Towards the optimal integrated production of biodiesel with internal recycling of methanol produced from glycerol

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Abstract.

In this paper, we present the optimization of the production methanol from glycerol and its integration in the production of biodiesel from algae. We propose a limited superstructure where the glycerol from biodiesel is first reformed for which steam reforming and autoreforming are evaluated. The gas obtained is cleaned up and its composition is adjusted in terms of the ratio CO / H_2 using three possible alternatives (bypass, PSA and water gas shift). Next, the removal of CO_2 is performed by means of PSA and the syngas is fed to the methanol synthesis reactor and the products obtained are separated. This synthesis is coupled with the production of biodiesel from algae using heterogeneous catalyzed reaction based on previous results. The optimization of the system is formulated as a Mixed Integer Non-linear Programming (MINLP) that is solved for the optimal production of biodiesel with recycle of methanol and simultaneous heat and water integration. The best process involves the use of autoreforming for a production cost 0f $0.61/gal, 3.34MJ/gal of energy consumption and 0.79gal/gal. The integrated process is $0.2/gal more expensive than the one that directly uses methanol but reduces in more than half the dependency of the process on fossil fuels.

Keywords: Energy, Biofuels, Hydrogen, Alternative fuels, Diesel, Fisher – Tropsch

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1.-Introduccion

The use of biomass to obtain liquid fuels has become attractive due to their compatibility with the current automobiles and petrol supply chains. However, the profitability of biofuels depends heavily on the economy of the byproducts. For some time glycerol has been a valuable byproduct in the biodiesel industry. However, the increase in the production of biodiesel results in an excess of glycerol with a limited market [1] reducing the price of glycerol to values below $0.102 /lb [2]. Under these expected revenues from glycerol, the production cost of biodiesel will increase at least $0.15/gal from the values presented by Martin & Grossmann [3], and thus its direct use to generate methanol for the process may become competitive in the concept of an integrated facility. Furthermore, the production of methanol from glycerol is also meant for reducing the dependency of biodiesel on fossil fuels.

The production of methanol from glycerol can be carried out using different paths. The most traditional is similar to the one that produces syngas from natural gas or coal, which can be traced back to the early 1900´s related to the Haber Bosch process and the Fischer Tropsch synthesis [4] . In order to generate the syngas out of the glycerol, a number of recent studies have evaluated the reforming of glycerol [5-8]. The gas resulting from this stage has to be further purified [9-14]. Next, the syngas reacts to produce methanol. The thermodynamics and kinetics of the process have been long studied [15-23]. In spite of the experience in methanol production, the mechanism is still not well understood [18, 19, 24]. Recently a new path to produce methanol from glycerol has been proposed with no reforming and operating at mild operating conditions, but requires the addition of hydrogen [25].

To improve the design and the energy efficiency as well as to decide whether it is profitable to produce methanol and reuse it for the production of biodiesel, mathematical optimization techniques can be used. The integration of biodiesel production, with a low investment cost, and the generation of methanol from glycerol, is a way to reduce the dependency on fossil fuel for the production of biodiesel. We propose a limited superstructure optimization approach where we first construct a flowsheet embedding the various process units involved in hydrogen production, and then consider alternatives for some of the processes. The particular feature is the modeling effort to obtain models for important equipment, in particular glycerol reformers, methanol reactor and biodiesel trasnesterification from experimental data to develop equation oriented models as function of operating variables, such as temperature or composition of the feed. The goal is to optimize the structure and the operating

conditions to maximize biodiesel integrating the use of the byproduct glycerol for the production of methanol due to the trasnesterification of the oil, while minimizing the energy input. The optimization of the system is formulated as a mixed integer nonlinear programming (MINLP) problem. We then design the optimal heat exchanger network of the resulting process followed by an economic evaluation to decide on the best technology. Finally, we design the optimal water network using the model by Ahmetovic and Grossmann [26] to evaluate the water consumption of the integrated process for further comparison. The integrated process developed in this paper will be compared to previous work by the authors where either glycerol is used as byproduct [3], or we simultaneously produce bioethanol and biodiesel form algae [27] to assess its competitiveness.

2. Overall Process Description

Figure 1 presents the integrated processes for the production of biodiesel from algae oil using methanol that is at least partially produced from the reforming of the biodiesel byproduct, glycerol. We can observe two main parts, the biodiesel production where not only the biodiesel (FAME) but also glycerol are produced, and a second section where the glycerol is reformed into syngas which is used to obtain methanol. In this section we describe the different process units involved in these two stages.

2.1.-Biodiesel production .

According to the results presented by Martín & Grossmann [3], the most promising transesterification technology for a flexible and robust operation in the production of biodiesel, independently of the raw material, uses an heterogeneous catalyst. Therefore, it is this technology the one that is considered. As it can be seen in Figure 1, the process starts from algae which are grown and harvested. The oils is extracted while the biomass is used for the production of energy. The oil is sent to trasnesterficiation. We mixing the raw materials, methanol and the oil, heat the mixture up to the operating conditions at the transesterification reactor (methanolysis) for the production of biodiesel. Next, the excess of methanol is separated to be recycled to the reactor while the mix of glycerol, biodiesel and oil is separated by gravity. The glycerol is sent to the process by which we produce methanol while the biodiesel is distilled. The methanol obtained is recycled to the transesterification reaction

where fresh methanol is also added. In section 3 we present the main modeling assumptions, while we refer the reader to the previous paper by the authors [3] for further reference regarding this process.

<u>2.2.-Methanol production from glycerol</u>

Once the glycerol is separated, see Figure 1, the production of methanol consists of five different parts. The first one the reforming of glycerol. Steam reforming and auto-reforming are evaluated. The last traces of hydrocarbons are removed in a PSA system with a bed of Silica gel.

Next, the composition of the syngas may need to be further adjusted in terms of CO, H_2 and CO_2 so that in the reactor the ratio of CO to H_2 is around 2 and the ratio $\dfrac{H_2 - CO_2}{CO + CO_2} \approx 2.1$ according to the results in the literature [21, 24, 28, 29]. In order to accomplish this objective water gas shift reactor, bypass and hybrid membrane / PSA for H_2 (with a bed of oxides) are considered [30]. The split fraction depends on the performance of the reforming stage.

Next, sour gases are removed. From the reforming of glycerol only CO_2 is present but we need to secure a concentration between 2 and 8% for the optimal operation of the reactor. A PSA system is considered together with a bypass [24, 31]. All these ratios must be kept at the entrance of the reactor.

Once the gas is purified, the methanol synthesis is carried out. Over a catalyst, typically $Cu/ZnO/Al_2O_3$, the synthesis gas consisting of H_2 , CO_2 and CO undergoes a series of chemical reactions in equilibrium the gas is transformed into methanol. The optimal working conditions (ratio of H_2 and CO and working temperature and pressure at the reactor) are optimized assuming that there is an equilibrium of the species in the reactor [15, 24,32] . Typical conversions per pass are of the order of 25%. Unreacted gases are separated from the methanol and recycled back to the reactor while the methanol is purified used at the transesterification reactor.
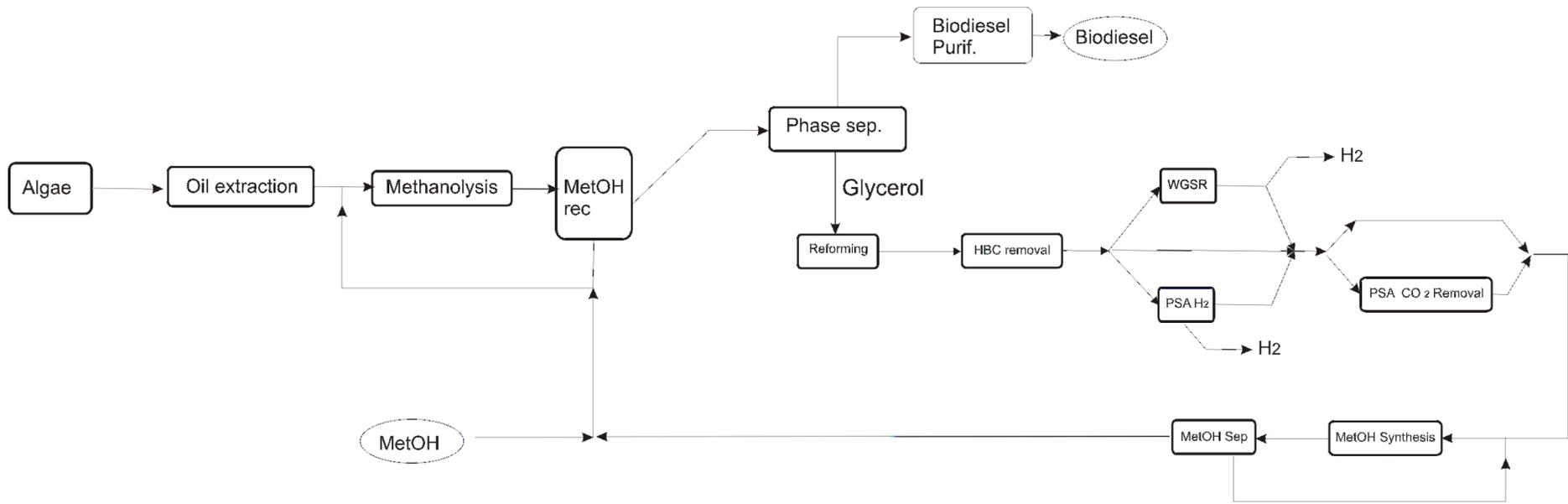
Figure 1.- Integrated production process for biodiesel production and glycerol recycling to produce methanol

3.-Mathematical modelling.

All the unit operations in the production process of liquid fuels and hydrogen from glycerol are modelled using surrogate models, design equations, 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 set of components is as follows J = { Wa, Glycerol, Methanol, Fame, Oil, CO2, CO, O2, N2, H2, CH4, C2H2, C2H4, Met, But, C}.The different units in the superstructure are modelled as described below. For the sake of the length of the paper we refer to previous papers by the authors [3, 33] for the details of the models for each equipment.

3.1.-Biodiesel production

The use of heterogeneous catalysts has proved to be flexible allowing the use of different raw materials, either cooking oil or algae oil, with very promising values of energy and water consumption and production cost [3] . These results are in part due to the fact that heterogeneous catalysts simplify the product purification stages since they can be easily separated or they can be packed in the reactor [34- 40] . Therefore, the process involves fewer units than other production processes such as the more common alkali catalyzed one, shown in Figure 1. For the sake of brevity, here we only present the model for the transesterification reactor in the description of the process to highlight the variables that we can control in the simultaneous optimization and heat integration, and we refer the reader to a previous paper [3]where the production of biodiesel is explained in detail

The reactants, namely oil and methanol, are mixed and heated up in mix 6 and HX 13 and fed to the transesterification reactor (methanolysis). The model of the reactor, given by eq. (1) predicts, the yield towards biodiesel (FAME) as function of the temperature, the catalyst load and the methanol ratio. Eq. (1) has been developed using experimental data in the literature [39]. The reaction time is fixed to 2h. Other models [40] are also available but they do not consider the effect of the temperature. Table 1 presents the bounds for the operating conditions.
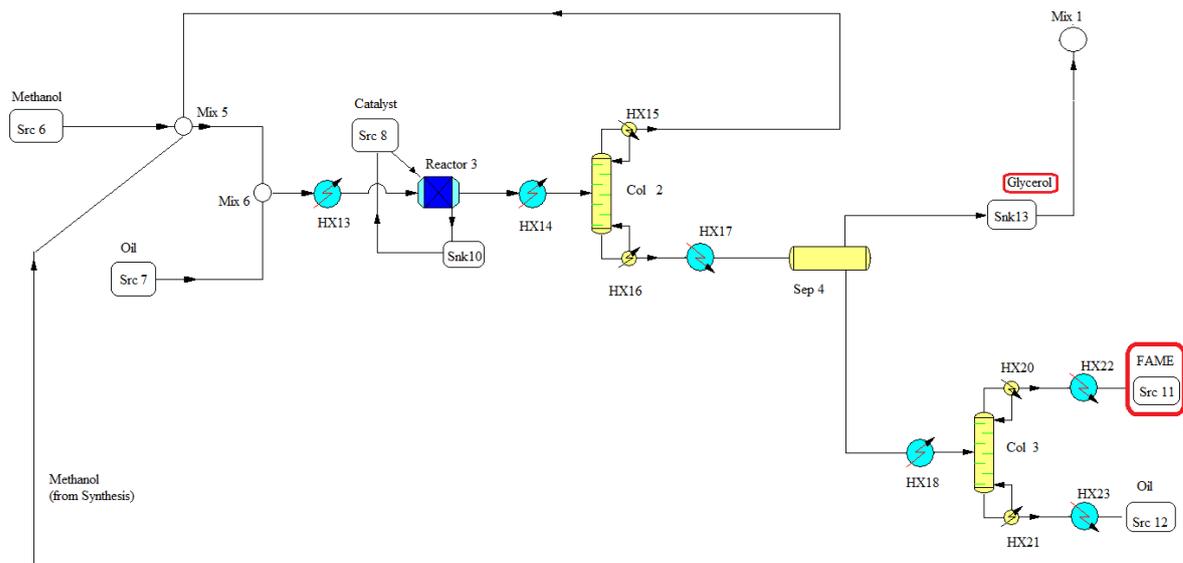
Figure 2.- Flowsheet for the production of biodiesel from oil via heterogeneous -catalyzed transesterification

$$yield = -73.6 + 2.5 * T(HX13, Reactor3) + 24.9 * Cat + 8.8 * ratio\_met - 0.01 * T(HX13, Reactor3)^2 - 1.29 * Cat^2 - 0.39 * ratio\_met^2 - 0.26 * T(HX13, Reactor3) * Cat \qquad (1)$$

Table 1.-Range of operation of the variables. Heterogeneous catalized

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

The energy involved in the reaction is calculated from the experimental results in the literature [3]. The stream exiting the reactor is distilled in column 2 to recover the excess of methanol so that it is recycled back to the reactor. A short cut method [41] is used to model all the distillation columns. The main features of the operating conditions are defined so as to avoid thermal decomposition of the different species and take into account the presence of two phases in terms of the vapour pressure calculation. To recover the methanol, the temperature at the bottoms cannot exceed 150ºC to avoid decomposition of the glycerol. Furthermore, at least 94% of the methanol is assumed to be recovered. These facts define the working pressure of column 2. The reflux ratio is key to determine the energy requirement for recovering the excess of methanol. Thus, based on the results by Dhar & Kirtania [42] we assume that the reflux ratio is within the range of 1 to 3, and it has to be always

greater or equal to the minimum reflux ratio as given by the Fenske equation assuming that the distillation involves 2 components, methanol and glycerol.

The bottoms are cooled down to 40ºC in HX7 before phase separation. To separate the aqueous phase from the oil phase, we consider a gravity separation step that allows the recovery of glycerol with a purity higher than 92% [43], while the biodiesel is purified in a distillation column (column 3). In this column, the temperature of the distillate and that of the bottoms have an upper bound to avoid product decomposition. The main challenge is to work below atmospheric pressure so that the distillate containing biodiesel exits the column below 250ºC to maintain biodiesel integrity, while the oil should remain below 350ºC. A short cut model is used for this column assuming variable reflux ratio from 2 to 3 [43].

3.2.-Gylcerol Reforming

Figure 3 shows a subset of the flowsheet presented in Figure 1 for the production of methanol from glycerol embedding the different alternatives.
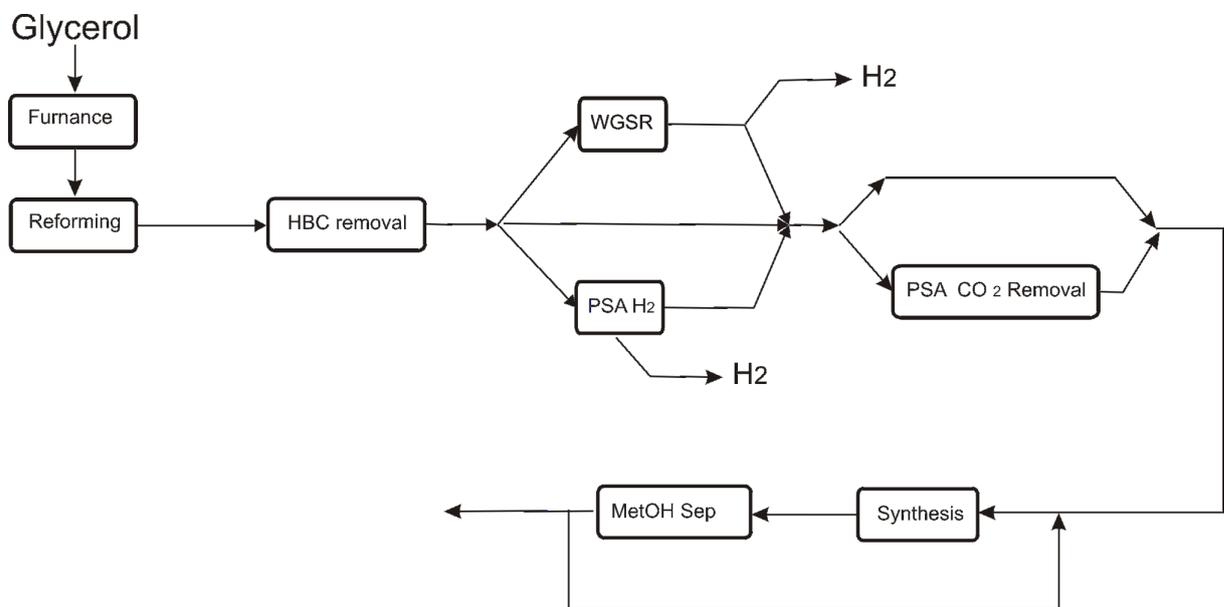
Figure 3.- Flowsheet for the production of hydrogen and FT-Fuels

The glycerol is fed to a furnace to heat it up and have it gasified. In this paper we consider steam reforming and auto-reforming to obtain raw syngas as, seen in Figure 4. Steam reforming is an endothermic process with high yield to hydrogen. On the other hand, autoreforming is a process which combines steam

reforming and partial oxidation so that the oxidation of part of the raw material provides energy for the steam reforming [44]. In order to develop the equation-oriented models, experimental data from the literature is used, see Martin & Grossmann [33] for further details.
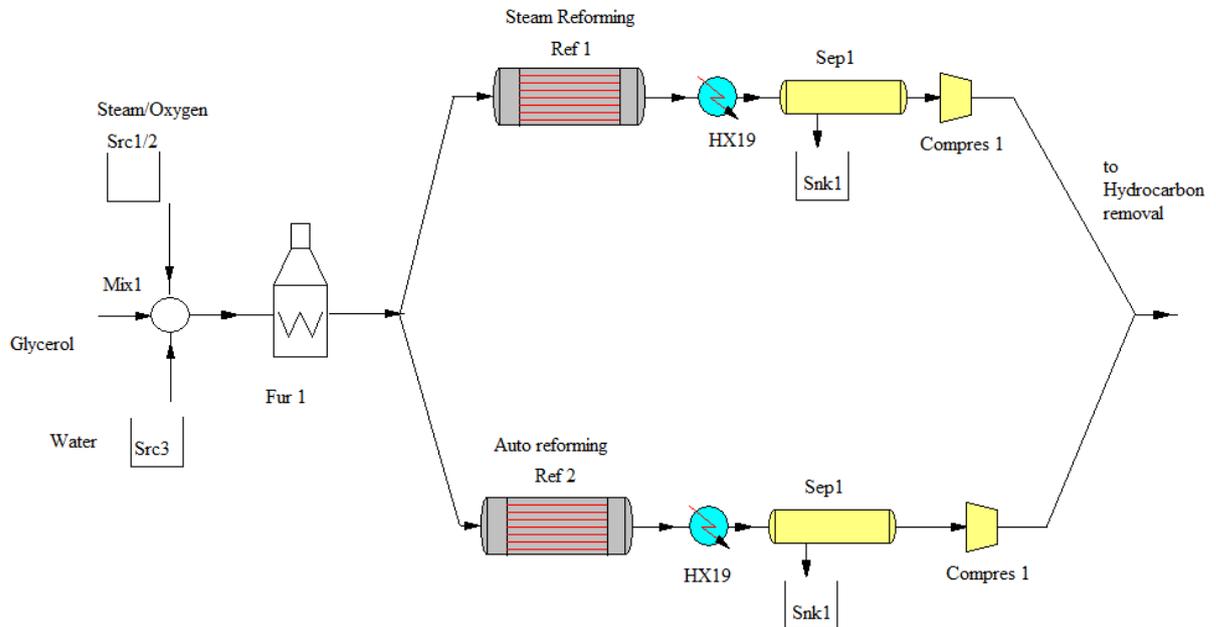
Figure 4.- Detail of the reforming alternatives

3.2.1.-Autoreforming

The chemical reaction taking place is of the form given by eq. (2). The mass balances to the species in the reformer are calculated based on the experimental results by Douette et al [6]. The experimental data shown in that paper are used to obtain a surrogate model for the reformer as function of temperature and feed composition (steam and oxygen added) . The model performs atomic balances to determine the species formed at the reformer. The complete model for autoreforming can be seen in Martín and Grossmann [33]

$$C_nH_m + xH_2O + yO_2 \longrightarrow aCO + bH_2 + cCH_4 + dCO_2 + eH_2O + ... \tag{2}$$

3.2.2.-Steam reforming

The stream coming from the furnace will be fed to the reformer. In this case the reactions taking place are of the form given by eq. (3).

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$$C_nH_m + nH_2O \longrightarrow nCO + (\frac{m}{2} + n)H_2 \qquad (3)$$
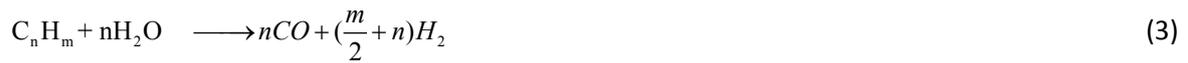
The model to predict the product gas composition is obtained from the results presented by Adhikari et al. [5]. The figures shown in that paper are used to obtain the data for the gas composition as function of the temperature and the steam added. The profiles of the gas composition as function of the temperature and the added steam are complex, and simple correlations are not enough to predict the outlet gas. A parameter estimation subproblem is defined based on a two step approach that is used to correlate the outlet gas as function of the temperature and the added steam. First, for each of the amounts of added steam, we correlate the outlet gas (CO, CO_2, H_2 and CH_4) as function of the temperature. Next, we include the effect of the ratio of steam added. The fitting of the experimental data with these equations was satisfactory as reported in the previous work [33]

3.3.-Clean up
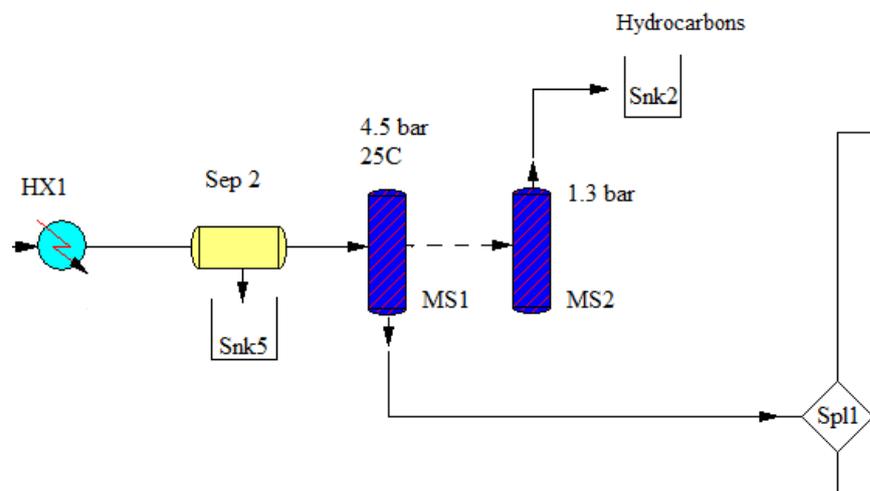
Figure 5.-Final hydrocarbon removal.

The traces of hydrocarbons generated in the reforming are withdrawn from the gas stream using a PSA system. The typical working conditions for PSA systems are low temperature (25 ºC) and moderate pressure (4.5 bar) so that there is adsorption of the different components on the bed [45]. Typically a bed of silica gel is the most appropriate for the removal of hydrocarbons. We assume that the PSA retains any hydrocarbon left in the

gas stream. Thus, we assume that the removal efficiency is 1 for hydrocarbons and nitrogen if present. Due to the low temperature, more water condenses in HX1 and it is discharged as seen in Figure 5

3.4.-Hydrogen production / Composition adjustment

Once the main contaminants are eliminated, the ratio between CO and H_2 may need to be adjusted so that the feed to the reactor is appropriate for the optimal production of methanol. In order to perform such adjustment, three alternatives are presented as seen in Figure 6. The first one is the use of water shift to reduce the amount of CO by producing more H_2. The second is a bypass. Finally, a hybrid membrane / PSA system with a bed of Zeolite 13X to remove the excess of hydrogen. It is possible that this surplus of hydrogen is sold to increase the profitability of the process [31, 46, 47].

Water Gas Shift.: The reaction taking place in the water shift reactor is widely known:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \tag{4}$$

The conversion is calculated using the model developed from the experimental data by Choi et al. [48] as function of the molar ratio of water to CO (H2O to CO) and the operating temperature. Eq.(5) was proposed by Martin and Grossman [49] to model the conversion in the reactor. The optimization determines the addition of water as well as the temperature and the conversion of the reaction. The model for the reactor is as follows:

$$CO\_shift\_conv = \frac{\left(0.0044 \cdot T\left(HX8, Reactor1\right) + 0.0924\right) \cdot H2OtoCO}{\left(H2OtoCO + \dfrac{46815}{T\left(HX8, Reactor1\right)^2}\right)}; \tag{5}$$

Thus, the products of the reactor are calculated as function of the conversion in the reactor and the stoichiometry given by eq. (4). The energy involved in the reaction is given by the heat of reaction and the conversion reached in the reactor.

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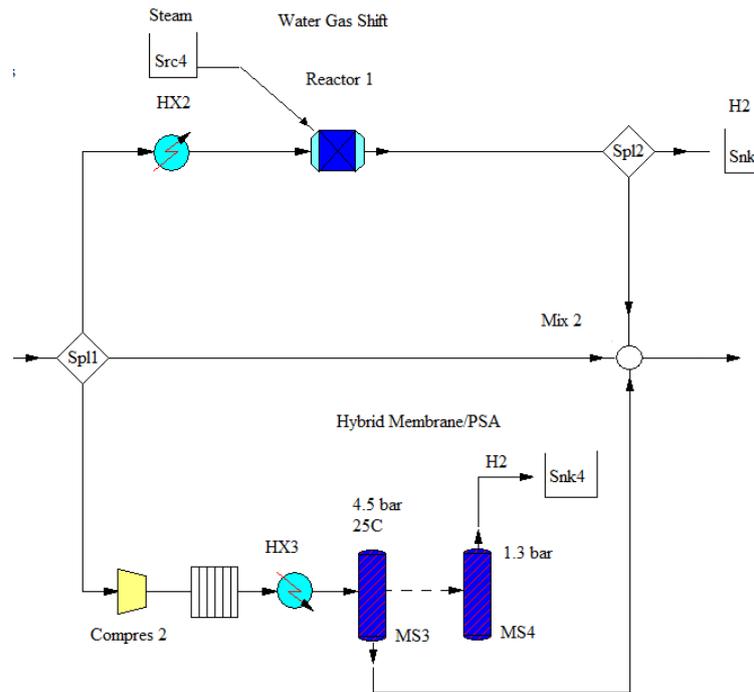
Figure 6.- Superstructure for the composition adjustment

Bypass: It may be possible that the stream does not need any adjustment in the CO:H_2 ratio due to the operating conditions at the reformer. Thus, a bypass is also allowed.

H_2 Membrane / PSA system: The stream to be treated in the membrane / PSA system for the recovery of pure hydrogen [50] will have to be adjusted in terms of temperature to 25 ºC, and pressure of 4.5 bar assuming that there is a 10% loss in the previous PSA system. The compression is modelled assuming polytropic behaviour to determine the final temperature and energy required. As a result of the cool down, water condenses in HX 10. The amount condensed is determined by the saturation conditions of the exiting gas. In this PSA it is assumed that only hydrogen is eliminated from the stream with an efficiency of 1 (100%). The other gases pass though. Finally, all the streams mix adiabatically.

3.5.-CO$_2$ removal by PSA system.

CO$_2$ must be partially removed from the gas stream to achieve the values recommended in the literature at the reactor from 2% to 8% in volume (Lee 2007). In order to achieve this concentration, we consider a bypass so that only part of the gas stream is treated in a PSA system to absorb the excess of CO$_2$ using Zeolite 5A or 13X. We assume that the removal of CO$_2$ is up to 95% of that in stream [31, 51, 52]. Figure 7 shows a scheme of

the process. The cycle is short the absorption capacity is around 0.1kg of CO_2 per kg of zeolite. The system is modelled as two beds, one operating and the second one in regeneration to allow continuous operation of the plant. The operating conditions are 25 ºC and 4.5 bar. Next, a three stage compressor with inter cooling is used, to adjusts the operating pressure to the one required at the reactor. Due to the high operating pressure at the reactor, from 50 to 100 bar, we consider a three stage compression system
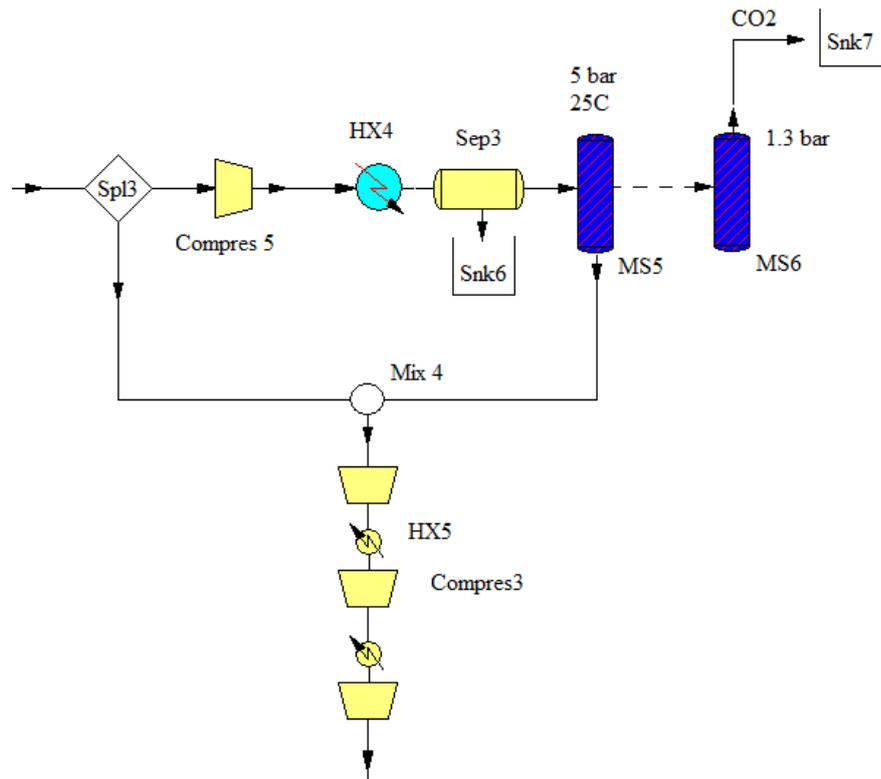
Figure 7.- PSA system for the removal of CO_2

3.6.-Methanol synthesis

Figure 8 presents the detail of the reaction and recycle flowsheet.. At present, methanol is produced from synthesis gas (a mixture of CO_2 , CO and H_2) and the reaction is catalyzed by a catalyst composed of (CuO $-ZnO -Al\,O$). The three main reactions that take place are the following:

$$CO + H_2 \leftrightarrow CH_3OH$$
$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad\qquad (6)$$
$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$$

13
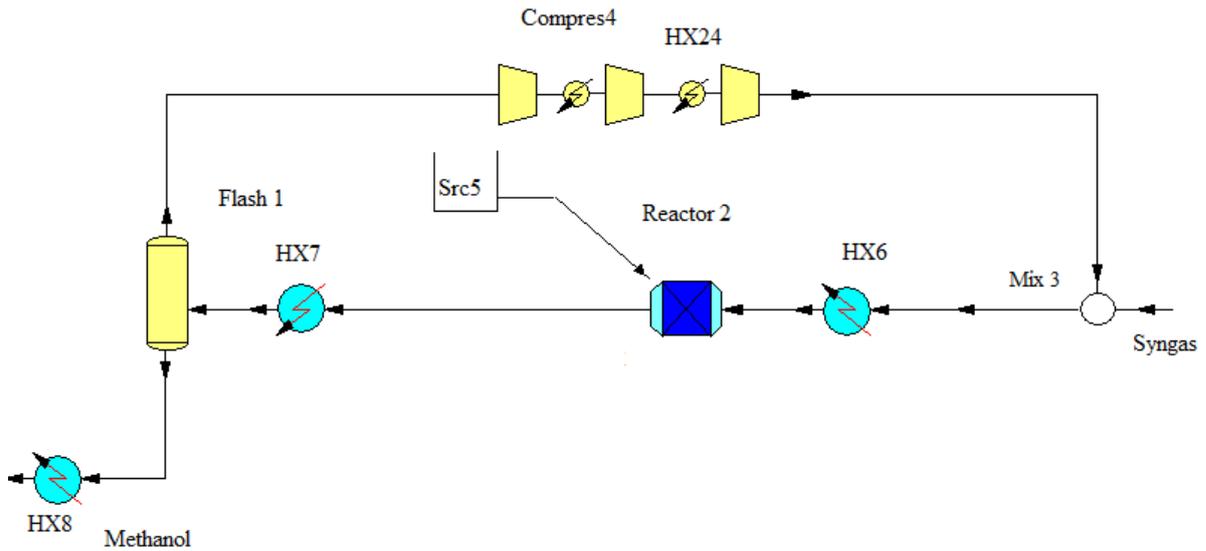
Figure 8.- Methanol synthesis section

However, since only two of the reactions are linearly independent we consider the reactions in equation (7):

$$CO + 2H_2 \leftrightarrow CH_3OH$$
$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

(7)

The equilibrium constants are given by the experimental results of Cherednichenko and Bisset [15, 32], respectively, with P in bars and T in K as presented by eqs. (8)-(9)

$$\frac{\left[P_{CH_3OH} \right]}{\left[P_{CO} \right]\left[P_{H_2} \right]^2} = 10^{\left[\frac{3971}{T} - 7.492 LogT + 1.77x10^{-3}T - 3.11x10^{-8}T^2 + 9.218 \right]}$$

(8)

$$\frac{\left[P_{CO} \right]\left[P_{H_2O} \right]}{\left[P_{CO_2} \right]\left[P_{H_2} \right]} = Exp\left[13.148 - \frac{5639.5}{T} - 1.077\ln T - 5.44x10^{-4}T + 1.125x10^{-7}T^2 + \frac{49170}{T^2} \right]$$

(9)

The reaction is favored by low temperatures and high pressures. Today's synthesis processes take place at low pressure (50-100 bar) since these processes use far less energy than the ones with high pressure as the synthesis gas compression is a costly operation. Furthermore, although the equilibrium conditions favor low temperatures, methanol converters must be operated at temperatures in the range 200–300 ∘C to ensure the

catalysts are active and to use the heat of reaction effectively [4, 21, 24, 28, 29, 31, 53]. Furthermore, the atomic mass balance must hold:

$$\text{H:} \quad \begin{aligned} & 2*\text{molh2} + 2*\text{molh2o}\big|_{in} \\ & -\left(2*\text{molh2} + 2*\text{molh2o} + 4*\text{molch3oh}\right)\big|_{out} = 0; \end{aligned} \tag{10}$$

$$\text{C:} \quad \begin{aligned} & \text{molCO} + \text{molCO2}\big|_{in} \\ & -\left(\text{molCO} + \text{molCO2} + \text{molch3oh}\right)\big|_{out} = 0; \end{aligned} \tag{11}$$

$$\text{O:} \quad \begin{aligned} & \text{molCO} + 2*\text{molCO2} + \text{molh2o}\big|_{in} \\ & -\left(\text{molCO} + 2*\text{molCO2} + \text{molh2o} + \text{molch3oh}\right)\big|_{out} = 0; \end{aligned} \tag{12}$$

There are two main operating variables that the feed to the reactor must meet for the optimal production of methanol, eqs. (13) and (14)

A) The ratio hydrogen to CO [31]

$$1.75 \leq \frac{H_2}{CO} \leq 3 \tag{13}$$

B) The role of CO_2 in the reaction mechanism has been and still is a subject of discussion in the literature. Its contribution in reaction models is certainly not well reflected. However, it is considered that the concentration of CO_2 should be 2% to 8% [4, 24] and the ratio of the syngas components involving CO_2 [31, 29] should be:

$$1.5 \leq \frac{H_2 - CO_2}{CO + CO_2} \leq 2.5 \tag{14}$$

The conversion is usually low and methanol and water must be separated from the gases, hydrogen, CO and CO_2 in a flash separation. The gases are recycled to the reactor and recompressed while the methanol must be purified, typically molecular sieves to remove the water since most of the water was condensed before the synthesis reactor. We consider the flash model [41] to determine the phase separation as function of the pressure and temperature.

3.8.-Solution procedure.

The MINLP problem is decomposed into 2 NLP's subproblems of about 2100 equations and 2300 variables each, one for each reforming mode, In that sense we will evaluate the production of methanol using each of the reforming technologies either autoreforming or steam reforming.

Each of the subproblems is solved as an NLP, which simultaneously optimizes the operating conditions such as the ratio CO/H_2 to be used at the reactor, the working temperature and the steam added at the WGSR, and the operating pressure and temperature at the methanol reactor, and the operating conditions at the transesterification reactor. The objective function to be maximized is given by a simple manufacturing cost involving the production of biodiesel, the cost of the methanol to be bought and the use of energy. We consider \$1/kg of liquid fuel biodiesel by default.

$$Z_{SR} = C_{FAME} * \mathrm{fc}(FAME) \ - C_{Cat\_Het} * \text{Catadded} - \ C_{MetOH} * \mathrm{fc}(MetOH)$$
$$- (0.06/3600) \cdot (\sum_i W(Compres_i)) \ -0.0005 \cdot 0.019 \cdot (Q + \mathrm{fc}(Wa, Reactor1) \cdot \lambda + \mathrm{fc}(Wa, Furnance) \cdot \lambda) \quad (15)$$
$$-4.687 \cdot 1.055 \cdot 0.000001 \cdot Q(Furnance)$$

$$Z_{AR} = C_{FAME} * \mathrm{fc}(FAME) \ - C_{Cat\_Het} * \text{Catadded} - \ C_{MetOH} * \mathrm{fc}(MetOH) \ - (0.06/3600) \cdot (\sum_i W(Compres_i))$$
$$-0.0005 \cdot 0.019 \cdot (Q + \mathrm{fc}(Wa, Reactor1) \cdot \lambda + \mathrm{fc}(Wa, Furnance) \cdot \lambda) \ -4.687 \cdot 1.055 \cdot 0.000001 \cdot Q(Furnance) \quad (16)$$
$$-0.021 \cdot \mathrm{fc}(O2, Furnance)$$

Thus, the main decision variables are the split fraction at the water gas shift reactor and hydrogen PSA system for the composition adjustment, the water gas shift operating conditions (temperature and steam needed) the operating conditions at the methanol synthesis reactor (temperature and CO/H_2 ratio) and at the furnace. Heat integration is performed using the Duran & Grossmann [54] model, and next we design the optimal heat exchanger network using SYNHEAT [55]. 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 the method by Sinnot [56] method; see also previous papers by the authors [30] for further details.

Finally, we develop the water network based on the work by Ahmetovic and Grossmann [26] and Martín, et al [57] to compare the results of water consumption with those presented in the integrated production of ethanol and biodiesel [27].

4.-Results and discussion.

The size of the plant is based on the production of biodiesel production facilities [3], 68 Mgal/yr of biodiesel. The economic evaluation is carried out based on the method by Sinnot [54] and input from industry as in previous papers by the authors [30]. The economic objective accounts for annualized equipment cost, management, labour, chemicals and utilities, which are updated from the literature (0.019$/kg Steam, 0.057$/ton cooling water, [58] 0.06$/kWh [59]; 0.021$/kg Oxygen, [60]) The cost of hydrogen is taken to be $1.6/kg based on DOE data, the cost of natural gas is $4.687/ Million BT [49, 61] Finally, the cost correlations for the different equipment can be found in the supplementary material of Martin and Grossmann [30]

Table (2) presents the main characteristics of the process. The optimal process involves the use of autoreforming. The theoretically maximum methanol produced out of 1 kg of glycerol is 0.70 kg where a molecule of CO must be released. The yield obtained by autoreforming (0.66 kg/kg) is close to 92% of the maximum theoretical yield even though we add steam and oxygen to the reformer to perform the decomposition of glycerol. Furthermore, the operating conditions at the transesterification reactor differ to the ones presented in the stand alone process [3] for the case of the autoreforming due to the improved heat integration of the whole process using this values while for the case of the steam reforming the values are similar. In terms of the operating conditions of the methanol synthesis reactor, the values obtained are close to the ones reported in the literature.

Table 2.- Process characteristics for methanol production and recycling from glycerol

	AR	SR
Ratio met	6.57	10.5
Cat	3.27	1
Temp (ºC)	60	60
O_2 added(mol/mol)	0.206	NA
Steam added (mol/mol)	0.5	0.613
Temperature(ºC)	700	629
R2 Temperature (ºC)	200	200
React. Pressure (bar)	50	50
H_2/CO	2.2	2.2
$\dfrac{H_2 - CO_2}{CO + CO_2}$	2.1	2.1

The economic evaluation and the design of the optimal water network yields the results shown in Table 3 for both alternative reforming modes. In Figure 9 we see the distribution of cost for the optimal alternative. We have a small amount of hydrogen as by product of the conversion of glycerol to methanol

Table 3.-Summary of results

	Autoreforming	Steam Reforming
$/gal_{biofuel}$	0.66	0.69
Energy (MJ/gal_{biofuel})	3.65	3.71
Water (gal/gal_{biofuel})	0.79	0.79
Investment (MM$)	118	121
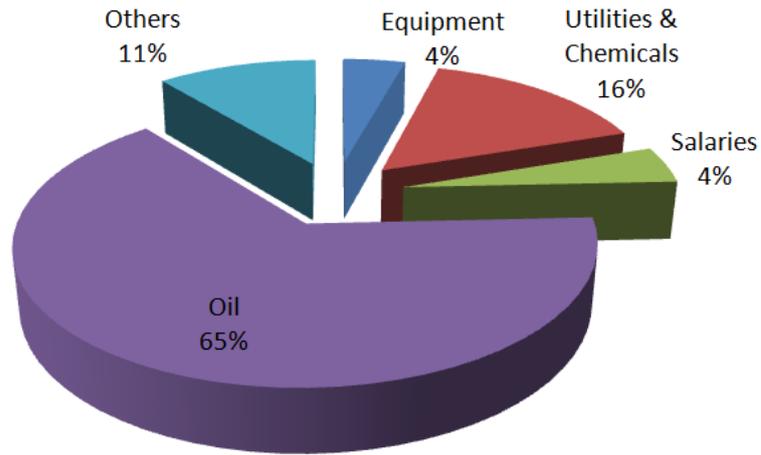
Figure 9.- Distribution of cost for the integrated production of biodiesel while recycling the methanol. Autoreforming

At the beginning of the paper it was mentioned that if the glycerol price decreases down to $0.102/lb, the production costs presented in Martín & Grossmann [3] for the production of biodiesel using methanol increase by $0.15/ gal to reach values of $0.6/gal (in case of using oil from algae). In Figure 10 we present the effect of the cost of glycerol on the production of biodiesel using an heterogeneous catalysis. We see that the integrated process is more expensive even for small glycerol costs even with the already low prices for glycerol $0.06/lb [62] In terms of the investment cost, the production of biodiesel and methanol from glycerol is slightly higher than that of the production of biodiesel from algae alone (110 MM$, [3]) reaching 118MM$ and 121 MM$ for the autoreforming and steam reforming options, respectively, with the same production level of biodiesel of 68.5 Mgal/yr. In spite of the higher investment and production costs, the use of glycerol presents the advantage of reducing the dependency of biodiesel on fossil fuels, since the process relies on a lesser extent to fossil fuel based methanol.
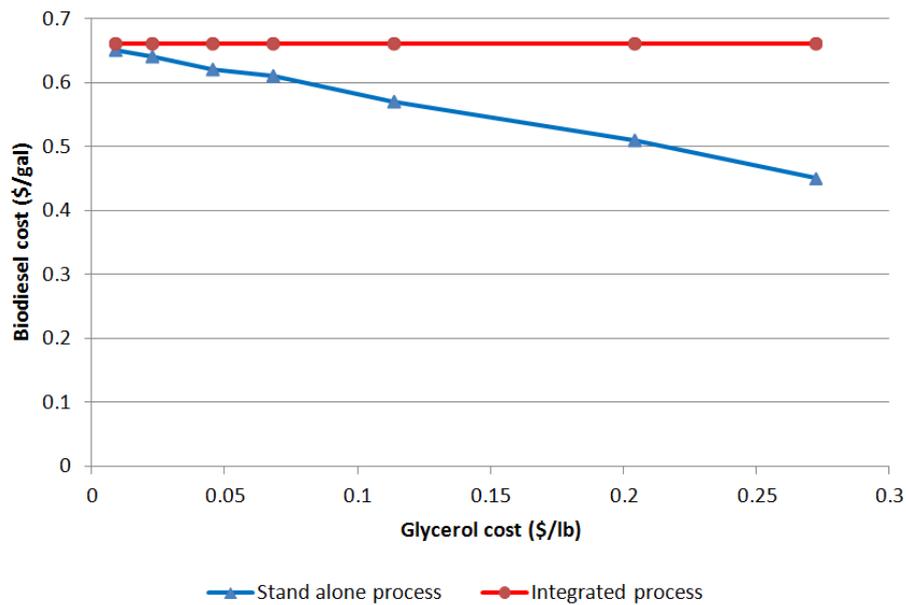
Figure 10.- Comparative costs of biodiesel production cost using glycerol as byproduct or integrating it towards methanol

There is another interesting comparison between integrated processes. For many years, the use of methanol for the production of biodiesel was supported on its lower price due to its production from natural gas. Recently, Martín & Grossmann [27] presented the simultaneous production of bioethanol and biodiesel from algae. Table (4) summarizes the production costs as well as the energy and water consumption [27]. Comparing the results in Table 3 with those in Table 4 we can see that the simultaneous production of ethanol and biodiesel is more economical and rather close in terms of energy and fresh water consumption. Thus, the use of methanol is no longer the clear option for the production of biodiesel. As it is presented in this paper, within an integrated bio-facility it makes perfect sense to use ethanol for the transesterification of oil. If we compare the investment costs for the integration of bioethanol and biodiesel [27] with those of biodiesel with recycling the glycerol to produce part of the methanol required, this last option has lower investment cost per gallon of biofuel produced, around 1.73 $ invested / gallon produced compared to 2.00 $ invested per gallon produced, but we still depend on a certain supply of fossil fuel based methanol to obtain biodiesel.

Table 4.-Summary of results

	Alkali cat	Enzymatic
$/gal$_{biofuel}$	0.32	0.35
Energy (MJ/gal$_{biofuel}$)	6.72	4.00
Water (gal/gal$_{biofuel}$)	0.77	0.59

5.-Conclusions

The superstructure modelling for the integrated production of biodiesel has been formulated as a MINLP. The problem is solved by decomposing the MINLP into two NLP's, one for each reforming mode. Each subproblem is optimized to determine the operating conditions at the reformer, the methanol synthesis reactor, the WGSR and the transesterification reactor.

The optimal process involves the use of autoreforming for the synthesis of methanol from glycerol for a production cost of $0.66/gal, consuming 3.65 MJ/gal and 0.79 gal of freshwater per gal of biodiesel produced. Hydrogen is obtained as byproduct of the methanol synthesis.

The results reveal that the integrated production of biodiesel and glycerol recycling to methanol is still more expensive even in the scenario of the reduced the glycerol price expected by the NERL. However, the integrated process is a promising option in our search for decreasing our dependency on fossil fuels since we can provide more than half the methanol needed for the process. Finally, the use of bioethanol for the production of biodiesel, traditionally discarded due to its higher price compared to methanol, becomes promising when methanol is to be produced from renewable raw materials not only in terms of production cost but also due to the lower energy and freshwater needs.

Acknowledgments

6.-Nomenclature.

atomh   atoms de hydro

atomo   atoms de Oxygen
atomc   atoms de Carbono
ni   mol of component i
CO_shift_conv   Conversion of CO in the water shift reactor
COtoH2   Molar ratio CO and H2 at mix1
COtoH2   Molar ratio CO and H2 at mix1
fc(j,unit1, unit2)   individual mass flow rate (kg/s)
F(unit1,unit2)   mass flow rate (kg/s)
H2OtoCO   Molar ratio H2o and Co
Oxygen_add   (mol steam per mor of carbon)
Pi: Partial pressure of component i.   (bar)
steam_add   mol steam per mo of carbon
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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