

Optimal biodiesel production using bioethanol: Towards process integration.

Kristen Severson, Mariano Martín, Ignacio E. Grossmann¹

Chemical Engineering Department. Carnegie Mellon University

Forbes Ave. Pittsburgh PA 15213

Abstract.

In this paper we optimize the production of biodiesel using bioethanol from algae following four different transesterification paths: alkali, enzymatic and heterogeneous catalysts and supercritical conditions. The reactors are modelled 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 column, gravity separators, etc.) in order to recover the ethanol, separate the polar and non polar phases and purify the glycerol and biodiesel produced to formulate the problem as a superstructure of alternatives. The aim of this paper 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 simply because these results take the separation stages into account. In terms of the best process, currently the alkali catalyzed process is the most profitable while the enzymatic based one is even more promising due to the lower consumption of energy and water, however it requires that the enzyme cost is reduced.

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

¹ Corresponding author. Tel.: +1-412-268-3642; Fax: +1-412-268-7139.
Email address: grossmann@cmu.edu (I.E. Grossmann)

1.-Introduction.

Biodiesel and bioethanol are the most important liquid biofuels employed in the transportation sector due to their similitude with current petrol-based fuels and their compatibility with current engines. These biofuels can be either used as fuels themselves or blended with petrol 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 (Gutierrez et al 2009)

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 acid, basic or enzymatic catalysts or under supercritical non catalyzed conditions. Typically, world biodiesel production is carried out employing methanol (Zhang et al 2003a&b; West et al. 2008; Helwani et al., 2009; Apostolakou et al., 2009; Pokoo-Aikins et al., 2009; Diaz et al., 2009; Glisic & Skala 2009; Al-Zuhair et al., 2010). The use of methanol has been based on its low cost compared to ethanol. 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 them are different, with methanolysis being much more rapid (Meneghetti et al., 2006). Because current biorefineries are becoming petrochemical complexes where a number of different products including ethanol and biodiesel are produced, integration of chemical processes has been reported to proved large economic savings. Therefore the use of ethanol can result in a large economical benefit in the actual operation of the complex (Gutierrez et al 2009, Kiss, 2010).

So far there are few processes reported for the production of biodiesel using ethanol (Santana et al 2010) and most of the studies are at laboratory scale evaluating the operating conditions at the reactor (Meneghetti et al., 2006). Thus the aim of this paper is to evaluate the 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 (Cristi, 2007) and the higher purity compared to the use of wastes. In terms of the process technologies, the use of alkali (KOH) catalyzed reaction is the most used (Gutierrez et al., 2009) while the use of enzymatic or heterogeneous catalyst or non-catalyzed reaction under supercritical conditions are becoming important

alternatives. There is a general lack of information in terms of modeling the transesterification 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 paper we propose 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 non catalyzed under supercritical conditions. We propose a limited 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. Next, we design the heat exchanger network using SYNHEAT (Yee & Grossmann 1990) 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 method proposed in Ahmetovic et al 2010, Grossmann and Martin (2010)

2.-Problem statement

We propose a superstructure for the production of biodiesel using ethanol as the alcohol and algal oil. The algal oil production is taken from the results of a previous paper (Martin & Grossmann 2011) involving algae growth, drying and oil extraction. The transesterification of the oil involves the four most common technologies for the transesterification of oil or ethanolysis based on the results in the literature. These data is used to write models for the reactor as 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 good data to develop the models. Due to the particularities of the process, the reactors operate with ethanol in a large excess. The economy of biodiesel production therefore relies on ethanol recovery and thus simultaneous optimization and heat integration is implemented, Duran and Grossmann 1986. Finally the water consumption of the different processes is calculated based on the paper by Ahmetovic et al 2010.

The paper is organized as follows. In section 3 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 section 4 we summarize the results of the optimization leading to the selection of the best process. Finally we compare the use of ethanol and methanol for the production of biodiesel in section 5 including a sensitivity analysis of the price of ethanol on the production cost of biodiesel.

3. Overall Process Description.

3.1.-Raw material.

The production of algae oil is attracting more attention due to the high yield from the ground to biofuels (Pokoo-Aikins 2009; Martin & Grossmann 2011). Microalgae production can be carried out either in ponds or photoreactors. The costs of running the ponds are lower but they are prone to contamination due to the open surface. Alternatively, photoreactors avoid contamination but have a higher capital and operating cost. For large scale, production ponds are usually recommended. (Mata et al. 2010).

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, giving a total unsaturated fatty acids content around 85%. (Zhang et al., 2009). Additionally it contains 0.01-0.02% moisture and 0.45-1.75 % free fatty acid (FFA) (Pokoo-Aikins et al 2009). Notably, FFA is always below 2% (Sanford et al., 2009). Based on these data, we assume that triolein and Oleic acid will represent the oil for further simulations with no impurities, therefore no pretreatment is needed.

3.2.- Biodiesel synthesis.

Once the oil is available, there are different processes to obtain biodiesel depending on the catalysis of the transesterification reaction, see fig 1 for the superstructure of alternatives. Fukuca, et al 2001, Helwani et al 2009. In all processes the lower bound for the purity of glycerol is 92% (Zhang et al 2003).

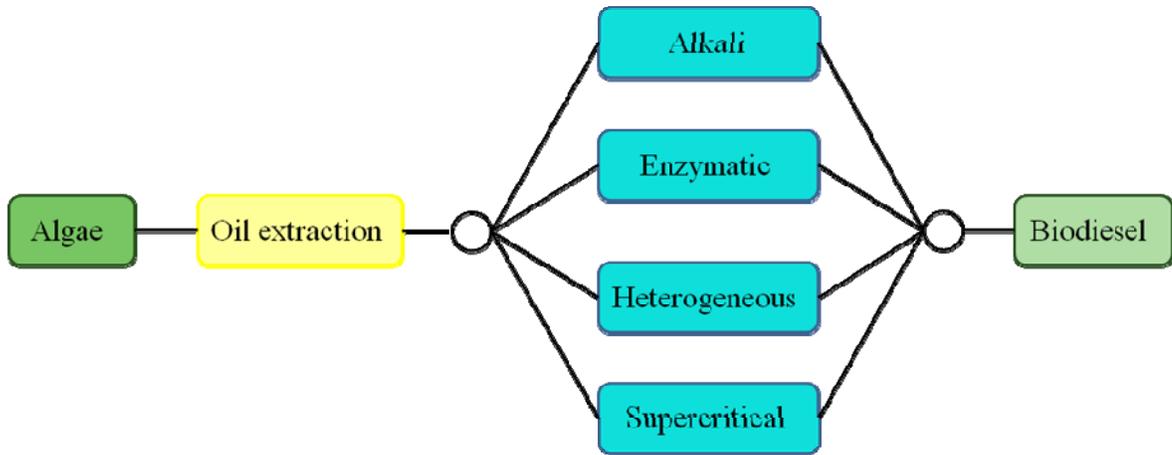


Figure 1.-Superstructure for the production of biodiesel using bioethanol

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

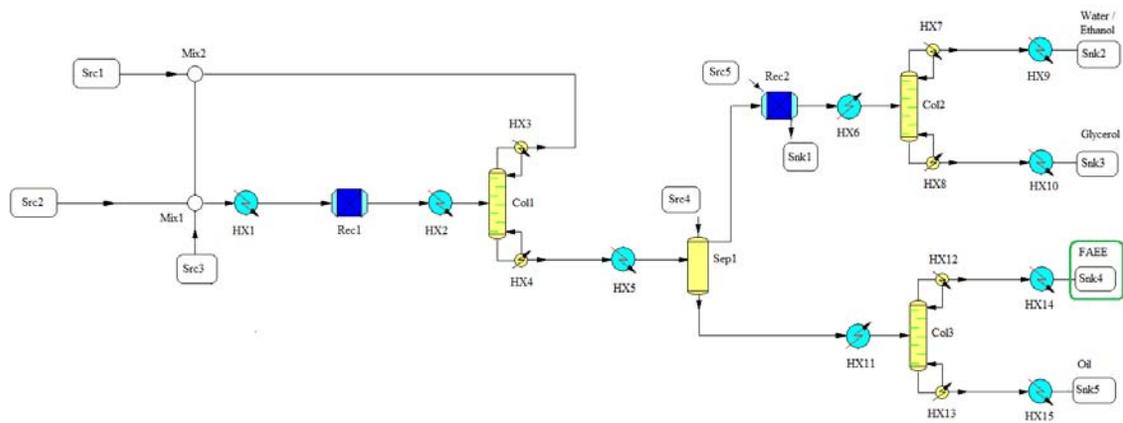


Figure 2.- Flowsheet for the production of biodiesel from oil via alkali -catalyzed transesterification

Alkaline Transesterification: The yield to biodiesel is function of a number of variables such as operation temperature, ethanol ratio to oil, and catalyst amount. Even though the operation conditions have been studied (Silva et al 2009, Joshi et al 2010) 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 trade-offs to get a high yield by adjusting the catalyst concentration, ethanol to oil ratio and working temperature. The catalyst used is KOH because K_3PO_4 can be

easy separated and used as fertilizer. The model for the transesterification reaction, Joshi et al (2010), eq (1), is taken from the literature

$$\begin{aligned} \text{yield} = & 22.94293 + 113.88 \cdot \text{cata_alk} + 2.828881 \cdot \text{Ratio_et} - 1.02734 \cdot T(\text{HX1,Rec1}) - 1.44522 \\ & \cdot \text{cata_alk} \cdot \text{Ratio_et} + 0.250723 \cdot \text{cata_alk} \cdot T(\text{HX1,Rec1}) + 0.023375 \cdot \text{Ratio_et} \cdot T(\text{HX1,Rec1}) \\ & - 41.4402 \cdot \text{cata_alk}^2 - 0.07568 \cdot \text{Ratio_et}^2 + 0.006226 \cdot T(\text{HX1,Rec1})^2; \end{aligned} \quad (1)$$

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

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

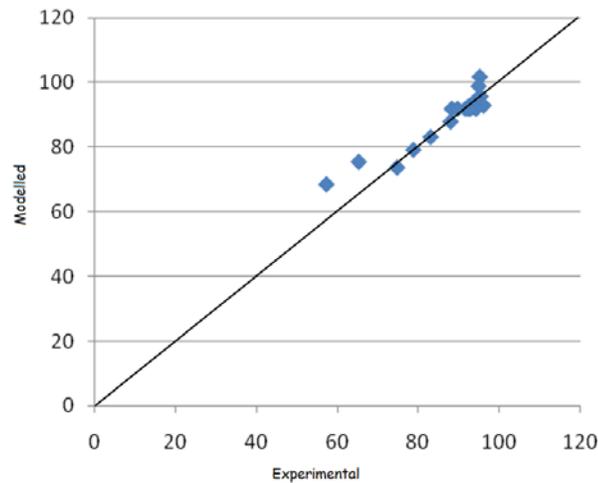


Figure 3.- Fitting of the data for the alkali catalyst

Ethanol recovery: A distillation column will be used to recover the excess of ethanol so that it is recycle back to the reactor. At least 94% of the ethanol is recycled. The reflux ratio is variable. The temperature at the bottom must not go over 150°C to avoid glycerin decomposition, thus vacuum operation is required. The bottoms is cooled down to 60°C before phase separation.

Water washing: The purpose of this stage is to separate the biodiesel from the glycerol, ethanol and catalyst. Following the typical approach (West, 2008, Zhang, 2003) 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 (Krawczyk 1996, West 2008. Based on Zhou et al 2006 and Cernoch et al 2009) we assume good phase

separation for ethanol. A small amount of water, 5% of the biodiesel phase, is added to the column (Cerboch et al. 2009) . The working temperature will be between 30 and 40°C. (Cerboch et al. 2009)

FAEE purification: The non polar phase containing biodiesel is purified in a distillation column. The main challenge is to work below atmospheric pressure so that the distillate containing biodiesel exist the column below 250°C (Zhang et al. 2003) to maintain the integrity of the biodiesel.

Alkali removal: In order to remove the alkali catalyst, KOH, phosphoric acid, H₃PO₄, is selected based on the fact that the salt generated in the neutralization reaction, K₃PO₄, can be easily removed using a gravity separator.

Glycerol purification: A distillation column is typically used to purify glycerol beyond 92% . Beyond this purity level, glycerol can be sold as a high quality by-product. However, the decomposition temperature of glycerol is reported to be 150°C which requires the distillation column to work below atmospheric pressure (Zhang et al. 2003). The reflux ratio is variable from 2 to 3 as well as the purity of the glycerol, using 0.92 as the lower bound. The final objective function is given in eq. (2)

$$Z = C_{FAME} * fc(FAEE) + C_{Glycerol} * fc(Glycerol) + C_{K_3PO_4} * fc(K_3PO_4) - C_{Steam} * (1 / \lambda) * (QS_max) - C_{KOH} * fc(KOH) - C_{MeOH} * fc(EtOH) - C_{H_3PO_4} * fc(H_3PO_4); \quad (2)$$

3.2.2.- Process 2: Enzymatic production of bio diesel

According to recent news from novozymes, one of the world leaders in enzyme production, while the current chemical process demands raw materials of high quality that can often also be used as food, a process based on enzymes will be able to use raw materials of poorer quality, such as animal fats, recycled restaurant oils, and waste products (Per Munk Nielson, senior science manager for Novozymes A/S). However, the enzymatic process has not been implemented at the industrial scale due to the lack of development (Ranganathan et al. 2008). Due to the high cost of the enzymes, the only economical way to produce biodiesel using them is if they are immobilized, allowing for reuse (Bajaj et al. 2010). 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 enzyme can be easily separated, there is no need for washing and the separation of glycerol does not require a distillation column.

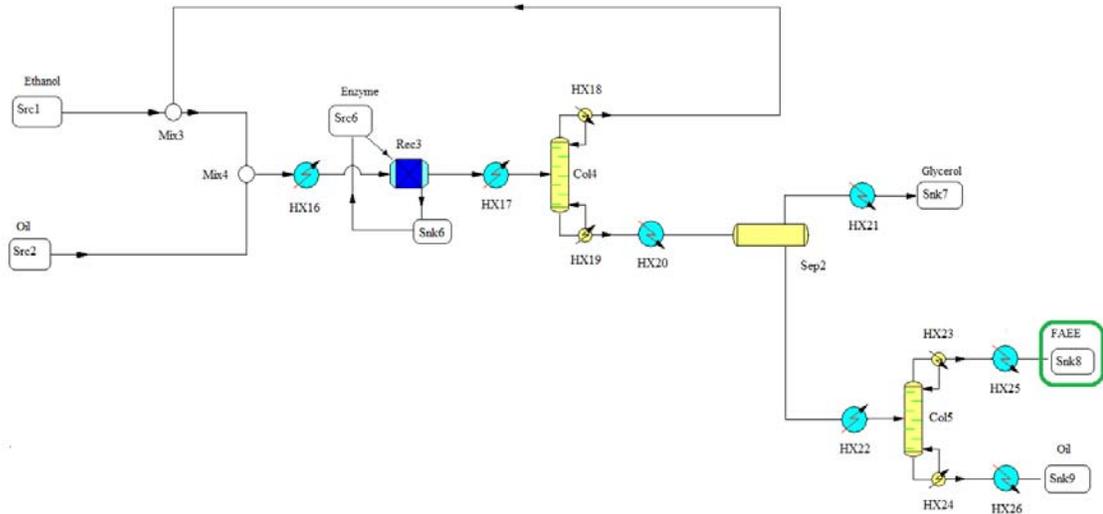


Figure 4.- Flowsheet for the production of biodiesel from oil via enzymatic transesterification

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. (de Oliveira et al. 2004, Rodrigues et al. 2008, Torres et al. 2004, Cavalcante et al. 2010, Pessoa et al. 2010). The paper by Rodrigues et al. (2008) 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. Eq. (3) presents the model. Despite the dispersion, reasonably good agreement is obtained. Figure 5 shows the goodness of the fitting and table 2 presents the range of operation of the variables.

$$\begin{aligned}
 \text{yield} = & 3.624996 - 1.64904 * T(\text{HX16}, \text{Rec3}) + 17.91299 * \text{time_enz} - 7.60104 * \text{Ratio_etE} + 10.59497 * \text{cata_enz} - \\
 & 0.49902 * \text{water_enz} + 0.014332 * T(\text{HX16}, \text{Rec3})^2 - 0.65091 * \text{time_enz}^2 - 0.33241 * \text{Ratio_etE}^2 - 0.31632 \\
 & * \text{cata_enz}^2 + 0.00692 * \text{water_enz}^2 - 0.0407 * T(\text{HX16}, \text{Rec3}) * \text{time_enz} + 0.17485 * T(\text{HX16}, \text{Rec3}) * \text{Ratio_etE} \\
 & - 0.0138 * T(\text{HX16}, \text{Rec3}) * \text{cata_enz} - 0.0156 * T(\text{HX16}, \text{Rec3}) * \text{water_enz} - 0.0601 * \text{time_enz} * \text{Ratio_etE} - \\
 & 0.4629 * \text{time_enz} * \text{cata_enz} + 0.11014 * \text{time_enz} * \text{water_enz} + 0.43481 * \text{Ratio_etE} * \text{cata_enz} + 0.21369 \\
 & * \text{Ratio_etE} * \text{water_enz} - 0.09614 * \text{cata_enz} * \text{water_enz};
 \end{aligned}$$

(3)

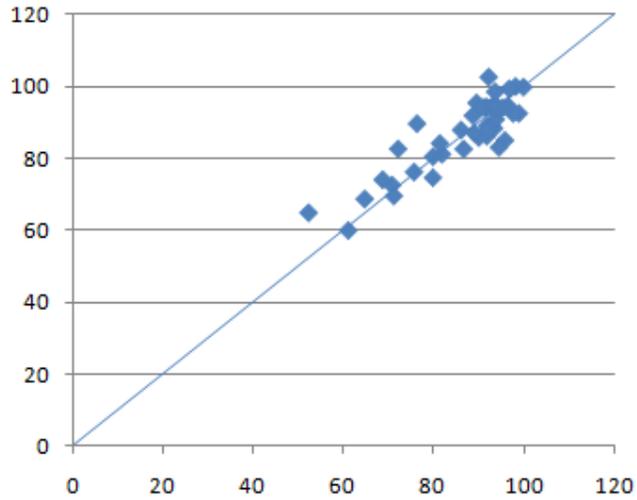


Figure 5.- Surface response model fitting for enzymatic transesterification.

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

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

The supported enzymes can be easily separated from the reactants and products, the ethanol is then separated to be reused and the biodiesel purified as in previous processes. The separation of the oil phase – polar phase is based on gravity and does not require the addition of any agent (Zhou et al. 2006 and Cernoch et al. 2009). The working temperature will be 40°C (Cerboch et al. 2009) similarly to the alkali case. Eq. (4) presents the objective function for this technology

$$Z = C_{FAME} * fc(FAEE) + C_{Glycerol} * fc(Glycerol) - C_{Steam} * (1 / \lambda) * (QS_max) - C_{enzy} * Enzymeadded * f_{recycle} - C_{MeOH} * fc(EtOH)$$

(4)

3.2.3.- Process 3: Supercritical production of biodiesel

The use of supercritical conditions for oil transesterification is deemed an efficient way to produce biodiesel since there is no catalyst involved, simplifying the separation of the products. However, the operating conditions of the reactor require the input of energy (electric and heat) to prepare the feed for the reaction (Valle et al. 2010, Gui et al. 2011). Figure 6 shows the flowsheet. The absence of 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 the experimental data in the literature (Valle et al. 2010) and is presented in eq. (5). Correlations for the yield and another one for the operating pressure are developed based on surface response methodology, see fig 7 and table 3 for the model range of variables and fitting.

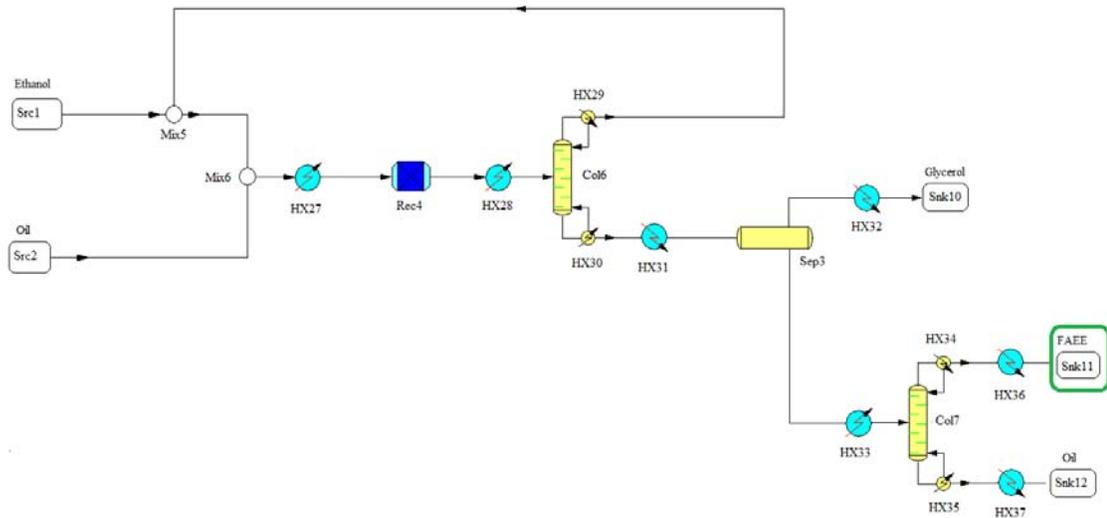


Figure 6.- Flowsheet for the production of biodiesel from oil via supercritical non catalyzed transesterification

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

(5)

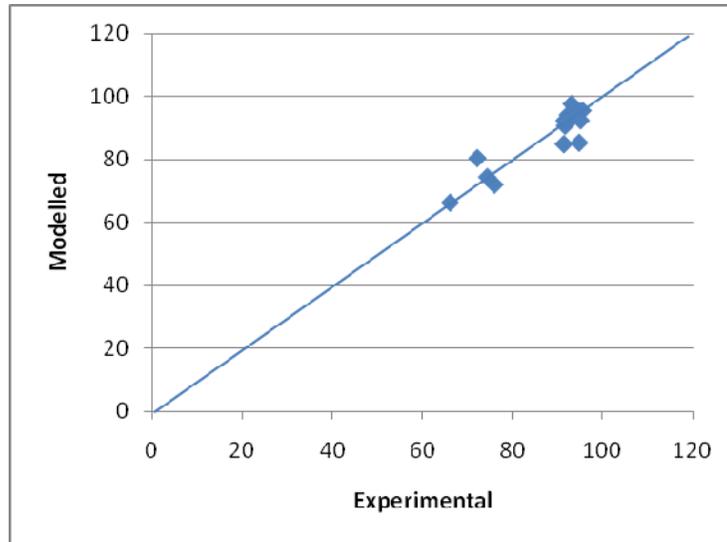


Figure 7.- Surface response fitting for supercritical non catalyzed transesterification

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

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

To determine the operating pressure we obtain a correlation using the data from the same source, Rodrigues et al. 2008, eq. (6). Figure 8 shows the fitting

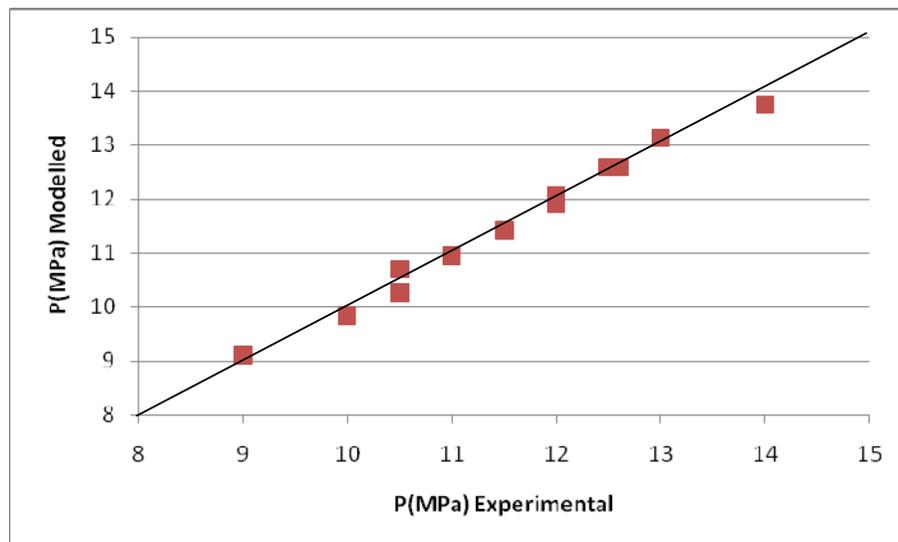


Figure 8.- Pressure as fuction of the temperature.

$$P(\text{MPa}) = -0.05387 + 0.030504 * T(\text{HX27,Rec4}) - 0.89026 * \text{RM} + 0.003033 * T(\text{HX27,Rec4}) * \text{Ratio_etS} \quad (6)$$

After the reactor, the stream is decompressed and a distillation column recovers the excess ethanol. There is a trade-off 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 will 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 contains mainly glycerol and biodiesel with small amounts of methanol, water, FFA and oil. A gravity separation allows the recovery of glycerol with a purity level higher than 92% while the biodiesel will be purified in a distillation column. In this column, as we have presented before, the temperature of the distillate - mainly biodiesel - must be kept below 250 °C to avoid diesel decomposition. Eq. (7) shows the objective function.

$$Z = C_{FAEE} * \text{fc}(\text{FAEE}) + C_{Glycerol} * \text{fc}(\text{Glycerol}) - C_{Steam} * (1/\lambda) * (\text{QS_max}) - C_{MeOH} * \text{fc}(\text{EtOH}) + C_{electricity} * (\text{W}(\text{Pump})); \quad (7)$$

3.2.4.- Process 4: Heterogeneous production of bio diesel

Over the last 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 been common (Cardoso et al. 2008, Li, et al. 2009, Kim et al. 2010, Jiménez Morales, et al. 2011; Cardoso et al. 2008) reported yields around 90% with SnCl₂, using fixed high molar ratios ethanol to oil of 120:1, which increases the energy consumption for the recycle of the ethanol excessively. Li et al. (2009) reported high yield working in a pressurized vessel with a lower ethanol 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 non polar phases and biodiesel purification. Based on the experimental results by Li et al. (2009) we have developed a surface response model for predicting the

performance of the reactor, see eq. (8). In figure 10 and table 4 we present the range of the variables and the fitting of the model with good agreement. The objective function is given by eq. (9).

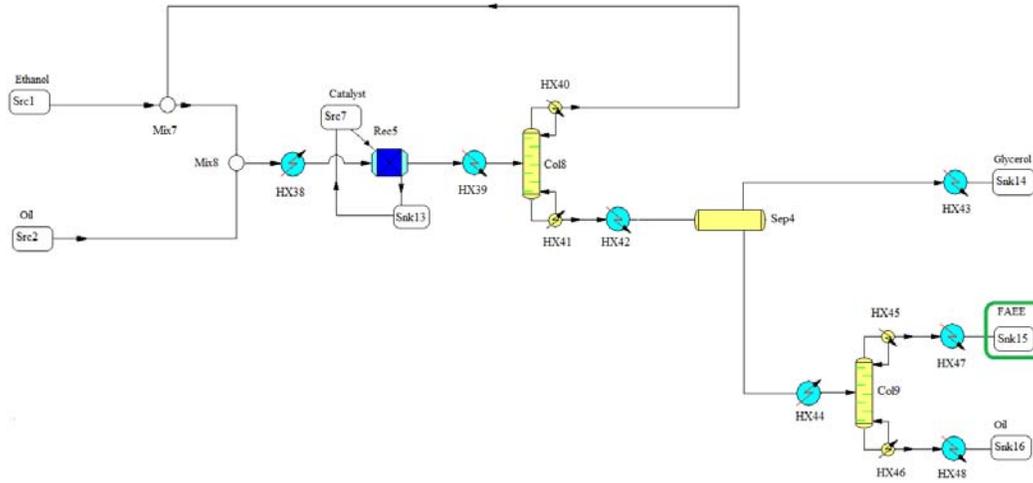


Figure 9.- Flowsheet for the production of biodiesel from oil via heterogeneous transesterification

$$\begin{aligned}
 \text{yield} = E = & -0.1247 + 3.1700 \cdot (T(\text{HX38}, \text{Rec5}) + 273) + 4.7602 \cdot \text{time_het} - 1.9494 \cdot \text{Ratio_eH} \\
 & + 0.0068 \cdot (T(\text{HX38}, \text{Rec5}) + 273)^2 - 0.0007 \cdot \text{time_het}^2 + 0.0567 \cdot \text{Ratio_eH}^2 - \\
 & 0.0092 \cdot (T(\text{HX38}, \text{Rec5}) + 273) \cdot \text{time_het} + 0.0079 \cdot (T(\text{HX38}, \text{Rec5}) + 273) \cdot \text{Ratio_eH} \\
 & + 0.0002 \cdot \text{time_het} \cdot \text{Ratio_eH};
 \end{aligned} \tag{8}$$

Table 4.-Range of operation of the variables. Enzymatic

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

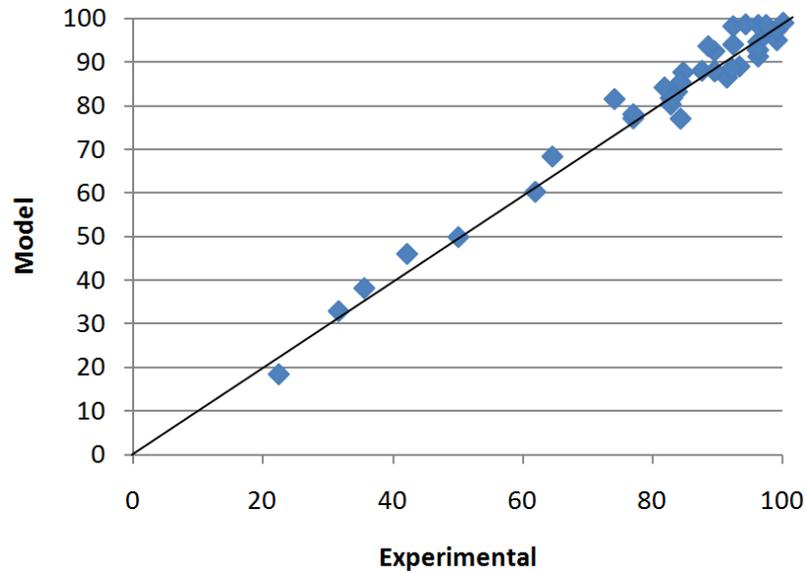


Figure 10. Fitting of the model

$$\begin{aligned}
 Z = & C_{FAEE} * fc(FAEE) + C_{Glycerol} * fc(Glycerol) \\
 - & C_{Steam} * (1 / \lambda) * (QS_max) - C_{EtOH} * fc(EtOH) - C_{cat_het} * fc(Oil) - C_{electricity} * (W(Pump)); \quad (9)
 \end{aligned}$$

4.-Results

4.1.-Flowsheet definition.

The typical biodiesel production capacity is 15Mgal/yr or 40000t/yr (1.3kg/s). In the future it is expected that the plants will produce 25kg/s of biodiesel (Apostolakou et al 2009). Currently the biggest plant in Europe produces 250000 t/yr (8kg/s) (<http://www.larioja.com>) while there are a number of them around 200000 t/yr (6.5 kg/s) so we will focus on the production of around 7kg/s (72MMgal per year)

The construction of the algae ponds ranges from 0.25 \$/m² to 1.25\$/m² (<http://www.aces.edu>, Putt 2007). The bigger the pond the lower the cost. We use a value of 0.61 \$/m² (<http://www.aces.edu>) to account for other minor equipment associated with the ponds because the size of the farm will allow a lower price. The cost of the digester and the generator (Putt 2007) are included so that we generate electricity from the biomass. The energy that can be obtained from the residue by digestion is computed using the data by Nielsen & Oleskiewicz-Popiel 2008 (522 kW/kg). From the ponds the amount of water lost due to evaporation is estimated to be 1.8kg/d.

However, this water is not necessary freshwater but saline water too. We assume a production cost for biodiesel so as to use in the objective function of 1\$/kg. In a production plant 0.083kwh of electricity are used per gallon of biodiesel (Radich 2002). 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) (Francheschin et al 2008). Electricity: 0.06 \$/kWh (Balat et al 2008), 4.876 \$/MMBTU for natural gas (<http://www.wtrg.com/daily/gasprice.html>) while table 5 shows the cost of the chemicals used.

Table 5.- Chemical cost

Chemical	Cost (\$/kg)	Source
Fertilizer	0.367 *	http://www.crystalsugar.com/agronomy/agtools/npk/Default.aspx
Enzyme	0.7	Sotof. Et al 2010
Tert butanol	2	Sotof. Et al 2010
Het. Catalyst	0.6	West et al 2008
CH ₃ OH	0.28	http://www.methanex.com/products/methanolprice.html
H ₂ SO ₄	0.329	http://www.purchasing.com/article/211930-Sulfuric_acid_prices_explode.php
KOH	1.6	http://www.echinachem.com/en/products/Product.aspx?SupplyOrRequestID=578325
CaO	0.06	www.lime.org
Gypsum	0.023	www.lime.org
H ₃ PO ₄	0.34	West et al 2008,
Glycerine	0.6	West et al 2008,
Hexane	0.41	Zhang et al 2003
Fe ₂ (SO ₄) ₃	0.447	http://www.abilenetx.com/Minutes/Council/2009/2009-10-08%20minutes.pdf
K ₃ PO ₄	1.9	http://www.sunivo.com/ennew/Products/Products_list.asp?sProdKw=potassium phosphate

(*) Mean value of a number of fertilizers

The typical operating conditions for the transesterification are shown in table 6 (a) Joshi et al. (2008) (b) Gui et al. (2009); (c) Valle et al. (2010) (d) Rodrigues et al. (2008) (e) Li et al. (2009). The simultaneous optimization of the performance of the reactor and heat integration reveals quite different values, see table 7, mainly in the operation of the reactor where 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.

Table 6.- Typical operating conditions

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

(a) Joshi et al (2008) (b) Gui et al. (2009); (c) Valle et al. (2010) (d) Rodrigues et al. (2008) (e) Li et al. (2009)

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
ratio_et	5.7	32	8.9	16
Time (h)	0.5	0.43	6.9	5
Cat/lipase(%)	1.5	--	14.0	2 ^f
Water added	-	-	0.0	-

^f fixed condition in the experimental data

After the optimization, see table 7, the objective function shows that the alkali one is the most promising process, see continuous lines in fig 12.

4.2.- 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 1990 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 (Martín et al. 2010), we design the water network based on the model by Ahmetovic et al. 2010. 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.

4.3.- Economic evaluation and discussion.

The production cost of oil from algae has been estimated to be \$0.07/lb in the best possible case (Pooko Aikins et al. 2009). This value can be obtained but not with the typical harvesting and drying technologies. The process is based on a new design for harvesting the algae recently released by Univenture Inc. 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.

So far, the transesterification costs have been estimated to be about \$0.58 per gallon with overhead of \$0.33 per gallon. If the co-product glycerol is credited at \$0.39 per gallon, the total cost for processing biodiesel is \$0.52 per gallon. (Wither and Noordam 1996). Other studies have estimated total operating costs of \$0.30-0.60 per gallon. (Bender 1997) 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 (Duffield, et al. 1998, Saka & Kusdiana 2001, Tao and Aden 2009). Previous results reported in the literature on energy consumption are from 3.3MJ/gal to 12MJ/gal (Pooko-Aikins et al. 2009, Saka & Kusdiana 2001, NDB 2009) with an industrial average of 4.4MJ/gal (NBD 2009). In terms of water consumption values of 1 to 3 gal/gal are reported (Pate et al. 2007). Table 8 summarizes the manufacturing costs, the energy and water consumption of the processes. 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 Martin & Grossmann (2011) presented that the optimal process was the one that used the alkali catalyst. Thus if we use this catalyst we can use either ethanol or

methanol for the production of biodiesel depending on the availability with small changes in the operating variables of the process. However, in case the oil comes from wastes the alkali catalyzed process requires pretreatment and therefore the heterogeneous based process is recommended (Martín & Grossmann, 2011)

Table 8.- Production costs, energy and water consumption (\$1/gal for ethanol)

	Alkali cat	Supercritical	Enzymatic	Heterogeneous
\$/gal	0.52	0.71	0.56	0.62
Energy (MJ/gal)	2.81	8.83	1.93	5.99
Water (gal/gal)	0.47	1.98	0.35	1.08

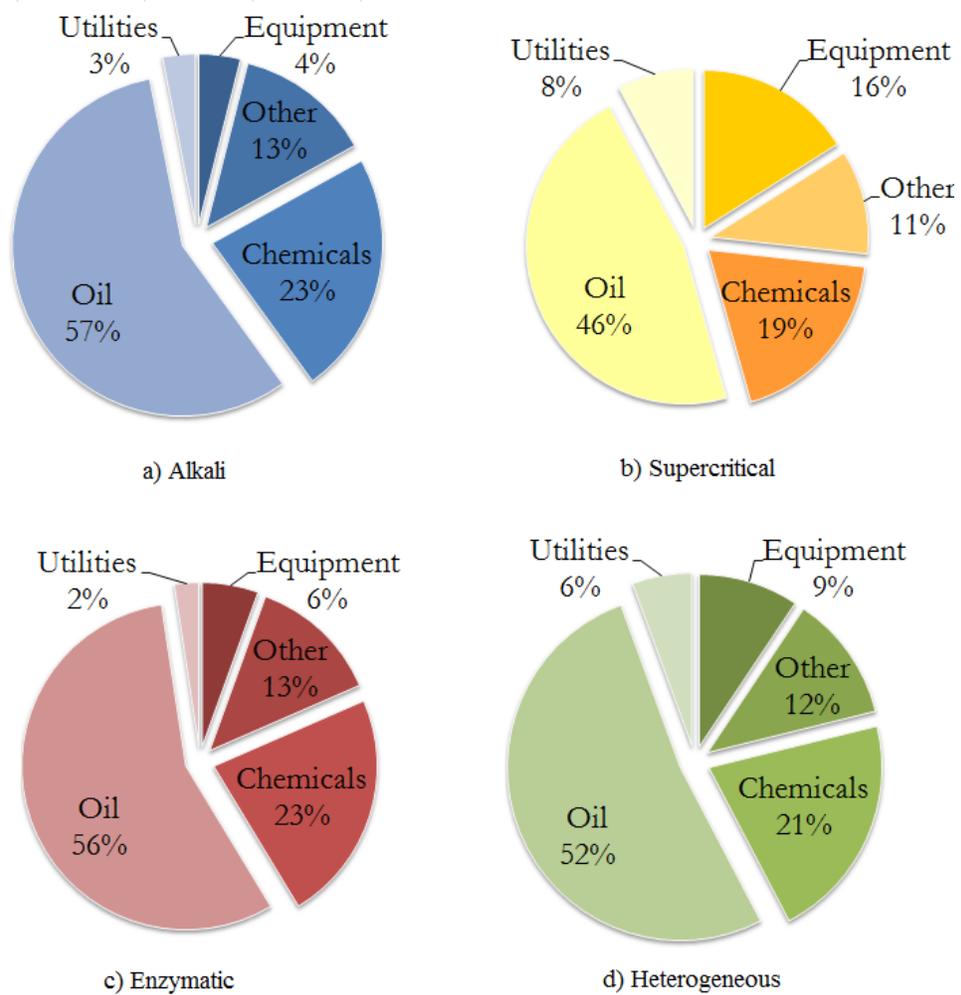


Figure 11.- Cost distribution for the four alternatives

In table 9 we present the comparison between the optimal design and the base case with neither optimization nor heat integration using the operating data from the literature, see table 9.

Table 9. Comparison between base case and optimal case

Alkali cat	Optimal	Base case
yield	0.98	0.89
\$/gal	0.52	0.58
Energy (MJ/gal)	2.81	4.86
Water (gal/gal)	0.47	1.53

Enzymatic	Optimal	Base case
yield	0.98	0.94
\$/gal	0.56	0.78
Energy (MJ/gal)	1.93	2.35
Water (gal/gal)	0.35	0.38

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 as well as in the case of the enzymatic based process. Furthermore, the quality of the glycerol in the base case is far from being interesting as by product due to the water added, thus it cannot be used as a valuable byproduct unless we purify it resulting in a higher production cost, \$0.78/gal vs. \$0.56/gal

4.4.- Sensitivity study.

The price of ethanol is the biggest uncertainty for the economic feasibility of this process compared to the traditional production facilities based on the use of methanol. Thus we evaluate the effect of the price of ethanol on the objective function. Fig. 12 shows the profiles. 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 10 we present the results of the alternatives based on a price of \$0/gal. These

values are similar to the ones obtained for the processes that use methanol (Martin & Grossmann 2011) so even though table 9 results 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 and if the production cost of ethanol decreases to the values reported by Martin & Grossmann 2011, around \$0.41/gal the use of the alkali process or even the supercritical one using ethanol are competitive with those using methanol (Martin & Grossmann 2012). Therefore, in the context of an integrated biorefinery, the use of ethanol becomes competitive and it is worth studying the process integration.

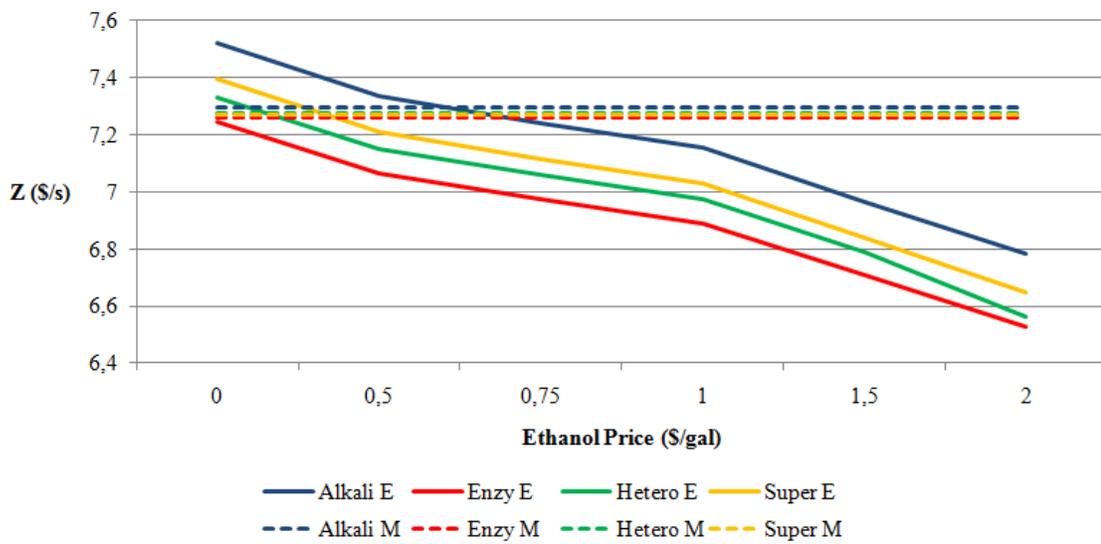


Figure 12.- Comparison of the results of the objective function using ethanol (E) or methanol (M)

Table 10.- Production costs, energy and water consumption (\$0/gal for ethanol)

	Alkali cat	Supercritical	Enzymatic	Heterogeneous
\$/gal	0.35	0.51	0.39	0.48
Energy (MJ/gal)	2.85	8.76	1.93	6.10
Water (gal/gal)	0.50	1.91	0.20	1.18

5.-Conclusions

In this paper 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. The objective function decides on the best process. Later 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 simply because the separation stages were not taking into account when deciding on the process design.

For the production of biodiesel using bioethanol we have identify two interesting technologies, alkali catalized and enzymatic catalyzed. The first one is currently the cheapest one and even competitive with the use of methanol as transesterifying agent but the energy and water consumptions are higher than in the case of using enzymatic catalyst whose main drawback currently is the enzyme cost. Even though the current prices of ethanol and methanol still support the use of the later for the production of biodiesel, the promising production costs presented by Martín & Grossmann 2011 and the advantages of integrated production of ethanol and biodiesel make the transesterification of oil with ethanol a future alternative in the context of a biorefinery complex.

6. References

- Ahmetovic, E.; Martín, M.; Grossmann, I.E. (2010) "Optimization of Water Consumption in Process industry: Corn – based ethanol case study" *Ind. Eng. Chem Res.* 49(17) 7972- 7982
- Al-Zuhair, S.; Almenhali, A.; Hamad, I.; Alshehhi, M.; Alsuwaidi, N.; Mohamed, S. (2010) Enzymatic production of biodiesel from used/waste vegetable oils: Design of a pilot plant. *Renew. Ener.*, doi:10.1016/j.renene.2010.05.010
- Apostolakou, A.A.; Kookos, I.K. ; Marazioti, C.; Angelopoulos, K.C. (2009) Techno-economic analysis of a biodiesel production process from vegetable oils. *Fuel Process. Technol.* 90 (2009) 1023–1031
- Balat, M.; Balat, H.; Öz, C. (2008) Progress in bioethanol processing *Progress in Energy and Combustion Science*, 34, 5, Pages 551-573

- Bender, M. (1997) Feasibility Study for Farmers' Biodiesel Cooperative. The Land Institute, April 1997.
- Kiany S.B. Cavalcante a,b,* , Maria N.C. Penha a, Karlene K.M. Mendonça a, Hilton C. Louzeiro a,b, Antonio C.S. Vasconcelos a,b, Adailton P. Maciel a, Antonio G. de Souza b, Fernando C. Silva a (2010) Optimization of transesterification of castor oil with ethanol using a central composite rotatable design (CCRD) Fuel 89 (2010) 1172–1176 (reactor alkali)
- Abiney L. Cardoso, Soraia Cristina Gonzaga Neves and Marcio J. da Silva, (2008) Esterification of Oleic Acid for Biodiesel Production Catalyzed by SnCl₂: A Kinetic Investigation *Energies* 2008, 1, 79-92; DOI
- Michal Cernoch, František Skopal and Martin Hájek Separation of reaction mixture after ethanolysis of rapeseed oil Eur. J. Lipid Sci. Technol. 2009, 111, 663–668 (separation)
- Chisti, Y., 2007, Biodiesel from microalgae. *Biotechnology Advances*, 25, 294-306.
- Diaz, M. S.; Espinosa, S.; Brignole, E. A. (2009) Model-Based Cost Minimization in Noncatalytic Biodiesel Production Plants. *Energy Fuels*, 23, 5587–5595
- Duffield, et.al. (1998) U.S. Biodiesel Development: New Markets for Conventional and Genetically Modified Agricultural Products. Agricultural Economic Report No. 770, September, 1998.
- Duran, M.A., Grossmann, I.E (1986) Simultaneous optimization and heat integration of chemical processes. *AIChE, J.*, 32, 123-138
- Glisic, S.; Skala, D. (2009) The problems in design and detailed analyses of energy consumption for biodiesel synthesis at supercritical conditions *J. of Supercritical Fluids* 49, 293–301
- Gui, M.M.; Lee, K.T.; Bhatia, S.; (2009) Supercritical technology for the production of biodiesel: Process optimization Studies. *J. Supercritical Fluids*, 49, 286-292
- Guo, Y.; Zhong, J.; Xing, Y.; Li, D.; and Lin, R (2007) Volatility of Blended Fuel of Biodiesel and Ethanol *Energy & Fuels*, 21, 1188-1192 (Vapour pressure FAEE)
- Luis F. Gutiérrez, Óscar J. Sánchez, Carlos A. Cardona (2009) Process integration possibilities for biodiesel production from palm oil using ethanol obtained from lignocellulosic residues of oil palm industry. *Bioresource Technology* 100 (2009) 1227–1237
- Franceschin, G.; Zamboni, A.; Bezzo, F.; Bertucco, A. (2008) Ethanol from corn: a technical and economical assessment based on different scenarios *Chem.Eng. Res. Des.*, 86, 5, 488-498
- Helwani, Z., Othman, M.R., Aziz, N., Kim, J.; Fernando, W.J.N. (2009) Solid heterogeneous catalysts for transesterification of triglycerides with methanol: a review., *Appl. Catal. A — Gen.* 363, 1–10.
- Jiménez-Morales, I., Santamaría –González, J., Maireles-Torres, P. , Jiménez-López, A. (2011) Calcined zirconium sulfate supported on MCM-41 silica as acid catalyst for ethanolysis of sunflower oil. *Appl. Catal. B. Environmen.*
- Hem Chandra Joshi; Joe Toler; Terry Walker Optimization of Cottonseed Oil Ethanolysis to Produce Biodiesel High in Gossypol Content *J Am Oil Chem Soc* DOI 10.1007/s11746-008-1200-7 (alkali reactor)
- Kim, M., Yan, S., Salley, S., Ng, K.Y.S. (2010) Competitive transesterification of soybean oil with mixed methanol/ethanol over heterogeneous catalysts. *Biores. Technol.* 101, 4409-4414

Kiss, A.A. (2010) Separative reactors for integrated production of bioethanol and biodiesel *Computers and Chemical Engineering* 34 (2010) 812–820

Krawczyk, T. (1996) Biodiesel Alternative Fuel Makes Inroads But Hurdles Remain, Inform 7 (8): 801-815

Eugena Li, Zhi Ping Xu, Victor Rudolph, (2009) MgCoAl-LDH derived heterogeneous catalyts for the etanol transesterification of canola oil to biodiesel. *Appl. Cat. B: Environ.* 88, 42-49

Ana V. Marjanovic´ , Olivera S. Stamenkovic´ , Zoran B. Todorovic´ , Miodrag L. Lazic´ , Vlada B. Veljkovic´ (2010) Kinetics of the base-catalyzed sunflower oil ethanolysis *Fuel* 89 (2010) 665–671 (alkali kinetic)

Mata, T. M., Martins, A.A., Nidia. S. Caetano, N.S. (2010) Microalgae for biodiesel production and other applications: A review *Renewable and Sustainable Energy Reviews* 14 (2010) 217–232

Martín, M.; Ahmetovic, E.; Grossmann, I.E. (2011) Optimization of Water Consumption in Second Generation bio-Ethanol Plants *I&ECR* 50(7), pp 3705–3721

Martín, M., Grossmann, I.E. Process optimization bioDiesel production from cooking oil and Algae. To be submitted to *Ind. Eng. Chem Res*

Martín, M., Grossmann, I.E. (2011) Energy optimization of lignocellulosic bioethanol production via gasification accepted *AIChE J.* | DOI: 10.1002/aic.12544

National Biodiesel Board 2009 Comprehensive Survey on Energy Use for Biodiesel Production
http://www.biodiesel.org/pdf_files/fueelfactsheets/Energy_Use_Survey.pdf (accessed june 2010)

Débora de Oliveira, Marco di luccio, Carina Faccio, Clarissa dalla Rosa, João Paulo Bender, Nádia Lipke, Silvana Menoncin, Cristiana Amroginski, and José Vladimir de Oliveira* (2004) Optimization of Enzymatic Production of Biodiesel from Castor Oil in Organic Solvent Medium. *Applied Biochemistry and Biotechnology* 113–116, 771-780 (Model conversion)

Pate, R. (2008) Biofuels and the Energy-Water Nexus AAAS/SWARM April 11, 2008 Albuquerque, NM

Fernando L. P. Pessoa & Shayane P. Magalhães & Pedro Wagner de Carvalho Falcão (2010) Production of Biodiesel via Enzymatic Ethanolysis of the Sunflower and Soybean Oils: Modeling *Appl Biochem Biotechnol* (2010) 161:238–244 (modelo reactor enzymes)

Pokoo-Aikins, G.; Nadim, A.; El-Halwagi, M.M.; Mahalec, V. (2010) Design and analysis of biodiesel production from algae grown through carbon sequestration *12,3*, 239-254

Rafael Costa Rodrigues & Giandra Volpato & Keiko Wada & Marco Antônio Záchia Ayub (2009) Improved Enzyme Stability in Lipase-Catalyzed Synthesis of Fatty Acid Ethyl Ester from Soybean Oil *Appl Biochem Biotechnol* (2009) 152:394–404 (Model reaction enzyme)

Rafael Costa Rodrigues, Giandra Volpato, Marco Antonio Zachia Ayub, and Keiko Wada (2008) Lipase-catalyzed ethanolysis of soybean oil in a solvent-free system using central composite design and response surface methodology *J Chem Technol Biotechnol* 83:849–854 (Model reaction enzyme)

Saka, S.; Kusdiana, D. (2001) Biodiesel fuel from rapeseed oil as prepared in supercritical methanol, *Fuel*, 80, 225-231

Nivea de Lima da Silva, Cesar Benedito Batistella, Rubens Maciel Filho, and Maria Regina Wolf Maciel (2009) Biodiesel Production from Castor Oil: Optimization of Alkaline Ethanolysis *Energy Fuels* 2009, 23, 5636–5642 (model alkaliv)

Simoni M. Plentz Meneghetti, Mario R. Meneghetti, Carlos R. Wolf, ‡ Eid C. Silva, Gilvan E. S. Lima, † Laelson de Lira Silva, † Tatiana M. Serra, Fernanda Cauduro, Lenise G. de Oliveira (2006) Biodiesel from Castor Oil: A Comparison of Ethanolysis versus Methanolysis *Energy & Fuels* **2006**, *20*, 2262-2265

Ernesto Camilo Zuleta Suárez*, Jair David Bonet Oballe, Luis Carlos Díaz Mueque, Marlon José Bastidas Barranco (2008) Optimización del proceso de obtención de biodiesel a partir de aceite de palma y etanol, mediante el método de superficie de respuesta *Vol. 6, No. 1, Enero - Julio 75-80*

Hary Sulisty, Suprihastuti S. Rahayu, I M. Suardjaja and Umar H. Setiadi (2009) Crude Candlenut Oil Ethanolysis to Produce Renewable Energy at Ambient Condition Proceedings of the World Congress on Engineering and Computer Science 2009 Vol I, WCECS 2009, October 20-22, 2009, San Francisco, USA

Tao, L., Aden, A. (2009) The economics of current and future biofuels. *In Vitro Cell. Dev. Biol. Plant.*, *45*, 199-217

Carlos F. Torres, Charles G. Hill Jr., and Cristina Otero (2004) Lipase-Catalyzed Ethanolysis of Borage Oil: A Kinetic Study *Biotechnol. Prog.* *20*, 756-763 (modelo reactor enzimas)

Valle, P.; Velez, A.; Hegel.; Mabe, G.; Brignole, E.A. (2010) Biodiesel production using supercritical alcohols with non edible vegetable oil in a batch reactor. *J. Supercritical fluids.* *54*, 61-70

Weiyang Zhou and D. G. B. Boocock (2008) Phase behavior of the base-catalyzed transesterification of soybean oil *Journal of the American Oil Chemists' Society*, *83*, *12*, 1041-1045

West, A.H.; Posarac, D.; Ellis, N. (2008) Assessment of four biodiesel production processes using HYSYS. *Plant Bioresour. Technol.* *99*, 6587-6601

Wither, R.V., and Noordam. M. (1996) Biodiesel From Canola: An Economic Feasibility Analysis, *Liquid Fuels Conference*, September 1996, Nashville, Tennessee.

Yee TF, Grossmann IE. Simultaneous optimization models for heat integration--II. Heat exchanger network synthesis. *Computers & Chemical Engineering.* 1990;*14*(10):1165-1184.

Zhang, Y.; Dube, M. A.; McLean, D. D.; Kates, M. (2003) Biodiesel Production from Waste Cooking Oil: 1. Process Design and Technological Assessment. *Bioresour. Technol.*, *89*, 1-16.

Zhang, Y.; Dube, M. A.; McLean, D. D.; Kates, M. (2003) Biodiesel production from waste cooking oil: 2. Economic assessment and sensitivity analysis *Bioresource Technology* *90*, 229-240

http://www.caer.uky.edu/energeia/PDF/vol15_6.pdf (heat of reaction based on the composition of the oil)

Santana, G.C.S., Martins, P.F., Da silva, N. de Lima., Batistella, C.B., Filho, R.M., Maciel, M.R.W. (2010) Simulation and cost estimate for biodiesel production using castor oil. *Chem. Eng. Res. Des.* *88*, 5-6, 626-632