Simultaneous optimization and heat integration for the co-production of diesel substitutes: Biodiesel (FAME & FAEE) and glycerol ethers from algae oil

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Abstract.

In this paper, we optimize the integration of the etherification of glycerol for the production of tert butyl glycerol with the production of biodiesel (using methanol or bioethanol) to increase the yield to diesel substitutes. The problem is formulated as a optimization model including algae oil production, production of ethanol from starch, transesterification of the oil with bioethanol or methanol, etherification of glycerol which depends on a dynamic model to compute the complex chemical equilibrium and purification of the ethers. We perform simultaneous optimization and heat integration using Duran & Grossmann's model and optimize the water consumption of the resulting process. The production of glycerol ethers increases the yield of diesel substitute by 20%. However, the current price of ibutylene increases the production cost of biofuel up to $1.05/gal in the best of the cases in which we integrate the production of bioethanol, biodiesel and glycerol ethers from algae. The energy and water consumptions are competitive with those of biodiesel when glycerol is the byproduct of the process or when we reuse it to obtain methanol.

Keywords: Energy, Biodiesel, glycerol, ethers, process integration

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1.-Introduccion

The use of biomass to obtain liquid fuels is potentially attractive due to their compatibility with the current automobiles and petrol supply chains. However, the profitability of biofuels depends heavily on the economics of the byproducts. For some time glycerol has been a valuable byproduct of the biodiesel industry. However, the increase in the production of biodiesel results in an excess of glycerol with limited market [1] reducing the price of glycerol to values of \$0.102 /lb[2] . Under these expected revenues from glycerol the production cost of biodiesel would increase \$0.15/gal from the values presented by Martin & Grossmann,[3] and thus its direct use to generate syngas and later methanol for the process may become competitive in an integrated facility as described by Martín & Grossmann[4] . Other synthetic paths that may be followed are to produce different chemicals such as propylene glycol, through hydrogenolysis, dehydration to yield acrolein, fermentation towards 1,3-propanediol, synthesis of Epichlorohydrin. Aside from these alternatives, the transformation of glycerol into fuel oxygenates by means of etherification and esterification reactions has been explored[5-10] because it represents a promising alternative since not only makes a good use of the glycerine, but it also increases the yield to biofuel in the overall biodiesel production process. In particular ethers are excellent oxygen additives for diesel fuel. Oxygenated diesel fuels are of importance for both environmental compliance and efficiency of diesel engines, which can be added to diesel or biodiesel increasing the production of biofuel from oil. A number of studies have recently dealt with the production of di and tri ethers of glycerol from its synthesis and characterization to process development[11-20]

So far only a few different process design alternatives for the manufacture of h- GTBEs have been proposed in the literature. The ARCO process[5] consisting of using a decanter that is placed after the reactor so that unconverted glycerol, p-toluenesulfonic acid, and MTBG can be recovered in the heavy phase and then recycled back to the reactor. The light phase is fed to a stripping column, followed by an extraction column (using water as solvent) for further separation. In this case a large amount of mono-ether is lost through the wastewater stream in the extraction column, thus a further separation and recycle is also required, which was not mentioned in the patent. In the Behr and Obendorf process[11-12] an extraction column is placed after the synthesis reactor, and glycerol feed is used as a solvent to extract unconverted glycerol, p-toluenesulfonic acid, and mono tert-butyl glycerol (MTBG). The extract stream is recycled back to the reactor, while the refined stream is fed to a flash tank followed by a vacuum column for further separation. Because mono-ethers and glycerol are recycled back to the reaction section, higher selectivity and conversion are obtained in this configuration in comparison with the ARCO process. Instead of reducing MTBG content from the product, in the Di Serio´s et al[21] process free fatty acid ester (FAME) is used as the solvent to extract GBTEs (including mono, di and tri tert butyl glycerol, MTBG, DTBG, and TTBG) to solve the problem of the low solubility of MTBG in fuel. A series of extraction steps in this process was proposed. The most recent one due to Cheng et al[13] claims a 22% decrease in the production cost by redirecting one recycle stream, using a stripping column to recover isobutylene, and using a rectifying column to purify the product.

The challenge is to go a step forward by integrating the production of ethers from glycerol with the biodiesel production facilities to evaluate the competitiveness of such facilities. The production process of ethers is characterized by a complex equilibrium between the five different species, glycerol, i- butane, mono, di and tri ethers whose kinetics also plays an important role. Thus, in this paper we use a dynamic optimization approach for the optimal heat and water integrated production of biodiesel from oil and high glycerol ethers to increase the production of diesel substitutes, while defining the operating conditions and performing heat and water integration. We present three case studies: the integrated production of TTBG and biodiesel from using a) methanol and bioethanol from oil (either cooking oil or algae oil), and b) the simultaneous production of ethanol, biodiesel and TTBG from algae. The biodiesel production is based on previous papers by the authors where they simultaneously optimize, heat and water integrate the production of the biodiesel using different catalyst and alcohols [3,4] [22,] while also considering the integration of the use of algae to produce the ethanol needed in the trasnesterification. [23] The organization of the paper is as follows. We describe the processes in section 2. Next, we comment on the modeling features in section 3 focusing on the new piece of the processes that is being integrated, while we refer to the literature for further details on already developed processes. In section 4 we discuss the results and compare them with stand alone biodiesel or biodiesel & bioethanol production and sensitivity study. Finally, we present the conclusions.

2. Overall Process Description

We divide the process in four sections, algae oil production, ethanol production from starch, biodiesel production from oil and finally high glycerol ethers (DTBG & TTBG = hTBG) production from the biodiesel byproduct. Figure 1 shows a superstructure involving the different case studies evaluated in the paper.

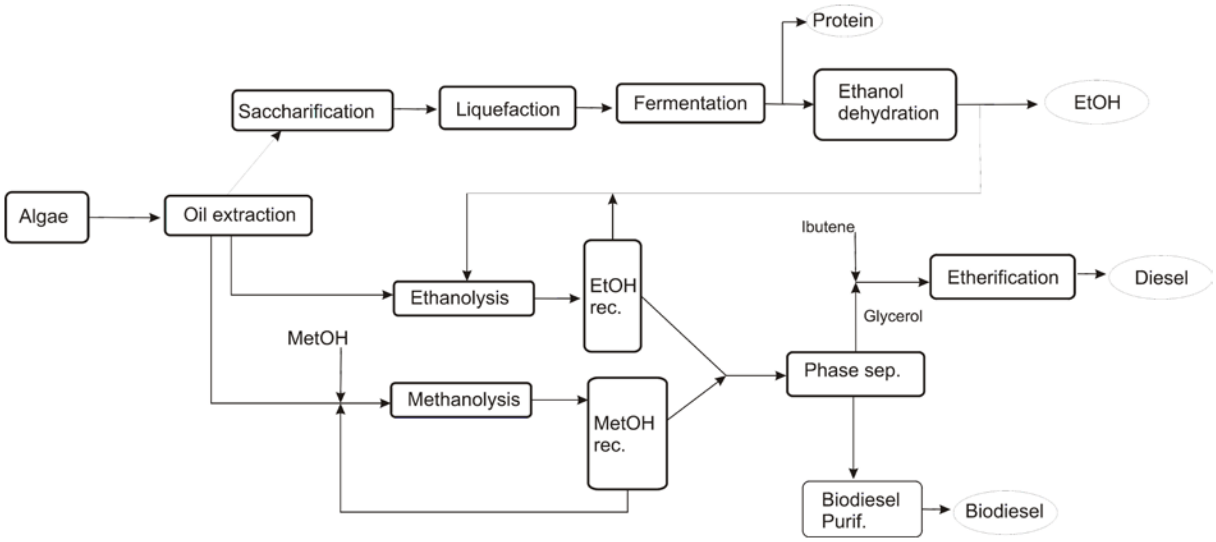


Figure 1.- Flowsheet for the integration of biodiesel production with glycerol ethers.

2.1.Algae oil production.

The production of oil and starch from algae (see Martín & Grossmann[3]) for further details of the models and the process) 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,[24] while the consumption of CO_2 depends on the growth rate, typically 50g/m^2 d [25] and it is given by the experimental results by Sazdanoff.[26] We assume that the dry algae biomass is composed by oil, up to a maximum of 60%w/w, starch and protein with a minimum of 10%w/w to be on feasible realistic values. Together with the algae, oxygen is produced and water is evaporated.[24] The energy consumed by the pond system is calculated based on the results by Sazdanoff.[26] Next, the algae are harvested from the pond. Recently Univenture inc. 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. The biomass is mixed with cyclo-hexane and compressed so that oil is extracted and the biomass is separated from the oil. The biomass can be used to obtain energy for the system[3] or it can also be further treated to obtain ethanol. The oil is used for trasnesterification and biodiesel production.

2.2.-Ethanol production from starch.

As it was presented in a previous paper in more detail [23] it is possible to obtain bioethanol from the starch from the algae. For that the starch has to follow a process similar to the production of bioethanol from corn.

The starch is first saccharified (85ºC), followed by liquefaction (65º) so that the polymers are broken down into glucose. Next, the glucose is fermented into ethanol at 38 ºC. The solid phase, mainly protein, is separated from the liquid phase and can be sold as animal food. The liquid phase, mainly ethanol and water, but containing other products in small amounts such as glycerol, succinic acid, lactic acid, is distilled in a multieffect distillation column to reduce the consumption of energy and cooling needs in the purification of ethanol. The last stage for the production of ethanol is the final dehydration using molecular sieves. Part of this ethanol will be used in the transesterification of the oil and the rest can be sold as biofuel.

2.3.-Biodiesel production .

a) Using methanol: According to the results presented by Martín & Grossmann[3] the most promising transesterification technology for a robust operation in the production of biodiesel from either cooking oil or algae oil uses an heterogeneous catalyst. The selection of this technology allows higher flexibility with regards to the raw material used. The process consists of mixing the raw materials, oil and alcohol, adjusting the pressure and temperature to the operating conditions of the transesterification reactor. We model this reactor using surface response approach based on data from the literature. Next the methanol is distilled and recycled to the reactor, while the mix of glycerol, biodiesel and oil is separated into two phases using a gravity separator. We need to keep the temperatures at the distillate and bottom of the columns within some limits, see Table 1, to avoid glycerol or biodiesel decomposition and to improve the liquid-liquid phase separation. The glycerol is sent to the process by which we produce ethers that can be added to biodiesel, and thus increase the production rate of diesel substitutes

b) Using ethanol: According to Severson et al[22] we can use competitively ethanol to transesterify the oil extracted from the algae . The results presented in that paper show that the use of enzymes as catalysts is promising in the sense that it consumes less energy and water than the one using KOH as catalysts one, but its current disadvantage is the high cost of the enzymes. We use surface response models obtained from experimental data in the literature to model the transesterification reactor. The mixture of ethanol, glycerol, biodiesel is distilled to recover and recycle the excess of ethanol used. The polar phase containing glycerol is separated from the non-polar phase containing the biodiesel, and while the biodiesel is purified in a distillation column to remove mainly the oil remaining, the glycerol is sent to etherification. The main process constraints can also be seen in Table 1.

Table 1.-Main operating constraints[3,22]

Equipment	Temperature limit
Alcohol separation column	Bottoms ≤150°C Reflux ratio 1-3
Biodiesel purification column	Top: ≤250°C Bottoms: ≤350-375°C Reflux ratio 2-3
Phase separation	30-40°C

2.4.-Biodiesel complements: Ethers from glycerol

For the production of the ethers of glycerol we adopt part of the solution by Cheng et al[13] briefly discussed in the introduction. After the etherification reaction we place a liquid-liquid separation stage that uses glycerol as solvent. The phase containing mainly the glycerol and the mono ether is recycled back to the reactor, while the other one, containing the di- and tri- ethers together with the isobutylene is separated. First, the ibutylene is separated in a stripping column, and the bottoms of the column are sent to a vacuum column where on the distillate we obtain the di- and tri- ethers and on the bottoms we get the monoether with a bit of higher ethers so as to recycle them to the reactor.

3.-Mathematical modeling.

All the unit operations in the production process of liquid fuels and hydrogen from glycerol are modeled using surrogate models, design equations, rules of thumb and mass and energy balances . The superstructure is written in terms of the total mass flows, component mass flows, component mass fractions, and temperatures of the streams in the network. The species in the system include those present in the algae, plus those produced during the process of ethanol production, and belong to the set *J* = { Wa, Glycerol, Methanol, FAME/FAEE, Oil, CO2, CO, O2, N2, H2, CH4, C2H2, C2H4, Met, But, C}. We describe the models below.

3.1.-Biodiesel production

The models for the stages that lead to the production of biodiesel from oil either using ethanol or methanol as transesterification agent can be seen in previous paper from the authors. For the sake of limiting the size of the paper we refer to previous papers[3, 22, 27,28] for the details of the models of each particular equipment from the ponds, algae drying, oil extraction, starch fermentation to ethanol, oil transesterification, either using heterogeneous catalyst in case of methanolysis, or enzymatic catalyst when se employ ethanolysis.

3.2.-Gylcerol etherification

3.2.1.-Reactor

The glycerol etherification reactions usually take place in the liquid phase at temperatures between 60 and 110 °C so that the operating pressure should be between 15 and 20 bar. The kinetics of the reactions catalyzed by different acid catalysts has been investigated by several authors. Among homogeneous catalysts, p-toluenesulfonic acid gave the best performance.

$$\begin{aligned}
&Glycerol + iButene \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MTBG\\
&MTBG + iButene \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} DTBG\\
&DTBG + iButene \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} TTBG
\end{aligned} \qquad (1)$$

The kinetics of the above reversible reactions are described using a power law model on the basis of the overall molar concentration of component i (Ci) with the following reaction rate expressions

$$\begin{aligned}
&\frac{dC_{Glycerol}}{dt} = -k_1 C_{Glycerol} C_{Ibutene} + k_{-1} C_{MTBG}\\
&\frac{dC_{MTBG}}{dt} = k_1 C_{Glycerol} C_{Ibutene} - k_{-1} C_{MTBG} - k_2 C_{MTBG} C_{Ibutene} + k_{-2} C_{DTBG}\\
&\frac{dC_{DTBG}}{dt} = k_2 C_{MTBG} C_{Ibutene} - k_{-2} C_{DTBG} - k_3 C_{DTGB} C_{Ibutene} + k_{-3} C_{TTBG}\\
&\frac{dC_{DTBG}}{dt} = k_3 C_{DTGB} C_{Ibutene} - k_{-3} C_{TTBG}\\
&\frac{dC_{Ibutene}}{dt} = -k_1 C_{Glycerol} C_{Ibutene} + k_{-1} C_{MTBG} - k_2 C_{MTBG} C_{Ibutene} + k_{-2} C_{DTBG}\\
&-k_3 C_{DTGB} C_{Ibutene} + k_{-3} C_{TTBG}
\end{aligned} \qquad (2)$$

The model parameters were taken from Behr and Obendorf[11-12] for glycerol etherification catalyzed by p-toluenesulfonic acid (pTS). The kinetic model parameters with Arrhenius form can be seen in Table 2. In order to integrate this reactor in the continuous operation of the plant, we propose the use of buffer tanks so that the tanks is filling while the reactor is operating and when the conversion is reached is discharged to another buffer tank that controls the flow downstream.

Table 2. Behr & Obendorf kinetic data[11-12]

Collision factor		Activation energies	
k_1 (min^{-1} mol^{-1})	$3.04 \cdot 10^{8}$	E_1 (kJ/mol)	74.04
k_{-1} (min^{-1} mol^{-1})	$3.69 \cdot 10^{13}$	E_{-1} (kJ/mol)	111.78
k_2 (min^{-1} mol^{-1})	$1.70 \cdot 10^{11}$	E_2 (kJ/mol)	92.80
k_{-2} (min^{-1} mol^{-1})	$8.54 \cdot 10^{14}$	E_{-2} (kJ/mol)	118.06
k_3 (min^{-1} mol^{-1})	$2.26 \cdot 10^{10}$	E_3 (kJ/mol)	92.56
k_{-3} (min^{-1} mol^{-1})	$6.35 \cdot 10^{15}$	E_{-4} (kJ/mol)	125.13

3.2.2.-Liquid liquid separation

Based on the modelling results obtained with Aspen Plus available in the literature,[11,12, 13 15,,21,] we have obtained reduced order models for the separation of the glycerol phase, containing MTBG and the i-butene phase containing DTBG and TTBG. Thus, we obtain correlations for each of the species involved in the liquid – liquid equilibrium of the form given by eq (3) based on a small parameter estimation problem using as variables the main components of each of the phases, glycerol and ibutene:

$$\text{Sep factor}_i = a + b\, x_{Glycerol} + c\, x_{Ibutene} + d\, x_{Glycerol} \cdot x_{Ibutene} \qquad (3)$$

where the parameters are given in Table 3.

Table 3.- Parameters for the correlation of the separation factor

	a	b	c	d
'Glycerol'	0.9544	0.247	0.430	0.0617
'MTBG'	0.1557	0.7239	5.376	1.662
Isobutene	-0.01755	0.5758	-0.467	-0.065
'DTBG'	-0.1358	1.18	-0.1889	0.0988
'TTBG'	-0.1936	1.381	0.02427	0.1890

3.2.3.-Columns modelling

Stripping column

The stripping column is designed based on the fact that it operates at 1 atm. From the top the ibutene comes out saturated with a mixture of glycerol, MTBG, DTBG and DDTB at the outlet temperature, while the rest comes out of the bottoms of the column. We fixed the recovery of the column based on literature results. [13]

fc(J,Col4,Compres1) = SepCol4(J)*fc(J,Sep2,Col4) ; (4)

fc(J,Col4,Compres1) + fc(J,Col4,Col8) = fc(J,Sep2,Col4) ; (5)

The top temperature is given so that the vapor phase can carry the volatile products and the bottoms comes as saturated liquid.

$$y_{sat} = \frac{molesvapor}{n_{ibutene}} \tag{6}$$

$$\text{molesvapor} = \sum_{i \in GMDT} n_i, \quad \text{i=Glycerol, MTBG,DTBG,TTBG} \tag{7}$$

$$\text{Pvaporiso} \cdot \left(1 + \text{ysat}\right) = \text{ysat} \cdot 760; \tag{8}$$

$$y_{i \in GMDT} = \frac{n_i}{molesvapor} \tag{9}$$

$$Pvaporiso = \sum_{i \in GMDT} y_i \cdot P_{vap,i} \tag{10}$$

We consider that the DTBG and the TTGB have the same vapor pressure, and we obtain an Antoine based correlation using the simulated results in the literature that relate boiling points and dew points to the operating pressure[11,12,13,15,21] The bottoms of the columns come at the boiling point of the mixture and the energy at the heat exchanger is calculated with an energy balance to the entire column.

$$Q(HX) = \sum_{bottoms} m_i cp_i (T_{bottoms} - T_{in}) + \sum_{top} m_i cp_i (T_{top} - T_{in}) + m_i \lambda_i \tag{11}$$

Vacuum column

In the vacuum column we obtain DTGB and TTGB from the top, and from the bottoms the stream to be recycle containing Glycerol and MTBG,

fc(J,Col8,HX35) =E= SepCol8(J)*fc(J,Col4,Col8) ; (12)

fc(J,Col8,Mix7) =E= (1-SepCol8(J))* fc(J,Col4,Col8) ; (13)

According to Chen et at.[13] low pressure (0.005 bar) is convenient to operate such a column. Thus, we consider the range from 0.005 to 0.05 bar. The operating pressures and temperatures are calculated using vapor pressures assuming negligible pressure drop across the column based on Chen et al.[13] and assuming that at the top only DTGB and TTGB are in that stream. Since the inlet temperature to the column in high, the global energy balance to the column determines the operating pressure and temperatures together with eq. (14) that assumes the same vapor pressure for DTGB and TTGB, due to the lack of experimental data. Eq. (15) is used for calculating the energy removed at the condenser .

$$\begin{aligned} P_{Vacum} &= \sum_{i \in GMDT} y_{i,top} \cdot P_{vap,i}(T_{top}) \\ P_{Vacum} &= \sum_{i \in GMDT} y_{i,bottoms} \cdot P_{vap,i}(T_{bottoms}) \end{aligned} \tag{14}$$

$$\mathrm{Q}(\mathrm{Cond}) = \sum_{top} m_i \lambda_i \tag{15}$$

3.3.-Solution procedure.

The particular feature of this problem relies on the equilibrium of the ethers production where we deal with a dynamic system to compute the conversion in the equilibrium for ethers formation. Using orthogonal collocation[29] the differential equations were discretized transforming the dynamic optimization problem for the etherification reactor into an NLP problem out that it is implemented together with the models for the various units involved in the process. Surface response models are used for the transesterification reactors, short cut models based on rigorous simulations, or experimental data from the literature are developed for the liquid- liquid separations or the distillation columns as presented before. Heat integration of the entire flowsheet is performed using the Duran & Grossmann [30] model. We use a simplified production cost as objective function, involving the biodiesel production, ethanol production and consumption, ethers production, ibutene and energy consumption.

Next we develop the optimal heat exchanger network using SYNHEAT.[31] Finally the cost analysis is performed involving raw material (oil) cost, maintenance, cost of utilities and chemicals, labor, annualized equipment cost and the cost for the management of the facility following Sinnot´s[32] method; see also previous papers by the authors[27] for further details.

We also develop the water network based on the paper by Ahmetovic and Grossmann[33] and Ahmetovic et al.[34] to compare the results of water consumption with those presented in the integrated production of ethanol and biodiesel[23]

We consider two cases studies. The first one is the optimization of the simultaneous production of biodiesel and glycerol ethers evaluating two typical alcohols, methanol, based on the studies by Martín & Grossmann[3] and ethanol, based on the work by Severson et al.[22]. This allows comparing with the production of biodiesel from oil alone in terms of production cost, as function of the glycerol selling price and due to the enhanced diesel substitutive production and the energy consumption involved. The second one evaluates the optimal algae design for the simultaneous production of ethanol, FAEE and ethers of glycerol

4.-Results and discussion.

The economic evaluation is carried out based on Sinnot method[32] and inputs from industry as in previous papers by the authors[27] taking into account annualized equipment cost, management, labour, based on other plants, chemicals and utilities, which are updated from the literature (0.019$/kg Steam; 0.057$/ton cooling water [35] (Franceschin et al 2008); 0.06$/kWh[36] , 0.021$/kg Oxygen[37] the cost of hydrogen is taken to be $1.6/kg based on DOE data[38], the cost of natural gas is $4.687/ MillionBTU.[39] The generation of an excess of steam is considered as a revenue of 0.0077$/kg$_{steam}$ (updated from Smith and Varbanov[40]). Finally, the cost correlations for the different equipment can be found in the supplementary material of Martín and Grossmann[27] and updated to the current 2012 prices.

4.1.-Integration of biodiesel production with glycerol ethers: Effect of the transesterifying alcohol

In this section we evaluate the integration of the production of biodiesel (FAME or FAEE) and glycerol ethers, where we simultaneously optimize the production of both when the byproduct glycerol is used for the production of more biofuel. Each of the problems involves around 5000 equations and 5500 variables. They are solved in GAMS for the optimal heat integration and process operation.

a) Simultaneous production of FAME and glycerol ethers as diesel substitutes

Figure 2 shows the flowsheet for the integrated production of FAME and glycerol ethers from oil. The optimization reveals small differences with the optimal conditions at the transesterification reactor presented in Martín & Grossmann,[3] see Table 4. With regards to the etherification reactor, Reactor 2, the dynamic simulation results in a operating temperature of 110 ºC. The total production of diesel substitutes increases by 20% when we use glycerol to produce DTBG and TTBG.

Table 4.-Operating conditions at the FAME trasnesterification reactor

	Heterog.	
	Alone(M&G)	Integrated
Temperature(ºC)	60	60
Pressure(bar)	1^f	1^f
Alcohol : oil ratio	11.190	10.920
Residence time(h)	2	2
Catalyst (%)	1	1

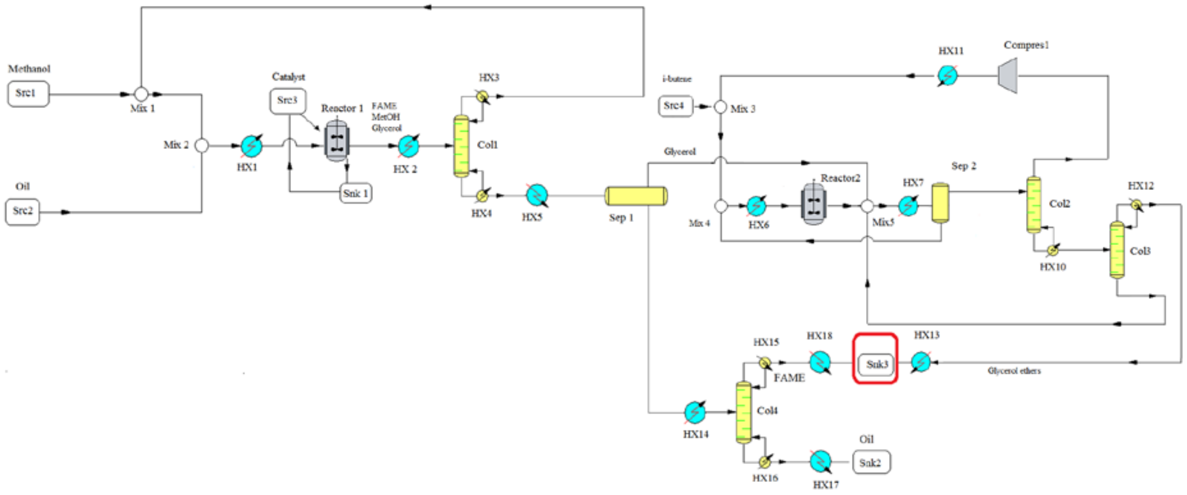


Figure 2.- Integrated flowsheet FAME & glycerol high ethers.

b) Simultaneous production of FAEE and glycerol ethers as diesel substitutes

Figure 3 presents the flowsheet for the optimal integration of the production of FAEE and high glycerol ethers from algae oil. Table 5 shows that the integration of the production of both diesel substitutes results in a modification of the operating conditions at the reactor to improve the heat integration of the flowsheet. The optimal operating conditions at the etherification reactor, Reactor 3, are 70 ºC.

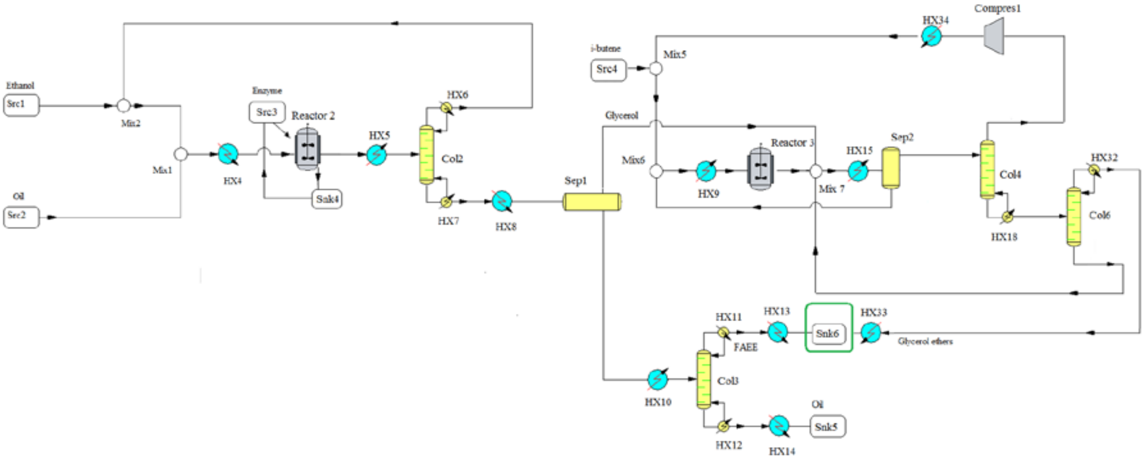


Figure 3.- Integrated flowsheet FAEE & glycerol high ethers.

Table 5.- Operating conditions at the FAEE trasnesterification reactor

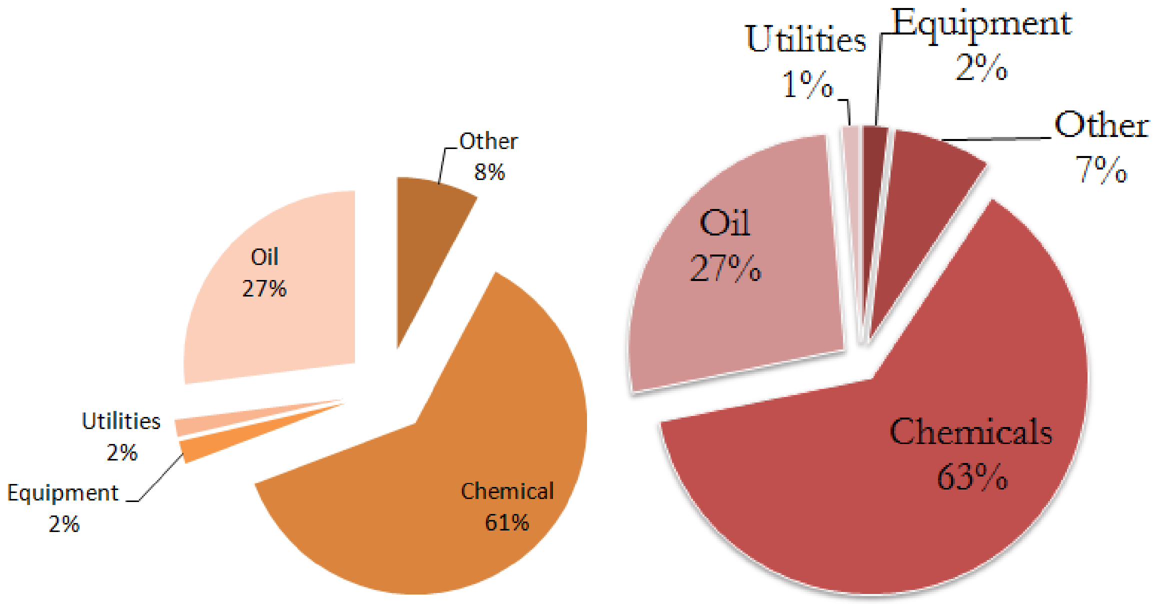
	Enzymatic	
	Alone(S et al)	Integrated
Temperature(ºC)	45	30
Pressure(bar)	4^f	4^f
Alcohol : oil ratio	8.9	4.5
Residence time (h)	6.9	7.9
Catalyst(%w/w)	14.0	13.3
Water added	0.0	0.0

The integration of the production of biodiesel and high glycerol ethers have the advantage that it increases the production of diesel substitutes up to 20% by using the by-product of the process. The disadvantage is related to the production cost of the biofuels obtained in this way since the ibutene is an expensive raw material, which increases the price of the biofuel by 3 compared to the stand-alone biodiesel [3,22] .

However, as we can seen in Table 6, from the energy and water consumption stand point, the integrated process is competitive with the stand-alone process and thus the key focus is to improve the economics of the process by the production of i-butene from renewable sources, which is already in progress [41,42,43] . In Figure 4 we present the contribution of the different items to the production cost of the integrated production of FAME or FAEE, and hTBG where the chemicals, where the i-butylene has almost 65% of the share of the cost due to its cost of \$2.2/kg [44]

Table 6.- Comparison between the stand alone and the integrated production

	Enz (Alone)	Enzymatic Integrated	Het (alone)	Heterogeneous Integrated
\$/gal	0.54	1.33	0.45	1.26
Energy (MJ/gal)	1.93	2.54	1.94	1.71
Water (gal/gal)	0.35	0.29	0.59	0.65
	(\$1/gal for ethanol) [22]		from algae [3]	



Using methanol Using ethanol

Figure 4.- Production cost break down

4.2.- Simultaneous production of gasoline and diesel substitutes from algae

For this case study we optimize the simultaneous production of ethanol, FAEE and glycerol ethers from algae. This work can be considered an extension of the previous paper by Martín & Grossmann[23] where the authors optimized the production of ethanol and FAEE by designing the algae composition. In this case, we go further, where due to the expected decrease in the selling price for glycerol we decide to produce ethanol and diesel substitutes, either FAEE or ethers of glycerol. In the Figure 5 we present the process flowsheet. We optimize the operation of the transesterification reactor, the production of ethanol from the starch contained in the algae, including multieffect columns implemented in the flowsheet (Cols 5-7) and not sequentially as in Karrupiah et al.[45] and the dynamic reactor that yields the glycerol ethers. This problem involves around 8000 equations and 9000 variables.

In Table 7 we present the optimal product distribution compared to that from Martín & Grossmann[23] . As we can see, the optimal algae composition is the same based on the fact that the production of ethanol requires a large amount of energy in order to dehydrate the ethanol. However, at the same time we need part of this ethanol for the transesterification of the oil together with the fact that we cannot produce more oil and the excess of ethanol is a good asset for the process.

Table 7. Optimal algae growth for the simultaneous production of FAEE, ethanol and high glycerol ethers

Enzymatic	(Byproduct Glyceol)		Enzymatic	(Glycerol Ethers)	
	Kg/s			Kg/s	
EtOH	0.866		EtOH	0.869	
Biodiesel	8.353		Biodiesel	8.350	
Prot	1.430		Prot	1.431	
Glycerol	0.869		DTBG&TTBG	1.865	
Algae comp	15		Algae comp	15	
Oil	9	60	Oil	9	60
Star	4.5	30	Star	4.5	30
Prot	1.5	10	Prot	1.5	10

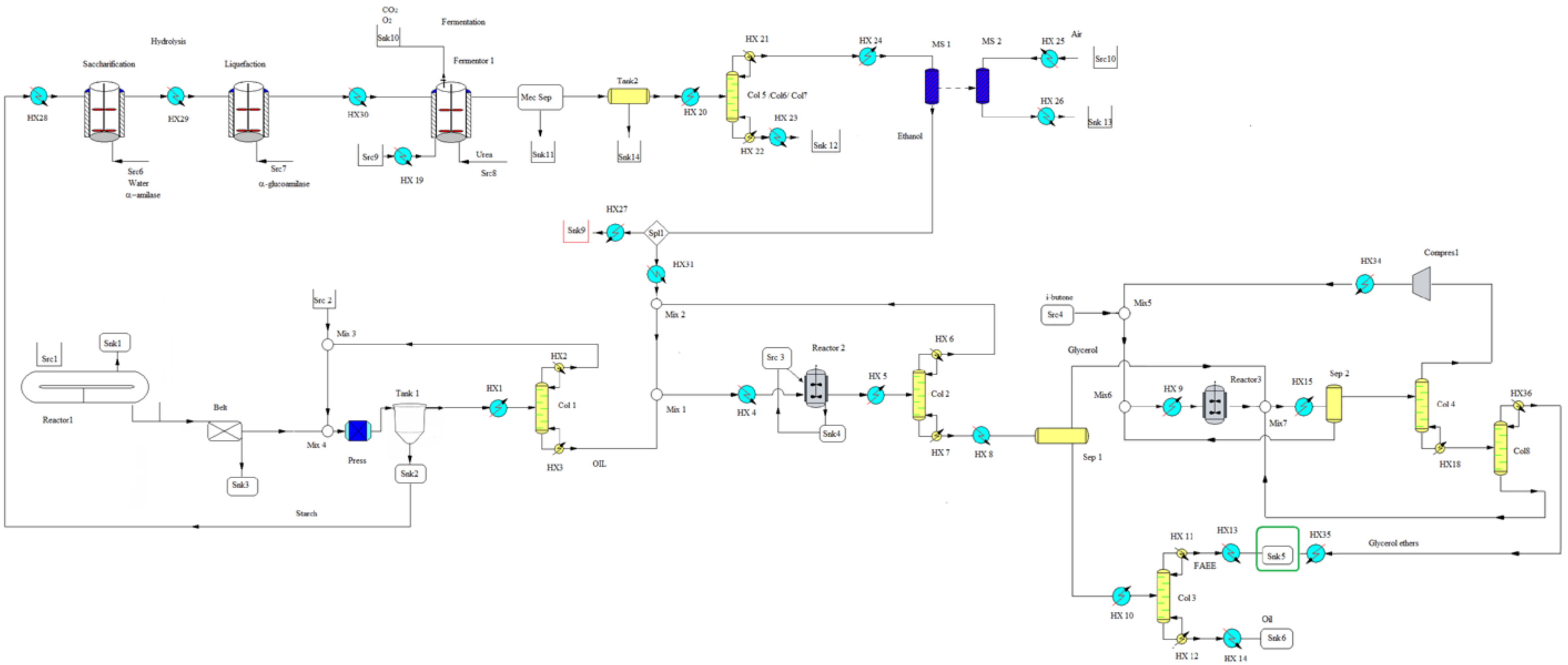


Figure 5. Integrated flowsheet FAEE & ethanol & glycerol high ethers.

When it comes to the operating conditions of the main equipment such as trasnesterification reactor, multieffect distillation column and etherification reactor it turns out (see Tables 8 and 9) that the integrated process requires different operating conditions at the transesterification reactor than the stand alone process. In this way we can better integrate the energy within the process providing energy to the transesterification reactor, and have similar operating conditions at the reactor and at the multieffect column as when we produce ethanol biodiesel and glycerol as byproduct. Finally, the operating conditions at the etherification reactor are the same as those obtained for the production of FAEE and hTBG alone since it operates at 70ºC but different both to the use of methanol since the highest operating temperatures at the transesterification modifies the energy integration within the process.

Table 8.- Operating conditions at the FAEE transnesterification reactor

	Enzymatic		
	Alone [22] (ethanol $1/gal)	Integrated[23]	Integrated + hTBG
Temperature(ºC)	45	30	30
Pressure(bar)	4[f]	4[f]	4[f]
ratio_et	8.9	4.1	4.1
Time (h)	6.9	8.0	8.0
Cat/lipase(%)	14.0	13.0	13.0
Water added	0.0	0.0	0.0

([f]) experimentally fixed

Table 9.- Summary of the operating condition of the distillation multieffect columns

	Column	α	β	P(LP) mmHg	LP/IP	IP/HP
Enzymatic	Col5-7	0.084	0.238	172	2.15	2.05

Legend: LP: Low pressure: IP: Intermediate pressure: HP: High pressure
α: fraction of total feed to LP column β: fraction of total feed to IP column

Figure 6 shows the profile of the different products in the etherification reactor, Reactor 3, at the optimal operating temperature of 70ºC. The conversion per pass is around 50%

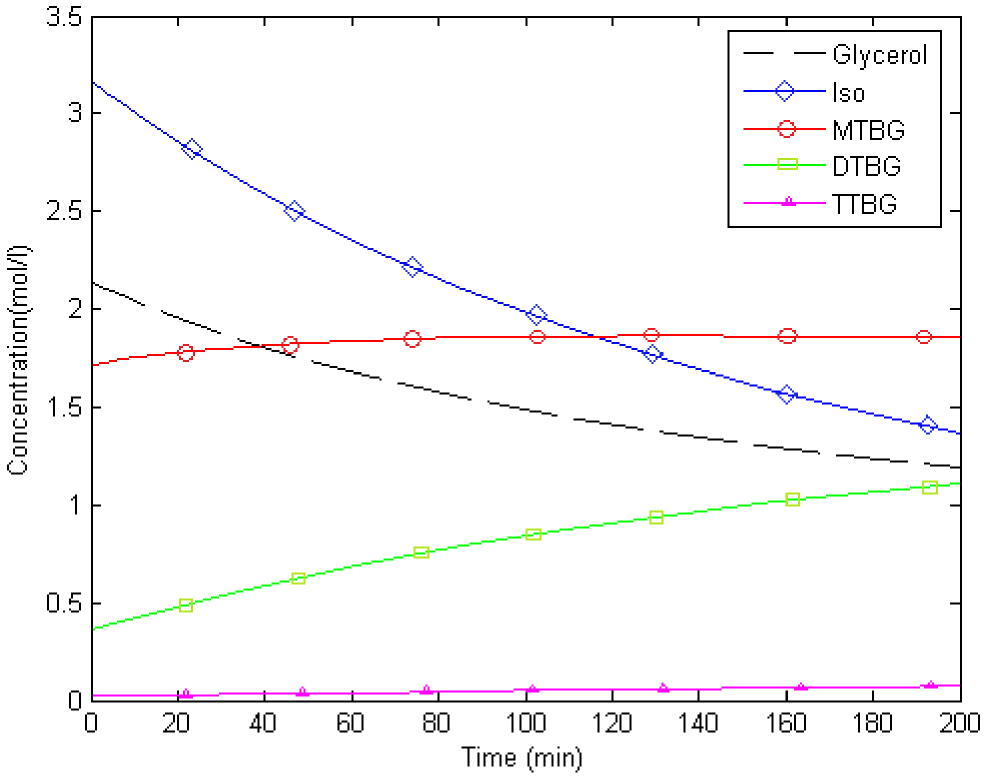


Figure 6.- Profiles of chemical species in the reactor

The advantage of the fully integrated process is that we are able to reduce the production cost to \$1.00/gal with an investment of 167M\$ for a production capacity of 108MMgal/yr of biofuels, 99MMgal of biodiesel and 9 MMgal/yr of bioethanol, which even though more expensive that biodiesel alone, becomes more competitive. The problem remains in the high cost of i-butene as can be seen in the share of the chemicals to the production cost of biofuels, see Figure 6. What is more important is that in terms of water and energy consumption the simultaneous production of FAEE, ethanol and h TBG is at least as good as the production of glycerol as by product, [23] and also compared to the production of FAME while integrating the use of glycerol to reduce the dependency of the process on methanol (reducing the dependency on fossil fuels) . Table 10 shows the comparison.

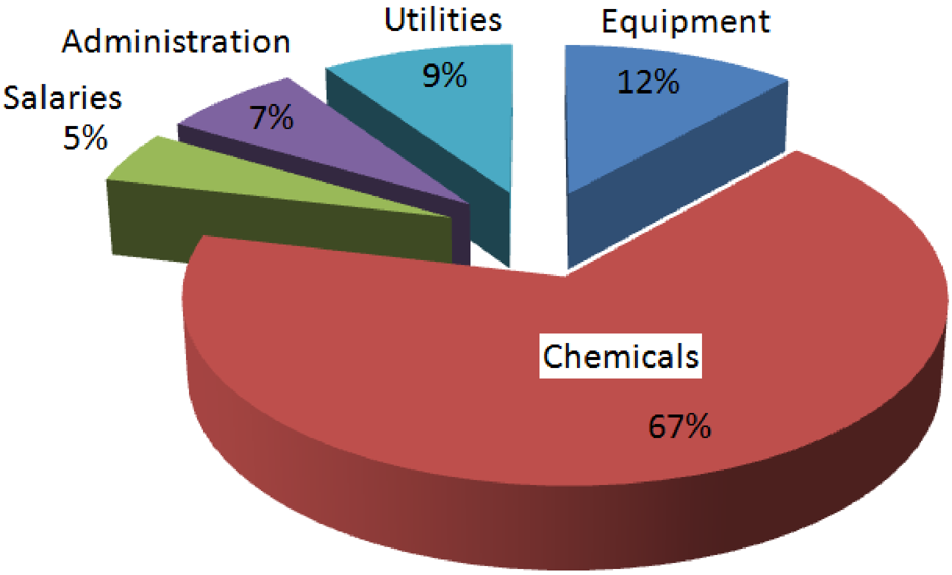


Figure 7.- Breakdown of the production cost of EtOH & D&TTBG & FAEE

Table 9.-Summary of results with simultaneous production

	Enzymatic (Ethanol and Gly)	Integrating MetOH (AR)	Enzymatic EtOH + D&TTBG & FAEE
$/gal$_{biofuel}$	0.35	0.66	1.00
Energy (MJ/gal$_{biofuel}$)	4.00	3.65	3.36
Water (gal/gal$_{biofuel}$)	0.59	0.79	0.59

4.3.- Sensityvity study

The paper is based on the assumption that the glycerol cost decreases due to the increase in the availability as a result of the production of biodiesel. Thus, in Figure 8 we present the effect of the price of the i-butene, to be read on the top x axis, and that of the price of glycerol, that can be red in the lower x axis on the cost of biofuels either glycerol is a byproduct (lines) or iw se used it to produce methanol (black line) or to produce glycerol ethers (discontinuos lines). As we can see the price of the i-butene must be reduced to half its current price for the processes to be competitive while the glycerol must reach the levels expected by the DOE at around \$0.2/kg[2] .

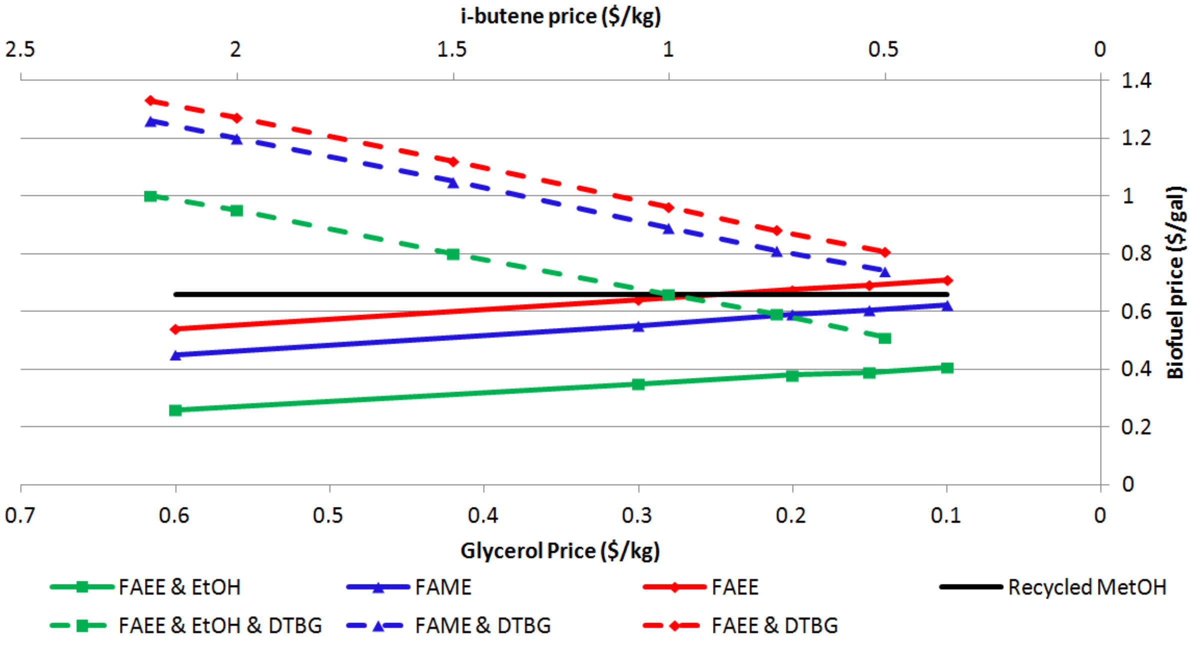


Figure 8.- Competitivity of the processes as function of the glycerol and I butylene cost.

The key problem related to the production of i- butene is the wide range of interesting products that use it as intermediate, such as MTBE. However, recently van Leeuwen et al[41] have proposed a conceptual design for the production of i-butene based on the fermentation of glucose. They report a production cost of i-butene of 0.9€/kg. As we can see in Figure 8, for this price, around $1/kg, the integration of the production of high ethers from glycerol becomes promising taking into account that according to Ahmed and Papalias[2] , the price of glycerol is expected to decrease down to $0.1/kg, roughly $0.2/kg. In this way, using ethanol instead of methanol, whose production from glycerol is not enough to avoid the dependence of the production of FAME from fossil fuel based methanol,[4] we can develop a process that has no dependency on fossil fuel to produce biodiesel and other diesel fuels substitutes.

5.-Conclusions

In this paper, we have optimized using algebraic and differential for equations for the synthesis of biodiesel and high glycerol ethers as crude based diesel substitutes. We have performed simultaneous optimization and heat integration of the process based on the discretization of the differential equations using orthogonal collocation.

The solution of the NLP problem indicates that the production of biodiesel (FAME or FAEE) from oil algae, coupled with the use of glycerol to obtain further amount of biofuels, increases the production of biofuels up to 10 to 20% with competitive consumptions of energy and water with respect to directly selling the glycerol as byproduct. The main disadvantage today is the price and source of i-butene. However, a number of current studies indicate that the use of glucose for the production of i-butene may be not only technically feasible, but economically competitive, which is promising for future integration of the processes.

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6.-Nomenclature.

Ci: Concentration of the chemical I in the reactor (mol/L)
Cpi: Heat capacity
fc(j,unit1, unit2) individual mass flow rate (kg/s)
F(unit1,unit2) mass flow rate (kg/s)
Pi: Partial pressure of component i. (bar)
T(unit1,unit2) Temperature of the stream from unit 1 to unit 2 (ºC)
x(J,unit1,unit2) mass fraction of stream from unit 1 to unit 2
λ : Vaporization heat (kJ/kg)

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