Soybean Oil (Markets Insider, 2021)	0.62
Soybean Acil Oil	0.31

For utilities prices, the values already defined in the software were used. In addition, some considerations have been made. For the acid oil, the consideration made was that its price was about half the price of soybean oil, information collected in the work of Soares (2014). For biokerosene, considering that in literature several prices are found depending on the production capacity of the plant, an intermediate value was used, of USD 0.93/kg. Using the price of biokerosene as USD 0.93/kg and the price of hydrogen as USD 1.25/kg, we have, for an annual production of 120 million liters of biokerosene using 27000 L/h of soybean acid oil, a return time on investment of 3.55 years, a value considered promising for plant implementation. The costs obtained can be observed in Table 4.

Table 4: Economic analysis of the simulated unit

Property	Value
Total capital cost (USD million)	10.17
Total operating cost (USD million/year)	55.64
Total raw materials cost (USDmillion/year)	49.51
Total product sales (USDmillion/year)	76.86
Total utilities cost (USD/year)	412,42
Return Time (Years)	3.55
Equipment cost (USD million)	1.71
Total installation cost (USD million)	4.37

As the price of hydrogen varied, an analysis was made considering what would be the maximum selling price of hydrogen for the plant to remain profitable with the sale of biokerosene at USD 0.93/kg. By analysis, it was observed that production will only be profitable if the selling price of hydrogen is less than USD 2/kg. The minimum selling price of biokerosene for the plant would be USD 0.67/kg, considering that the plant did not make any profit from the process and the hydrogen price was USD 1.25/kg. As it is of interest to keep profit, if we kept the selling price at USD 0.93/kg, the price of biokerosene would be close to current conventional kerosene price, which showed a considerable price increase last year, being approximately USD 0.9/kg (IATA, 2023). Also, the plant presented lower sales values than some found in the literature, such as the value stipulated by Pearlson (2013), of USD 1.37/kg for the same annual production and Martinez-Hernandez et al. (2019), that estimated approximately USD 1.64/kg, considering a higher hydrogen price of USD 2/kg and an annual production of 11.9 million liters. A near minimum selling price was obtained by Klein et al (2018), using a different strategy of cost reduction involving on-site H_2 production in integrated biorefineries, of USD 0.87/kg for a 228 million liters production. It is also possible to observe that the material that represents most part of the raw materials costs of this simulation is the soybean acid oil, despite being a residual raw material. The cost of hydrogen has become lower than the acid oil cost due to the recycling of hydrogen in the process, being an essential strategy for reducing costs. The cost per hour for soybean acid oil and hydrogen were 3096.932 USD/h and 2519.376 USD/h, representing approximately 55 % and 45 % of raw materials costs, respectively.

4. Environmental Analysis

The emission of greenhouse gases generated for the plant configuration before and after the addition of energy integration exchangers by the energy analysis was compared. According to the results presented in simulation, a reduction of 57.3 % in CO_2e (carbon dioxide equivalent) emissions is observed with the use of energy integrations. The result is expected, considering that the use of integration exchangers enables energy transfer between streams without the need of an external source of heating, generating an internal reuse power. Despite the reduction, the CO_2 generated in simulation is mainly composed by the use of utilities, heated by combustion of a fuel that, in this case, was considered biogas. By the greenhouse gases balance generated on the cradle-to-gate cycle, it is possible to evaluate the total emissions generated throughout the biofuel generation cycle, considering the production and transport of main raw materials (soybean, hydrogen, and biogas). The results obtained are shown in Table 5.

According to Marzullo (2007), the absorption of CO_2 per hectare of soybeans during the photosynthesis process is around 8.433 t CO_2/ha. Dividing the total emission value by this factor, we see that the necessary amount of hectares to absorb all the CO2 emitted in the production cycle of 1 ton of biokerosene is 0.123 ha/t BAF. When comparing the emissions related to the biokerosene cycle generated with other raw materials, in a study defined by Roitman (2018), we see that the value obtained for the cycle using acid soybean oil is slightly lower than that of the HEFA route using used cooking oil, and considerably lower than the HEFA route cycle using camelina oil and the conventional fossil kerosene cycle. To compare the results, the values presented in the work by Roitman (2018) were converted from g CO_2e/MJ BAF to t CO_2e/t BAF, using the minimum value of lower calorific value defined by the ASTM D1655 standard (Peres et al., 2018), of 42.8 MJ/kg ATF. The compared values are shown in Table 6.

Table 5: Total Carbon Emissions

System	Emission (t CO_2e/t BAF)
Soybean Cultivation	0.16
Soybean Transport	4.29e-05
Soybean Refining	0.01
Soybean Acidification	1.65e-03
Biokerosene Production	0.12
Hydrogen Transport	6.18e-05
Hydrogen Production	0.72
Biogas Transport	4.85e-06
Biogas Production	0.02
Total	1.04

Table 6: Total Carbon Emissions

Route	Raw Material	Emission (tCO_2e/t BAF)
HEFA (BAF)	Soybean acid oil	1.04
HEFA (BAF)	Used cooking oil	1.16
HEFA (BAF)	Camelina oil	2.01
Refine (ATF)	Petroleum	3.77

It is possible to observe that the use of acid soybean oil is advantageous in environmental terms, since its emission is lower when compared to the used cooking oil route. Despite the value obtained being lower than that analyzed by Roitman (2018), it cannot be concluded that the emission of the cycle is effectively lower, considering that the considerations by different authors may have been different in some points of analysis of the subsystems. Despite this, the values generated by the present work are consistent with the average values found in the literature. Comparing with the emissions generated by fossil aviation kerosene, the environmental gains with the use of biofuel are remarkable. With the value obtained, there is a reduction of 72 % in the value of emissions compared to conventional kerosene. Observing the value estimated by IATA (2017), of 80 %, the value is reasonably close. Other studies also indicate that the expected reduction would be around 61 to 63 %, according to Zemanek et al. (2020), being at an intermediate value to that presented by these references. Looking at the impact of each system on the cycle, we see that most of the emissions refer to the production of hydrogen gas, biokerosene itself and soybean cultivation for this study.

5. Conclusions

Considering the potential for applying the HEFA route for production of aviation biokerosene, it is possible to observe that large-scale production is promising from soybean acid oil. The biokerosene presented adequate characteristics under the R-02 reactor conditions of 300 ºC, 50 bar and 500 hydrogen/oil molar ratio, with low aromatic content and i/n ratio of 6.8. For those conditions, the yield was approximately 86.3 %. In addition, the energy analysis and application of energy integration exchangers also reduced about 86 % of the energy initially used in simulation, showing some cost reduction related to these resources. For a profitable simulation, the biojet fuel price obtained was closed to the current conventional jet fuel price, which had a considerable price increase in the last year, showing that the application of the residual raw material and only one reactor for hydroprocessing can be useful alternatives to make the biojet fuel production competitive to fossil kerosene. The soybean acid oil, not very explored in the aviation sector, is an interesting alternative for reducing expenses, even though it represents the major cost related to raw materials in the process, representing 55% of raw materials costs per hour. Hydrogen, despite being a raw material with the highest added value, had its impact reduced by using recycling in the process, but it still represents 45% of operating costs, which makes the acid oil with the highest participation in these costs. Therefore, the application of a single-step route, and the hydrogen recycle can be interesting alternatives that reduce gas-related expenditures. Furthermore, for an annual production of 120 million liters of biokerosene, the payback period was about 3.55 years, which is considered a reasonable time for an industrial plant. Also, the environmental study of emissions developed showed an emission factor of 1.04 t CO_2e/t BAF and a reduction in greenhouse gas emissions of 72 % when compared to the fossil kerosene cycle. This shows us that studies involving alternatives in obtaining biofuels are essential to accelerate the process of energy transition to renewable energies and reduce the impacts generated by the aviation sector.

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