Optimal Integration for Biodiesel Production Using Bioethanol

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The production of biodiesel from algae is optimized using bioethanol following four different transesterification paths: alkali, enzymatic, and heterogeneous catalysts and supercritical conditions. The reactors are modeled using response surface methodology based on experimental results from the literature. These reactor models are implemented together with short-cut methods for the other equipment (distillation columns, gravity separators, etc.) in order to recover the ethanol, separate the polar and nonpolar phases, and purify the glycerol and biodiesel produced to formulate the problem as a superstructure of alternatives. The aim is to simultaneously optimize and heat integrate the production of biodiesel using ethanol in terms of the reaction technology and the operating conditions. The optimal conditions in the reactors differ from the ones traditionally used because these results take the separation stages into account. In terms of the optimal process, the alkali catalyzed process is the most profitable, while the enzymatic one is also promising due to the lower consumption of energy and water, although it requires significant enzyme cost. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 834–844, 2013

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Introduction

Biodiesel and bioethanol are the most important liquid biofuels employed in the transportation sector due to their similarity with current crude oil-based fuels and their compatibility with current engines. These biofuels can be used either as fuels themselves, or blended with petroleum based diesel and gasoline to enhance the oxygen content of such fuels. These oxygenated blends allow the reduction of polluting gases, mostly aromatic hydrocarbons and CO_2.[1]

For producing biodiesel, the transesterification of vegetable oils with low-molecular-weight alcohols, like methanol or ethanol, has been the traditional process instead of emulsification. This reaction is accomplished with the help of acidic, basic or enzymatic catalysts or under supercritical noncatalyzed conditions. Current world biodiesel production is carried out employing methanol[2–10] due to its low cost compared to ethanol. Recently, it has been reported that similar yields of biodiesel can be obtained via the transesterification of oil using either ethanol or methanol as the transesterification agent. However, the reaction times required to attain these yields are different: methanolysis is much more rapid.[11,12] Because current biorefineries are becoming chemical complexes where a number of different products including ethanol and biodiesel are produced, integration of chemical processes has been reported to produce large economic savings. Therefore, the use of ethanol can result in a large economic benefit in the operation of the complex.[1,13]

So far there are few processes reported for the production of biodiesel using ethanol,[14] and most of the studies are at laboratory scale evaluating the operating conditions of the reactor.[11,12] Thus, the aim of this article is to evaluate the industrial production of biodiesel from oil and ethanol. The most promising raw material for oil is microalgae, due to the high yield from the field to oil,[15] and the higher purity compared to the use of wastes. In terms of the process technologies, the use of an alkali (KOH) catalyzed reaction is the most widely used,[1] while the use of enzymatic or heterogeneous catalyst or noncatalyzed reaction under supercritical conditions are becoming important alternatives. There is a general lack of information in terms of modeling the transesterification reaction due to the less frequent use of ethanol. This fact represents a major challenge. The expected increase in the production of ethanol and the advantages of process integration suggest that the use of ethanol for the transesterification of oil may be competitive.

In this article, we investigate the conceptual optimal design for the production of biodiesel using bioethanol within the context of a biorefinery. We evaluate four different technologies, catalyzed (alkali, heterogeneous and enzymatic), and noncatalyzed under supercritical conditions. We propose a superstructure optimization approach where we first construct a flowsheet embedding the various process units involved. The problem is formulated as an MINLP for the simultaneous optimization and heat integration of the process. Given the small number of alternatives, the solution is obtained by enumeration of the NLP subproblems to obtain the optimal solution and to identify other promising alternatives. Next, we design the heat exchanger network using SYNHEAT,[16] and perform an economic evaluation to determine the production cost. Finally, to address the concern of water consumption in biofuel production processes, we determine the freshwater consumption following the method proposed in Ahmetovic et al.[17] and Grossmann and Martín[18]

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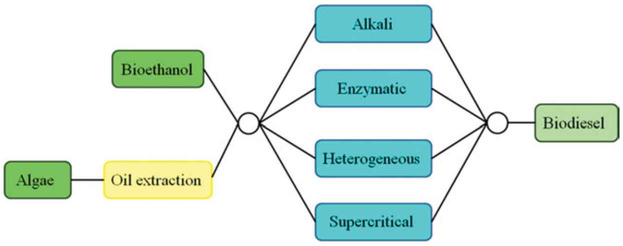

Figure 1. Superstructure for the production of biodiesel using bioethanol.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Problem Statement

We propose a superstructure for the production of biodiesel using ethanol as the alcohol and algae oil. The algae oil production is taken from the results of a previous article[19] involving algae growth, drying and oil extraction. The transesterification of the oil involves the four most common technologies for the transesterification of oil with ethanol, or ethanolysis, based on the results in the literature. These data are used to write models for the reactor as a function of the operating variables such as temperature, ethanol to oil ratio, amount of catalysts, if any, pressure and time. There is a lack of research in some of the technologies, and, therefore, it has been difficult to find reliable data to develop the models. Due to the special features of the process, the reactors operate with ethanol in large excess. The economy of biodiesel production, therefore, relies on ethanol recovery, and, thus, simultaneous optimization and heat integration are implemented.[20] Finally, the water consumption of the different processes is calculated based on previous articles.[17,21]

The article is organized as follows. In the "Overall Process Description" section, we present the main assumptions related to the different units involved in the production of biodiesel from algae oil and ethanol, with special focus on the development of models for the transesterification reactor. In the "Results" section, we summarize the results of the optimization leading to the selection of the best process. Finally, in the "Conclusions" section, we compare the use of ethanol and methanol for the production of biodiesel, including a sensitivity analysis of the price of ethanol on the production cost of biodiesel.

Overall Process Description

Raw material

The production of algae oil is attracting attention due to the high yield from the ground to biofuels.[7,19] Microalgae production can be carried out either in ponds or photoreactors. The cost of running the ponds is lower, but they are prone to contamination due to the open surface. Alternatively, photorreators avoid contamination, but have a higher capital and operating cost. For large-scale production ponds are usually recommended.[22]

The Microalgae oil 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, yielding total content of unsaturated fatty acids of around 85%.[23] Additionally, it contains 0.01–0.02% moisture and 0.45–1.75% free fatty acid (FFA).[7] Notably, FFA is always below 2%.[24] Based on these data, we assume that triolein and oleic acid represent the oil for further simulations with no impurities, and, therefore, no pretreatment is needed.

Biodiesel synthesis

Once the oil is available, there are different processes[5,25] to obtain biodiesel depending on the catalyst of the transesterification reaction (see Figure 1 for the superstructure of alternatives). In all processes the lower bound for the purity of glycerol is 92%.[2] In the next subsections, we discuss the modeling features for each of the stages involved in the production of biodiesel using bioethanol and microalgae oil. In general, we use short cut methods and experimental data from the literature to model the different equipment. For the sake of reducing the length of the article, we refer to the supplementary material of a previous article by the authors[19] for the models of typical equipment such as distillation columns, liquid–liquid separations and heat exchangers, while in this article we focus on modeling the reactors. Since the reactors and liquid–liquid separations models are based on experimental data, we consider those models to be validated, while for the distillation columns we validate the results from the optimization using process simulators (ASPEN), taking into account that biodiesel from bioethanol is not the same compound as when methanol is used in the transesterification.

Process 1: Alkali-Catalyzed Process. Figure 2 shows the flowsheet for the use of alkali catalyst in the transesterification of oil. It consists of five stages, transesterification,

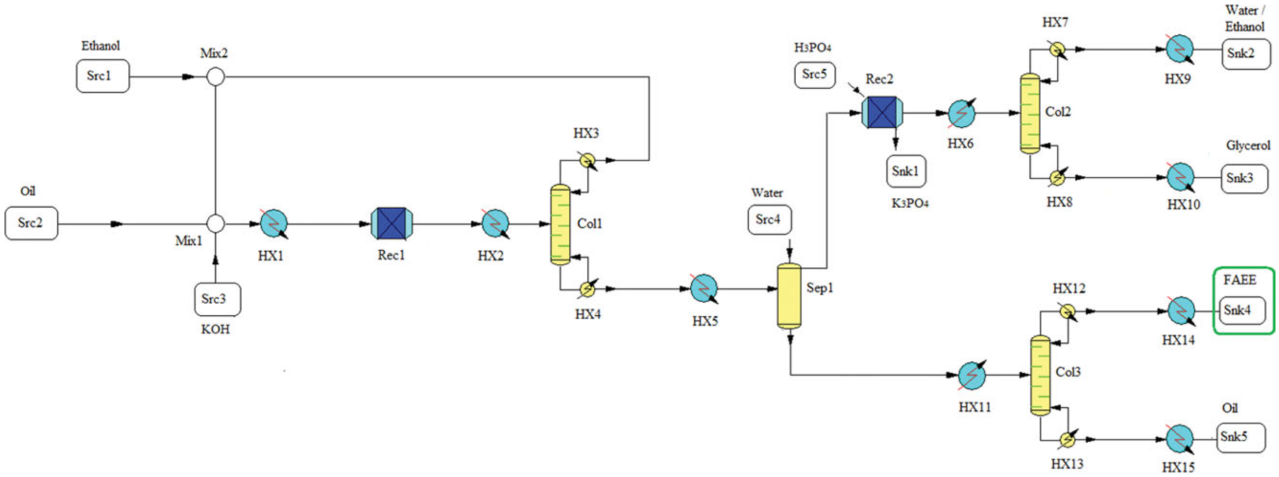

Figure 2. Flowsheet for the production of biodiesel from oil via alkali—catalyzed transesterification.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

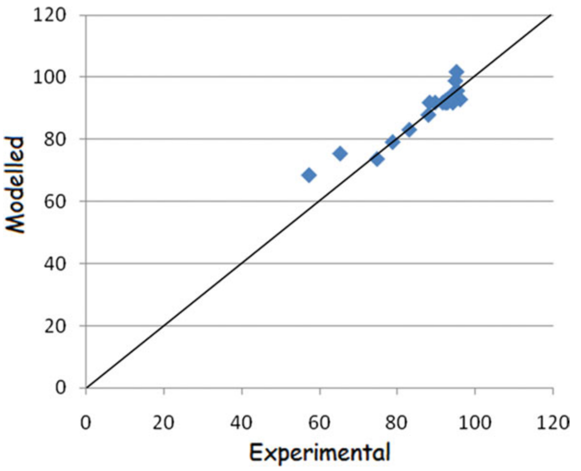

Figure 3. Fitting of the data for yield of the alkali catalyst.

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ethanol recovery, catalyst washing, glycerol purification, and biodiesel recovery.

Alkaline Transesterification. The yield of biodiesel is a function of a number of variables such as operation temperature, ethanol:oil ratio, and catalyst amount. Even though the operating conditions have been studied,[26,27] they have been optimized only in the context of the reactor to obtain approximately 90–98% oil conversion to ethyl esters using different alkali catalysts without considering the energy required in the separation stages. There are a number of tradeoffs to obtain a high yield by adjusting the catalyst concentration, ethanol; oil ratio and working temperature. The catalyst used is KOH because K_3PO_4 can be easily separated and used as fertilizer. The model for the transesterification reaction,[27] Eq. 1, is taken from the literature and Table 1 presents the range of operating variables

$$\begin{aligned}\text{yield} &= 22.94293 + 113.88^*\text{cata\_alk} + 2.828881^*\\ &\quad \text{Ratio\_et} - 1.02734^*\text{T(HX1, Rec1)} - 1.44522\\ &\quad ^*\text{cata\_alk}^*\text{Ratio\_et} \quad + 0.250723^*\text{cata\_alk}^*\text{T(HX1, Rec1)}\\ &\quad + 0.023375^*\text{Ratio\_et}^*\text{T(HX1, Rec1)} - 41.4402^*\text{cata\_alk}^2\\ &\quad - 0.07568^*\text{Ratio\_et}^2 + 0.006226^*\text{T(HX1, Rec1)}^2; \qquad (1)\end{aligned}$$

Ethanol Recovery. A distillation column will be used to recover the excess of ethanol so that it is recycled back to the reactor. At least 94% of the ethanol is recycled. The reflux ratio is variable. The temperature at the bottom must not be higher than 150°C to avoid glycerol decomposition; thus, vacuum operation is required. The bottoms are cooled down to 60°C before phase separation. We have used short cut methods to model the distillation columns; see Martin and Grossman[19] for the details. We validate the operating conditions of the column using process simulators.

Water Washing. The purpose of this stage is to separate the biodiesel from the glycerol, ethanol and catalyst. Following the usual approach,[2,4] we assume that a water washing column is used to fully separate both phases. There is controversy as to whether gravity separation alone is sufficient.[4,28] Based on the experimental results presented by Zhou and Boocock[29] and Cernoch et al.[30] we assume good phase separation for ethanol. A small amount of water, 5% of the biodiesel phase, is added to the column.[30] The working temperature is between 30 and 40°C.[30]

FAEE Purification. The nonpolar phase containing biodiesel is purified in a distillation column. The main challenge is to operate below atmospheric pressure so that the distillate containing biodiesel exits the column below 250°C to maintain the integrity of the biodiesel.[2]

Alkali Removal. In order to remove the alkali catalyst, KOH, phosphoric acid, H_3PO_4 is selected based on the fact that the salt generated in the neutralization reaction, K_3PO_4, can be easily removed using a gravity separator.

Glycerol Purification. A distillation column is typically used to purify glycerol above a concentration of 92%. Beyond this purity level, glycerol can be sold as a high-quality byproduct. However, the decomposition temperature of glycerol is reported to be 150°C, which requires the distillation column to operate below atmospheric pressure.[2] The reflux ratio is variable from 2 to 3 as is the purity of the glycerol, using 0.92 as the lower bound. The final objective function is given in Eq. 2

$$\begin{aligned}Z &= C_{\text{FAEE}}{}^*\text{fc(FAEE)} + C_{\text{Glycerol}}{}^*\text{fc(Glycerol)}\\ &\quad + C_{K_3PO_4}{}^*\text{fc(K3PO4)} - C_{\text{Steam}}{}^*(1/\lambda)^*(\text{QS\_max})\\ &\quad - C_{\text{KOH}}{}^*\text{fc(KOH)} - C_{\text{EtOH}}{}^*\text{fc(EtOH)}\\ &\quad - C_{H_3PO_4}{}^*\text{fc(H3PO4)}; \qquad (2)\end{aligned}$$

Process 2: Enzymatic-Catalyzed Production of Biodiesel. According to recent reports from Novozymes, one of the world leaders in enzyme production, a transesterification process based on enzymes will be able to use raw materials of lower quality, such as animal fats, recycled restaurant oils, and waste products as opposed to current chemical processes which require high-quality raw materials in competition with food.[31] However, the enzymatic process has not been implemented at industrial scale due to the lack of process scale up research.[32] Due to the high cost of the enzymes, the only economical way to produce biodiesel is using them in immobilized form allowing for their reuse.[33] Figure 4 shows the flowsheet for the production of biodiesel using enzymatic catalysts. The stages are similar to the ones for the previous process, but because the immobilized enzymes can be easily separated, there is no need for washing and the separation of glycerol does not require a distillation column.

Transesterification Reduced Order Model. There are a number of recent models based on design of experiments for the transesterification reaction using enzymatic catalysts to obtain biodiesel.[34–38] The article by Rodrigues et al.[38] is used as reference due to the yield achieved and the variables studied. From their experimental results it is possible to obtain a model using bilinear and quadratic terms given by Eq. 3. Despite the dispersion, there is reasonably good agreement. Figure 5 shows the goodness of the fit, and Table 2 presents the range of operation of the variables

Table 1. Range of Operation of the Variables

Variable	Lower bound	Upper bound
Temperature (°C)	25	80
Ratio ethanol (mol/mol)	3	20
Catalyst	0.5	1.5

Alkali pretreatment

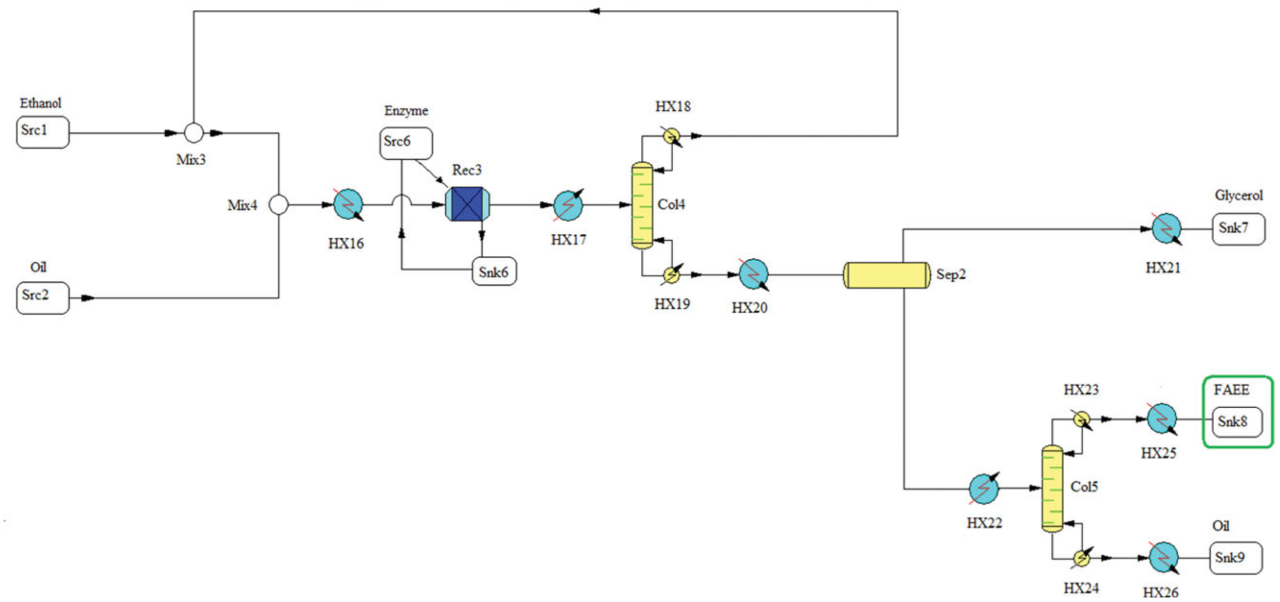

Figure 4. Flowsheet for the production of biodiesel from oil via enzymatic transesterification.

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$$\begin{aligned}\text{yield} = {} & 3.624996 - 1.64904^{*}\text{T(HX16, Rec3)} + 17.91299^{*}\text{time\_enz} - 7.60104^{*}\text{Ratio\_etE} + 10.59497^{*}\text{cata\_enz} \\ & - 0.49902^{*}\text{water\_enz} + 0.014332^{*}\text{T(HX16, Rec3)}^{2} - 0.65091^{*}\text{time\_enz}^{2} - 0.33241^{*}\text{Ratio\_etE}^{2} - 0.31632 \\ & {}^{*}\text{cata\_enz}^{2} + 0.00692^{*}\text{water\_enz}^{2} - 0.0407^{*}\text{T(HX16, Rec3)}^{*}\text{time\_enz} + 0.17485^{*}\text{T(HX16, Rec3)}^{*}\text{Ratio\_etE} \\ & - 0.0138^{*}\text{T(HX16, Rec3)}^{*}\text{cata\_enz} - 0.0156^{*}\text{T(HX16, Rec3)}^{*}\text{water\_enz} - 0.0601^{*}\text{time\_enz}^{*}\text{Ratio\_etE} \\ & - 0.4629^{*}\text{time\_enz}^{*}\text{cata\_enz} + 0.11014^{*}\text{time\_enz}^{*}\text{water\_enz} + 0.43481^{*}\text{Ratio\_etE}^{*}\text{cata\_enz} \\ & + 0.21369^{*}\text{Ratio\_etE}^{*}\text{water\_enz} - 0.09614^{*}\text{cata\_enz}^{*}\text{water\_enz}; \qquad (3)\end{aligned}$$

The supported enzymes can be easily separated from the reactants and products. The ethanol is then separated to be reused. The separation of the oil and polar phases is based on gravity and does not require the addition of any agent.[29,30] The working temperature is 40°C[30], similarly to the alkali case. Finally, the biodiesel is purified by distillation. Equation 4 presents the objective function for this technology

$$\begin{aligned}Z = {} & C_{\text{FAEE}}{}^{*}\text{fc(FAEE)} + C_{\text{Glycerol}}{}^{*}\text{fc(Glycerol)} \\ & - C_{\text{Steam}}{}^{*}(1/\lambda)^{*}(\text{QS\_max}) - C_{\text{enzy}}{}^{*}\text{Enzymeadded}^{*} \\ & \text{f}_{\text{recylce}} - C_{\text{EtOH}}{}^{*}\text{fc(EtOH)} \qquad (4)\end{aligned}$$

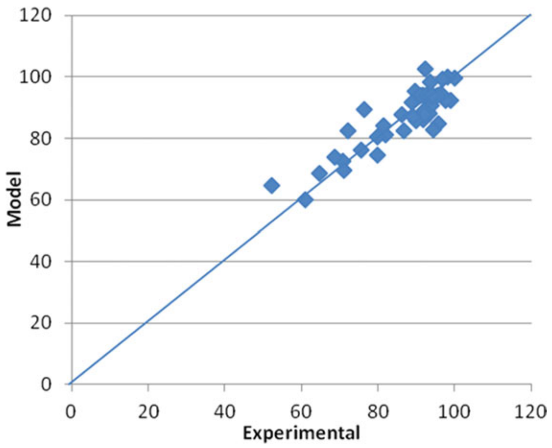

Figure 5. Surface response model fitting for the yield of enzymatic transesterification.

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Process 3: Supercritical Production of Biodiesel. The use of supercritical conditions for oil transesterification is deemed to be an efficient way to produce biodiesel since there is no catalyst involved, which simplifies the separation of the products. However, the operating conditions of the reactor require energy (electricity and heat) to prepare the feed for the reaction.[39,40] Figure 6 shows the flowsheet. The absence of the catalyst simplifies the flowsheet because the only steps are ethanol recovery, phase separation via gravity and biodiesel purification. The model for the reactor is obtained from experimental data in the literature[40] and is presented in Eq. 5. Correlations for the yield and for the operating pressure are developed based on surface response methodology (see Figure 6 and Table 3 for the model's range of variables and fitting)

$$\begin{aligned}\text{yield} = {} & 0.2243 - 2.8332^{*}\text{T(HX27, Rec4)} + 9.2281^{*}\text{time\_sup} \\ & + 19.3431^{*}\text{Ratio\_etS} - 0.1075^{*}\text{Ratio\_etS}^{2} + 0.007844^{*}\text{T} \\ & \text{(HX27, Rec4)}^{2} - 0.0849^{*}\text{time\_sup}^{2} - 0.0136^{*}\text{time\_sup}^{*} \\ & \text{T(HX27, Rec4)} - 0.0358^{*}\text{Ratio\_etS}^{*}\text{T(HX27, Rec4)} \\ & - 0.0105^{*}\text{time\_sup}^{*}\text{Ratio\_etS}; \qquad (5)\end{aligned}$$

Table 2. Range of Operation of the Variables

Variable	Lower bound	Upper bound
Temperature (°C)	20	45
Ratio ethanol (mol/mol)	3	12
Catalyst(%w/w)	5	16
Added water(%w/w)	0	20
Time (h)	6	13

Enzymatic transesterification

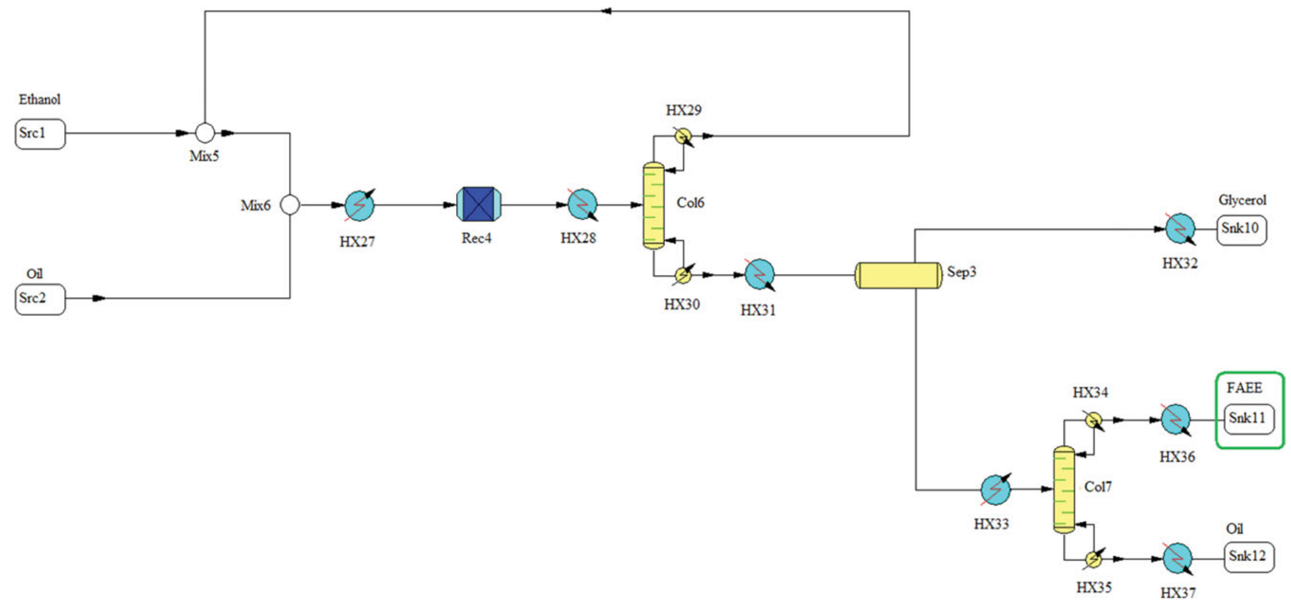

Figure 6. Flowsheet for the production of biodiesel from oil via supercritical noncatalyzed transesterification.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

To determine the operating pressure we obtain a correlation (Eq. 6), using the data from the same source.[39,40] Figure 8 shows the fit.

$$\begin{aligned} \mathrm{P(MPa)} = {} & -0.05387 + 0.030504^{*}\mathrm{T(HX27, Rec4)} \\ & - 0.89026^{*}\mathrm{Ratio\_etS} + 0.003033^{*}\mathrm{T(HX27, Rec4)}^{*} \\ & \mathrm{Ratio\_etS} \end{aligned} \quad (6)$$

After the reactor, the stream is decompressed and a distillation column recovers the excess ethanol. There is a tradeoff between the operating conditions in the reactor and the separation stages: the larger the excess of ethanol the higher the yield. However, more energy is required to recover the excess. If less ethanol is used in the reactor, we have to compensate for the loss of yield by modifying either the pressure, the residence time, or the inlet temperature.

The bottoms of the distillation column contain mainly glycerol and biodiesel with small amounts of ethanol, water, FFA, and oil. A gravity separation allows the recovery of glycerol with purity higher than 92%, while the biodiesel is purified in a distillation column. In this column, as we have discussed before, the temperature of the distillate, mainly biodiesel, must be kept below 250°C to avoid biodiesel decomposition. The objective function is given by Eq. 7

$$\begin{aligned} Z = {} & C_{\mathrm{FAEE}}{}^{*}\mathrm{fc(FAEE)} + C_{\mathrm{Glycerol}}{}^{*}\mathrm{fc(Glycerol)} \\ & - C_{\mathrm{Steam}}{}^{*}(1/\lambda)^{*}(\mathrm{QS\_max}) - C_{\mathrm{EtOH}}{}^{*}\mathrm{fc(EtOH)} \\ & + C_{\mathrm{electricity}}{}^{*}(\mathrm{W(Pump)}); \end{aligned} \quad (7)$$

Table 3. Range of Operation of the Variables

Variable	Lower bound	Upper bound
Temperature (°C)	290	325
Ratio ethanol (mol/mol)	30	52
Pressure (MPa)	10	15
Time (min)	25	30

Supercritical transesterification

Process 4: Heterogeneous Production of Biodiesel. Over the last few years there has been an increasing interest in synthesizing heterogeneous catalysts for the production of biodiesel using ethanol. However, until recently only low yields have commonly been obtained [41–44] (ca. 90% with $SnCl_2$, using high-molar ratios ethanol:oil, 120:1, which excessively increases the energy consumption for ethanol recycle). Li et al.[44] reported high-yields working in a pressurized vessel with a lower ethanol:oil ratio. The flowsheet for the use of heterogeneous catalysis in the production of biodiesel is shown in Figure 9. It is similar to the one used for the enzymatic catalyzed transesterification requiring catalyst separation, ethanol recovery, separation of the polar and nonpolar phases and biodiesel purification. Based on the experimental results by Li et al.[44] we have developed a surface response model for predicting the performance of the reactor (Eq. 8). In Figure 10 and Table 4, we present the range of the variables and the fit of the model with good agreement. The objective function is given by Eq. 9

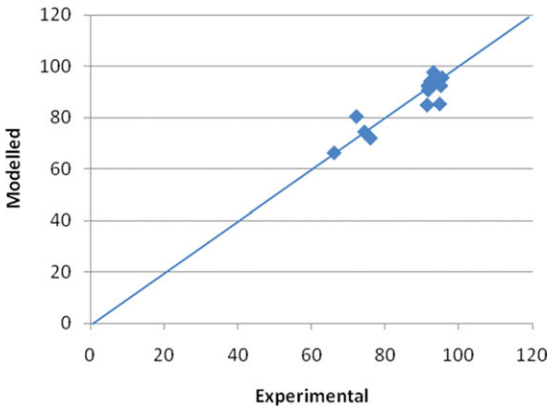

Figure 7. Surface response fitting for the yield of supercritical noncatalyzed transesterification.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

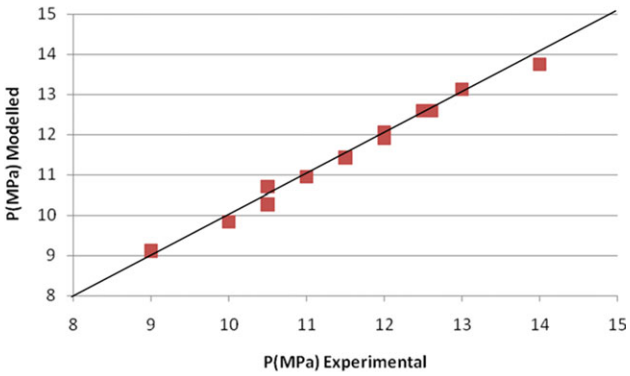

Figure 8. Pressure as function of the temperature.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\begin{aligned}\text{yield} = {} & -0.1247 + -3.1700^{*}(\text{T(HX38, Rec}') + 273) \\ & + 4.7602^{*}\text{time\_het} - 1.9494^{*}\text{Ratio\_etH} \\ & + 0.0068^{*}(\text{T(HX38, Rec5)} + 273)^{2} - 0.0007^{*}\text{time\_het}^{2} \\ & + -0.0567^{*}\text{Ratio\_etH}^{2} - 0.0092^{*}(\text{T(HX38, Rec5)} + 273)^{*} \\ & \text{time\_het} + 0.0079^{*}(\text{T(HX38, Rec5)} + 273)^{*}\text{Ratio\_etH} \\ & + 0.0002^{*}\text{time\_het}^{*}\text{Ratio\_etH}; \qquad (8)\end{aligned}$$

$$\begin{aligned}\text{Z} = {} & C_{\text{FAEE}}{}^{*}\text{fc(FAEE)} + C_{\text{Glycerol}}{}^{*}\text{fc(Glycerol)} \\ & - C^{*}_{\text{Steam}}(1/\lambda)^{*}(\text{QS\_max}) - C_{\text{EtOH}}{}^{*}\text{fc(EtOH)} \\ & - C_{\text{cat\_het}}{}^{*}\text{fc}(Oil) - C_{\text{electricity}}{}^{*}(\text{W(Pump)}); \qquad (9)\end{aligned}$$

Results

Flowsheet design

The typical biodiesel production capacity is 15 Mgal/yr or 40,000 t/yr (1.3 kg/s). In the future it is expected that biofuel plants will produce 25 kg/s of biodiesel.[6] Currently the largest plant in Europe produces 250,000 t/yr (8 kg/s),[45] while there are a number of them around 200,000 t/yr (6.5 kg/s).[46]

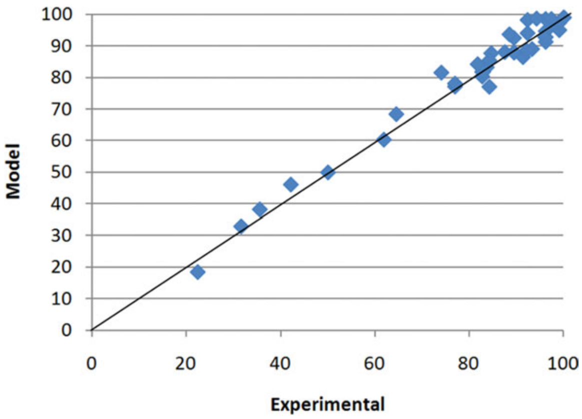

Figure 10. Fitting of the yield for heterogeneous catalyst.

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Therefore, we will focus on the production of 7 kg/s (68 MMgal/y).

The construction of algae ponds ranges from 0.25 \$/m^2 to 1.25 \$/m^2.[47,48] The bigger the pond the lower the cost per area. We use a value of 0.61 \$/m^2 [47] to account for other minor equipment associated with the ponds. The cost of the digester and the generator[48] are included so that we generate electricity from the biomass. The energy that can be obtained from the residue by digestion is 522 kW/kg.[49] The amount of water lost due to evaporation from the ponds is estimated to be 1.8 kg/d per pound. This water is saline water so no freshwater is necessary. We assume a \$1/kg production cost basis for biodiesel for use in the objective function. In a production plant of biodiesel, 0.083 kwh of electricity is used per gallon.[50] Additional energy is used for the supercritical and heterogeneous process because of the pressure of the reactor.

The costs for utilities are taken from the literature (0.019 \$/kg steam, 0.057 \$/ton cooling water)[51] 0.06 \$/kWh[52] electricity, 4.876 \$/MMBTU for natural gas.[53] Table 5 shows the cost of the chemicals used.

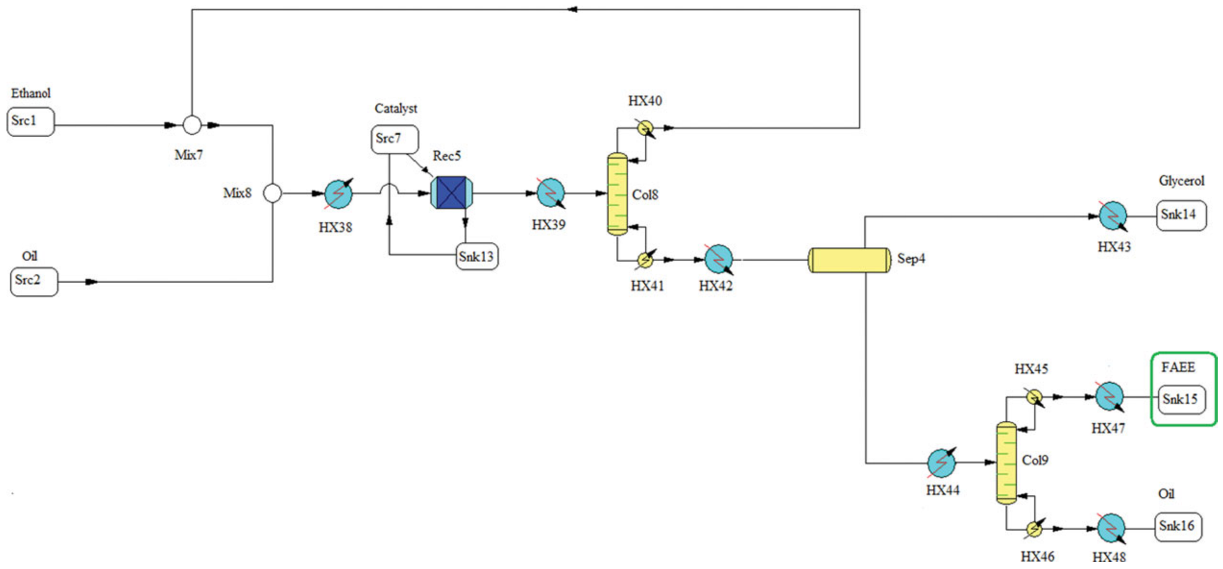


Figure 9. Flowsheet for the production of biodiesel from oil via heterogeneous transesterification.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 4. Range of Operation of the Variables

Variable	Lower bound	Upper bound
Temperature (°C)	170	200
Ratio ethanol (mol/mol)	7	16
Time (min)	120	300
Cat (%)	2%	
Presssure (atm)	25	

Heterogeneous catalyzed

Table 5. Chemical Cost

Chemical	Cost ($/kg)	Source
Fertilizer	0.367 *	55
Enzyme	0.7	56
Het. Catalyst	0.6	4
CH_3OH	0.28	57
H_2SO_4	0.329	58
KOH	1.6	59
CaO	0.06	60
Gypsum	0.023	60
H_3PO_4	0.34	4
Glycerol	0.6	4
Hexane	0.41	4
$Fe_2(SO_4)_3$	0.447	61
K_3PO_4	1.9	62

(*) Mean value of a number of fertilizers

The typical operating conditions for the transesterification are shown in Table 6. For all the cases we assume the same heat of reaction.[54] The simultaneous optimization of the performance of the reactor and heat integration yields quite different values (see Table 7), mainly in the operation of the reactor where the temperatures and alcohol:oil ratios differ due to the fact that the operating conditions at the reactor are optimized simultaneously with the process including energy integration.

After the optimization for each design alternative (see Table 7), the objective function shows that the alkali option is the most promising process (see continuous lines in Figure 12).

Design of the heat exchanger network, water network

Once the flowsheet is optimized, for costing purposes we need to define the optimal heat exchanger network (HEN). We use the model by Yee and Grossmann[16] to design the optimal HEN. 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 in bioethanol production processes, we design the water network based on the models by Ahmetovic et al.[17] We identify the equipment involved, boiler and cooling tower, assuming that the algae are grown in sea water, and optimize the superstructure leading to the water network to determine the freshwater consumption.

Economic evaluation and discussion

The production cost of oil from algae has been estimated to be $0.07/lb in the best case.[7] This value cannot be obtained with typical harvesting and drying technologies, but can be obtained with a process based on a new design recently released by Univenture, Inc.[19] 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.

The transesterification costs have been estimated to be about $0.58 per gallon with an overhead of $0.33 per gallon. If the coproduct glycerol is credited at $0.39 per gallon, the total cost for processing biodiesel is $0.52 per gallon.[63] Other studies have estimated total operating costs of $0.30–0.60 per gallon,[64] The total operating cost for converting fats and oils to biodiesel ranges from $1.39 to $2.52 per gallon, depending on which feedstocks are used.[65–67] Previous results reported in the literature on energy consumption are from 3.3 MJ/gal to 12 MJ/gal[7,65,67] with an industrial average of 4.4 MJ/gal[68] (NBD, 2009). In terms of water consumption, values of 1–3 gal/gal are reported.[69]

The method used to determine the production cost is based on Sinnot[70] and previous articles by the authors[19,71] involving labor, raw materials, chemicals, utilities, maintenance and annualized cost of the equipment. Table 8 summarizes the manufacturing costs, the energy and water consumption of the processes, and Figure 11 presents the production cost breakdown while in Table 9 we present the detailed breakdown of the costs for the two most promising alternatives, the alkali and the enzymatic catalyzed reactions. The most profitable process is the one that uses alkali catalyst. It can be seen that this process is predicted by the objective function (see Figure 12), and also turns out to be the best one when a more detailed economic evaluation is performed. However, the most environmentally friendly process is the enzymatic-based one, which consumes less energy and water. Thus, it is expected that further development of the enzymes will result in decreases in the production cost, and, therefore, the enzymatic process will be preferred for the production of biodiesel using ethanol.

One important point in integrated biorefineries is the flexibility of the process. For the production of biodiesel from methanol using algae as raw material, Martín and Grossmann[19] reported that the optimal process was the one that used the alkali catalyst. Thus, if we use this catalyst, small changes in the operating variables of the process allow either ethanol or methanol to be used for the production of biodiesel depending on the availability. However, in the case where the oil comes from waste, the alkali catalyzed process requires pretreatment, and, therefore, the heterogeneous based process is recommended.[19] For the case of the use of ethanol, the enzymatic is more promising for a flexible operation.

Out of the four alternatives (alkali, heterogeneous or enzymatic catalyzed and noncatalyzed under supercritical

Table 6. Typical Operating Conditions

	Alkali(27,39)	Supercritical(39,40)	Enzymatic(37)	Heterogeneous(44)
	KOH			
Temperature(°C)	25	320	31.5	200
Pressure (bar)	4	140	1	25
Alcohol : oil ratio(mol/mol)	20:1	39:1	7.5:1	16
Residence time(h)	0.5	0.1-0.75	7	3
Catalyst(%w/w)	1.07	N/A	15	2
Water added (%w/w)	--	--	4%	--

Table 7. Optimal Operating Conditions (Ethanol $1/gal)

	Alkali	Supercritical	Enzymatic	Heterogeneous
Temperature(°C)	75	317	45	200
Pressure(bar)	4^f	115	4^f	25^f
Alcohol : oil ratio (mol/mol)	5.7	32	8.9	16
Residence time (h)	0.5	0.43	6.9	5
Catalyst(%w/w)	1.5	--	14.0	2^f
Water added (%w/w)	--	--	0.0	--

^{f}fixed condition in the experimental data.

Table 8. Production Costs, Energy and Water Consumption ($1/gal for Ethanol)

	Alkali cat	Supercritical	Enzymatic	Heterogeneous
$/gal	0.51	0.61	0.54	0.57
Energy (MJ/gal)	2.81	8.83	1.93	5.99
Water (gal/gal)	0.47	1.98	0.35	1.08

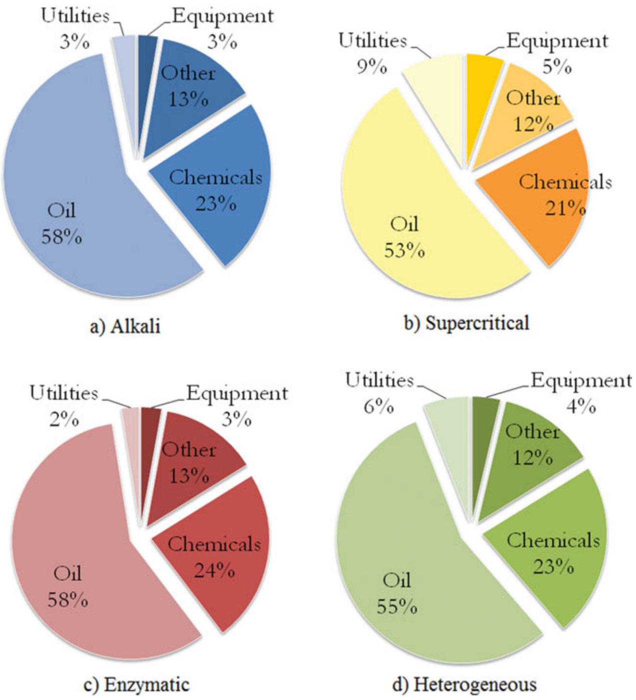
conditions), there are two that are promising in terms of production cost, the alkali catalyzed and the enzymatic catalyzed. The production cost using ethanol is slightly higher than the values obtained when using methanol as the raw material (Martín and Grossmann[20]) due to the current higher cost of ethanol. However, due to the expected decrease in the cost of ethanol production and its increasing availability, cost is not the only important decision variable. In Table 8 we also present the energy and water consumption. Water consumption is based on the treatment and recycle of the water needed in the boiler that generates the steam required for the plant and the cooling tower, so that we cool down the water used for cooling in the process plus the process water used depending on the case. We used the method proposed in Ahmetovic et al.[17] and Grossmann and Martín[18] to develop the optimal water network. We see that energy consumption for the enzymatic case is almost the same as that obtained for the heterogeneous catalyzed alternative when using methanol,[19] while water consumption is lower. This points to the enzymatic catalyzed process as the most promising design, despite the major drawback of its current production cost.

In Table 10, we present the comparison between the optimal design and the base case using the operating data from the literature with neither optimization nor heat integration.

As it can be seen, for the alkali process, there is a clear improvement in terms of heat and water consumption, as well as yield due to the simultaneous optimization and heat integration. The same trend is true in the case of the enzymatic based process. Furthermore, the quality of the glycerol in the base case is far from being of interest as a byproduct due to the added water. Therefore, it cannot be used as a valuable byproduct resulting in an increased production cost of biodiesel of $0.78/gal vs. $0.56/gal.

Table 9. Detailed Production Costs

	(Algae Oil - Alkali)	(Enzymatic catalyzed)
Cost type	*Annual Costs (MM)*	*Annual Costs (MM)*
Equipment (annualized)	1.34	1.42
Electricity	0.34	0.34
Salaries	3.27	3.27
Other expenses	3.41	3.41
Chemicals	−4.27	−1.56
Oil	29.21	29.11
Steam	0.95	0.65
Cooling water	0.30	0.25
Total	34.56	36.90
$ / gallon diesel	**0.51**	**0.54**



a) Alkali

b) Supercritical

c) Enzymatic

d) Heterogeneous

Figure 11. Cost distribution for the four alternatives.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

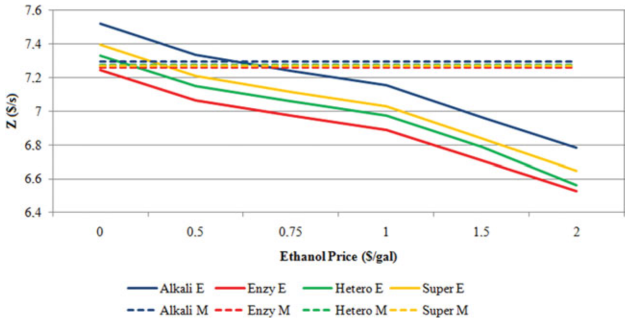


Figure 12. Comparison of the results of the objective function using ethanol (E) or methanol (M).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 10. Comparison between Base Case and Optimal Case

Alkali cat	Optimal	Base case
yield	0.98	0.89
$/gal	0.51	0.62
Energy (MJ/gal)	2.81	4.86
Water (gal/gal)	0.47	1.53
Enzymatic	Optimal	Base case
yield	0.98	0.94
$/gal	0.54	0.78
Energy (MJ/gal)	1.93	2.35
Water (gal/gal)	0.35	0.38

Table 11. Production Costs, Energy and Water Consumption ($0/gal for Ethanol)

	Alkali cat	Supercritical	Enzymatic	Heterogeneous
$/gal	0.34	0.43	0.38	0.41
Energy (MJ/gal)	2.85	8.76	1.93	6.10
Water (gal/gal)	0.50	1.91	0.20	1.18

Sensitivity analysis

The price of ethanol represents the largest uncertainty for the economic feasibility of this process compared to the traditional production facilities based on the use of methanol. We evaluate the effect of the price of ethanol on the objective function as seen in Figure 12 to find the breakeven point when ethanol may become competitive with current use of methanol. The only ethanol based process that can compete with the use of methanol is the one that uses the alkali catalysts. The results presented in Table 8 are based on a target price of $1/gal, while in Table 11 we present the results of the alternatives based on a price of $0/gal as a minimum production cost. Assuming linear contribution of the ethanol price on the production cost of biodiesel, based on Figure 12, and the production costs given in Tables 8 and 11, respectively, the breakeven point is around $0.5/gal of ethanol, a value that is in the range of the one presented by Martín and Grossmann[71] for the production of ethanol from gasification of switchgrass followed by catalyst mixed alcohol synthesis. Therefore, even though the results in Table 9 support the fact that it will be cheaper to produce biodiesel using methanol at the current prices of ethanol and methanol, in terms of energy and water consumption they are as competitive as the ones that use methanol. If the production cost of ethanol decreases to the values reported by Martín and Grossmann,[71] around $0.41/gal. The use of the alkali process, or even the enzymatic one using ethanol, are competitive with those using methanol.[19] Thus, in the context of an integrated biorefinery, the use of ethanol becomes competitive.

Conclusions

In this article, we have optimized the production of biodiesel from algae oil by proposing a superstructure of alternative technologies for the transesterification of the oil. We solve the superstructure by decomposing it for each of the technologies so that they are simultaneously optimized and heat integrated according to a specified objective function. The optimal heat exchanger and water networks and an economic evaluation are determined after this optimization.

Simultaneous optimization and heat integration of the flowsheets result in optimal operating conditions in the reactors that differ significantly from the ones traditionally used because the separation stages were not taken into account when deciding on the reactor design.

For the production of biodiesel using bioethanol we have identified two interesting technologies, alkali catalyzed and enzyme catalyzed. The first one is currently the cheapest one and is even competitive with the use of methanol as a transesterfying agent, but the energy and water consumptions are higher than in the case of using an enzymatic catalyst whose main drawback currently is the cost of the enzyme. Even though the current prices of ethanol and methanol support the use of the latter for the production of biodiesel, the promising production costs presented by Martín and Grossmann[71] and the advantages of integrated production of ethanol and biodiesel, make the transesterification of oil with ethanol a promising alternative in the context of a biorefinery complex. The results look promising, even though we acknowledge that further validation of these results is needed at pilot plant scale due to the conceptual nature of our work.

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Notation

C_i = cost of material I, $/Kg or kW
cata_alk = mass percentage alkali catalyst to oil
cata_enz = (%w/w) enzyme catalyst to oil
Enzymeadded = mass of enzyme added, kg
$F(i)$ = mass flow of component i produced or used, kg/s
Q(unit) = Thermal energy involved in unit, kW
QS_max = integrated hot utility, kW
Ratio_etE = molar ratio ethanol to oil in the enzymatic reactor
Ratio_et = molar ratio ethanol to oil in the alkali catalyzed reactor
Ratio_etH = molar ratio ethanol to oil in the heterogeneous catalyzed reactor
Ratio_etS = molar ratio ethanol to oil in the supercritical trasnesterification reactor
time_enz = reaction time in enzymatic catalyzed reactor, h
time_sup = reaction time in supercritical reactor, min
time_het = reaction time in heterogeneous catalyzed reactor, h
*T*pinch (pinches) = temperature pinch, °C
T (unit, unit1) = *t* of the stream from unit to unit 1, °C
water_enz = (%w/w) water added to oil
W(unit) = electrical energy involved in unit, kW
yield = yield of the reaction
λ = latent heat steam, kJ/kg

Materials

Wa = water
EtOH = ethanol
Glycerol: = glycerol (byproduct of the transesterification reaction enzyme)
FAEE = fatty acid ethyl ester or biodiesel
FFA = free fatty acid
Oil = either cooking oil or the oil extracted from the algae
KOH = potassium hydroxide, homogeneous alkali catalyst
K_2SO_4 = potassium sulfate, fertilizer
H_3PO_4 = phosphoric acid
K_3PO_4 = potassium phosphate
Algae = algae

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