



## Reaction Analysis and Simulation of Fatty Esters Production from Acid Oil using a Hybrid Process

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The use of residual oils as raw materials to produce fatty esters in the biodiesel industry is of great interest, as it may improve both the economic and environmental aspects of a process. The use of these residual materials in biofuel production can aggregate value to something that would otherwise be solely disposed of and, as they have lower costs related to the refined oil, its use could reduce operating costs in the industry. However, these resources usually present high free fatty acid (FFA) content. Therefore, considering the traditional biodiesel production process, these fatty acids must be removed before entering the transesterification reactor due to soap formation, which reduces the reaction yield. As a result, to remove these FFA, one of the most common procedures is through the inclusion of a previous step, the esterification reaction. In both esterification and transesterification, short-chain alcohols are generally used to promote FFA and triglycerides conversion into long-chain esters. Concerning the influence associated with the choice of different alcohols, there is a wide variety of process analyses presented in the literature focusing on using only one type of alcohol, usually methanol or ethanol, in both reactions. Nevertheless, the study of a biodiesel production process evaluating the possibility of using the two alcohols at distinct parts in the process is a significant gap to be filled. In this study, an in-depth analysis of the esterification and transesterification reaction kinetics using methanol and ethanol was carried out as a possible optimization variable. In addition, the process simulation concerning the use of different alcohols for each reaction was performed. Several conditions were tested in both reactors before the final alcohol selection, and the use of methanol in the esterification and ethanol in the transesterification reaction presented the most promising results, indicating that a hybrid process concerning alcohol use may bring significant advantages to the process. To validate this theory, a complete process and economic analysis were carried out, evaluating not only the results obtained from the reaction but also the purification steps. Another essential aspect considered in the project is the fatty acid content in the oil, which may vary according to storage conditions and prior use. Thus, the impact due to this fluctuation in the economic aspects was verified. With the simulated base project, different optimizations were made to reduce the entire process's equipment and operational costs. An energy analysis was also developed with the inclusion of energy-saving heat exchangers, which reduced utility costs. Finally, an economic evaluation of the final process was obtained to assess the main variables affecting the project and its payback time. It is essential to say that the kinetic study was based on the content present in the literature, and the simulation was performed on the software Aspen Plus® V10, including the energy and economic analyses. Considering the importance of optimizing the industrial process for biodiesel production and improving its economic aspects, the main target of this study is to demonstrate how the use of different alcohols for the esterification and transesterification reactions may enrich these previously reported vital aspects.

## 1. Introduction

The constant search for process cost reduction and optimization is of extreme importance. It promotes the use of different materials as substitutes for the original ones, improving the diversity of process types and ways to produce the same final product. It can also add value to materials that would otherwise be discarded. In the biodiesel industry, the type of oil or fat is important, but the possibility of using other alcohols is of great interest. Although most studies focus on using one type of alcohol, usually a short-chain one (Musa, 2016), little is known about using different alcohols in the same process. The most common alcohols used in the biodiesel industry are methanol and ethanol, and the final product characteristics vary to the use of each of these alcohols. Fatty acid methyl esters (FAME), for example, have a lower viscosity and acid value at the cost of lower stability toward oxidation, heat content, and cetane number (Knothe, 2005). However, fatty acid ethyl esters (FAEE) have better lubricity (Joshi et al., 2010) and lower cloud and pour points (Stamenković et al., 2011).

There are various studies available in the literature evaluating the use of methanol (Vinay et al., 2015) or ethanol (Margarida et al., in press) in process simulation. However, an analysis considering the use of different alcohols in distinct parts of the process is still necessary. In this study, the possibility of using residual oils varying acid concentrations and using different alcohols in the esterification and transesterification reactions in the biodiesel industry is assessed, verifying both the reaction and economic aspects of the process.

## 2. Results and Discussion

### 2.1 Alcohol and Reaction Kinetics Analysis

The biodiesel production process from residual oils demands removing the FFA before the transesterification reaction with a base catalyst. Therefore, the esterification reaction kinetics with methanol (Rani et al., 2013) and ethanol (Murad et al., 2017) using sulfuric acid as catalyst was simulated and evaluated at different conditions, as presented in Table 1. A reaction period of 90 minutes was used in all esterification reactions, and lauric acid was adopted as the base fatty acid for analysis.

Table 1: Results from the esterification reaction simulation using methanol and ethanol with Aspen Plus®

Methanol								
Temp. (°C)	Lauric Acid (mol)	Methanol/Acid Molar Ratio	Conv. (%)	Equipment Costs (million USD)	Utility Cost (million USD/year)	Product Sales (million USD/year)	Operating Cost (million USD/year)	Product Sales vs. Operating Cost
50	100	60:1	63.05	3.209	4.511	82.866	90.111	0.920
60		40:1	97.26	2.231	3.032	127.836	89.808	1.423
60		60:1	97.92	2.978	4.246	128.710	93.350	1.379
60		80:1	98.44	3.640	5.567	129.389	96.101	1.346
Ethanol								
Temp. (°C)	Lauric Acid (mol)	Ethanol/Acid Molar Ratio	Conv. (%)	Equipment Costs (million USD)	Utility Cost (million USD/year)	Product Sales (million USD/year)	Operating Cost (million USD/year)	Product Sales vs. Operating Cost
60	100	6:1	62.04	1.685	1.691	86.878	86.104	1.009
60		9:1	67.58	1.687	2.201	94.642	99.266	0.953
60		12:1	74.09	1.852	2.710	103.749	104.591	0.992
70		9:1	72.26	1.694	2.183	101.196	99.279	1.019
70		12:1	75.43	1.871	2.771	105.630	112.431	0.940

The system assessed for this analysis was composed of the esterification reactor and a distillation column for alcohol recycling with a condenser and reboiler. It can be seen that methanol's use would improve reaction conversion and had a better product sales to operating cost ratio. High conversion in the esterification reaction is crucial, as a presence of FFA lower than 0.5 wt.% (West, 2006) is demanded for the transesterification to occur without soap formation. The catalyst concentration used in the reactions was 5 wt.% of FFA for the methanol unit and 0.33 wt.% of FFA and ethanol for the ethanol unit, which are values commonly present in the literature. Further tests with higher catalyst concentration (0.66 wt.%) in the ethanol unit had little impact on the conversion (less than 1 % difference). As can be seen, methanol use in this reaction would benefit the process, and therefore it was chosen for esterification. Another essential aspect of methanol is the easier separation of water, as it is known that water presence prejudices not only the esterification and transesterification reactions

(Yusoff et al., 2014), but also the final biodiesel properties. It is important to say that higher temperatures were not tested to guarantee that the alcohols' boiling point would not be reached.

The kinetics used for the transesterification reaction analysis were obtained from Nouredini and Zhu (1997) when using methanol and from (Reyero et al., 2015) when using ethanol. The simulated results using the two types of alcohol are presented in Table 2. Sodium hydroxide was adopted as the catalyst for this reaction and triolein as the base triglyceride. The reaction temperature and time (with a range allowed by the kinetic equation) were varied to analyze the reaction behavior. In Table 2, the final conversion to ethyl and methyl-oleate and the remaining quantities of the formed byproducts were included in the analysis. In these tests, a higher pressure (1.5 bar) was used to avoid methanol vaporization.

*Table 2: Results from the transesterification reaction simulation using methanol and ethanol with Aspen Plus®*

Methanol							
Temp. (°C)	Methanol/Triolein Molar Ratio	Time (min)	Methyl-Oleate (mol)	Conv. (%)	Monoolein (mol)	Diolein (mol)	Triolein (mol)
50	6:1 (Triolein addition of 100 mol)	15	247.87	82.62	1.76	7.23	11.97
		30	249.67	83.22	1.72	7.07	11.49
		60	253.73	84.58	1.70	6.99	11.24
15		253.73	84.58	2.10	6.95	10.09	
30		254.77	84.92	2.07	6.86	9.81	
60		255.30	85.10	2.05	6.82	9.67	
70		15	258.32	86.11	2.49	6.71	8.59
		30	258.95	86.32	2.46	6.65	8.43
		60	259.27	86.42	2.45	6.62	8.35
Ethanol							
Temp. (°C)	Ethanol/Triolein Molar ratio	Time (min)	Ethyl-Oleate (mol)	Conv. (%)	Monoolein (mol)	Diolein (mol)	Triolein (mol)
50	6:1 (Triolein addition of 100 mol)	15	294.48	98.16	1.87	0.83	0.67
		30	295.96	98.65	1.60	0.62	0.40
		60	296.72	98.91	1.46	0.52	0.26
15		295.74	98.58	1.63	0.65	0.44	
30		296.61	98.87	1.48	0.53	0.29	
60		297.04	99.01	1.40	0.47	0.21	
70		15	296.44	98.81	1.50	0.55	0.32
		30	296.96	98.99	1.41	0.48	0.22
		60	297.22	99.07	1.37	0.45	0.17

The obtained overall conversion is better when using ethanol at any temperature and reaction time. An important fact is that in the transesterification using methanol, apart from the desired product, there is still a high concentration of triolein followed by diolein and monoolein. Ethanol, however, has a higher concentration of monoolein, followed by diolein and triolein. The higher proportion of monoolein is advantageous as the biodiesel specifications allow a higher presence of this component (0.7 wt.%) about to diolein and triolein (0.2 wt.%). Also, with a higher proportion of diolein and triolein in the final product, a more expensive separation process is needed, either to remove these undesired components or to recycle them to the transesterification reactor. Therefore, ethanol was chosen as the best alcohol option for this transesterification process.

## 2.2 Process Evaluation

Once the alcohols for each reaction were defined, the biodiesel production process was designed using the Aspen Plus® simulation tool. The process starts with the injection of methanol and waste oil under different FFA concentrations in the acid-catalyzed esterification reaction using a CSTR (Continuous Stirred Tank Reactor). This equipment operates at 60 °C and with a residence time of 110 minutes to guarantee that the final biodiesel is within acidity specifications. The esterification reactor is followed by a methanol-recycling distillation column, a neutralization reactor, a flash for water removal, and a base-catalyzed transesterification reactor, operating at 70 °C and with a residence time of 30 minutes. The conditions chosen for the transesterification reactor were based on the study developed by Reyero et al. (2015). In the end, crude glycerol is obtained and sold within specifications for this product, also returning part of the ethanol that remained from the decanter's heavy phase to the transesterification reactor. The biodiesel formed is purified to achieve specifications, and the non-reacted ethanol with a small water concentration was recycled to the transesterification reactor.

With the base project completed, different optimizations were tested to reduce costs. The first test considered the use of energy-saving heat exchangers for heat integration. By verifying the possible configurations that would bring higher energy and cost savings, a scenario with three exchangers was proposed as the most favorable choice. The use of more heat exchangers would result in an energy-saving of less than 1 %, and therefore three heat exchangers were considered suitable for the proposed objective. With the three equipment, the utility usage and utility cost could be reduced by 14 and 30 %, respectively.

To verify the impact of acid content in oil in the project, the amount of FFA, represented by lauric acid (Margarida et al., in press), was varied from 5 to 10 wt.% related to triolein. It could be noticed that the process showed high stability, with little modifications on the pressure of the water removal flash and a slight variation in payback time (2.66 years using waste oil with 5 wt.% acid concentration, 2.73 years with 7 wt.% acid concentration, and 2.89 years with 10 wt.% acid concentration).

The process proposed using the Aspen Plus® simulation tool can be observed in **Errore. L'origine riferimento non è stata trovata.**

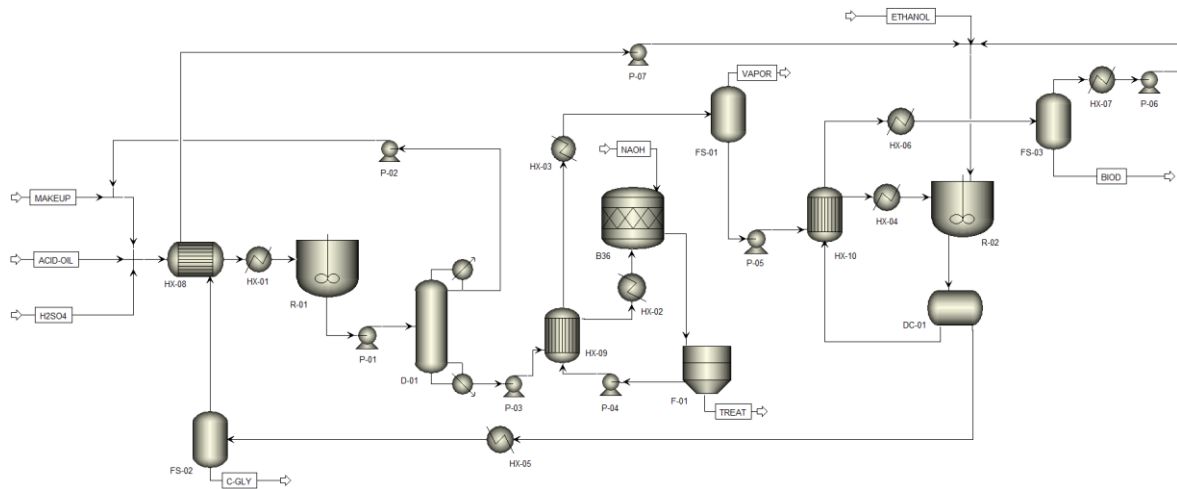


Figure 1: Biodiesel production process using a hybrid route and with energy-saving heat exchangers

The energy-saving heat exchangers were represented in the process as HX-08, HX-09, and HX-10. Some exchangers were also placed after the energy-saving heat exchangers for the start-up of the process and to complement heat exchange. Finally, it was possible to reduce cold and hot utilities by 15 and 13 %, respectively. The TREAT, C-GLY, and BIOD streams represent the sodium sulfate, crude glycerol, and biodiesel product, respectively. The MAKEUP, H2SO4, and ACID-OIL streams represent the methanol's make-up, the sulfuric acid catalyst, and the residual oil with different acid concentrations used as feedstock, respectively. In the neutralization step, stream NAOH, containing a sodium hydroxide solution (50 wt.%), is used to form the sodium sulfate. As ethanol is used in the transesterification reaction, the ETHANOL stream is used for this component's make-up. The first flash equipment (FS-01) is used to improve the transesterification conversion by removing water from the process, which requires a maximum water concentration of 0.06 % (Silva and Oliveira, 2014). In the simulation, 255,000 m<sup>3</sup>/year of biodiesel is produced within specifications from the European Standard (EN 14214) and ANP (National Agency for Petroleum, Natural Gas and Biofuels), as can be seen in Table 3.

Table 3: Simulation and standard specifications of biodiesel

Property	ANP	EN 14214	Simulation
Density (kg/m <sup>3</sup> , 15 °C for EN 14214 and 20 °C for ANP)	850-900	860-900	870
Kinematic Viscosity (cSt, 40 °C)	3.0-6.0	3.5-5.0	4.18
Water Content (mg/kg)	200 max	500 max	10.9
Monoglyceride Content (wt.%)	0.70 max	0.80 max	0.36
Diglyceride Content (wt.%)	0.20 max	0.20 max	0.18
Triglyceride Content (wt.%)	0.20 max	0.20 max	0.12
Alcohol Content (wt.%)	0.20 max	0.20 max	0.18
Acid Value (mg KOH / g)	0.50 max	0.50 max	0.47
Ester Content (wt.%)	96.5 min	96.5 min	98.8

For the economic evaluation, all utility prices used in the project were obtained from the Aspen Plus® databank. In contrast, the product's and reagent's prices, despite the acid oil, were taken from the current market price. The waste oil's price was considered 60 % of the soybean oil price, as the oil's price is strongly linked to the FFA presence (Mahesar et al., 2014), and no specific value for residual oil was found in the literature. Therefore, it is expected that the waste oil value is considerably lower than the refined oil.

As raw material costs significantly influence the operating cost, stream recycling is of great interest. Apart from the first distillation column for ethanol recycling, two other process streams containing high contents of ethanol were recycled to the transesterification reactor. Comparisons considering the inclusion of those recycling streams are presented in Figure 2. By only reconnecting two streams in the process, the total operating costs, which comprises raw material, utilities, maintenances, and other expenses, could be reduced by 15 %.

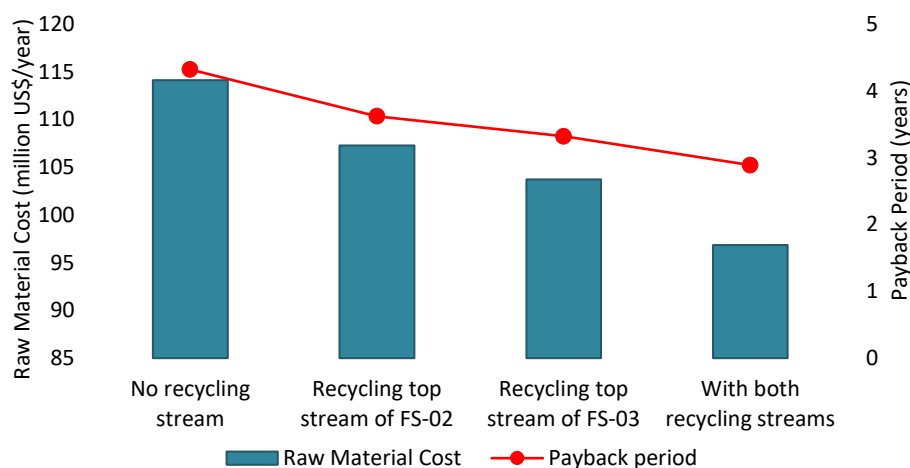


Figure 2: Economic influence in raw material cost and payback period to the use of recycling streams

Another essential aspect is the influence of raw material cost, as it represents almost 90 % of the total operating cost. With an in-depth analysis of the components contributing to the raw material cost, it was seen that the acid oil and ethanol represent the main expenses in the process with a participation of 82 and 16 %, respectively. In Figure 3, the raw material cost and payback period are evaluated considering an acid oil price variation of 10%.

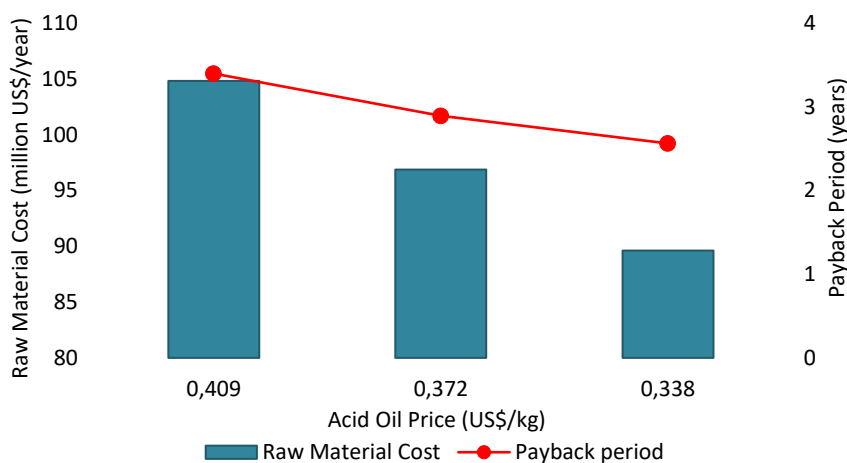


Figure 3: Raw material cost and payback period comparison to different acid oil price

These results confirm the considerable influence of the waste oil price in the project and the importance of working with residual materials to reduce costs. However, with any of the tested acid oil prices, the obtained payout period was very satisfactory.

Using the acid oil price as 60 % of the soybean oil price, the payback time of the process obtained using waste oil with 10 wt.% of FFA related to triolein was 2.9 years.

### 3. Conclusions

Through a kinetics evaluation of both the esterification and transesterification reactions, it was concluded that using different alcohols would benefit the process, increasing product conversion and reducing costs. The use of methanol in the esterification increased conversion and reduced the operating cost. The use of ethanol in the transesterification increased conversion with a lower concentration of the intermediate products with stricter limits by the biodiesel specifications. With the process design, the addition of three energy-saving heat exchangers reduced utility costs by 30 %, an investment that would pay for itself in half a year. The recycling of process streams was also evaluated. It was already expected that the use of the first methanol-recycling distillation column was vital for the process, as the project would have a payback period of more than 10 years without this equipment. Additionally, by reconnecting the top streams of the second and third flash equipment to the transesterification reactor, it was possible to reduce the payback period by 33 %. The proposed process presented high stability concerning the FFA concentration in the waste oil, where a variation of lauric acid concentration in triolein from 5 to 10 wt.% would increase the payback period by 8 % and with only a slight change in the first flash pressure. Finally, tests varying acid oil prices showed that the waste oil price has vital importance in the project's cost, participating in more than 80 % of the raw material cost. Considering all optimizations developed in this project, 255,000 m<sup>3</sup>/year of biodiesel is produced within the specifications from both the European Standard and ANP with a very optimistic payback period of less than 3 years. Therefore, it was proved that the idea of working with two types of alcohol at different parts in the process can be economically favorable, environmentally friendly, and may improve process stability and controllability.

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### References

- Margarida B.R., Flores L.I., Hamerski F., Voll F.A.P., Luz Jr. L.F. de L., in press, Simulation, optimization, and economic analysis of process to obtain esters from fatty acids, *Biofuels, Bioproducts and Biorefining*. doi:10.1002/bbb.2186.
- Mahesar S.A., Sherazi S.T.H., Khaskheli A.R., Kandhro A.A., Uddin S., 2014, Analytical approaches for the assessment of free fatty acids in oils and fats, *Analytical Methods*, 6, 4956–4963.
- Murad P.C., Hamerski F., Corazza M.L., Luz I.F.L., Voll F.A.P., 2017, Acid-catalyzed esterification of free fatty acids with ethanol: an assessment of acid oil pretreatment, kinetic modeling and simulation, *Reaction Kinetics, Mechanisms and Catalysis*, 123, 505–515.
- Musa I.A., 2016, The effects of alcohol to oil molar ratios and the type of alcohol on biodiesel production using transesterification process, *Egyptian Journal of Petroleum*, 25, 21–31.
- Knothe, G., 2005, Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters, *Fuel Processing Technology*, 86, 1059–1070.
- Joshi H., Moser B.R., Toler J., Walker T., 2010, Preparation and fuel properties of mixtures of soybean oil methyl and ethyl esters, *Biomass and Bioenergy*, 34, 14–20.
- Stamenković O.S., Veličković A.V., Veljković V.B., 2011, The production of biodiesel from vegetable oils by ethanolysis: current state and perspectives, *Fuel*, 90, 3141–3155.
- Noureddini H., Zhu D., 1997, Kinetics of transesterification of soybean oil, *Journal of the American Oil Chemists' Society*, 74, 1457–63.
- Rani K.N.P, Kumar T.P., Neeharika T.S.V.R., Satyavathi B., Prasad R.B.N, 2013, Kinetic studies on the esterification of free fatty acids in jatropha oil. *European Journal of Lipid Science Technology*, 115(6), 691–697.
- Reyero I., Arzamendi G., Zabala S., Gandía I.M., 2015, Kinetics of the NaOH-catalyzed transesterification of sunflower oil with ethanol to produce biodiesel, *Fuel Processing Technology*, 129, 147–55.
- Silva C., Oliveira J.V., 2014, Biodiesel production through non-catalytic supercritical transesterification: Current state and perspectives, *Brazilian Journal of Chemical Engineering*, 31, 271–85.
- Vinay K.S, Krishnam R.A.V., Rajendra K., Sarath C.S., 2015, Production of Bio-Diesel From Sesame Oil Using Aspen Simulation, BSc Thesis, Bapatla Engineering College, Bapatla, IN.
- West A.H., 2006, Process Simulation and Catalyst Development for Biodiesel Production, MSc Thesis, University of British Columbia, Vancouver, CA.

Yusoff M.F.M., Xu X., Guo Z., 2014, Comparison of fatty acid methyl and ethyl esters as biodiesel base stock: A review on processing and production requirements, *Journal of the American Oil Chemists' Society*, 91, 525–531.