Optimization and heat and water integration for biodiesel production from cooking oil and algae

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Abstract.

In this paper we address the optimal production of second generation of biodiesel using waste cooking oil and algae oil. We consider 5 different technologies for the transesterification of the oil (homogeneous acid or alkali catalyzed, heterogeneous basic catalyzed, enzymatic and supercritical non catalyzed). We formulate the problem as an MINLP where the models for each of the reactors are based on surface response methodology to capture the effect of the variables on the yield. The aim is to simultaneously optimize and heat integrate the production of biodiesel from each of the different oil sources in terms of the technology to use and the operating conditions required. The optimal conditions in the reactors differ from the ones traditionally used because the separation stages were not taking into account in the design. When using algae oil, the optimal process employs alkali as catalyst with a production cost of 0.42\$/gal, 1.94 MJ/gal of energy consumption and freshwater consumption 0.60 gal_{water} / $gal_{ethanol}$. For cooking oil the optimal process is the one with heterogeneous catalyst, with production cost, energy and water consumption of \$0.66/gal, 1.94 MJ/gal and 0.33gal_{water} / $gal_{ethanol}$, respectively.

Keywords: Energy, Biofuels, Biodiesel, Cooking Oil, Mathematical optimization, Algae

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1.-Introduccion

Many researchers have concluded that vegetable oils hold promise as alternative fuels for diesel engines. [1,2] However, using raw vegetable oils for diesel engines can cause numerous engine-related problems. [3] The increased viscosity, low volatility, and poor cold flow properties of vegetable oils lead to severe engine deposits, injector coking, and piston ring sticking. [4,5] Thus, research has focused on developing transformation products like pyrolysis, micro emulsion and transesterification. The process of transesterification has been used widely. It removes glycerol from the triglycerides and replaces it with radicals from the alcohol used for the conversion process. [6] This process decreases the fuel's viscosity, but maintains the cetane number and heating value. The monoesters produced by transesterifying vegetable oils with alcohol are known as *biodiesel.* [7,8] The first generation of biodiesel has been produced using vegetable oils such as sunflower, cottonseed oil, rapeseed oil, soybean oil, palm oil, peanut oil and canola oil as raw materials. [9] However, the competition with the food chain and the high cost of the raw material requires focusing on alternative sources of oil. [10]

Among oils, waste cooking oil is a promising alternative to vegetable oil for biodiesel production because it is much less expensive than pure vegetable oil. Typically, waste oils have been sold commercially as animal feed. However, since 2002, the EU has enforced a ban on feeding these mixtures to animals because during frying many harmful compounds are formed. [11] Hence, the waste cooking oil must be disposed of safely, or used in a way that is not harmful to human beings. The quantity of waste cooking oil generated per year by any country is huge. [12-14] The disposal of waste cooking oil is problematic because disposal methods may contaminate water. Many developed countries have set policies that penalize the disposal of waste oil through the water drainage. Therefore, a substantial amount of biodiesel can be produced from this material representing one of the better alternatives to reuse and dispose cooking oil efficiently and economically. [15-17] However, the high demand of diesel fuel and the availability of waste cooking oil [11,13, 14, 18] indicates that biodiesel from cooking oil cannot replace diesel fuel, but it can contribute to reduce the dependency on petrol based diesel.

Microalgae are also a source of biomass with great potential. The algae convert sunlight, nutrients and CO_2 into proteins carbohydrates and lipids with a growth rate that doubles their biomass up to five times a day.

Subsequently, growth is stopped by limitation of the nutrient so that lipids are produced. Algae can grow not only on normal carbon sources, such as glucose, fructose, etc, but on wastes from agriculture and food industries, and using saline water or wastewater, eliminating the problem of water usage, thus lowering the cost of microalgae oil while algae growth can also be used to treat water in order to remove NH_4^+, NO_3^-, PO_4^{3-} . [19-21] Thus, microalgae oils are now believed to be a promising feedstock for biodiesel production since the oil they generate has a fatty acid composition similar to that of vegetable oils [20, 22,23] with a high yield as seen in Figure 1, capable of meeting the US diesel need with 2-5% of the current US cropland. [24-27] However, the industrial production of biodiesel from algae is still facing technical and economical challenges. In order to produce a fair amount of oil, microalgae must be carefully selected so that they are capable of producing large quantities of lipids that are tolerant to fluctuation in the operating conditions. Furthermore, the growing of algae requires a concentrated and plentiful source of CO_2, and its harvesting costs are still high.

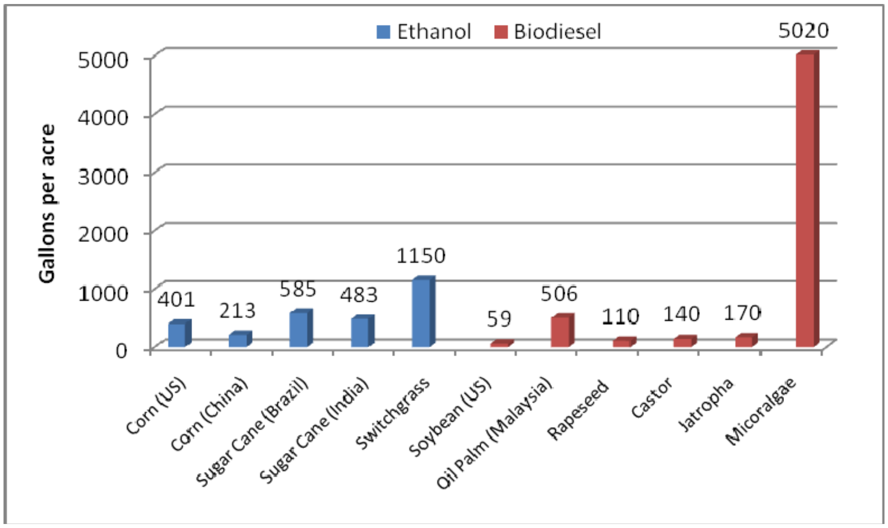


Figure 1.- Yield of biofuel for different raw material per area

In this paper, we propose the conceptual design for the production of biodiesel from waste cooking oil and microalgae oil (including the production of the oil from algae) evaluating five of the most common technologies for the transesterification of the oil: catalyzed (acid, alkali, heterogeneous and enzymatic) and non catalyzed under supercritical conditions. [13,28-36] We propose a limited superstructure optimization where we first construct a flowsheet embedding the various process units involved. These units are interconnected to each other through network flows and other utility streams. So far the optimization of the operating conditions for the transesterification has been focused on the reactor alone. [11] However, it is clear that a broader view to the process including the separation and recycle should provide better operating parameters. Reduced order models obtained from experimental data are used to simultaneously optimize and heat integrate the flowsheet maximizing the gross profit to decide on the transesterification technology, the operating conditions at the reactor and the separation of the products. The optimization of the system is formulated as a mixed-integer non linear programming problem. Next, we design the heat exchanger network using SYNHEAT [37] and perform an economic evaluation to determine the production cost. Finally, to address the concern on water consumption in biofuel production processes, we determine the freshwater consumption following the approach proposed in Grossmann and Martin [38]

2. Overall Process Description

Figure 2 shows the superstructure for the production of biodiesel from waste cooking oil and algae. In case of using algae, the production of oil involves three stages: algae growing, harvesting (including drying) and oil extraction. We consider two alternatives for the harvesting of algae: the traditional one based on centrifugation, and the new one recently proposed in the literature.[39] Once the oil is available, five technologies for the production of biodiesel are evaluated: whether the oil is transesterified using homogeneous alkali (KOH) or acid (H_2SO_4) catalysts, heterogeneous catalysts (CaO), immobilized enzymes, or non catalytic transesterification under supercritical conditions. In short, each technology consists of the preparation of the reactants, the transesterification reactor and the recovery and purification stages of methanol, glycerol and biodiesel. In the next section we describe the different processes and units involved in Figure 2, and the assumptions used for modeling. For the sake of limiting the length of the paper, we include the models of the different units in the supplementary material for further reference.

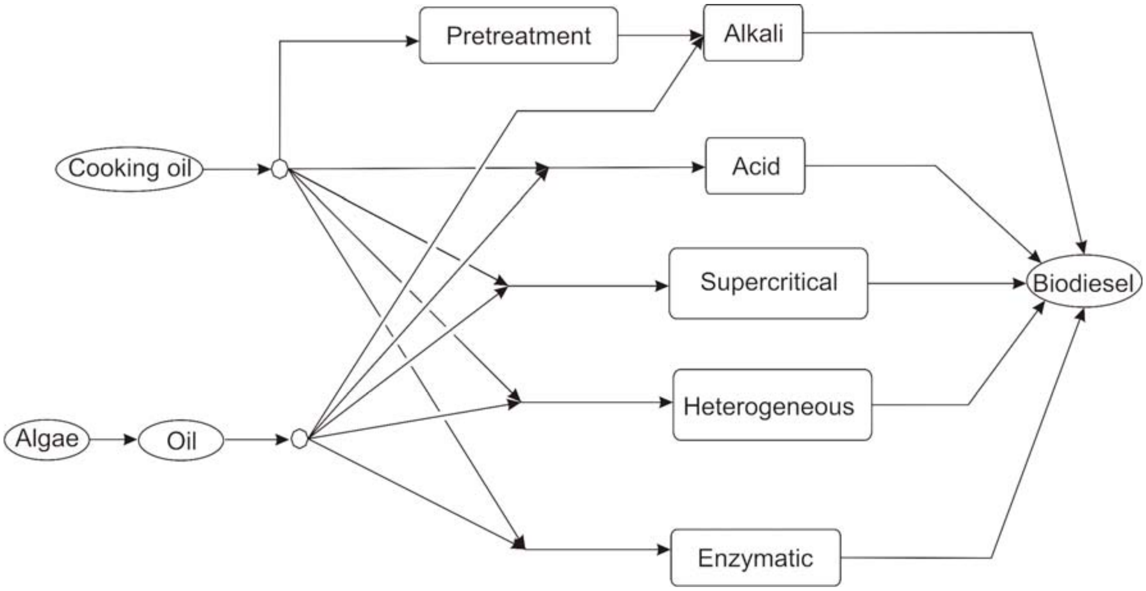


Figure 2 .-Supersctructure of alternative processes.

3.-Mathematical modeling

All the unit operations in the production process of biodiesel from oil are modeled using reduced order models, mass and energy balances, and design equations. The model is formulated in terms of the total mass flows, component mass flows, component mass fractions, and temperatures of the streams in the network. The components in the system include { Wa, MetOH, Glycerol, FAME, FFA, Oil, Hexa, tButa, H_2SO_4, KOH, K_2SO_4, H_3PO_4, K_3PO_4, Algae, Biomass, CO_2, O_2 }. We assume stream mixing to be adiabatic.

Duran & Grossmann[40] showed that the simultaneous optimization and heat integration of process flowsheets results in large energy and cost savings. In this process the recycle of methanol is energy intensive, and therefore it is an opportunity for integrating the model presented by Duran & Grossmann[40] in the problem formulation. Thus, in the objective function we can see QS_max, which represents the minimum heating predicted by the model together with other operating costs and credits. For further explanation on the model see also Bielger et al.[41] In the next subsections we present the assumptions for modeling the different units.

3.1.-Raw material

3.2.1.-Cooking oil

The composition of the cooking oil in terms of impurities is not fixed. On average, it has 0.25% moisture, 2.75 % free fatty acid, FFA,[42] but it can range from 1.5% from food processors to 4% FFA from restaurants in the winter, to as high as 10% or 15% FFA in the summer (depending on how frequently the grease is collected)[43] (Tyson et al., 2004). In general the chemical composition of the oil is mainly oleic and linoleic (45% Oleic, 40 Linoleic, 10/ Palmitic, 5% Stearic acid) but it depends on the kind of oil. For example Olive oil and canola oil reach 85% Oleic acid. [11,44] For our modeling, we assume that the oil can be characterized as triolein and oleic acid, in agreement with the literature[11, 39], containing 5% FFA (West et al., 2008) and 0.25% of water.

3.1.2.-Algae oil.

Figure 3 presents the superstructure for the production of algae oil. It consists of three stages, growing of the microalgae, harvesting and oil extraction. The growing of the microalgae can be carried out either in ponds or photorreactors. The costs of running the ponds are lower, but they are prone to contamination due to the open surface. On the other hand, to avoid contamination photoreators can be used at a higher cost. For this study we focus on ponds since they are the most widely used system for large-scale outdoor microalgae cultivation because they are cheaper, easy to build and operate. [45]

The production of oil from algae is performed by injecting CO_2 into the water, which can be saline water so that the consumption of freshwater is reduced together with air and fertilizers. The amount of water needed and the concentration of fertilizers is taken from the report by Pate [46], while the consumption of CO_2 depends on the growth rate, typically 50g/m^2 d [47], and is given by the experimental results by Sazdanoff [48]. Together with the algae, oxygen is produced and water is evaporated. [48] The energy consumed by the pond system is calculated based on the results by Sazdanoff [48].

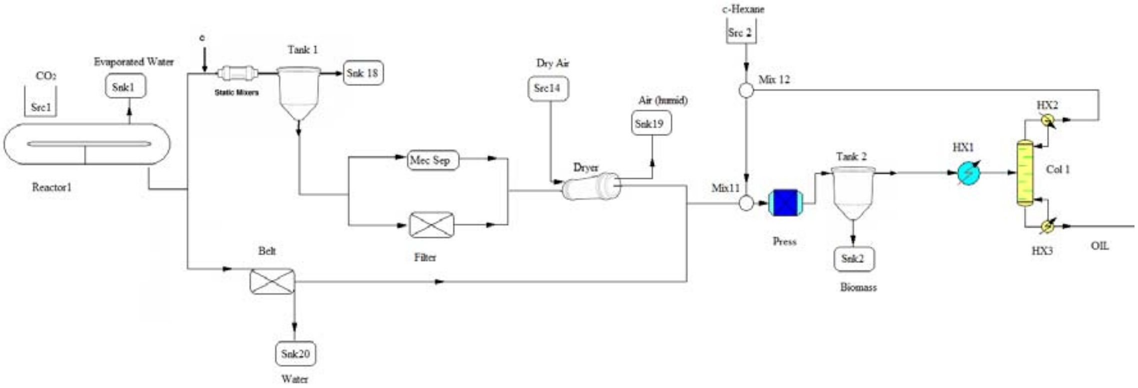


Figure 3.- Oil production from microalgae.

Given the relatively low biomass concentration obtainable in microalgae cultivation systems, due to the limit of light penetration (typically in the range of 1–5 g/L) and the small size of microalgae cells (typically in the range of 2–20 μm in diameter), the costs and energy consumption for biomass harvesting are significant. This section is the most important in the economy of the production of oil from algae. We consider two alternatives as shown in Figure 3.

1) Traditionally, different technologies, including chemical flocculation, biological flocculation, filtration centrifugation, and ultrasonic aggregation have been investigated for microalgae biomass harvesting. The selection of appropriate harvesting technology depends on the value of the target products, the biomass concentration, and the size of microalgal cells of interest. In general, chemical and biological flocculation require low operating costs. However, they have the disadvantage of requiring a long processing period, and having the risk of bioreactive product decomposition. On the other hand, filtration, centrifuge, and ultrasonic flocculation are more efficient but more costly, and they are the selected technology so far and thus is our technology of choice. The energy required for this option is calculated based on the results available in the literature. [48-50]

Biomass drying before further lipid/bioproduct extraction and/ or thermochemical processing is another step that needs to be taken into consideration after algae concentration. Sun drying is probably the cheapest drying method that has been employed for the processing of microalgae biomass. However, this method requires long drying time and large drying surface, and risks the loss of some bioreactive products. Low-pressure shelf drying is another low-cost drying technology that has been investigated. It is nevertheless also of low efficiency. More efficient but more costly drying technologies that have been investigated for drying microalgae include, drum drying, freeze drying, and refractance window dehydration technology. It is important to find the balance between the drying efficiency and cost-effectiveness to maximize the net energy output of the fuels from microalgae strategy. [51,52] We consider drum drying as it is currently common practice to be able to obtain 5% wet algae. The energy involved in this stage is considered that of evaporating the water accompanying the solids.

2) Recently, Univenture Inc.[39] has presented an innovative technology capable of integrating harvesting and drying the algae with low energy consumption. It is based on the use of capillarity, membrane systems and paint drying to obtain 5% wet algae with a consumption of 40W for 500L/h of flow. Figure 4 shows a scheme of the laboratory scale device proposed by this company.

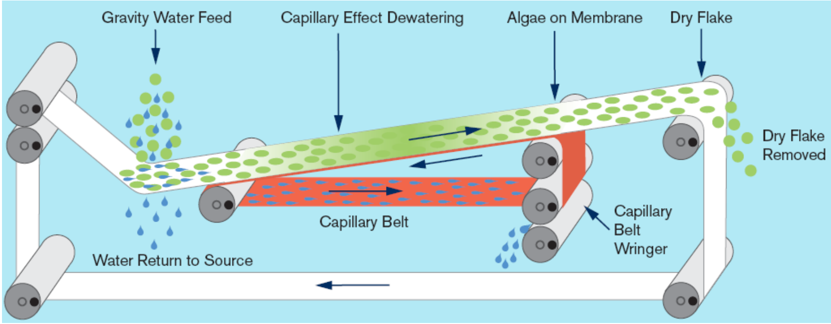


Figure 4. New harvesting process

Once the algae are dried, oil extraction from biological materials may be performed by chemical means, physical means, or a combination of the two [53] For large scale oil extraction from microalgae, the process is usually accomplished with mechanical cell disruption followed by solvent extraction. In this work we consider Hexane solvent *extraction* used along with the oil press/expeller method. After the oil has been extracted using an expeller, the pulp is mixed with cyclo-hexane to extract the remaining oil content. The oil dissolves in the cyclohexane, and the pulp is filtered out from the solution. The oil and cyclohexane are separated by means of distillation in column 1. The ratio of hexane to algae is set to 1 and the oil recovery reaches 97% according to the results by Mulbry et al. [54] while the energy needs for the mechanical press are taken from www.ascof.com.[55] We minimize the energy consumption in the production of microalgae oil to define the best process.

The microalgae oil mainly contains 7.44% palmitic acid, 2.78% palmitoleic acid, 6.58% stearic acid, 68.10% oleic acid, 10.07% octadecadienoic acid, 4.02% octadecatrienoic acid, and the total unsaturated fatty acids content reaches around 85% [23] , 0.01 % - 0.02% moisture, 0.45-1.75 % FFA[32] and always below 2%.[42] Thus, no pretreatment is needed. For the model, we assume that oleic acid with no impurities will represent the oil for further simulations.

3.2.- Biodiesel synthesis.

Once the oil is available, either from cooking or from algae, there are different processes to obtain biodiesel depending on the technology for the transesterification reaction. [7,30] In all processes the lower bound for the purity of glycerin is set to 92%[11, 28] so as to sell it as a valuable byproduct.

3.2.1.-Process 1: Alkali-catalyzed process

3.2.1.1.-Pretreatment.

The alkali catalyzed reaction is sensitive to impurities such as water or FFA. Thus, a pretreatment stage to remove the FFA and transform them into methyl esters is needed in case we use waste cooking oil as raw material. The pretreatment stage includes esterification of the free fatty acids, glycerin washing and methanol recovery as it can be seen in Figure 5.

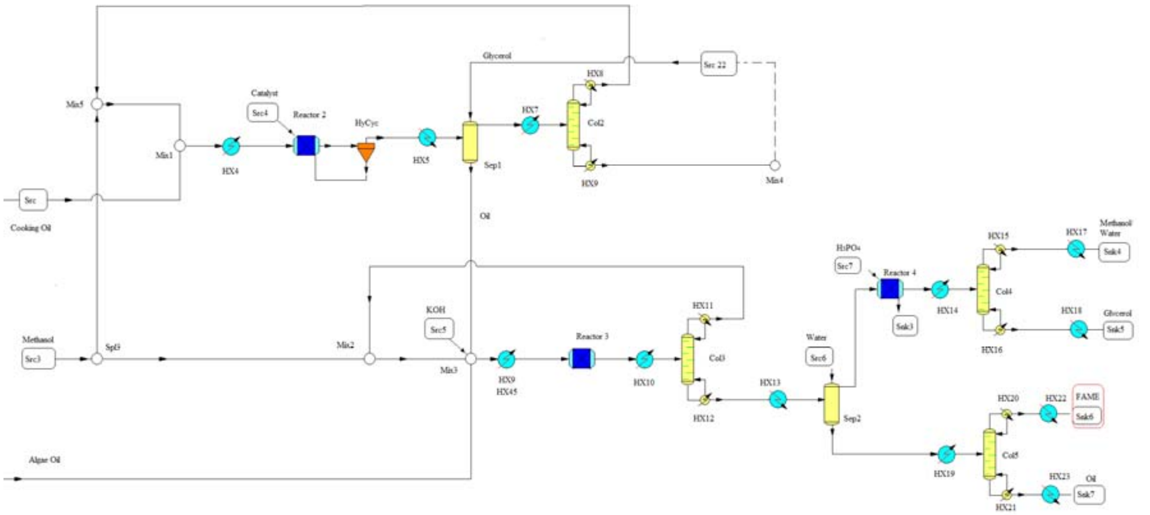


Figure 5.- Flowsheet for the production of biodiesel from oil via alkali -catalyzed transesterification

The cooking oil (Src) is mixed with fresh methanol and recycled in mix 1. The stream is heated in HX4 to be prepared for transesterification. The model for the pretreatment reactor is based on the results by Wan Omar et al. [56] (who used ferric sulfate as catalyst). The use of the solid catalyzed reaction allows simple recovery of the products since the catalyst is removed by filtration. Using the data reported in that paper we developed a surface response model, eq. (1). for the yield towards biodiesel as a function of the reaction time, the molar ratio between methanol and oil, and the operating temperature at the reactor. In Figure 6 we present the fitting of equation (1) and the experimental data. We fixed the yield to be 98%. Table 1 shows the range of the operating variables.

$$\begin{aligned}
&\mathrm{yield\_FFA} = 31.03104 + 1.486403123 * \mathrm{T}\left(\mathrm{HX1, Reactor1}\right) - 6.97793097 * \mathrm{ratio\_met} + 19.77691899 * \mathrm{time} \\
&-0.00018078 * \mathrm{T}\left(\mathrm{HX1, Reactor1}\right)^2 - 0.16677756 * \mathrm{ratio\_met}^2 - 1.6230585 * \mathrm{time}^2 \\
&+0.02516368 * \mathrm{T}\left(\mathrm{HX1, Reactor1}\right) * \mathrm{ratio\_met} - \\
&0.41625815 * \mathrm{T}\left(\mathrm{HX1, Reactor1}\right) * \mathrm{time} + 2.37322062 * \mathrm{ratio\_met}\ \ * \mathrm{time};
\end{aligned} \tag{1}$$

Table 1.-Range of operation of the variables. Alkali pretreatment

Variable	Lower bound	Upper bound
Temperature (ºC)	50	80
Ratio methanol (mol/mol)	1	15
Time (h)	2.5	5
Catalyst	0.4% of oil	
Pressure	400kPa	

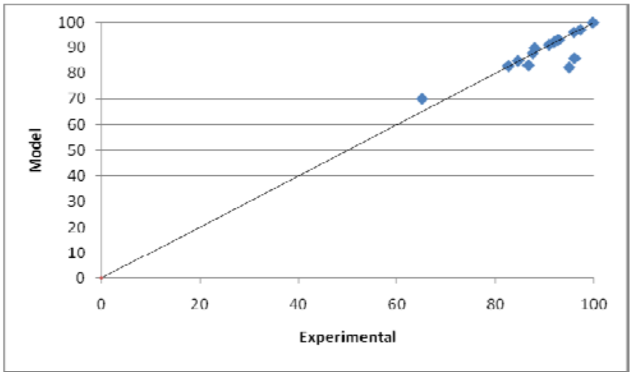


Figure 6.- Surface response model for pretreatment

The products of the reaction are calculated based on the yield and the stoichiometry of the reaction. The mixture coming from the previous reactor is cooled down to 46ºC and glycerol at room temperature is added to separate the phases in Sep1, aqueous (including methanol, glycerol, water) from the oil phase (containing the FAME and the rest of the oil). The oil is sent to transesterification. On the other hand, the stream containing methanol, glycerol and water is distillated recovering most of the methanol in Col 2. We model the distillation column using short cut methods as it is detailed in the supplementary material The presence of water in the glycerin prevents complete recycle of the stream. However, it can be dehydrated and reused.

Alkaline Transesterification: The yield to biodiesel is a function of a number of variables such as operating temperature, methanol ratio to oil, catalyst amount. Even though the operating conditions have been studied in detail, [16, 57-60] they have been optimized in the context of the reactor alone without considering the energy required in the separation stages. There are a number of trade-offs to get a high yield by adjusting the catalyst concentration, methanol phase and working temperature. The catalyst used is KOH due to the possible use of the byproduct K_3PO_4 as a fertilizer. The model for the transesterification reaction is given by eq. (2). [61,62] Table 2 presents the range of operating variables.

$$\begin{aligned}\text{yield} = {} & 74.6301 + 0.4209*\text{T}(\text{reactor}) + 15.1582*\text{Cat} + 3.1561*\text{ratio\_met} - 0.0019*\text{T}(\text{reactor})^2 \\ & -0.2022*\text{T}(\text{reactor})*\text{Cat} - 0.01925*\text{T}(\text{reactor})*\text{ratio\_met} - 4.0143*\text{Cat}^2 - 0.3400*\text{Cat}*\text{ratio\_met} \\ & -0.1459*\text{ratio\_met}^2\end{aligned} \qquad (2)$$

Table 2.-Range of operation of the variables. Alkali

Variable	Lower bound	Upper bound
Temperature (ºC)	45	65
Ratio methanol (mol/mol)	4.5	7.5
Cat (%)	0.5	1.5

The energy involved in the reaction is calculated from the experimental results in the literature.[63] We assume the same value for all the technologies. The stream exiting the reactor is distilled in column 3 to recover the excess of methanol so that it is recycled back to the reactor. A short cut method[41] is used to model all the distillation columns. The main features of the operating conditions are defined so as to avoid thermal decomposition of the different species and the presence of two phases in terms of the vapour pressure calculation. To recover the methanol, the main characteristic is that the temperature at the bottoms cannot exceed 150ºC to avoid decomposition of the glycerol. This fact defines the working pressure of column 3. Furthermore, at least 94% of the methanol is recycled. The reflux ratio is key to determine the energy requirement for recovering the excess of methanol. Thus, based on the results by Dhar & Kirtania [64] we assume that the reflux ratio is within the range of 1 to 3, and it has to be always greater or equal to the minimum reflux ratio as given by the Fenske equation for determining the minimum reflux ratio in distillation processes involving 2 components, methanol and glycerol.

The bottoms are cooled down to 40ºC in HX13 before phase separation. To separate the aqueous phase from the oil phase we consider the use of a washing column, following the commonly used approach. [13,29] We assume that a small amount of water, 1% of the biodiesel phase, at 20ºC, is added to the mixture coming from the methanol column[13] . We also acknowledge the fact that there is controversy whether gravity separation alone can do the work. [29, 65]

The oil phase is sent to column 5 to purify the biodiesel from the unreacted oil. The main challenge is to work below atmospheric pressure so that the distillate containing biodiesel exits the column below 250ºC[13] to maintain biodiesel integrity, while the oil should remain below 350ºC. A short cut model is used for this column assuming variable reflux ratio from 2 to 3. [13]

The aqueous phase is treated to remove the alkali, KOH. We propose the use of phosphoric acid based on the fact that the salt generated in the neutralization reaction, K_3PO_4 , can be easily removed using a gravity separator and it can also be sold as a fertilizer. The reaction is given by eq. (3) :

$$H_3PO_4 + 3KOH \longrightarrow K_3PO_4 + 3H_2O \tag{3}$$

The products of the reactor are calculated based on the stoichiometry of the reaction, and the final temperature is calculated assuming adiabatic operation of the reactor taking into account the heat of neutralization. Once neutralized, the stream is sent to column 4 to purify the glycerol. Above 92% purity, glycerol can be sold as a high quality by-product. However, the decomposition temperature of glycerin is reported to be 150ºC, which makes this distillation column to operate below atmospheric pressure.[13] The reflux ratio is variable from 2 to 3, as well as the purity of the glycerin using 0.92 as the lower bound.

The objective function to determine the optimal operating conditions is given by a gross profit calculation involving the cost of the products and byproducts minus the cost of the raw materials and is given by eq. (4) and eq. (5) for a constant flow of oil and a fixed minimum conversion at the reactor.

$$\begin{aligned}
\mathrm{Z} = {} & C_{FAME} * \mathrm{fc}\left(\mathrm{FAME, Col5, HX22}\right) + C_{Glycerol} * \mathrm{fc}\left(\mathrm{Glycerol, Col4, HX18}\right) + C_{K_3PO_4} * \mathrm{fc}\left(\mathrm{K3PO4, Reactor4, Snk3}\right) \\
& - C_{Steam} * (1/\lambda) * \left(\mathrm{QS\_max}\right) - C_{KOH} * \mathrm{fc}\left(\mathrm{KOH, Src5, Mix3}\right) - C_{MetOH} * \mathrm{fc}\left(\mathrm{MetOH, Src23, Mix2}\right) \\
& - C_{H_3PO_4} * \mathrm{fc}\left(\mathrm{H3PO4, Src7, Reactor4}\right) + \mathrm{Z'};
\end{aligned} \tag{4}$$

where Z’ is given by

$$\begin{aligned}
\mathrm{Z'} = {} & - C_{Glycerol,\,pure} * \mathrm{fc}\left(\mathrm{Glycerol, Mix4, Sep1}\right) + C_{GLycerol,rec} * \mathrm{fc}\left(\mathrm{Glycerol, Col2, Mix4}\right) \\
& - C_{Cat} * \mathrm{Cat\_pret\_add} - C_{MetOH} * \left(\mathrm{MetOH, Src3, Spl2}\right);
\end{aligned} \tag{5}$$

or zero in the case of algae oil.

3.2.2.-Process 2: acid-catalyzed transesterification

Despite its insensitivity to free fatty acids in the feedstock, acid-catalyzed transesterification has been largely ignored mainly because of its relatively slower reaction rate. Freedman et al.[56] and Canakci and Gerpen[8] have reported biodiesel production and the effects of the molar ratio of alcohol to oil, the reaction temperature, the amount of catalyst, and the reaction time on the ester conversion by acid-catalyzed transesterification. However, no cross effects were studied. The kinetics of the acid-catalyzed transesterification has also been investigated and it is believed that the forward and reverse reactions follow pseudo-first-order and second-order kinetics, respectively. [56,66-67]

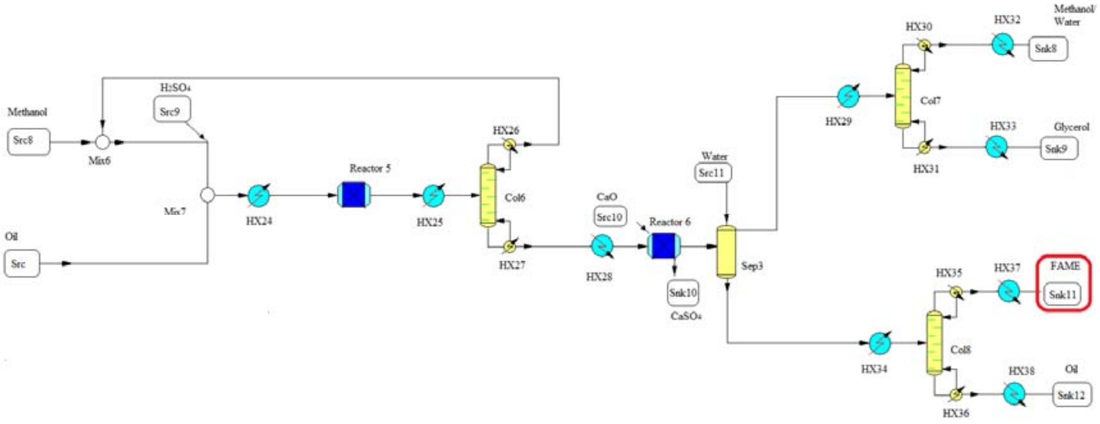


Figure 7.- Flowsheet for the production of biodiesel from oil via acid -catalyzed transesterification

Figure 7 shows the flowsheet for this technology. As in the previous cases the raw materials are prepared for the reaction in mix 7 and HX 24. In order to model the reactor, a surface response model is used based on the experimental results by Canakci and Gerpen[8] and Kulkarni & Dalai.[11] Figure 8 shows the fitting of the model given by eq. (6), and the experimental data. There are a number of variables that determine the yield of biodiesel such as the amount of catalyst, the excess of methanol, and the working temperature at the reactor. Table 3 gives the ranges of operation of these variables

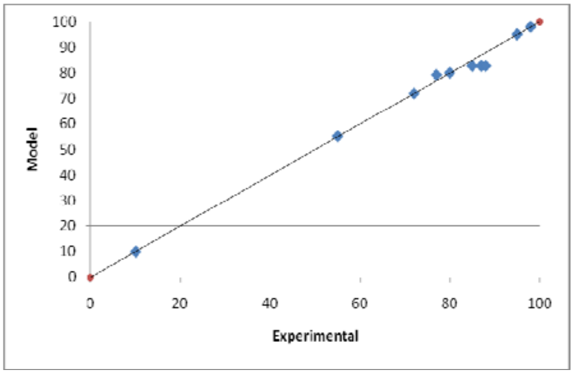


Figure 8.- Surface response fitting foo acid catalized transesterification.

$$\begin{aligned}\text{yield } &= (79.444523 - 1.59614107 * \mathrm{T}(\mathrm{HX24,Reactor5}) - 3.12722176 * \mathrm{ratio\_met} - 1.14234895 * \mathrm{Cat} - \\ &0.01193003 * (\mathrm{T}(\mathrm{HX24,Reactor5}))^2 + 0.75330856 * (\mathrm{T}(\mathrm{HX24,Reactor5})) * \mathrm{Cat} + \\ &0.40574243 * (\mathrm{T}(\mathrm{HX24,Reactor5})) * \mathrm{ratio\_met} + 0.175788313 * \mathrm{Cat}^2 - 6.56010529 * \mathrm{Cat} * \mathrm{ratio\_met} - \\ &0.02509877 * \mathrm{ratio\_met}^2 \text{);}\end{aligned} \qquad (6)$$

Table 3.-Range of operation of the variables. Acid

Variable	Lower bound	Upper bound
Temperature (ºC)	25	65
Ratio methanol (mol/mol)	3.3	30
Cat (%)	1	5

The stream exiting the reactor is calculated based on the yield of the reaction and is fed to column 6 to recover the excess of methanol. The model and assumptions for this column are similar to the ones for column 3 where the reflux ratio is variable, and the temperature at the bottoms must not go over 150ºC to avoid glycerin decomposition. The bottoms are cooled to 40ºC and neutralized.[13] The sulfuric acid used as catalyst in the trasnesterification reactor is completely removed in a neutralization reaction by adding calcium oxide (CaO) to produce $CaSO_4$ and H_2O. Calcium oxide is used primarily due to its low-cost relative to other alkali substances and due to the precipitation of the salt which simplifies the separation. Gypsum ($CaSO_4$) can also be sold to increase the revenue. The neutralization reaction is given by eq. (7):

$$H_2SO_4 + CaO(\text{lime}) \longrightarrow CaSO_4(gypsum) + H_2O \qquad (7)$$

The products of the reactor are calculated based on the stoichiometry of the reaction. We assume adiabatic operation. The product stream is sent to phase separation in sep 3. For performing the phase separation a washing step using water has been recommended.[13] In Sep 3, we add a small amount of water, 0.01 the biodiesel, to separate glycerol, water, methanol from oil, FFA and biodiesel. Each of the phases are purified using distillation columns.

The polar phase is sent to column 8 where glycerol is purified beyond 92% to be sold as a byproduct. The model is similar to column 4.[13] The non polar phase containing biodiesel is purified in column 7 whose characteristics have already been presented. The objective function is a gross profit evaluation given by eq. (8):

$$\begin{aligned} \mathrm{Z} &= C_{FAME} * \mathrm{fc}\left(\mathrm{FAME},\mathrm{Col7},\mathrm{HX32}\right) + C_{Glycerol} * \mathrm{fc}\left(\mathrm{Glycerol},\mathrm{Col8},\mathrm{HX38}\right) + C_{gypsum} * \mathrm{gypsum} \\ &- C_{Steam} * (1/\lambda) * \left(\mathrm{QS\_max}\right) - C_{\mathrm{lim}e} * \mathrm{lime} - C_{MetOH} * \mathrm{fc}\left(\mathrm{MetOH},\mathrm{Src8},\mathrm{Mix6}\right) \\ &- C_{H_2SO_4} * \mathrm{fc}\left(\mathrm{H2SO4},\mathrm{Src9},\mathrm{Mix7}\right) \end{aligned} \tag{8}$$

3.2.3.- Process 3: Heterogeneous production of bio diesel

The use of heterogeneous catalysts for the production of biodiesel simplifies the purification stages since they can be easily removed from the products, or they can be packed in the reactor[11, 29, 30, 68,69] Therefore, the process is simpler than the previous ones as it can be seen in Figure 9.

The reactants are prepared in mix 14 and HX 53 and fed to the reactor. The model of the reactor is taken from the literature, [70] which predicts the yield towards biodiesel as function of the temperature, the catalyst load and the methanol ratio. The reaction time is fixed to 2h. Other models[71] are also available but they do not consider the effect of the temperature. Eq. (9) predicts the yield of the transesterification reaction, and table 4 presents the bounds for the operating conditions.

$$\begin{aligned} \mathrm{yield} &= -73.6 + 2.5 * \mathrm{T}\left(\mathrm{HX39},\mathrm{Reactor7}\right) + 24.9 * \mathrm{Cat} + 8.8 * \mathrm{ratio\_met} - 0.01 * \mathrm{T}\left(\mathrm{HX39},\mathrm{Reactor7}\right)^2 - \\ &\quad 1.29 * \mathrm{Cat}^2 - 0.39 * \mathrm{ratio\_met}^2 - 0.26 * \mathrm{T}\left(\mathrm{HX39},\mathrm{Reactor7}\right) * \mathrm{Cat} \end{aligned} \tag{9}$$

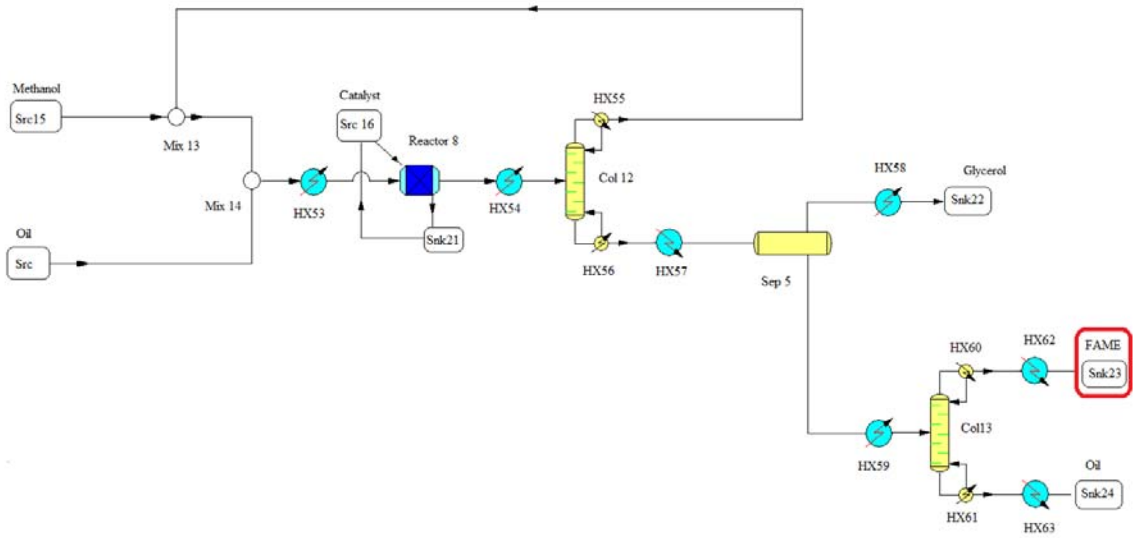


Figure 9.- Flowsheet for the production of biodiesel from oil via heterogeneous -catalyzed transesterification

Table 4.-Range of operation of the variables. Heterogeneous catalized

Variable	Lower bound	Upper bound
Temperature (ºC)	40	60
Ratio methanol (mol/mol)	6	12
Cat (%)	1	4

After the reactor, distillation column 12 is used to recover the excess of methanol. The model is similar to previous methanol recovery columns. The bottoms of the distillation column contain mainly glycerol and biodiesel with small amounts of methanol, water, FFA and oil. A gravity separation allows the recovery of glycerol with a purity higher than 92%[13] while the biodiesel is purified in a distillation column (column 13). In this column, as we have presented before, the temperatures of the distillate and that of the bottoms have an upper bound to avoid product decomposition. The objective function is similar to the previous cases and it is given in eq. (10).

$$\begin{aligned} Z \ &= C_{FAME} * \mathrm{fc}\left(\mathrm{FAME}, \mathrm{Col13}, \mathrm{HX62}\right) \ + \ C_{Glucerol} * \mathrm{fc}\left(\mathrm{Glycerol}, \mathrm{HX58}, \mathrm{Snk22}\right) \\ &- C_{Steam} * (1/\lambda) * \left(\mathrm{QS\_max}\right) \ - C_{Cat\_Het} * \ \mathrm{Catadded} - \ C_{MetOH} * \mathrm{fc}\left(\mathrm{MetOH}, \mathrm{Src13}, \mathrm{Mix13}\right); \end{aligned} \tag{10}$$

3.2.4.- Process 4: Enzymatic production of bio diesel

Most of the previous studies regarding the production of biodiesel [13,29,31,72-77] have neglected the possibility of using enzymes. However, recently interest in it is increasing. [35, 36, 78] According to Novozymes, there is high potential for the use of enzymes (lipases) since they can process raw materials such as wastes, animal fats, or recycled restaurant oil (Per Munk Nielson, senior science manager for Novozymes A/S). [79] However, the process has not been implemented at industrial scale due to the lack of development. [80] Due to the high cost of the enzymes, the only way to produce biodiesel using them as catalysis is if they are immobilized and reused.[81] Furthermore, only by combining different lipases is it possible to reach high yields of biodiesel. [82]

Figure 10 shows the flowsheet for the production of biodiesel using enzymatic catalysts. As in previous technologies the raw materials are prepared and fed to the reactor. There are a number of recent models based on design of experiments for the transesterification of oil using methanol and enzymes. [82-84] Among them, the last one by Huang[82] reports high yields by using tert-butanol as cosolvent . From their experimental results it is possible to obtain a model involving bilinear and quadratic terms on the five variables that characterize the process, amount of lipase, the ratio between the two types of lipases used, the ratios of methanol and t-butanol, and the reaction time, given by eq. (11). Figure 11 shows the goodness of the fit and Table 5 the range of the operating variables.

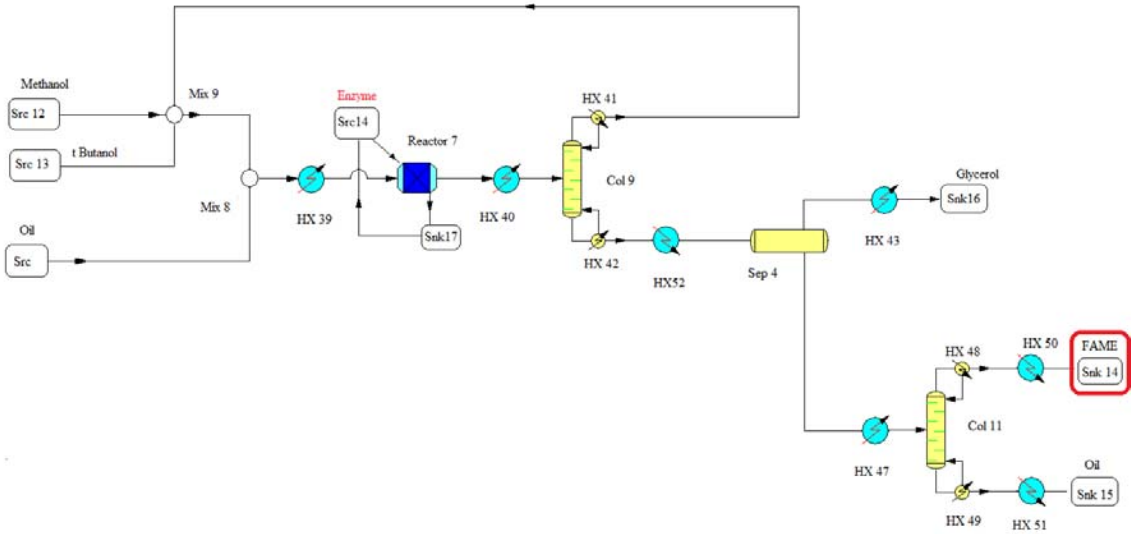


Figure 10.- Flowsheet for the production of biodiesel from oil via enzymatic transesterification

$$\begin{aligned}
&\mathrm{yield} = (-58.05 + 39.505*\mathrm{lipase} + 169.65*\mathrm{lipratio} + 37.19*\mathrm{ratio\_tbuta} + 13.55*\mathrm{ratio\_met} + 4.415*\mathrm{time} \\
&-2.484*\mathrm{lipase}^2 - 13.300*\mathrm{lipase}*\mathrm{lipratio} + 1.534*\mathrm{lipase}*\mathrm{ratio\_tbuta} + 75.56*\mathrm{lipase}*\mathrm{ratio\_met} \\
&-7.747*\mathrm{lipase}*\mathrm{time} - 142.38*\mathrm{lipratio}^2 \\
&-64.666*\mathrm{lipratio}*\mathrm{ratio\_tbuta} + 6.9726*\mathrm{lipratio}*\mathrm{ratio\_met} - 0.464*\mathrm{lipratio}*\mathrm{time} - 7.876*\mathrm{ratio\_tbuta}^2 \\
&+9.988*\mathrm{ratio\_tbuta}*\mathrm{ratio\_met} - 0.6411*\mathrm{ratio\_tbuta}*\mathrm{time} \\
&-3.09*\mathrm{ratio\_met}^2 + 0.2421*\mathrm{ratio\_met}*\mathrm{time} - 0.1105*\mathrm{time}^2)*(-0.000204715*\left(\mathrm{T}\left(\mathrm{Reactor7}\right)\right)^2 \\
&+ 0.0279679*\mathrm{T}\left(\mathrm{Reactor7}\right) + 0.112717)
\end{aligned} \tag{11}$$

Table 5.-Range of operation of the variables. Enzymatic.

Variable	Lower bound	Upper bound
Temperature (ºC)	40	60
Lipase to oil(w/w)	0.02	0.04
Lip ratio(w/w)	0.4	0.6
Ratio t-butanol to oil (v/v)	0.4	0.8
Ratio methanol to oil (mol/mol)	3	6
Time (h)	19	25

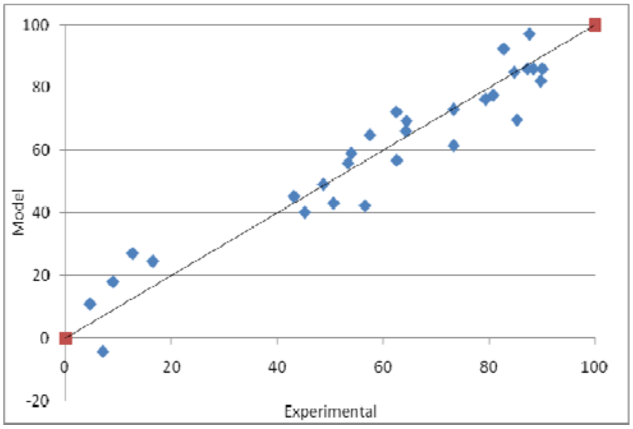


Figure 11.- Surface response model fitting for enzymatic transesterification.

The supported enzymes can be easily separated from the reactants and products, and subsequently the methanol is separated to be reused in column 9, and the biodiesel purified in column 11. The characteristics of these columns have been described in previous alternatives. The separation stages are also similar to the ones used for the reaction catalyzed by heterogeneous acids. To resolve the tradeoffs presented in the reactor and separation stages the objective function to be maximised is given by eq. (12)

$$Z = C_{FAME} * \mathrm{fc}\left(\mathrm{FAME}, \mathrm{Col11}, \mathrm{HX50}\right) + C_{Glycerol} * \mathrm{fc}\left(\mathrm{Glycerol}, \mathrm{HX43}, \mathrm{Snk16}\right) - C_{Steam} * (1/\lambda) * \left(\mathrm{QS\_max}\right)$$
$$- \; C_{enzy} * \mathrm{Enzymeadded} * \mathrm{f}_{recylce} - C_{MetOH} * \mathrm{fc}\left(\mathrm{MetOH}, \mathrm{Src12}, \mathrm{Mix9}\right) - C_{tButa} * \mathrm{fc}\left(\mathrm{tButa}, \mathrm{Src13}, \mathrm{Mix9}\right) \quad (12)$$

3.2.5.- Process 5: Supercritical production of bio diesel

Several studies also recommend the use of supercritical conditions as an efficient way to produce biodiesel since there are no catalysts involved. [11, 33,75] Based on the studies by West et al.[75] and Glisic and Skala[34] in which no other co-solvent is used together with methanol, the process flowsheet is similar to the previous ones. Figure 12 shows the flowsheet. Some other studies use propane as cosolvent producing also high yields. [44, 85]

The liquid methanol and oil are compressed and heated up to the operating conditions in the reactor. However, developing the surface response model for the reactor is more challenging due to the lack of complete studies and experimental data. Thus, we have combined the results from the studies by Babcock et al., [86] Deshpande et al., [86], Valle et al. [87] and Tan et al.[88] to come up with a surface response model that predicts the yield of the transesterfication as a function of the operating pressure, temperature, reaction time and molar ratio of methanol to oil. Eq. (13) shows the model, and the fit between the model and the experimental results is shown in Figure 13. The agreement is worse than in the previous examples but acceptable at high yields which are the ones we expect. Table 6 presents the range of the operating variables in the reactor.

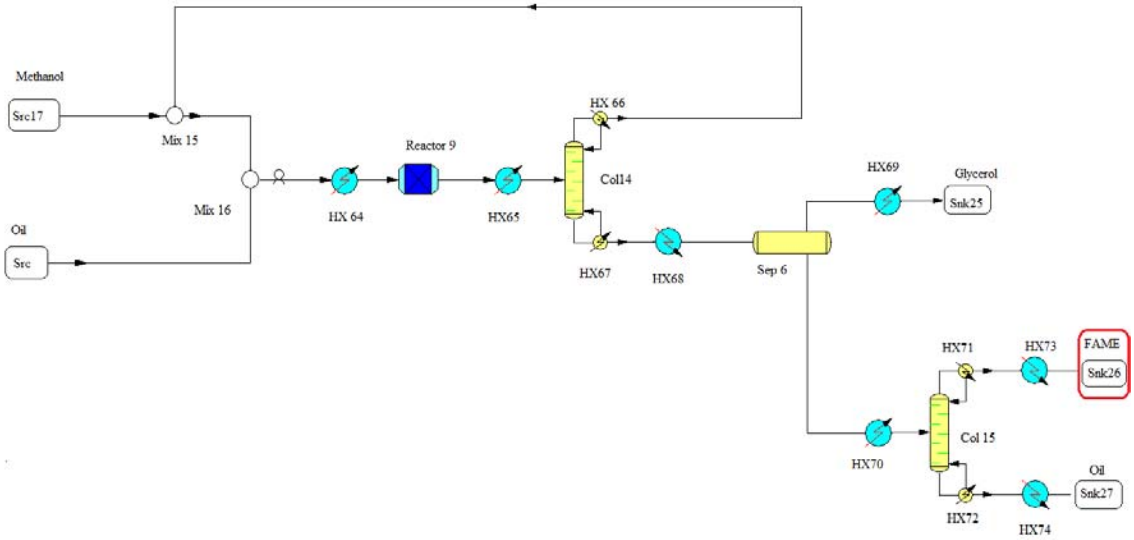


Figure 12.- Flowsheet for the production of biodiesel from oil via supercritical non catalyzed transesterification

$$\begin{aligned}\text{yield} = {} & 0.0010086 + 0.0554953 * \text{ratio\_met} + 0.15400198 * T(\text{reactor}) + 0.01244766 * \text{time} - 0.4591294 * P \\ & -0.059753 * \text{ratio\_met}^{2} - 0.0079404 * \text{ratio\_met} * T(\text{reactor}) - 0.0152524 * \text{ratio\_met} * \text{time} \\ & +0.0446531 * \text{ratio\_met} * P \; 0.0010993 * T(\text{reactor})^{2} + 0.0069208 * T(\text{reactor}) * \text{time} - 0.0023881 * T(\text{reactor}) * P \\ & -0.0014844 * \text{time}^{2} - 0.0035 * \text{time} * P - 0.00066982 * P^{2}\end{aligned} \tag{13}$$

Table 6.-Range of operation of the variables. Supercritical conditions

Variable	Lower bound	Upper bound
Temperature (ºC)	240	450
Ratio methanol (mol/mol)	10	50
Time (min)	2	600
Pressure(bar)	100	450

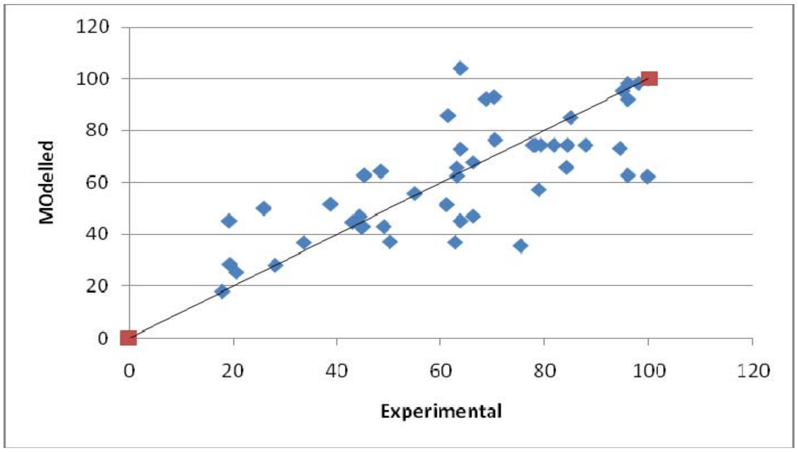


Figure 13.- Surface response fitting for supercritical non catalyzed transesterification

After the reactor, the product stream is decompressed and the excess of methanol is recovered in column 14. The model is similar to previous methanol recovery columns. The bottoms of the distillation column contains mainly glycerol and biodiesel with small amounts of methanol, water, FFA and oil. A gravity separation, Sep 6, allows the recovery of glycerol with a purity lever higher than 92% while the biodiesel is sent to column 15 where it is separated from unreacted oil.

In order to establish the optimal trade-offs related to the operating conditions of this process, the objective function to be maximized is the gross profit, as in previous cases, given by eq. (14):

$$\begin{aligned} Z \;=\; & C_{FAME} * \mathrm{fc}\left(\mathrm{FAME}, \mathrm{Col15}, \mathrm{HX73}\right) \; + C_{Glycerol} * \mathrm{fc}\left(\mathrm{Glycerol}, \mathrm{HX69}, \mathrm{Snk25}\right) \\ & - C_{Steam} * (1/\lambda) * (\; \mathrm{QS\_max}) - C_{MetOH} * \mathrm{fc}\left(\mathrm{MetOH}, \mathrm{Src17}, \mathrm{Mix15}\right) \; + \; C_{electricity} * \left(\mathrm{W}\left(\mathrm{Pump}\right)\right); \end{aligned} \tag{14}$$

3.3.-Solution procedure.

The superstructure comprises 6 sections, the production of oil from algae as well as each of the biodiesel production processes. We decompose the problem into two: that related to oil production (either from algae or cooking oil) and the biodiesel synthesis. For the algae the model is simple, since the optimization between the two technologies is favourable to the belt dehydration of the algae. The decision among the biodiesel production processes consists of solving a MINLP since the optimal production only selects one of the five alternatives.

$$\begin{gathered} \begin{bmatrix} Y_1 = true \\ Alkali \\ z_1 = f_1(\theta) \end{bmatrix} \vee \begin{bmatrix} Y_2 = true \\ Acid \\ z_2 = f_2(\theta) \end{bmatrix} \vee \begin{bmatrix} Y_3 = true \\ Enzymatic \\ z_3 = f_3(\theta) \end{bmatrix} \vee \begin{bmatrix} Y_4 = true \\ Heterogeneous \\ z_4 = f_4(\theta) \end{bmatrix} \vee \begin{bmatrix} Y_5 = true \\ Supercritical \\ z_5 = f_5(\theta) \end{bmatrix} \\ Y_1 \veebar Y_2 \veebar Y_3 \veebar Y_4 \veebar Y_5 \end{gathered} \tag{15}$$

Simultaneous optimization and heat integration is implemented within each of five processes to determine the optimal operating conditions. To decide upon the best process we maximize the objective function Z of each of the processes. Specifically we maximize a simplified profit function for each of the technologies and raw materials, algae oil and cooking oil with a minimum yield at the reactor of 0.98. Next, we design the optimal heat exchanger network (HEN) using the software SYNHEAT[37] to determine the number of heat exchangers and their specifications for costing purposes. Finally, the production cost for the production of biodiesel is computed once all the equipment needed for the production plant have been defined.

Following the link between energy and water consumption[38] for each of the optimized flowsheets, we also determine the water consumption using the model developed in Ahmetovic and Grossmann.[89] For this particular case the water network is simple since it basically reduces to the utility system, the boiler and cooling tower).

4.-Results

4.1.-Flowsheet definition.

The typical production capacity is 15Mgal/yr or around 40,000t/yr (1.3kg/s). In the future it is expected that the plants will produce 25kg/s of biodiesel.[31] Nowadays the biggest plant in Europe produces 250,000 t/yr (8kg/s) [90] while there are a number of them of around 200,000 t/yr (6.5 kg/s). Thus, we consider a plant capacity of about 7 kg/s.

The cost for the construction of the ponds ranges from 0.25 $\$/m^2$ to 1.25$\$/m^2$. [49,91] The bigger the pond the lower the cost. We use a value of 0.61 $\$/m^2$ [91] because even though our system will be large, this will allow to account for other minor equipment associated with the ponds such as the cost of the digester and the electricity generator. [49] The energy that can be obtained from the residue by digestion is computed using the data by Nielsen & Oleskowicz-Popiel[92] (522 kW/kg). In the ponds water is lost due to evaporation, 1.8kg/d. However, it is expected that the ponds use saline water, and thus this water is not accounted in the water balance.

According to the literature the microalgae oil obtained following the growing , harvesting and extraction yields a price of 0.25 $/lb[93] but the optimal production cost is expected to be as low as 0.07$/lb [32] . In Table 10 we present the results of our analysis revealing a production cost of $0.131/kg, which verifies the values predicted by Pokoo-Aikins et al.[32] as long as the new technology proposed by Univenture[39] is used.

We assume a production cost for biodiesel for the gross profit evaluation in the objective function of 1$/kg. For the operation of a biodiesel plant 0.083kwh of electricity are used per gallon of biodiesel[94] not including the supercritical process. The costs for utilities are updated from the literature (0.019 $/kg Steam, 0.057 $/ton cooling water[95] . Electricity: 0.06 $/kWh [96] 4.876 $/MMBTU [97] for natural gas while Table 7 summarizes the cost of the different chemicals used. We assume that the glycerol for washing in pretreamtent is twice as expensive as the byproduct of the transesterification process since its purity is 100% (http://www.ruralsementes.com), while the glycerol byproduct from the pretreatment is 25% more expensive than the by product of the transesterification since it is also of higher purity.

The typical operating conditions for the transesterification are shown in Table 8 [13,29,35]. The simultaneous optimization of the performance of the reactor, methanol recycle and heat integration yield different values for the reactor operation. The temperatures and alcohol to oil ratios differ due to the fact that the operating conditions at the reactor are optimized simultaneously with the process including energy integration in contrast to the optimization of the reactor alone. The results are summarized in Table 9.

Table 7.- Chemicals cost

Chemical	Price ($/kg)	Source
Fertilizer	0.367 *	98
Enzyme	0.7	35
Tert butanol	2	35
Het. Catalyst	0.6	29
CH_3OH	0.28	99
H_2SO_4	0.329	100
KOH	1.6	101
CaO	0.06	102
Gypsum	0.023	102
H_3PO_4	0.34	29
Glycerin	0.6	29
Hexane	0.41	13
$Fe_2(SO_4)_3$	0.447	103
K_3PO_4	1.9	104

(*) Mean value of a number of fertilizers

Table 8.- Typical operating conditions

	Alkali (13, 29)	Acid(13, 29)	Heterog. (29,69)	Supercritical (29)	Enzymatic (35)
	H_2SO_4/NaOH				
Temperature(ºC)	70/60	80	60[29] ;67.5[69]	350	25
Pressure (bar)	4/4	4	1	200	1
Alcohol : oil ratio	6:1/6:1	50:1	4.5:1[29] 6:1[69]	42:1	3:1 met
Ratio_but					12:1 t-butanol
Residence time(h)	1 / 4	4	3[29, 69]	0.333	
Catalyst	1/1(%w/w)	1.3:1 molar to oil	1[29], 3[69] (%w/w)	N/A	4(%w/w)

Table 9.- Optimal operating conditions

	Alkali cat	Acid Cat	Het -CaO	Supercritical	Enzymatic
(Algae / Cooking Oil)					
Temperature(ºC)	45/45 (64.6)[*]	47.5/47.5	60/60	328/328	60/60
Pressure(bar)	4/4(4)[f]	4[f]	1[f]	105/105	1[f]
Alcohol : oil ratio	6.6/6.6(1)[*]	20/20	11.190/10.920	10.969/10.215	4.966/ 4.964
Ratio_but					0.671/0.672
Residence time(h)	2/2(2.45)[*]	48	2	0.5/0.5	21.661/ 21.658
Catalyst (%)	1.06/1.063(0.4)[*]	2/2	1/1	N/A	2/2
Lipase ratio					0.529/0.529

(*) Pretreatment (f) fixed

Instead of presenting directly the optimal case resulting from the optimization, in Table 10 we present the values for the objective function for the different cases which allows us to identify not only the process with the best gross profit but promising alternatives. The objective function shows that, in the case of algae oil, the alkali catalyst is the best one while when the raw material is cooking oil, the best process is the heterogeneous one. As we can see in the table, if the feedstock is uncertain or we prefer to have a flexible plant capable of dealing with different oil characteristics, the best process is the heterogeneous one since its objective function value is not only the best for cooking oil but it is also quite close to the one obtained for the alkali catalyzed one in case of algae oil.

Table 10.- Simplified profit evaluation

	Price ($/kg)
Algae production	0.131
Cooking oil	0.2[28]

		Objective function ($/s) Algae/ Cooking oil
Biodiesel production	Alkali Cat.	7.297/ 6.875
	Acid Cat.	7.093 / 7.076
	Supercritical	7.268 / 7.247
	Enzymatic	7.262 / 7.239
	Heterogeneous	7.274 / 7.253

4.2.- Design of the heat exchanger network, water network

Once the flowsheet is optimized, we need to synthesize the optimal heat exchanger network (HEN) for which the model by Yee and Grossmann [37] is used. Next, since water consumption is a current concern in biofuel production processes, it is our aim to determine the minimum water consumption. Similarly as we have studied the water consumption in the bioethanol production processes [105,106], we design the water network based on the model by Ahmetovic and Grossmann[89]. We identify the equipment involved, boiler and cooling tower, assuming that the algae are grown in sea water and we optimize the superstructure leading to the water network to determine the freshwater consumption, Table 11 shows the results.

4.3.- Economic evaluation and discussion.

We use the same method as presented in Martin & Grossmann [107] based on industrial data for the economic evaluation, which allows further comparison of the results with previous papers by the authors.

The production cost of oil from algae has been estimated to be as low as \$0.07/lb in the best possible scenario. [32] This value can be achieved as long as the process is based on a new design for harvesting the algae recently released by Univenture [39] see (Fig. 3&4). When using this new technology based on membranes, the energy to remove the water and dry the algae is drastically reduced, and the production costs can be as low as \$0.06/lb. Figure 14 shows the breakdown of the production costs including the ponds and auxiliary equipment as part of the equipment costs, the fertilizers for the growth of algae, steam, electricity and cooling water, and management of the plant. We assume that the cost of CO_2 is zero either coming from the biorefinery [107] or from power plants.

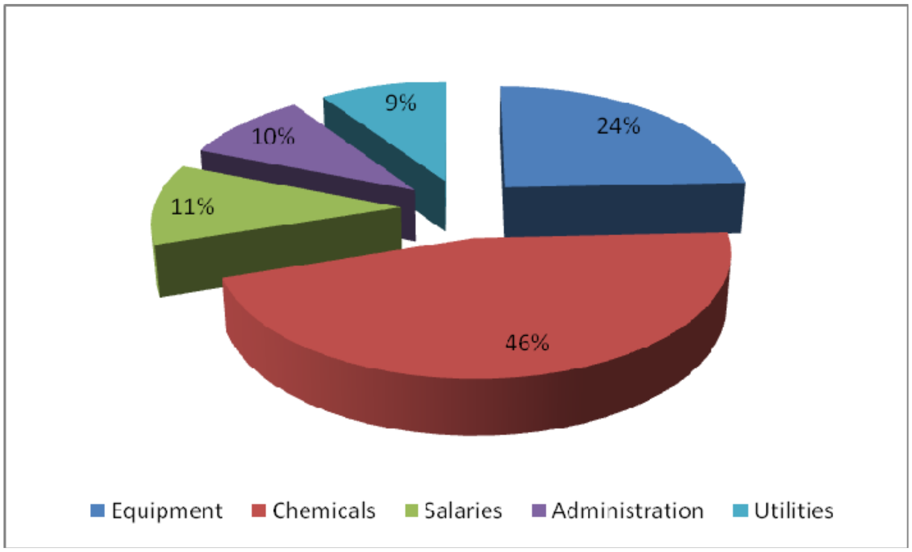


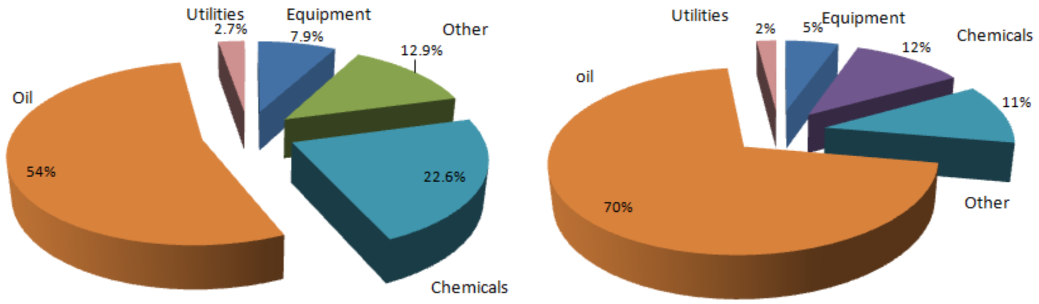
Figure 14. Cost distribution for the produciton of oil from algae.

Wither and Noordam in 1996[108] estimated the transesterification costs to be about 58 cents per gallon and overhead cost 33 cents per gallon. If the byproduct glycerol is credited at 39 cents per gallon, the total cost for processing biodiesel is 52 cents per gallon. Other studies have estimated total operating costs of 30-60 cents per gallon. [109] The total operating cost for converting fats and oils to biodiesel ranges from \$1.39 to \$2.52 per gallon, depending on what feedstocks are used. [110-112] Previous results reported in the literature on energy consumption range from 3.3 MJ/gal to 12 MJ/gal [32, 111,113] with and industrial average of 4.4 MJ/gal (National Biodiesel Board 2009). In terms of water consumption, values of 1 to 3 gal/gal are reported by Pate and coworkers.[114] Table 11 summarizes the manufacturing costs, the energy and water consumption of the processes. Since the production cost of the oil from the algae includes the energy consumption, for the sake of the comparison in Table 11 we only include the energy consumption in the transesterification step. It can be seen that the best processes predicted by the objective function in Table 10, also turn out to be the best ones when a more detailed economic evaluation is performed. Figure 15 shows the breakdown of the costs.

Table 11.- Production costs, energy and water consumption.

	Alkali cat	Acid Cat	Supercritical	Het –CaO	Enzymatic
$/gal					
Algae	0.42	0.50	0.49	0.45	0.48
Cooking	0.83	0.72	0.92	0.66	0.71
Thermal Energy (MJ/gal)					
Algae	1.94	1.94	3.91	1.94	2.08
Cooking	2.20	2.19	4.32	1.94	3.36
Water (gal/gal)					
Algae	0.60	0.87	0.78	0.59	0.72
Cooking	0.32	0.67	0.61	0.33	0.59

Based on the results of the optimization, the optimal process from biodiesel production from algae oil is the alkali catalyzed one. After heat integration, the energy required when using algae oil is 1.94MJ/gal. The water consumption, by developing a water network as in Ahmetovic et al. [89] yields 0.60 gal/gal with a final production cost of $0.42 /gal. The other competitive process is the heterogeneous catalyzed one for which algae oil results in a energy consumption of 1.94MJ/gal, 0.59 gal/gal of water consumption and $0.45 /gal. If cooking oil is used, only the heterogeneous catalyst is recommended. In this case also 1.94MJ/gal are required, consuming 0.33 gal/gal of water and with a production cost of $0.66/gal. The main differences between the two processes are the price of the raw material, and the fact that the process for the production of oil from algae can be integrated with the biodiesel production to reduce transportation costs and the heat integration since the oil comes at a higher temperature, and can be used to provide energy for the transesterification. The cost of this energy is taken into account in the production cost of the oil from algae. The results are very promising for the production of biodiesel since half the energy reported in the literature is used and between half and a third of the best value reported for water consumption reported.[114]



Optimal Algae Oil Optimal cooking oil

Figure 15. Contribution of the different costs to the total production cost. [118]

However, if we prefer to be flexible in terms of design so that we can work with good yield no matter what raw material we have to process, from Table 5 we suggest the use of the heterogeneous process since it represents the best trade-off since the production cost for algae is just \$0.01/gal more expensive that the optimal process, and consumes almost the same energy and water.

In Table 12 we present the comparison between the results for the optimal cases for the production of biodiesel from algae and cooking oil implementing simultaneous optimization and heat integration, and the ones obtained by fixing the variables to those typically used in the literature and obtaining a feasible solution for the flowsheet without optimization and heat integration. A clear advantage is shown when the approach presented in this paper is used, which is translated in lower production costs and energy consumption for a higher conversion in the reactor.

Biodiesel competes with the synthetic diesel produced using Fischer–Tropsch technology. If we compare the production or biodiesel with that of the FT-Diesel [115] , the results show a tradeoff. are promising. On the one hand, the FT-Diesel production process is more flexible since it generates gasoline and diesels while biodiesel production is focused on the production of biodiesel only. Moreover, the production cost is similar, below 0.75 \$/gal and highly dependent of the raw material. However the complexities of the process varies. The FT-Diesel process requires more equipment and purification stages for the syngas as well as for the products resulting in an investment cost of \$216MM. On the other hand, the economics of biodiesel plants depends on the raw material.

In case of using cooking oil, the investment cost is reduced to \$17MM and a production price competitive with that of FT-Diesel, \$0.71/gal. However, if we use algae the investment cost including the construction of ponds requires a facility involving large ponds increasing the investment cost up to \$105MM, which is still half the one required for the FT-Diesel plant, while the operating costs, \$0.42/gal, are 2/3 of those of the FT-Diesel.

Table 12.-Comparison of the base case based on literature results and the optimal case

	Algae Oil	Cooking Oil
conversion		
Optimal	0.98	0.98
Base	0.96[b]	0.80[b]
\$/gal		
Optimal	0.42	0.68
Base	0.44[b]	0.80[b]
Energy (MJ/gal)		
Optimal	1.94	1.94
Base	1.94[b]	2.34[b]
Water (gal/gal)		
Optimal	0.60	0.33
Base	0.56[b]	0.25[b]

([b] reactor operating conditions as in table 8)

Finally, there is an opportunity for process integration between algae production and the production of lignocellulosic based biofuels. Processes such as the production of ethanol, hydrogen or FT-diesel via gasification generate a fair amount of CO_2 that can be used in algae growth. The case of the production of hydrogen[116] is particularly interesting because in that case only the hydrogen from the lignocellulosic raw material is used and thus algae production represents an opportunity for the use of the carbon.

5.-Conclusions

In this paper, we have optimized the conceptual design for the production of biodiesel from cooking oil and algae oil by proposing a superstructure of alternative technologies for the transesterfication of the oil. We solve the superstructure by decomposing it for each of the technologies so that they are simultaneously optimized and heat integrated. The gross profit decides on the best process. Next we design the optimal heat exchanger network and perform an economic evaluation. Simultaneous optimization and heat integration of the flowsheets result in the fact that the optimal operating conditions in the reactors differ from the ones traditionally used because in previous work the separation tasks were not taking into account when deciding on the process design.

In terms of the optimized process, for algae oil the alkali catalyzed one is the best with a production cost of 0.42$/gal, 1.94 MJ/gal of energy consumption and water consumption of $0.60gal_{water} / gal_{biodiesel}$. For cooking oil the best one is the heterogeneous catalyzed with lower operational cost due to the ease separation of products ($0.66/gal, 1.94 MJ/gal of energy consumption and $0.33gal_{water} / gal_{biodiesel}$) The energy values are half the ones reported in the literature while the water consumption is one third to a half of the best values reported. Although promising, the results must be validated experimentally at the pilot plant level.

6.-Nomenclature

C_i	Material cost ($/Kg or kW)
Fcp(unit)	Flow heat capacily (kg/s· kJ(kg K))
Tpinch(pinches)	Temperature pinch (ºC)
T(Unit, Unit1)	Temperature of the stream from unit to unit 1 (ºC)
Fc(J,Unit, Unit1)	mass flow of component J from unit to unit 1 (kg/s)
F(Unit, Unit1)	total mass flow from unit to unit 1 (kg/s)
Q(unit)	thermal energy involved in unit (kW)
W(unit)	electrical energy involved in unit (kW)
QS_max	Integrated hot utility (kW)
yield	yield of the reaction
Cat_alka	fraction mass catalizer ;
Cat:	fraction in mass of H2SO4
ratio_met	ratio methanol to oil
yield_FFA	yield of the pretreatment reaction
yield	yield of the transesterification reaction
time	reaction time (h) ;
Cat_pret_add	mass fraction of catalysts added ;
conver	conversion /0.98/;
conver_FFA	conversion of the pretreatment reaction /0.99/;
λ	Latent heat steam (kJ/kg)

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