Optimal Simultaneous Production of Hydrogen and Liquid Fuels from Glycerol: Integrating the Use of Biodiesel Byproducts

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Abstract.

In this paper, we present the optimization of the production of hydrogen and/or liquid fuels from glycerol. We propose a limited superstructure embedding the alternative technologies involved. Glycerol is first reformed using either aqueous phase reforming, steam reforming or autoreforming. The gas obtained is cleaned up and its composition is adjusted in terms of the ratio CO / H_2 (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 Fischer - Tropsch reactor. The products obtained are separated while the heavy products are hydrocracked. The optimization of the system is formulated as a Mixed - integer Non-linear Programming (MINLP) that is solved first for the optimal production of hydrogen alone, and next for the simultaneous production of liquid fuels and hydrogen. The production of hydrogen is competitive with that obtained from switchgrass as long as the glycerol price is below \$0.05/lb using aqueous phase reforming, while for the liquid fuels to be attractive the price needs to be below \$0.025/lb using auto reforming.

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

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1.-Introduccion

The use of biomass to obtain liquid fuels has attracted interest due to their compatibility with the current automobile and gasoline supply chains. However, the profitability of biofuels depends heavily on the economy of the byproducts. This is the case of corn ethanol, where the DDGS provide an important credit (Karuppiah et al., 2008), or the lignocellulosic based ethanol, in which case the hydrogen produced is an important asset (Martín & Grossmann, 2011a). In the case of biodiesel obtained from the transesterification of oil (vegetal, cooking oil or the one obtained from microalgae (Martín & Grossmann, 2012), glycerol is a valuable byproduct of the reaction that can contribute to the profitability of the production process due to the large number of compounds that can be produced from it and its many potential applications (Pagliaro & Rossi, 2010; Fan et al 2010). Figure 1 shows the distribution of its use as ingredient for different products (Pagliaro & Rossi, 2010). The expected increase in the amount of glycerol produced resulting from the production of biodiesel presents a new scenario with the need to find new markets to the excess of glycerol with scope for the production of fuels. Among these fuels, hydrogen (Ahmed & Papadias, 2010) and FT-fuels (Wilhelm et al., 2001) are promising due to their straightforward use within the biorefinery. Furthermore, biodiesel production requires energy (Martín & Grossmann, 2012). Therefore, this is another incentive to increase the profitability and improve the energy balance of biodiesel production.
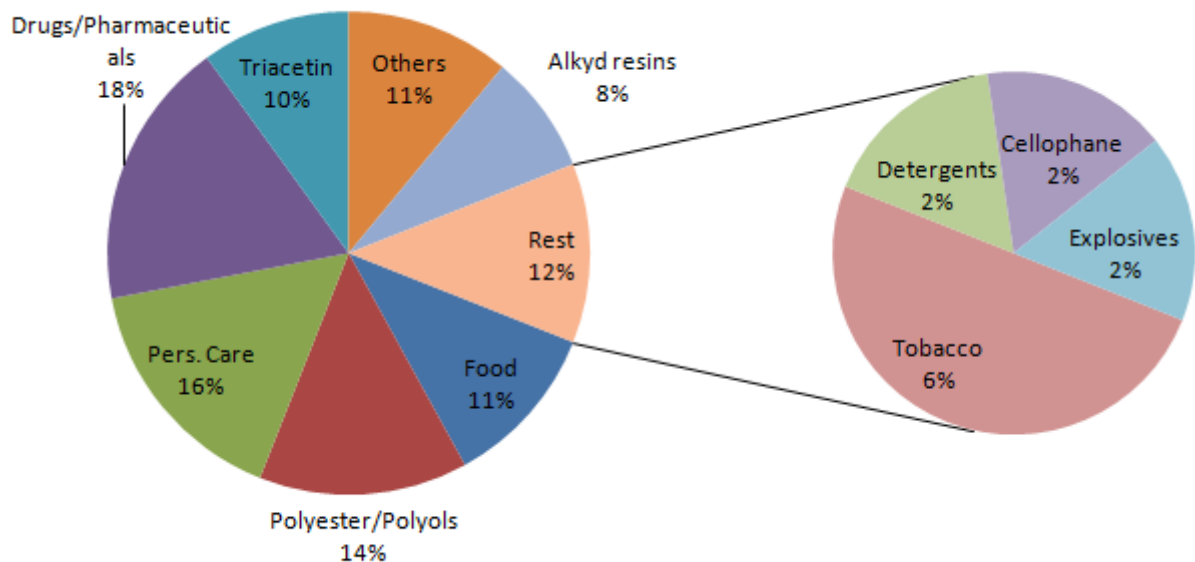

Figure 1.-Distribution of products obtained from glycerol

Hydrogen was first proposed as an energy carrier by Cecil (Cecil, 1820). Current developments on fuel cell technology for both stationary generation of electricity and for road transportation represent an important step towards energy security, where the hydrogen economy becomes key for the feasibility of the technology (Ahmed & Papadias, 2010). However, as any other alternative fuel, the availability and low cost of fossil fuels has slowed down their development (Cole, 2007; Ran and Dell, 2008)

On the other hand, the Fischer-Tropsch synthesis has been used in moments of difficult access to crude oil to produce synthetic gasoline and diesel from coal and it is now spreading to biomass and other sources of syngas (Swanson, 2010; Martín & Grossmann, 2011b).

In order to generate the syngas from glycerol, a number of recent studies evaluate the reforming of glycerol (Adhikari et al 2007; Douette et al 2007, Wang et al 2008, da Silva et al 2009). However, the gas resulting from this stage has to be further purified and converted (Mueller-Langer, 2007; Feng et al., 2009; Gao, et al., 2009;Ji et al., 2009a&b, Kunkes et al 2009).

In this paper, we focus on the simultaneous production of FT-diesel and hydrogen from glycerol so as to increase the yield to fuels from oil. To improve the design and the energy efficiency as well as to decide whether it is interesting to produce hydrogen, FT-liquid fuels or both, mathematical optimization techniques (Grossmann et al., 1999) are used in this work. We propose a limited superstructure optimization approach where we first construct a flowsheet embedding the various process units involved in hydrogen and synthetic liquid fuels production, considering various technological alternatives for some of the processes. The particular feature is the modeling effort to obtain models for the most important equipment, in particular glycerol reformers to develop from experimental data equation oriented models as a function of the operating variables, such as temperature or composition of the feed (Martín & Grossmann, 2012). These units are interconnected to each other through network flows and other utility streams. The goal is to optimize the structure and the operating conditions to maximize synthetic diesel production, while minimizing the energy input. The optimization of the system is formulated as a mixed-integer nonlinear programming (MINLP) problem, where the model involves a set of constraints representing mass and energy balances for all the units in the system. We then perform heat integration of the resulting process followed by an economic evaluation to decide on the best technology.

2. Overall Process Description

The process consists of five different parts. The first one is the reforming of the raw material. Three different technologies are evaluated: (1) steam reforming, (2) auto-reforming and (3) aqueous phase reforming (APR). The two first ones generate syngas operating at high temperature, while the last one generates only H_2 and CO_2 at a much lower temperature but it requires a large amount of liquid water. The last traces of hydrocarbons are removed in a PSA system with a bed of silica gel.

After reforming, the composition may need to be adjusted to a molar ratio of $CO : H_2$, from 1 to 2 according to the results by Wang et al (2008), or else hydrogen is obtained and purified. In order to do so a water gas shift reactor, bypass and hybrid membrane / PSA for H_2 (with a bed of oxides) are considered. The splitting fraction depends on the performance of the glycerol reformer.

The third part corresponds to the removal of sour gases, CO_2. According to the study by Martín & Grossmann (2011a), a PSA system with a bed of Zeolite 5A is recommended.

Once the gas is purified, the Fischer-Tropsch synthesis is carried out. Over a catalyst of iron or cobalt, the synthesis gas consisting of H_2 and CO undergoes a series of chemical reactions where it is transformed into liquid hydrocarbons. The optimal conditions (ratio of H_2 and CO and working temperature at the reactor) are to be optimized using the Anderson-Schulz-Flory (ASF) distribution (Schulz, 1999). Synthetic biodiesel is produced together with gasoline, gas products and heavy fuels (Opdal & Skreiberg, 2006). The working pressure is assumed to be 30 atm according to experimental results (Wang, 2008).

Finally, the FT liquids produced are separated from the gas products and fractionated using an atmospheric distillation column. The heavy oil is then hydrotreated in order to produce more diesel and gasoline. The results from Bezergianni et al. (2009) are used to provide a model for the hydrocraking of the heavy oil. Figure 1 shows the flowsheet embedding the different alternatives.
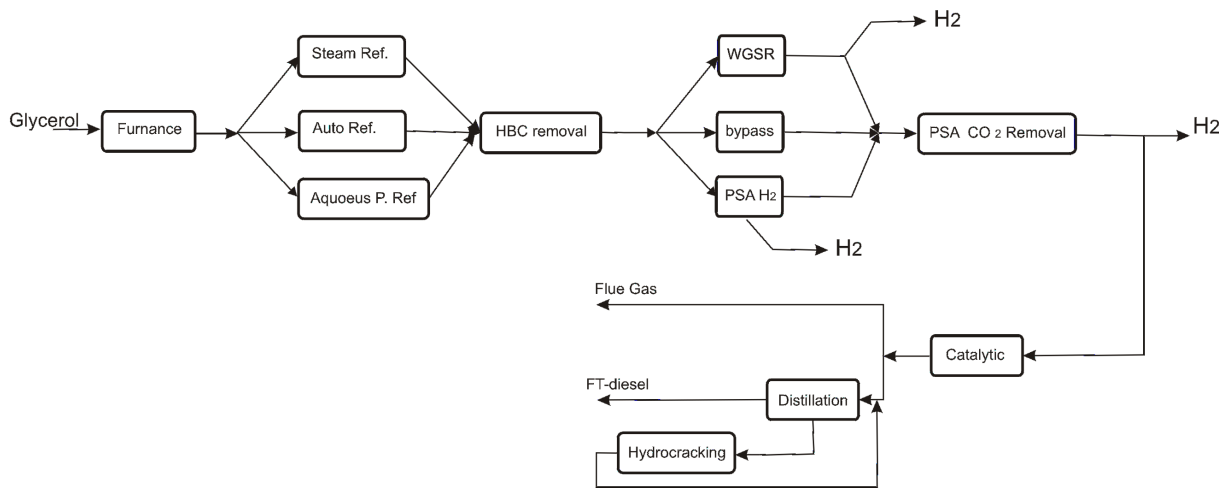
Figure 2.- Flowsheet for the production of hydrogen and FT-Fuels

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, pressures and temperatures of the streams in the network. The components in the system belong to the set J = { Wa, Glycerol, Gasoline, Diesel, Heavy, 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 reducing the length of the paper, we refer to previous papers by the authors for the detailed models of particular equipment related to gas treatment and FT synthesis (Martín & Grossman 2011a,b,c)

3.1.-Reforming

In this paper we consider three of the most promising reforming technologies to obtain a gas phase from glycerol. The first ones is steam reforming, an endothermic process with high yield to hydrogen The second one is autoreforming, a process which combines steam reforming and partial oxidation so that the oxidation provides the energy required for the steam reforming reactions (Rand & Dell, 2008). Finally, we consider aqueous phase, a method that produces only H_2 and CO_2 using water in liquid state (Shabaker et al., 2004). In order to develop the equation-oriented models, experimental data from the literature is used. The glycerol is fed to a furnace to heat it up and gasify it to a point depending on the reforming mode, see Figure 3. Eq. (3a) is used for steam and auto

reforming and eq. (3b) is used for aqueous phase reforming. Next, correlations for the composition of the different gas species are developed
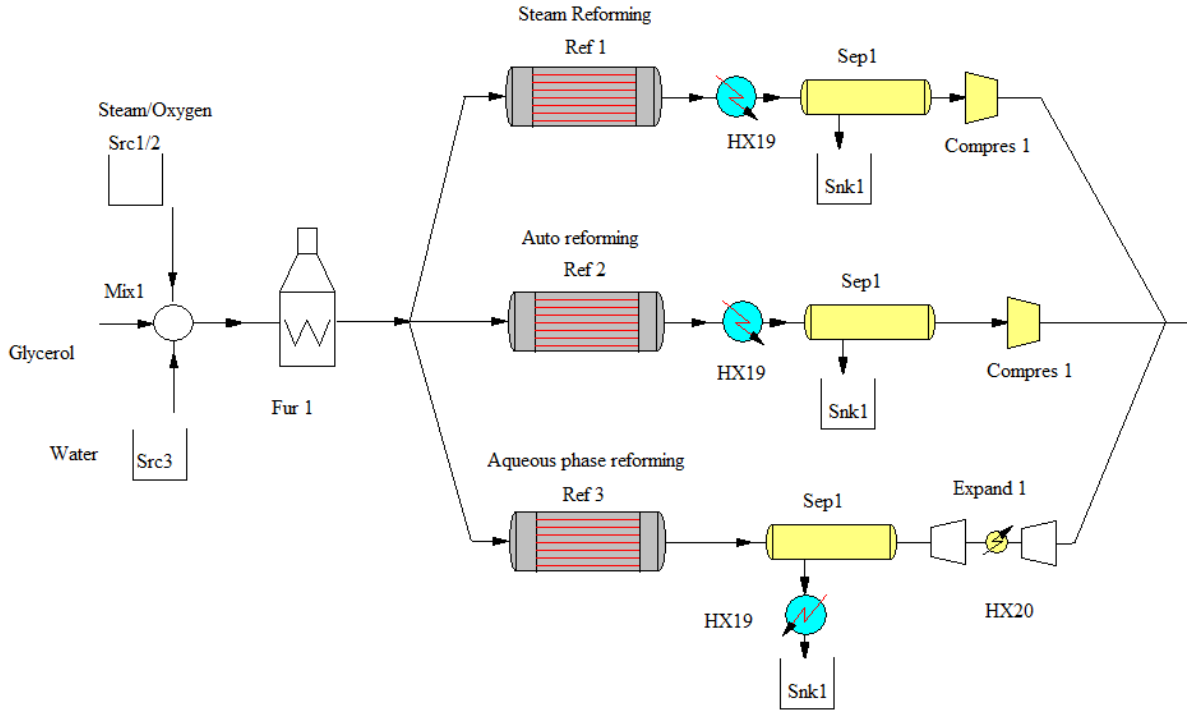

Figure 3 Detail of the reforming process

$$Q(\text{Furnance}) = \text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})*(c\_p\_\text{ind}(\text{Glycerol})*(\text{Tb}(\text{Glycerol}) - T\_\text{amb}) +$$

$$\text{dH}\_\text{vap}\_0(\text{Glycerol})\int_{\text{Tb}('\text{Glycerol}')}^{T_{Furnance}} c\_p\_v(j)dT) + \text{fc}(\text{Wa}, \text{Src2}, \text{Furnance})\int_{T\_\text{amb}}^{T_{Furnance}} c\_p\_v(j)dT + \qquad (3a)$$

$$\text{fc}(O_2, \text{Src2}, \text{Furnance})\int_{T\_\text{amb}}^{T_{Furnance}} c\_p\_v(j)dT)$$

$$Q(\text{Furnance}) = \text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})*(c\_p\_\text{ind}(\text{Glycerol})*(T(\text{Furnance,Ref})\text{-}T\_\text{amb}) +$$
$$\text{fc}(\text{Wa}, \text{Src1}, \text{Furnance})*(c\_p\_\text{ind}(\text{Wa})*(T(\text{Furnance,Ref}) - T\_\text{amb})) \qquad (3b)$$

3.1.1.-Autoreforming Oxidation (AR)

The chemical reactions taking place are of the form given by eq. (4). The mass balances to the species in the reformer are calculated based on the experimental results by Douette et al. (2007). The experimental data shown in Douette's paper are used to obtain a surrogate model for the reformer as function of temperature and feed composition (steam and oxygen added). The model fitting is shown in Figure 4. As can be seen, good agreement is found between eqs. (11)-(14) and the experimental data.

$$C_3H_8O_3 + xH_2O + yO_2 \longrightarrow aCO + bH_2 + cCH_4 + dCO_2 + eH_2O + \ldots \tag{4}$$
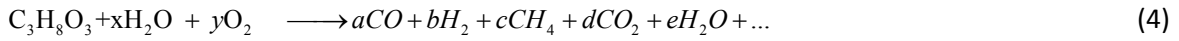
$$0 \le \text{Oxygen\_add} \le 0.8 \tag{5}$$

$$1 \le \text{steam\_add} \le 3 \tag{6}$$

$$700 \le T(\text{Furnance}, \text{Ref}) \le 1000 \tag{7}$$

$$\text{fc}(O2, \text{Src3}, \text{Furnance}) = \text{Oxygen\_add} * \frac{\text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})}{\text{MW}(\text{Glycerol})} * 3 * \text{MW}(O2); \tag{8}$$

$$\text{fc}(\text{Wa}, \text{Src2}, \text{Furnance}) = \text{steam\_add} \frac{\text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})}{\text{MW}(\text{Glycerol})} * 3 * \text{MW}(\text{Wa}); \tag{9}$$

$$\text{fc}(J, \text{Src2}, \text{Furnance}) + \text{fc}(J, \text{Src1}, \text{Furnance}) + \text{fc}(J, \text{Src3}, \text{Furnance}) = \text{fc}(J, \text{Furnance}, Ref); \tag{10}$$

The product gas composition is calculated using the correlations below:

$$\text{molh2} = \frac{\text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})}{\text{MW}(\text{Glycerol})} * (0.0909255 + 0.1018091 * \text{Oxygen\_add} + 0.1846624 * \text{steam\_add} +$$
$$0.0079854 * T(\text{Ref}) + 0.2262167 * \text{Oxygen\_add} * \text{steam\_add} -$$
$$0.0090133 * \text{Oxygen\_add} * T(\text{Ref}) - 0.0005252 * \text{steam\_add} * T(\text{Ref})$$
$$-0.000067076 * \text{Oxygen\_add} * \text{steam\_add} * T(\text{Ref}))$$
$$\tag{11}$$

$$\text{molCO} = \frac{\text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})}{\text{MW}(\text{Glycerol})} (0.4501756 - 1.7314193 * \text{Oxygen\_add} -$$
$$0.4162428 * \text{steam\_add} + 0.0039189 * T(\text{Ref})$$
$$+1.1865907 * \text{Oxygen\_add} * \text{steam\_add} - 0.001192 * \text{Oxygen\_add} * T(\text{Ref})$$
$$-0.000104 * \text{steam\_add} * T(\text{Ref}) - 0.0007666 * \text{Oxygen\_add} * \text{steam\_add} * T(\text{Ref}))$$
$$\tag{12}$$

$$\text{molCO2} = \frac{\text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})}{\text{MW}('\text{Glycerol}')} (0.3906452 + 0.2148554 * \text{Oxygen\_add} + 0.8711465 * \text{steam\_add}$$
$$+0.0008662 * T(\text{Ref}) + 0.4791314 * \text{Oxygen\_add} * \text{steam\_add}$$
$$+0.0013223 * \text{Oxygen\_add} * T(\text{Ref}) - 0.0008126 * \text{steam\_add} * T(\text{Ref})$$
$$-0.0007268 * \text{Oxygen\_add} * \text{steam\_add} * T(\text{Ref}));$$
$$\tag{13}$$

$$\text{molC}H4 = \frac{\text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})}{\text{MW}('\text{Glycerol}')} (-3.726e-8 - 3.773e-8 * \text{Oxygen\_add} - 3.108e-7 * \text{steam\_add}$$
$$+4.317e-5 * T(\text{Ref}) - 1.445e-7 * \text{Oxygen\_add} * \text{steam\_add}$$
$$+1.002e-5 * \text{Oxygen\_add} * T(\text{Ref}) + 9.767e-6 * \text{steam\_add} * T(\text{Ref})$$
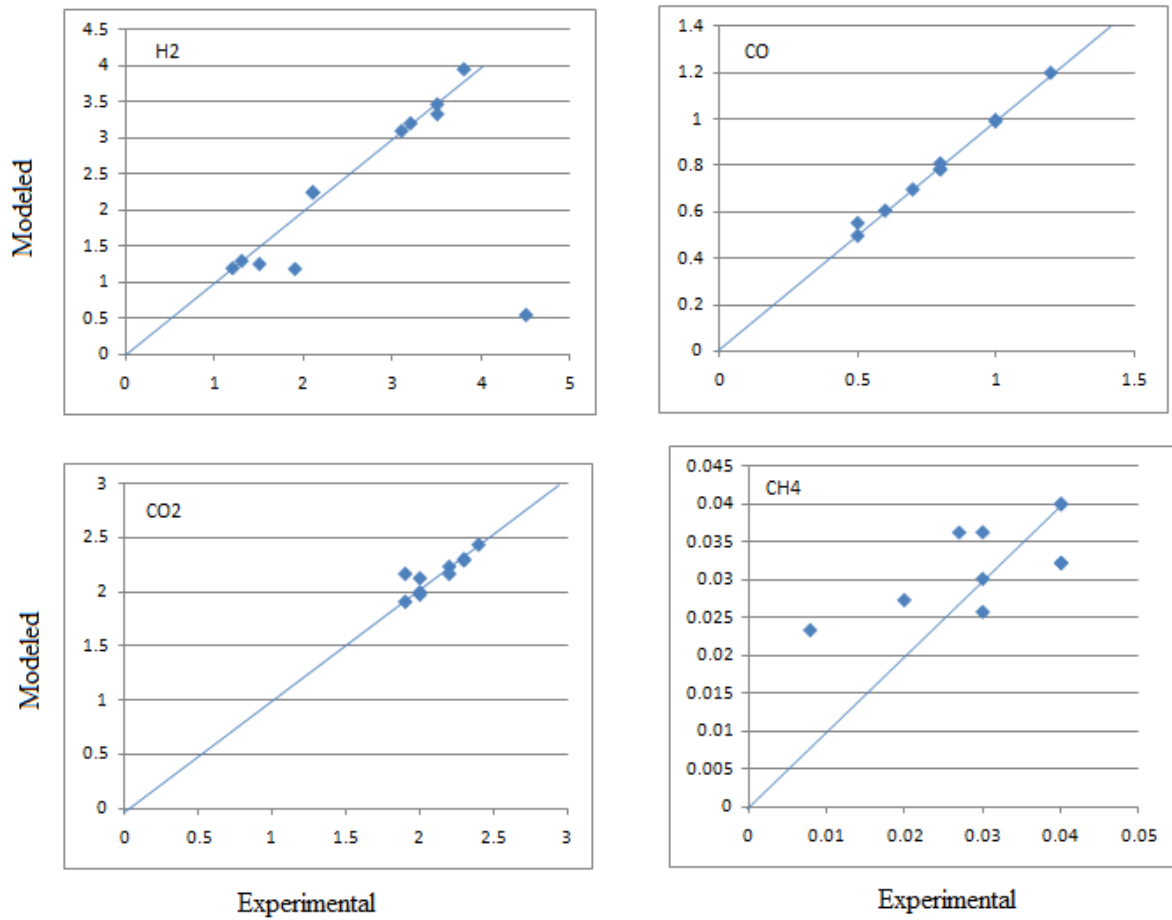$$-2.453e-5 * \text{Oxygen\_add} * \text{steam\_add} * T(\text{Ref}));$$

Figure 4.- Model fit for the autoreforming

Atomic balances:

H:
$$\left(2*\text{steam\_add}*3+8\right)\frac{\text{fc}\left(\text{Glycerol},Src1,\text{Furnance}\right)}{\text{MW}\left(\text{Glycerol}\right)}$$
$$-\left(2*\text{molh2}+4*\text{molch4}+2*\text{molh2o}+2*\text{molc2h2}+4*\text{molc2h4}\right)=0; \tag{15}$$

C:
$$\left(3\right)\frac{\text{fc}\left(\text{Glycerol},Src1,\text{Furnance}\right)}{\text{MW}\left(\text{Glycerol}\right)}$$
$$-\left(\text{molCO}+\text{molCO2}+\text{molch4}+\text{molc}+2*\text{molc2h2}+2*\text{molc2h4}\right)=0; \tag{16}$$

O:
$$\left(2*\text{Oxygen\_add}*3+3+\text{steam\_add}*3\right)\frac{\text{fc}\left(\text{Glycerol},Src1,\text{Furnance}\right)}{\text{MW}\left(\text{Glycerol}\right)}$$
$$-\left(\text{molco}+2*\text{molCO2}+2*\text{molo2}+\text{molh2o}\right)=0; \tag{17}$$

Oulet stream

$$\text{fc}(J, \text{Ref}, \text{HX11}) = \text{mol}_j * \text{MW}(J); \qquad \forall j \tag{18}$$

$$Q_{react} = \sum_j \Delta H_j^f \Big|_{T(furnance)} \tag{19}$$

$$Q_{prod} = \sum_j \Delta H_j^f \Big|_{T(furnance)} \tag{20}$$

$$Q_{prod} \approx Q_{react} \tag{21}$$

3.1.2.-Steam reforming (SR)

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. (22). The model is obtained from the results presented by Adhikari et al. (2007). 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 hence simple correlations are not enough to predict the outlet gas. A two step procedure 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 so as to develop an equation-oriented model to predict the gas composition as function of the temperature and the steam injected in the reformer. Due to the complexity of the profiles for the gas generated at the reformer, eqs. (25-28), are also complex. However, the fitting of the experimental data with these equations is satisfactory as seen in Figure 5.

$$C_3H_8O_3 + nH_2O \longrightarrow aCO + bH_2 + cCO_2 + dCH_4 + ... \tag{22}$$
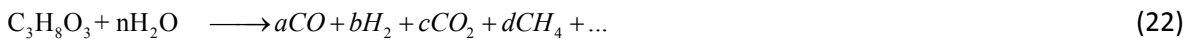
$$\text{fc}(Wa, \text{Src2}, \text{Furnance}) = \text{steam\_add} \frac{\text{fc}(\text{Glycerol}, \text{Src1}, \text{Furnance})}{\text{MW}(\text{Glycerol})} \text{MW}(Wa) \tag{23}$$

$$\text{fc}(J, \text{Src2}, \text{Furnance}) + \text{fc}(J, \text{Src1}, \text{Furnance}) = \text{fc}(J, \text{Furnance}, \text{Ref}); \tag{24}$$

$$molh2 = \frac{fc\left(Glycerol, Src1, Furnance\right)}{MW\left(Glycerol\right)} ($$

$$\left(\begin{array}{l} -0.0000000000112*\left(steam\_add^3\right) + 0.0000000001948*\left(steam\_add^2\right) \\ - 0.0000000008677*steam\_add + 0.0000000007681 \end{array}\right)*\left(T\_reforming + 273\right)^4 +$$

$$\left(\begin{array}{l} 0.000000035751*\left(steam\_add^3\right) - 0.00000061754*steam\_add^2 \\ + 0.0000027097*steam\_add - 0.0000024456 \end{array}\right)*\left(T\_reforming + 273\right)^3 +$$

$$\left(\begin{array}{l} -0.000042181*\left(steam\_add^3\right) + 0.00072376*\left(steam\_add^2\right) \\ - 0.0031299*steam\_add + 0.0028955 \end{array}\right)*\left(T\_reforming + 273\right)^2 +$$

$$\left(0.021807*\left(steam\_add^3\right) - 0.37172*\left(steam\_add^2\right) + 1.5866*steam\_add - 1.5026\right)*\left(T\_reforming + 273\right) +$$

$$\left(-4.171*steam\_add^3 + 70.653*steam\_add^2 - 298.11*steam\_add + 288.16\right))$$

$$(25)$$

$$molCO = \frac{fc\left(Glycerol, Src1, Furnance\right)}{MW\left(Glycerol\right)} ($$

$$\left(0.000000000073154*steam\_add - 0.00000000071134\right)*\left(T\_reforming + 273\right)^4 +$$

$$\left(-0.00000023117*steam\_add + 0.0000022197\right)*\left(T\_reforming + 273\right)^3 +$$

$$\left(0.00026955*steam\_add - 0.0025493\right)*\left(T\_reforming + 273\right)^2 +$$

$$\left(-0.13769*steam\_add + 1.2817\right)*\left(T\_reforming + 273\right) +$$

$$\left(26.028*steam\_add - 238.55\right))$$

$$(26)$$

$$molCO2 = \frac{fc\left(Glycerol, Src1, Furnance\right)}{MW\left(Glycerol\right)}$$

$$\left(\begin{array}{l} -0.000000021725*\left(T\_reforming + 273\right)^3 + 0.000043132*\left(T\_reforming + 273\right)^2 \\ - 0.027228*\left(T\_reforming + 273\right) + 6.3326 \end{array}\right) *$$

$$\left(steam\_add\right)^{\left(\begin{array}{l} 0.00000000006628*\left(T\_reforming+273\right)^4 - 0.00000019627*\left(T\_reforming+273\right)^3 \\ + 0.00021633*\left(T\_reforming+273\right)^2 - 0.10479*\left(T\_reforming+273\right) + 19.06 \end{array}\right)})$$

$$(27)$$

$$molCH4 = \frac{fc\left(Glycerol, Src1, Furnance\right)}{MW\left(Glycerol\right)}$$

$$(\frac{\left(-0.479*\log\left(steam\_add\right) + 8.1713\right) + \left(\begin{array}{l} -0.0000097452*steam\_add^3 \\ + 0.00020612*steam\_add^2 \\ - 0.0013085*steam\_add \\ - 0.0033209 \end{array}\right)*\left(T\_reforming + 273\right)}{1 + \exp\left(-\left(T\_reforming + 273\right)*\left(0.000051956*steam\_add^2 - 0.00027429*steam\_add + 0.0028799\right)\right)} +$$

$$\left(0.0155*steam\_add^3 - 0.3021*steam\_add^2 + 1.7829*steam\_add - 4.8415\right))$$

$$(28)$$

Atomic balance

H:
$$(2*steam\_add+8)\frac{fc(Glycerol,Src1,Furnance)}{MW(Glycerol)}$$
$$-(2*molh2+4*molch4+2*molh2o+2*molc2h2+4*molc2h4)=0; \qquad (29)$$

C:
$$(3)\frac{fc(Glycerol,Src1,Furnance)}{MW(Glycerol)}$$
$$-(molCO+molCO2+molch4+molc+2*molc2h2+2*molc2h4)=0; \qquad (30)$$

O:
$$(3+steam\_add)\frac{fc(Glycerol,Src1,Furnance)}{MW(Glycerol)}$$
$$-(molco+2*molCO2+2*molo2+molh2o)=0; \qquad (31)$$
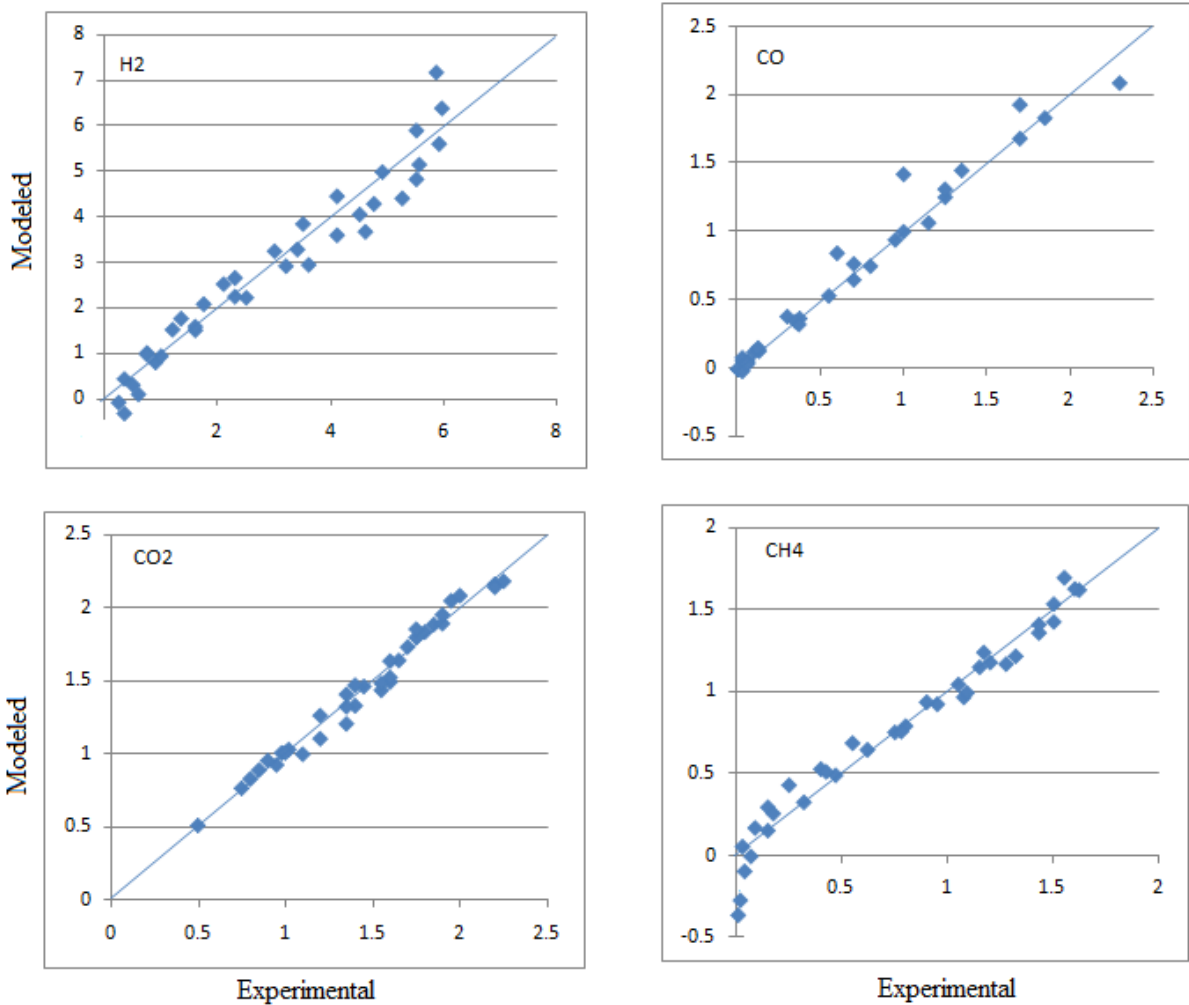
Figure 5.- Model fit for the steam reformer

Outlet stream:

$$fc(J,Ref,HX11)=mol_j*MW(J); \qquad \forall j \qquad (32)$$

$$T\_reforming = 0.5*\left(T\left(Furnance, Ref\right) + T\left(Ref, HX11\right)\right); \tag{33}$$

$$Q_{react} = \sum_{j} \Delta H_{j}^{f}\Big|_{T(furnance)} \tag{34}$$

$$Q_{prod} = \sum_{j} \Delta H_{j}^{f}\Big|_{T(Reforming)} \tag{35}$$

$$Q_{prod} = Q_{react} \tag{36}$$

3.1.3.-Aquoeus phase reforming

Recently another technology has been proposed that allows the generation of hydrogen from glycerol directly. It is called aqueous phase reforming (APR) in which the water is kept in liquid state by increasing the operating pressure. Using the experimental results from Shabaker et al. (2004), we propose a simple model for this reformer where the composition of the gas depends linearly on the temperature within the range of experimental values.

$$y_{h_2} = 0.66 + \frac{(0.64 - 0.66)}{40}\left(T\left(Furnance, Ref\right) - 225\right); \tag{37}$$

$$y_{CO_2} = 0.3; \tag{38}$$

$$y_{CH_4} = 0.04 + \frac{(0.058 - 0.04)}{40} * \left(T\left(Furnance, Ref\right) - 225\right); \tag{39}$$

$$y_{C_2H_6} = \frac{0.002}{40} * \left(T\left(Furnance, Ref\right) - 225\right); \tag{40}$$

$$press * 760 = Exp\left(coef\_p\left(Wa, 1\right) - \frac{coef\_p\left(Wa, 2\right)}{\left(coef\_p\left(Wa, 3\right) + T\left(Furnance, Ref\right)\right)}\right) \tag{41}$$

$$x_j = \frac{y_j \cdot MW(j)}{\sum_{j} y_j \cdot MW(j)}; \quad \forall j \in \left\{H_2, CO_2, CH_4, C_2H_6\right\} \tag{42}$$

$$fracCgas = 0.86 + \frac{0.12}{40}\left(T\left(Furnance, Ref\right) - 225\right); \tag{43}$$

$$mcarbon = \left(\frac{MW(C)}{MW(CO2)}\right) * xco2 + \left(\frac{MW(C)}{MW(CH4)}\right) * xch4 + \left(2 * \frac{MW(C)}{MW(C2H6)}\right) * xc2h6; \tag{44}$$

$$\text{frac}_j = \dfrac{\left(\text{fracCgas} * \dfrac{\text{fc}\left(\text{Glycerol}, \text{Furnance}, \text{Ref}\right)*\text{MW}\left(\text{C}\right)*3}{\text{MW}\left(\text{Glycerol}\right)}\right)*\left(\text{x}_j*\left(\dfrac{\text{n}_{\text{Cj}}*\text{MW}\left(\text{C}\right)}{\text{MW}\left(j\right)}\right)\right)}{\text{mcarbon}} \; ; j = \left\{CO_2, CH_4, C_2H_6\right\}$$

(45)

$$\text{fc}\left(j, \text{Ref}, \text{HX11}\right) = \text{frac}_j * \dfrac{\text{MW}\left(j\right)}{\text{n}_{\text{Cj}}*\text{MW}\left(\text{C}\right)}; j = \left\{CO_2, CH_4, C_2H_6\right\}$$

(46)

$$\text{fc}\left(\text{H2}, \text{Ref}, \text{HX11}\right) = \text{fc}\left(\text{CO2}, \text{Ref}, \text{HX11}\right) * \dfrac{\text{xh2}}{\text{xco2}};$$

(47)

In order to meet the mass balance we assume that in the liquid phase ethanol, propanediol and methanol (in this order of amount) are the most important byproducts (Shabaker et al., 2004).

$$\left(\dfrac{2*\text{fc}\left(\text{EtOH}, \text{Ref}, \text{HX11}\right)}{\text{MW}\left(\text{EtOH}\right)}\right) + \left(\dfrac{\text{fc}\left(\text{MetOH}, \text{Ref}, \text{HX11}\right)}{\text{MW}\left(\text{MetOH}\right)}\right) +$$
$$\left(\dfrac{3*\text{fc}\left(\text{PropDi}, \text{Ref}, \text{HX11}\right)}{\text{MW}\left(\text{PropDi}\right)}\right) = \left(1 - \text{fracCgas}\right)*\dfrac{\text{fc}\left(\text{Glycerol}, \text{Furnance}, \text{Ref}\right)*3}{\text{MW}(\text{Glycerol})}$$

(48)

Atomic balance of H, C and O must also hold. Finally, we assume adiabatic operation of the reformer as follows:

$$Q_{react} = \sum_j \Delta H_j^f \Big|_{T(furnance)}$$

(49)

$$Q_{prod} = \sum_j \Delta H_j^f \Big|_{T(furnance)}$$

(50)

$$Q_{prod} \approx Q_{react}$$

(51)

We assume a feed to the reformer with 10% glycerol in water based on the results by Liu et al (2006) and Shabaker et al. (2004) since the less amount of water the less energy required in the furnace as long as the process is feasible. Lower concentrations result in an excessive consumption of energy to heat up the aqueous mixture.

3.2.-Clean up

The trace 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 (Olofsson et al., 2005). 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 as well as the ammonia. Thus, the removal efficiency is 100% for hydrocarbons. Due to the low temperature, more water condenses in HX6 and it is discharged to Snk5 in Figure 6.
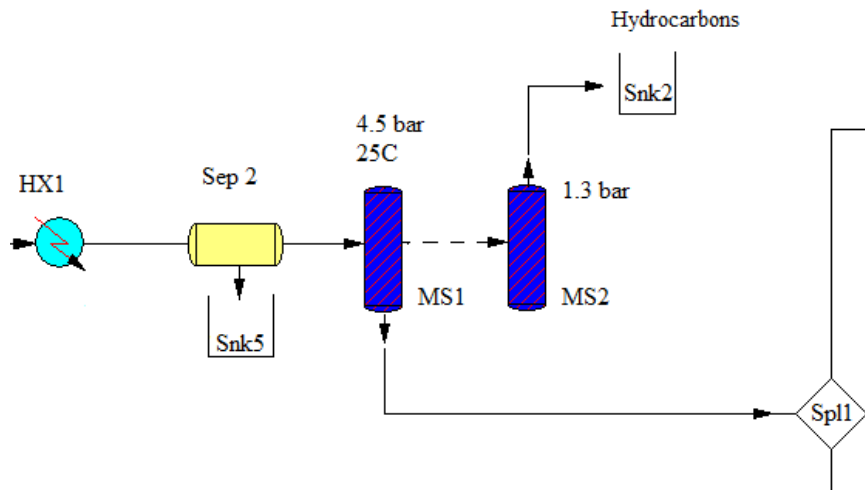

Figure 6.-Final hydrocarbon removal.

3.3.-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 FT-reactor is appropriate for the optimal production of diesel fraction, or we can produce only hydrogen. In order to perform such an adjustment, apart from modifying the operating conditions at the reformer, three alternatives are presented: The first one is the use of water gas shift to reduce the amount of CO by producing more H_2, or to produce only hydrogen. The second is a bypass. Finally, a hybrid membrane / PSA system with a bed of zeolite 13X to remove the excess of hydrogen, see Figure 7. It is possible that this surplus of hydrogen is sold to increase the profitability of the process (Neves & Schvartzman, 2005; Choi et al 2009).

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

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{49}$$

However, the conversion is calculated using the model developed from the experimental data by Choi et al (2003) as function of the molar ratio of water to CO (H2OtoCO) and the operating temperature. Eq.(50) was proposed by Martín and Grossman (2011c) to model the conversion in the reactor as function of the ratio steam to CO and the operating temperature at the reactors.

$$CO\_shift\_conv = \frac{\left(0.0044 \cdot T\left(Reactor1\right) + 0.0924\right) \cdot H2OtoCO}{\left(H2OtoCO + \dfrac{46815}{T\left(Reactor1\right)^2}\right)};$$
(50)

Thus, the products of the reactor are calculated as function of the conversion in the reactor and the stoichiometry given by eq. 49. The energy involved in the reaction is given by the heat of reaction and the conversion reached in the reactor.
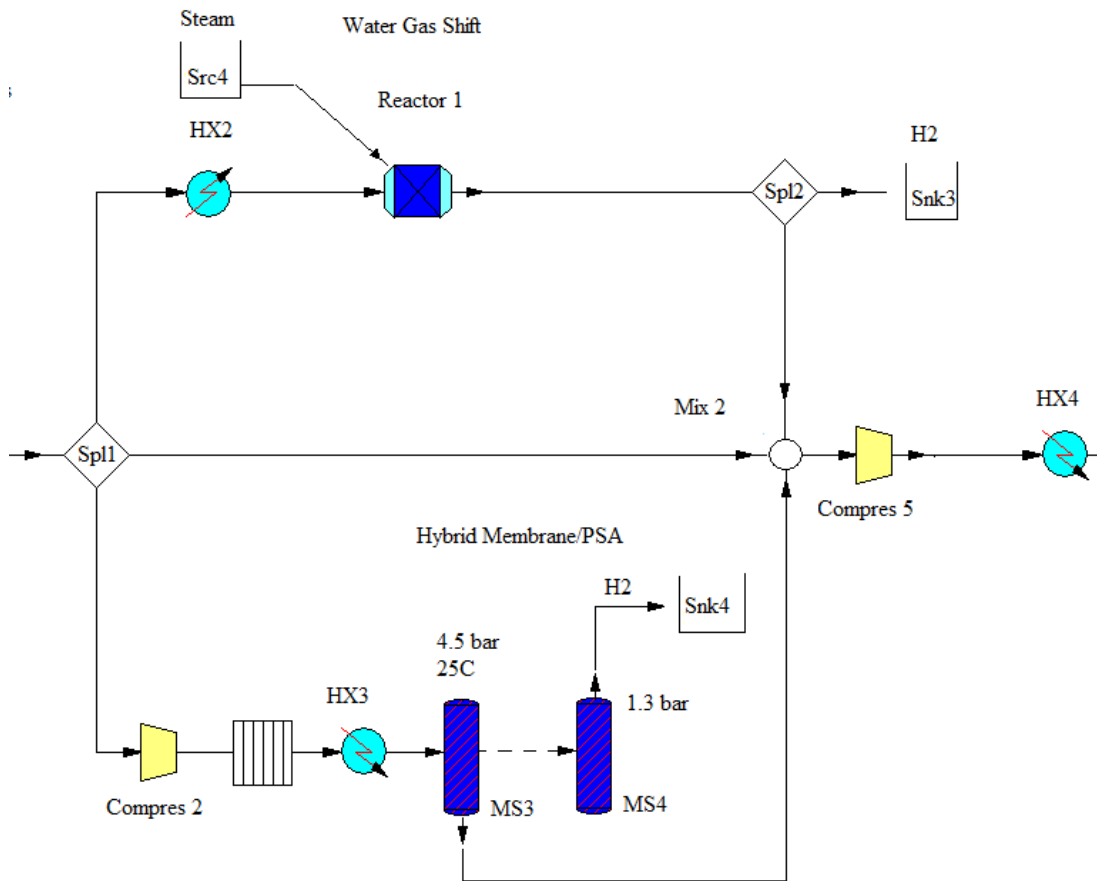

Figure 7.- Superstructure for the composition adjustment

Bypass: It may be possible that the stream does not need any adjustment in the CO:H_2 ratio for the optimal operation of the FT reactor.

H_2 Membrane / PSA system: The stream to be treated in the membrane / PSA system for the recovery of pure hydrogen (http://www.ist-world.org) will have to be adjusted in terms of temperature to 25 ºC, and pressure 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 cooling, water condenses in HX 3. 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 100%. The other gases pass though. Finally all the streams mix adiabatically. The ratio CO and H_2 is determined by the needs of the reactor to maximize the FT diesel production.

3.4.-CO_2 removal by PSA system.
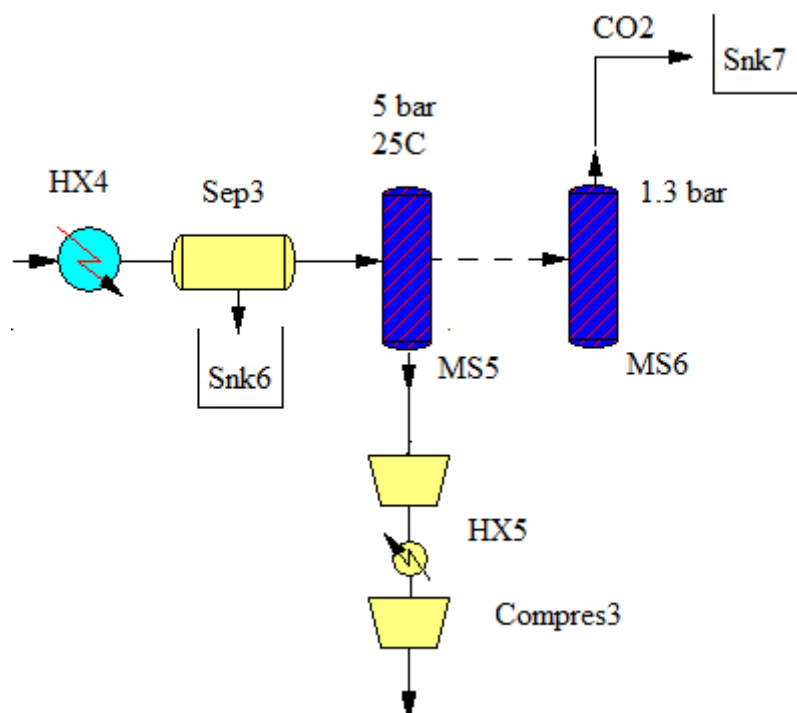

Figure 8.- PSA system for the removal of CO_2

In the case the syngas is used for the production of liquid fuels, CO_2 must be removed from the gas stream. Thus, the gas is first treated in a PSA system to remove CO_2 by using zeolite 5A or 13X capable of removing 95% of CO_2 in the stream (Ko et al., 2003; Ritler, 2004). 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, thus in HX 4 water condenses. Figure 8 shows a scheme of the process.

3.5.-Liquid fuel synthesis

The catalysts, either cobalt or iron based, and operating conditions at the FT – reactor, either low (200–240 °C) or high (300–350 °C) temperatures, and pressures from 10 to 40 bar depend on the types and quantities of products desired. In particular, the iron catalyst provides high selectivity towards synthetic diesel, $C_{10} - C_{18}$, and they are the catalysts of choice. Moreover, the reactions with iron catalyst are usually conducted at 30 bar. Furthermore, Fischer-Tropsch synthesis requires careful control of the H_2:CO ratio to satisfy the stoichiometry of the synthesis reactions as well as to avoid deposition of carbon on the catalysts (coking). An optimal H_2:CO ratio from 1:1 to 2:1 for the production of diesel and gasoline is recommended (Wang et al., 2008) while a minimum ratio of 1.7 is required for iron catalysts, (Dry, 2002). Figure 9 shows the detail of the flowsheet for the synthesis where heat exchanger 7 heats up the feed to the reactor operating conditions.
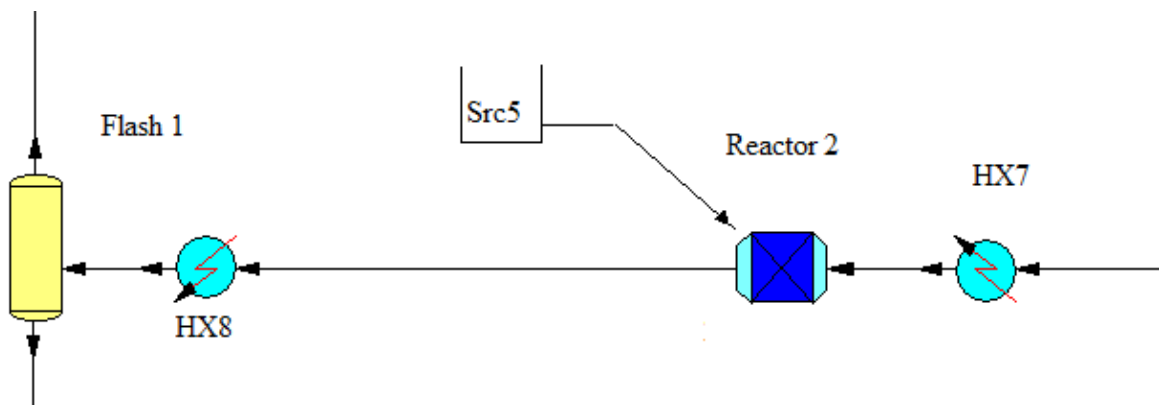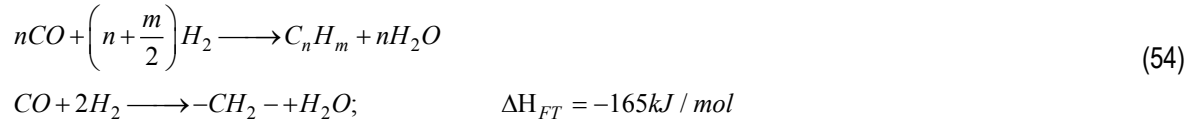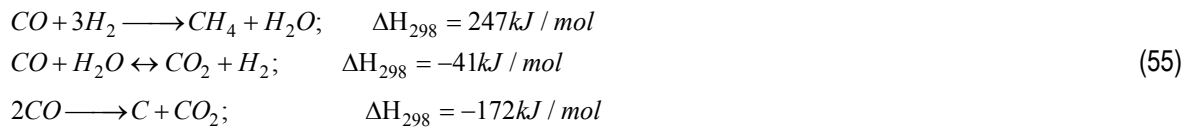

Figure 9.- FT Reactor

The reaction given in eq. (51) is the desired one and is the most dominant reaction when applying cobalt-based FT catalyst. When using iron-based (Fe) catalyst the WGS, second reaction in eq. (52), reaction also readily takes place since Fe catalyzes the WGS enabling the operation at a lower temperature.

$$nCO + \left(n + \frac{m}{2} \right) H_2 \longrightarrow C_n H_m + n H_2 O$$

$$CO + 2H_2 \longrightarrow -CH_2 - +H_2 O; \qquad \Delta H_{FT} = -165 kJ \, / \, mol$$

(54)

Apart from this reaction, a large number of chemical reactions also take place such as methanation, the first reaction in eq. (52), the water gas shift (WGS), the second one, and the Boudouard equilibrium. Both, the methanation reaction and the Boudouard reaction are undesirable.

$$CO + 3H_2 \longrightarrow CH_4 + H_2 O; \qquad \Delta H_{298} = 247 kJ \, / \, mol$$
$$CO + H_2 O \leftrightarrow CO_2 + H_2; \qquad \Delta H_{298} = -41 kJ \, / \, mol$$
$$2CO \longrightarrow C + CO_2; \qquad \Delta H_{298} = -172 kJ \, / \, mol$$

(55)

In order to model the length of the hydrocarbons generated, we use the Anderson-Schulz-Flory (ASF) distribution that describes the probability of hydrocarbon chain growth (Schulz, 1999). The probability of chain growth can be denoted as α. The operating temperature of the reactor is calculated based on the correlation obtained by Song (2004) for α, combined with the model for the mass fraction of each hydrocarbon (w_i, i = number of C) assuming that the Fischer - Tropsch reactor works as a polymerization reactor (Fürnsinn et al., 2005). A conversion of 0.8 – 0.9 in CO is considered (Park & Norbeck, 2009) which is used to determine the share of the different fractions, C1-C2, C3-C4, gasoline, diesel and heavy product

$$w_i = \alpha^{i-1} (1-\alpha)^2 \cdot i$$

(56)

$$\alpha = \left(0.2332 * \left(\frac{y_{CO}}{y_{H_2} + y_{CO}} \right) + 0.633 \right) * \left(1 - 0.0039 * \left(\left(T\_Synthesis + 273 \right) - 533 \right) \right)$$

(57)

The mass balances in the reactor are simplified using the values calculated for the different fractions of the products from eq. (56).

3.6.-Separation and hydrotreatment.

The separation of hydrocarbons is very common in the petrochemical industry. The most important problem is the fact that we are dealing with a mixture of fractions instead of single compounds. The gas fractions can be separated by flash separation. In order to separate the gas phase from the liquid phase and avoid losing liquid, the flash operates at the same pressure of the reactor but we cool down the mixture to 30ºC in HX21. The recovery of the flash is considered to be 100% for the gases and light hydrocarbons and 0% for the gasoline, diesel, wax and water. The gases can be further separated into methane and butane fractions, or can be used together are flue gas to produce energy.

The water is next separated from the organic phase using a decanter. Next, the three fuel fractions are separated as in any crude distillation system as shown in Figure 10. According to Speight (1991), the typical distillation towers for crude oil have 30 trays and the typical temperatures are 125 ºC for the top (Gasoline), 220 ºC for the diesel and 280 ºC at the bottom for the heavier components. The outlet of the fractionation columns are mainly gasoline from the top, diesel from the middle, and the heavy fraction from the bottom. The reflux ratio is assumed to be 2 (Parkash, 2003). These kind of columns do not have reboiler since steam is directly injected at the bottom. We assume that we recover the steam used and recycle it after heating it up again, and thus the energy consumption of the column is given by the furnace to heat up the feed to the operating temperature, around 220ºC, HX11 in Figure 10, and the steam required is assumed to be around 0.18 kg of steam per kg of residue based on the results by Jonas & Pujado (2006). The conditions are on the conservative side due to the range of results reported in the literature and the fact that most of the data are reported for crude and not for FT products (Marcel & Dekker, 1997; Parkash, 2003; Jonas & Pujado, 2006; More et al., 2010)

The bottoms of the column can be treated to obtain more diesel. Hydrocracking (reactor 3) is the best option in order to produce diesel virtually free from aromatics (Dry, 2002). The temperature of operation is given by the optimum performance towards the production of diesel, thus is a decision variable.
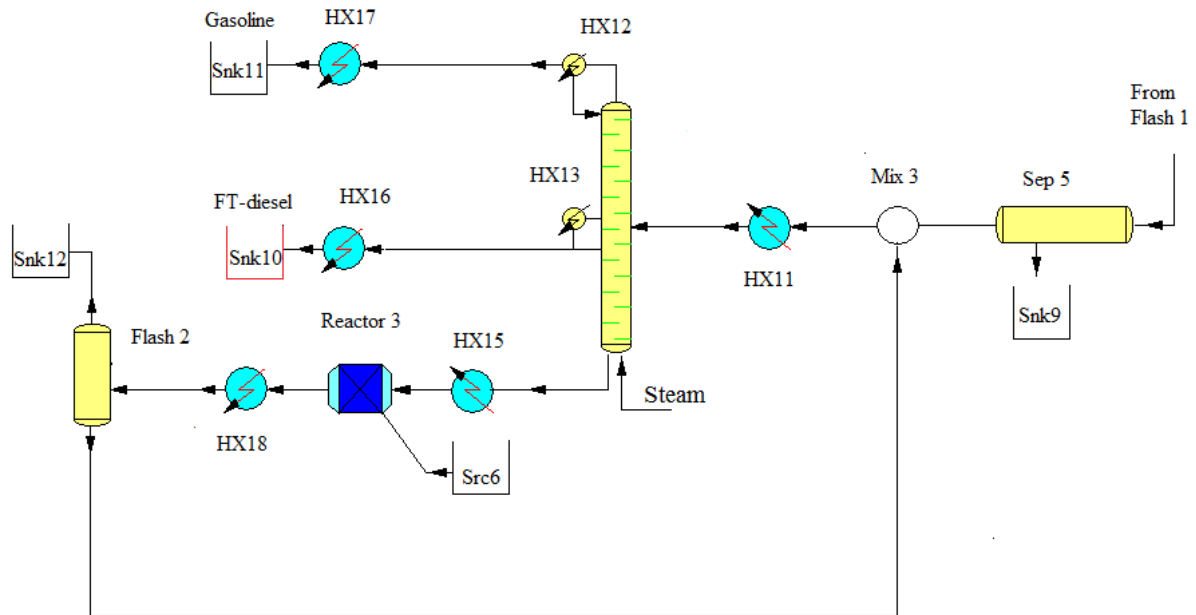
Figure 10.- Diesel and gasoline fractionation

To model the hydrocracking reactor we use the experimental data for the conversion and selectively as function of the temperature from the paper presented by Bezergianni et al. (2009). We correlate these profiles (Martín & Grossmann, 2011b) using polynomials to develop a reduced order model for the hydrocracking reactor, eqs (58-59).

$$X\_R3 = 0.000185714*(T\_reactor3)^2 - 0.128829*T\_reactor3 + 22.6931; \tag{58}$$

$$S\_diesel = -0.00014286*(T\_reactor3)^2 + 0.099514*T\_reactor3 - 16.383; \tag{59}$$

The reactor also requires a hydrogen stream. We assume 600 ft^3 of hydrogen per bbl to be left with the products, and this represents around 7.5% of the total hydrogen fed to the hydrocracker (Speight, 1991). These values depend on the composition of the feed, the catalysts and operating conditions, and a range is available in the literature. Thus, the products from the reactor are calculated based on the conversion and selectivity .The products will be separated by cooling them to 30 ºC in a flash so that the gasoline and diesel fractions are recycled to the column to be separated, while the H$_2$ is recycled to the system so that only a small amount of make-up of hydrogen is fed. Meanwhile, the liquids (gasoline, diesel and heavy) are recycled to the column to be separated again

3.7.-Solution procedure.

The original MINLP problem is decomposed into 3 NLP's subproblems, one for each reforming mode, due to the fact that aqueous reforming is capable of producing only hydrogen. In that sense we will evaluate the production of hydrogen using three alternatives. Next, for autoreforming and steam reforming we evaluate the possibility of producing FT-diesel, hydrogen or both at the same time, the optimal ratio and the operating conditions by solving the superstructure that involves the three options for hydrogen production or separation.

Each of the subproblems, for each of the reforming modes, is solved as an NLP to optimize the operating conditions of the reformer, the WGSR, the Fischer - Tropsch reactor, and at the hydrocracking unit. The objective function to be maximized is the benefit cost involving the production of diesel and the use of energy to prepare the feed for the reformer, the WGSR and the FT reactor as well as the cost of hydrogen used in hydrocracking must be minimized. Eqs. (60)-(62) are used in the optimization of the hydrogen production for the three reforming modes, AFR, SR and AR respectively:

$$Z_{AFR} = C_{H_2} \cdot \text{fc}\left(\text{H2, Ref, Sep1}\right) - C_{NatGas} \cdot Q\left(\text{Furnance}\right) - C_{Water} \cdot \text{fc}\left(\text{Wa, Src1, Furnance}\right) \quad (60)$$

$$Z_{SR} = C_{H_2} \cdot \text{fc}\left(\text{H2, Spl2, Snk3}\right) - C_{NatGas} \cdot Q\left(\text{Furnance}\right)$$
$$-C_{Steam} \cdot \left(Q\left(\text{HX2}\right) + \text{fc}\left(\text{Wa, Src4, Reactor1}\right) \cdot \lambda + \text{fc}\left(\text{Wa, Src2, Furnance}\right) \cdot \lambda\right) \quad (61)$$

$$Z_{AR} = C_{H_2} \cdot \text{fc}\left(\text{H2, Spl2, Snk3}\right) - C_{NatGas} \cdot Q\left(\text{Furnance}\right) - C_{O_2} \cdot \text{fc}\left(\text{O2, Src3, Furnance}\right)$$
$$-C_{Steam} \cdot \left(Q\left(\text{HX2}\right) + \text{fc}\left(\text{Wa, Src4, Reactor1}\right) \cdot \lambda + \text{fc}\left(\text{Wa, Src2, Furnance}\right) \cdot \lambda\right); \quad (62)$$

For the simultaneous production of hydrogen and liquid fluids, we use eqs. (60) and (61) for autoreforming and steam reforming, respectively:

$$Z_{AR} = C_{H_2} \left(\text{fc}\left(\text{H2, Spl2, Snk3}\right) + \text{fc}\left(\text{H2, MS4, Snk4}\right)\right) + C_{Diesel}\text{fc}\left(\text{Diesel, HX11, Col1}\right) +$$
$$-C_{Steam} * \left(Q\left(\text{HX7}\right) + \text{fc}\left(\text{Wa, Src4, Reactor1}\right)\lambda + \text{fc}\left(\text{Wa, Src2, Furnance}\right)\lambda\right)$$
$$-C_{NatGas}Q\left(\text{Furnance}\right) - C_{O_2}\text{fc}\left(\text{O2, Src3, Furnance}\right) - C_{H_2}0.01*\text{fc}\left(\text{Nafta, HX11, Col1}\right);$$

$$(60)$$

$$Z_{\text{steam}} = C_{H_2} \cdot (\text{fc}(H2, Spl2, Snk3) + \text{fc}(H2, MS4, Snk4)) + C_{Diesel} \cdot \text{fc}(Diesel, HX11, Col1)$$
$$-C_{Steam} \cdot (Q(HX7) + \text{fc}(Wa, Src4, Reactor1)\lambda + \text{fc}(Wa, Src2, Furnance)\lambda) \qquad (61)$$
$$-C_{NatGas} \cdot Q(Furnance) - C_{H_2} \cdot 0.01 * \text{fc}(Nafta, HX11, Col1)$$

Thus, the main decision variables are the the steam and/or oxygen added to the reformer and its operating temperature, 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 Fisher-Tropsch reactor (Temperature and CO/H$_2$ ratio) and the hydrocracking conditions.

4.-Results and discussion.

The size of the plant is fixed to 1kg/s of glycerol, which is approximately the production of glycerol in typical biodiesel production facilities. The cost for facilities is updated from the literature (0.019$/kg, steam, 0.057$/ton cooling water, Franceschin et al., 2008; 0.06$/kWh, Balat et al., 2008; 0.021$/kg Oxygen, Forsberg & Gorensek, 2007). The cost of hydrogen is taken to be $1.6/kg established by the DOE for the long term. We consider $1/kg of liquid fuel and the cost of natural gas at $4.687/ Million BTU since it was quite stable for more than a year. However, lately the price has decreased as a result of the development of shale gas. Therefore, we evaluate its effect on the solution in the sensitivity analysis section (http://www.eia.gov/naturalgas/weekly). The generation of an excess of steam is considered as a revenue of 0.0077$/kg$_{\text{steam}}$ (updated from Smith and Varbanov, 2005). We determine the production cost as in previous papers by the authors (Martín & Grossmann, 2011a) based on Coulson's methodology (Sinnot, 1999) including raw material cost, chemicals and utilities, labour, maintenance, management and equipment annualized cost. The production level is based on the processing of the glycerol produced in a typical biodiesel production plant (Martín & Grossmann, 2012), around 1kg/s of glycerol.

4.1.-Hydrogen production

All three technologies are capable of producing hydrogen as only the fuel, it we optimize the production of hydrogen alone in the first place. Table 1 summarizes the results of the optimization

Table 1.- Process characteristics for hydrogen production

	Autoreforming	Steam Reforming	Aqueous phase
Oxygen added(mol/mol)	0.187		
Steam added (mol/mol)	3.038	2.738	
Temperature(ºC)	746	587	241

Figure 11 presents the cooling and energy needs for each of the processes including the furnace, and the generation of steam if any. The APR generates energy in the form of low pressure steam, but requires a large amount of cooling due to the fact that it uses liquid water at high pressure for decomposing the glycerol. Either steam reforming (SR) or autoreforming (AR) are energy intensive.
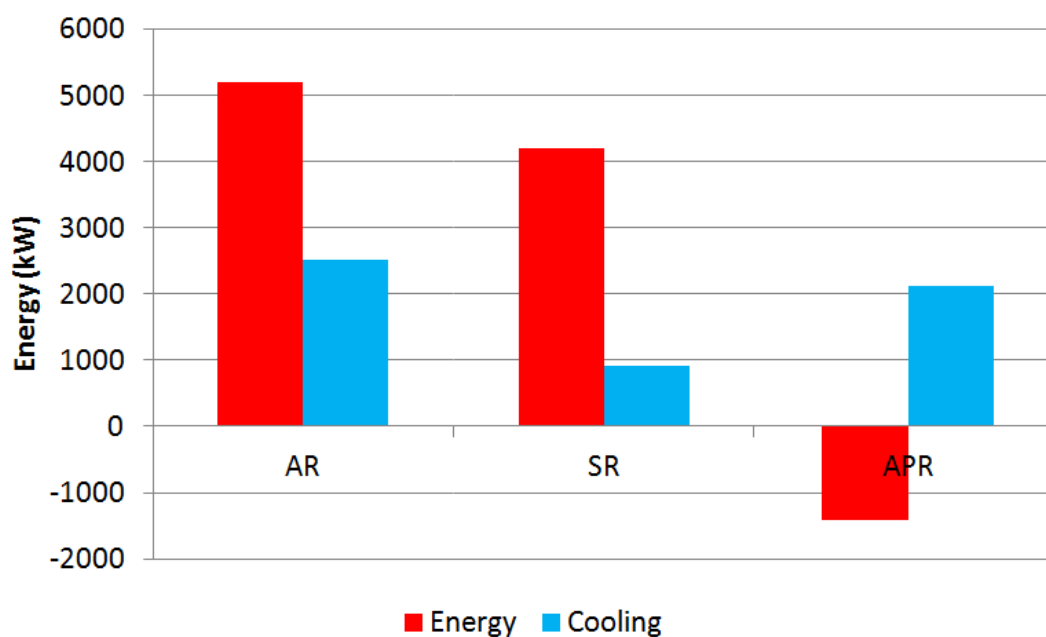

Figure 11. Net energy balance for the production of hydrogen (1kg/s of glycerol)

As seen in Table 2, total annualized cost indicates that the aqueous phase reforming has an advantage in terms of the composition obtained, even though the energy input to the process is higher. We perform an economic analysis after heat integration of the streams using SYNHEAT following the procedure presented in Martín & Grossmann (2011). The results can be seen in Table 2 assuming glycerol cost of $0/gal Later in the paper we evaluate the effect of the cost of glycerol on the production of hydrogen. Even though the highest yield

to hydrogen corresponds to autoreforming, the higher consumption of utilities, oxygen and steam, and the larger number of process equipment for purification of the gas leaving the reformer results in the aqueous phase reforming being the most attractive process. The production cost of the ARP based process is $0.55/kg at zero cost of glycerol with the lowest investment cost of $11.4MM, see Figure 12.
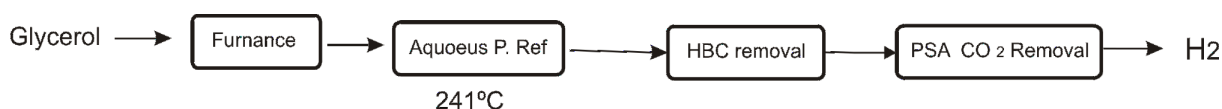
Glycerol → [Furnance] → [Aquoeus P. Ref 241°C] → [HBC removal] → [PSA CO₂ Removal] → H2

Figure 12.- Optimal flowsheet for the production of hydrogen from glycerol

Table 2. Hydrogen Production (Glycerol cost $0/kg)

	Autoreforming	Steam reforming	APR
Utilities contribution (%)	36.0	33.7	10.0
Biofuel yield (kg/kg$_{wet}$)	0.123	0.084	0.111
Production cost ($/kg)	0.83	0.87	**0.55**
Investment ($MM)	14.8	10.6	**11.4**

4.2.-Liquid fuels and hydrogen production

The simultaneous production of hydrogen and liquid fuels from glycerol means solving the complete superstructure deciding on the separation of hydrogen and the technology used, as well as the composition adjustment for the synthesis of liquid fuels from syngas following a FT reaction. In this case the ratio H_2/CO entering the FT reactor is key for the process. According to Wang et al. (2008), increasing the inlet H_2/CO ratio causes an increase of lighter distillates and a decrease of heavier distillates. Higher gasoline and diesel product selectivity is obtained when the inlet H_2/CO ratio is between 1.0 to 2. However, Dry (2002) reported that for Fe catalysis a minimum of 1.7 is required. These experimental results are verified by the results of the optimization. Adjusting the composition requires energy, and thus the results lead to the lower bound, 1.7. Table 3 presents the main operating parameters of both alternatives after energy integration, while Figure 13 shows the optimal product distribution for the optimal FT-diesel production where the peak is shown for the range of chain length corresponding to diesel.

Table 3.- Process characteristics for hydrogen and liquid fuels production from glycerol

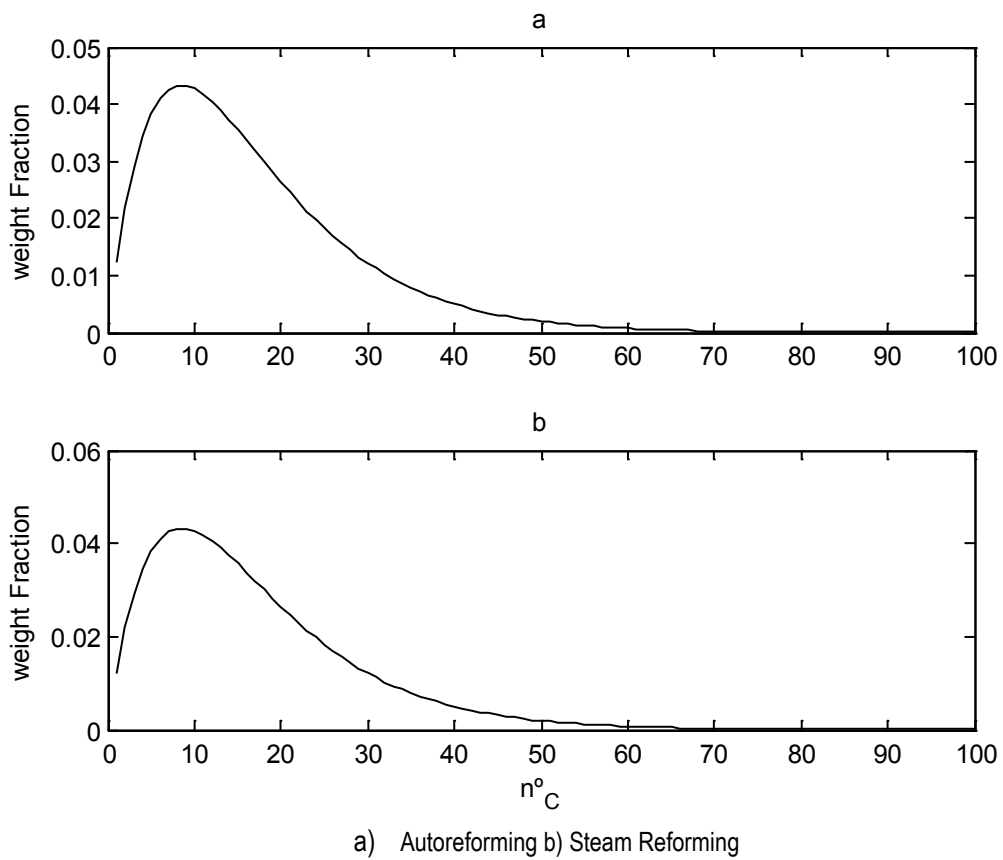|	Autoreforming	Steam Reforming
Oxygen added(mol/mol)	0.101	NA
Steam added (mol/mol)	1	1
Temperature(C)	684	605
FT Temperature	200	201
α	0.9	0.89
H_2/CO	1.7	1.7

a

b

a) Autoreforming b) Steam Reforming

Figure 13.- Optimized distribution of products

In Figure 14 we present the net energy balance for both reforming technologies. Autoreforming requires less energy and more cooling than the steam reforming since the process is a combination of exothermic and endothermic reactions, while the steam reforming is only endothermic reactions resulting in lower final temperature and higher energy input for the reforming to take place.
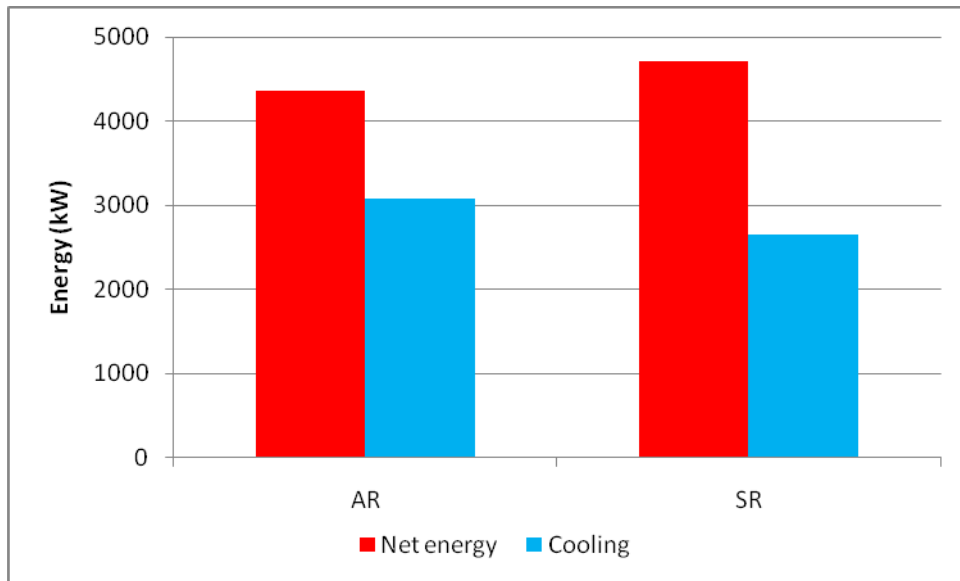
Figure 14. Net energy balance for the production of fuels (1kg/s of glycerol)

The results of the optimization indicate that the optimal operation of the process produces hydrogen and liquid fuels simultaneously. Next, we perform an economic evaluation for both alternatives as in previous cases, and the results are summarized in Table 4 assuming glycerol cost of $0/kg. In the next section, we evaluate the effect of the glycerol price on the cost of liquid fuels. There is a trade off between the investment cost and the production cost since autoreforming has higher yield, and thus lower production cost but the investment is slightly higher. The main advantage of autoreforming is the fact that it produces a surplus of hydrogen (we assume $1.58/kg DOE final target) that not only covers the needs of hydrocracking, but it provides extra revenue increasing the total yield of liquid biofuels and reducing the utilities cost even though the selectivity to diesel is slightly lower than steam reforming. The optimal flowsheet is shown in Figure 15.

Table 4. Liquid fuels production 2MMgal/yr (Glycerol cost $0/kg)

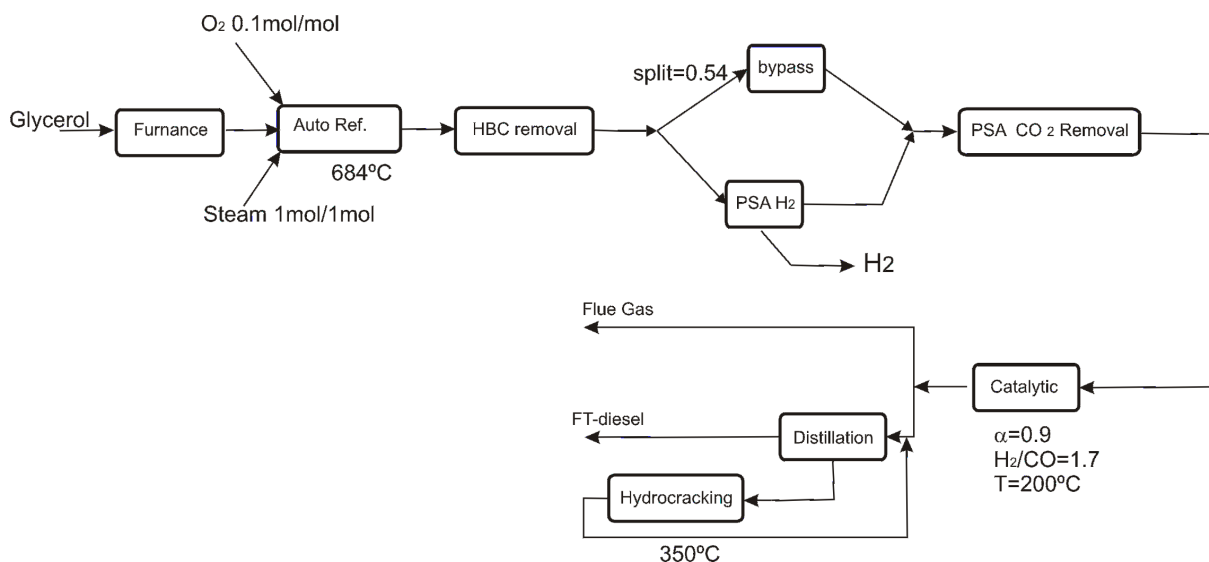|	Autoreforming	Steam reforming
Biofuel yield (kg/kg$_{wet}$)	0.23	0.16
Selectivity to Diesel	0.58	0.64
Selectivity to H$_2$	0.20	0.18
Production cost ($/gal)	**0.02**	0.73
Investment ($MM)	18.2	15.6

Figure 15.- Optimal flowsheet for the simultaneous production of hydrogen and liquid fuels.

4.3.-Raw materials cost sensitivity analysis

a) For Hydrogen

The cost of glycerol is an uncertain parameter in the process since the increase in its production as byproduct of the biodiesel industry will result in a decrease in its price. Ahmed and Papadias (2010) considered a raw material cost of $0.102/lb which results in a production cost of hydrogen of $2.8/kg which is reasonable for the initial target of the DOE, but almost twice as expensive as the expected cost of $1.58/kg in the long run. To reach this goal the glycerol cost must be $0.052/lb, which in fact is the expected final value for glycerol according to the USDOE (Chi et al., 2007). Figure 15 presents the profile of the cost of hydrogen as function of the glycerol cost.

On the other hand, if we compare in Figure 15 the production of hydrogen from glycerol with that which uses switchgrass as raw material (Martín & Grossmann, 2011c), the hydrogen from glycerol is competitive as long as the glycerol cost is below $0.05/lb to reach the target of $1.58/kg suggested by the DOE, or if we compare the use of glycerol with switchgrass, the cost of the switchgrass must be at least $90/ t. We realize that the production capacity of both plants is not the same. However, what is similar is the production capacity of the biodiesel plant which generates the glycerol as byproduct and the hydrogen plant. In this sense, this comparison is more realistic than if we scale up the production plant that uses glycerol as raw material to the levels of a

biorefinery of swichgrass since we will probably not be able to obtain that amount of glycerol within a reasonable distance.
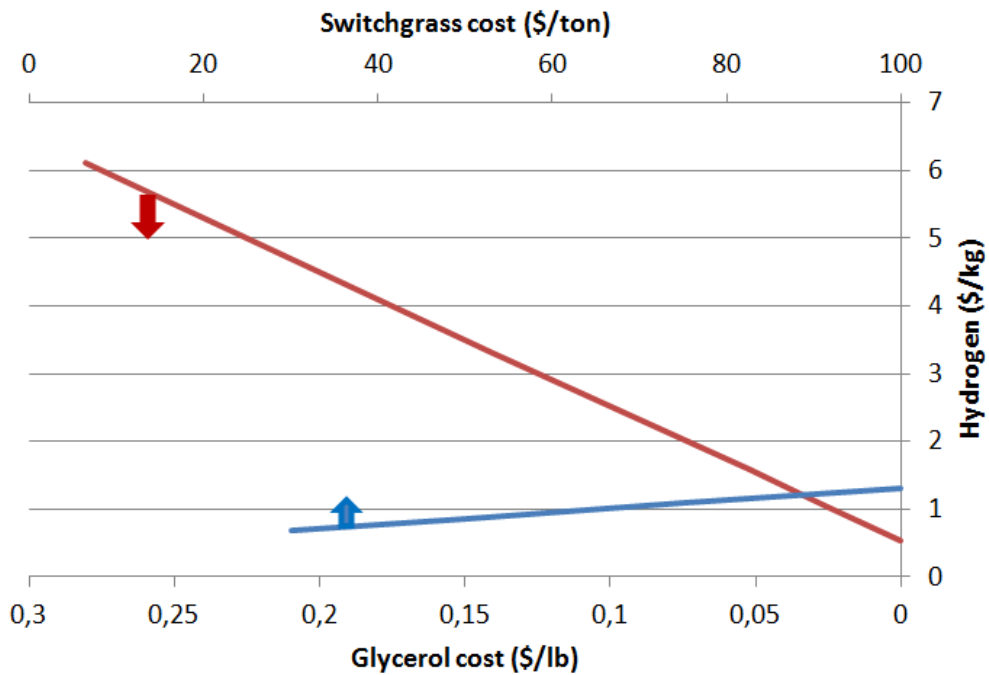

Figure 15.- Competition between the use of switchgrass and glycerol for the production of hydrogen

As a result of the discovery of shale gas, the latest values available for the natural gas are around $2/MMBTU. Thus, the production cost of hydrogen using this value is reduced by $0.2/kg so that the use of glycerol is competitive with switchgrass if it reaches $80/t, and it is possible to reach the target by the DOE for glycerol costs of $0.06/lb.

Finally, In order to reuse the carbon in the form of CO_2 it is convenient to capture it and its use in algae ponds which is an attractive alternative to generate more fuels, (Martín & Grossmann, 2012).

b)   For Liquid fuels

If the glycerol cost reaches $0.102/lb (Ahmed and Papadias, 2010) the production cost of liquid fuels following the optimal alternative that uses autoreforming increases up to $3.70/gal, while to meet the $1/gal of liquid fuel the price of glycerol has to be no higher than $0.025/lb, which is half the value expected in the long term by the DOE (see Figure 16).

If we compare the use of glycerol and switchgrass for the production of liquid fuels, we see that as in the previous case for the hydrogen production, switchgrass must reach $90/ton and glycerol reduce its cost to less than $0.05/lb.
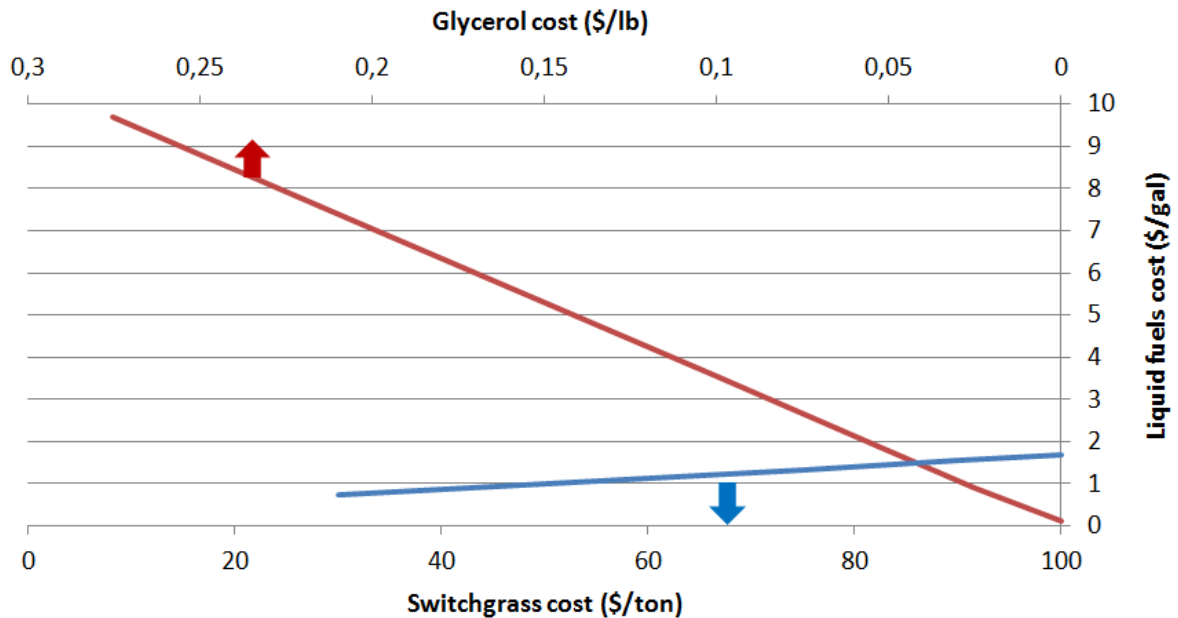

Figure 16.- Competition between the use of swichgrass and glycerol for the production of liquid fuels

In Figure 16 the flue gas from the FT reactor has not been considered as a source of energy. However, there is potential to improve the profitability of the process by using the flue gas to generate steam and sell it. In doing so, we can get around 2.3 MW of energy from each of the technologies, either autoreforming or steam reforming, which represents a reduction in $0.35/gal of biofuel. In this case the production cost of biofuels using the autoreforming path is $3.24/gal if the glycerol reaches $0.102/lb (Ahmed and Papadias, 2010) and for the limit of $1/gal the price of glycerol can go up to $0.04/lb.

Furthermore, since the price of natural gas is very volatile with the development in shale gas, its current price has decreased to values of $2 /MMBTU. This fact, together with the use of flue gas as a revenue, reduces the production cost of liquid fuels to around $0.5/gal of liquid fuel with respect to the values presented by the red line in Figure 16. In this case, the production of liquid fuels out of glycerol becomes competitive if the switchgrass reaches $80/t, and glycerol reaches the DOE target of $0.05/lb.

5.-Conclusions

A superstructure modelling the flowsheet has been formulated be including three glycerol reforming modes, gas clean up, several alternatives for composition adjustment, sour gases removal and, for liquid fuels, FT synthesis. The corresponding MINLP problem is solved by decomposing it into hydrogen production and simultaneous production of hydrogen and liquid biofuels production since aqueous phase reforming can only produce hydrogen. Each subproblem is optimized to determine the operating conditions.

The results indicate that the production of fuels from glycerol is not competitive with the use of lignocellulosic switchgrass unless the price for glycerol is low. For the production of hydrogen alone, aqueous phase reforming is recommended. However, in order for this process to be competitive the prices of glycerol need to be $0.05/lb, around half the prediction of the DOE in the medium term.

Hydrogen production from glycerol produces CO_2. Due to the fact that glycerol is also a source of carbon we propose the simultaneous production of biofuels and hydrogen resulting in the fact that the simultaneous synthesis of FT-diesel, green gasoline and hydrogen, using glycerol autoreforming is suggested by the optimization. However, due to the number of pieces of equipment needed, and in spite of the net production of energy from the process, only if the glycerol cost goes down to $0.05/lb the production process becomes competitive with the production of FT-diesel from switchgrass even if the hydrogen is sold as a credit. Further experimental results at pilot plant level are needed to validate these results.

Acknowledgments

6.-Nomenclature.

Alpha   chain length
atomh   atoms de hydro
atomo   atoms de Oxygen
atomc   atoms de Carbono
CO_shift_conv   Conversion of CO in the water shift reactor
COtoH2   Molar ratio CO and H2 at mix1
Condensed_j   Water condensed before equipment j (kg/s)
COtoH2   Molar ratio CO and H2 at mix1
C_p_ind(J)   liquid phase heat capacity of element J   (kJ / kg*K)
c_p_v(J)   vapor phase heat capacity of element J   (kJ / kg*K)

coef_p(J,i) Coefficients of the Antoine equation for vapor pressure for element J.
dH_shift_reac Heat of reactor   (kJ/kmol)
fracCH4   fraction of gases C1 and C2
fracC3C4   fraction of gases C3-C4
fracgasolina   fraction of gasoline produced
fracdiesel   fraction of diesel produced
fracheavy   fraction of heavy products
fc(j,unit1, unit2)   individual mass flow rate (kg/s)
F(unit1,unit2)   mass flow rate (kg/s)
H2OtoCO   Molar ratio H2o and Co
Massproduct   Mass flow of liquid products   (kg/s)
Masshydro   Mass flow of hydrogen   (kg/s)
MassGas   mass of gas generated   (kg)
mol(j)   mol of component (J) j={H2,CO2, CO, CH4, H2O, C2H4, C2H2, C,O2} (kmol/s)
mea_conc   MEA concentration in water
MW_gas_j   Molecular weight in equipment j   (kg/kmol)
NonCondensed_j   Amount of water non condensed after equipment j (kg)
Oxygen_add   (mol steam per mor of carbon)
p_sat_j   saturation pressure equipment j (mmHg)
P_MEA   Working pressure at mea column   (bar)
P_PSA   Presure required for PSA bar   (bar)   ;
p_air   desorption pressue in mmHq (consitent with Antoine eq.) - 1 atm /760/ (mmHg)
P_flash2   Pressure at the flash   /760/   (mmHg)
Q_prod   Energy products   (kJ/s)
Q_reac;   Energy reactants   (kJ/s)
Rec_col4   reflux ratio at column 4   /2/
steam_add   mol steam per mo of carbon
S_diesel   Selectivity to diesel
S_gasoline   Selectivity to gasoline
T_compr(n)_st1   Temperature in the interstage of compressor (n) system   (ºC)
T_amb   ambient temperature /20/   (ºC)
 T_PSA   Working temperature of PSA systhems /25/   (ºC)
dT_min   EMAT /5/   (ºC)
T_cooldown   Cool down temperature /25/   (ºC)
T_flash2   /30/;   (ºC)
T_in_col4   /220/   (ºC)
T_dest   /125/   (ºC)
T_dest2   /220/   (ºC)
T_colas   /280/   (ºC)
T_Synthesis   Temperature at FT reactor   (ºC)
T_reactor3   Temperature at hydrocracking   (ºC)
T(unit1,unit2) Temperature of the stream from unit 1 to unit 2   (ºC)
Waterdecomp mass of water decomposed   (kg/s)
X_R3
x(J,unit1,unit2)   mass fraction of stream from unit 1 to unit 2
λ : Vaporization heat (kJ/kg)

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