Process Optimization of FT-Diesel Production

from Lignocellulosic Switchgrass

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Abstract.

In this paper we present the conceptual design for the optimization of FT-diesel production process from switchgrass via gasification of biomass. We propose a limited superstructure where the process starts with the gasification of the biomass. Two different alternatives are evaluated, direct and indirect gasification. The gas obtained is cleaned up and its composition adjusted in terms of the ratio CO / H_2 considering a bypass, a PSA system and water gas shift reaction. Next, the removal of CO_2 and H_2S is performed using absorption in ethanolamines and PSA. Once the syngas is prepared the Fischer - Tropsch reaction is conducted and the products separated. Hydrocracking of the heavy products is also considered to increase the yield towards green diesel. The optimization of the system is formulated as an equation-based Mixed-Integer Non-linear Programming (MINLP) problem that is solved for the optimal production of the biodiesel fraction while minimizing the energy consumption and the hydrogen consumption. The optimal solution requires the use of indirect gasification followed by steam reforming. The ratio CO /H_2 is left as the one obtained after gas reforming while adjusting the temperature at the FT reactor and the operating conditions of the hydrocracking to increase the FT-diesel production. A promising production cost of 0.72 $/gallon is obtained and only 0.15 gal $_{Water}$ / gal $_{bioifuel}$ of water consumption is requried if air cooling is implemented in the plant.

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

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1.-Introduccion

A number of reasons such as the limited nature of the energy resources together with the increasing demand and dependency on fossil fuels have encouraged the development of clean and renewable fuels. Among the different alternatives like solar, hydroelectric, geothermic, wind, only biomass provides a raw material capable of entering the market in the short term because of the similarity of its products with the current liquid fuels and the possibility of sharing their supply chain. Biomass has focused the effort for producing biofuels over the last decades (primarily corn-based ethanol but also biodiesel derived from soybeans and canola oil). However, the impacts on the food supply chain (Rosegrant, 2008) and indirect land for growing biomass for energy on croplands (Searchinger, 2008; Fargione et al. 2008) have raised some concerns, thereby driving the efforts towards the use of lignocellulosic feedstocks, a non-food biomass (various crop and forest residues and energy crops that can be grown on degraded lands). These options include cellulosic ethanol produced biochemically and synthetic fuels derived thermochemically via biomass gasification, the so called biomass to liquids (BTL) technologies based on Fischer-Tropsch synthesis (Wilhelm et al., 2001)

Fischer-Tropsch liquids can be refined to various amounts of renewable (green) gasoline, diesel fuel, and aviation fuel by selecting appropriate process conditions. Depending on the types and quantities of Fischer-Tropsch products desired, either low (200–240 °C) or high temperature (300–350 °C) synthesis at pressures ranging between 10 to 40 bar are used with either cobalt or iron based catalysts (Brown & Wright, 2009).

Diesel fuel has gained adepts in Europe since the technology in the automobiles has become competitive with that of gasoline, and currently represents half the fuel consumed by road transportation in the EU, while in the US it accounts for 22% of the road transportation (Shelley, 2008). Thus, the FT production method has recently been received great attention as a way of exploiting natural gas reserves, coal or biomasses, to produce a mixture of gaseous, liquid and solid hydrocarbons with high added-value. However, Choi et al. (1996) suggested that the FT-gasoline and FT-diesel is 10.07 $/bbl (0.24 $/gallon) and 7.19 $/bbl (0.17 $/gallon) more expensive than transportation fuels derived from crude oil. So far most of the work has focused on the optimization of the reactor conditions (Wang et al., 2008, Teles & Fernandes, 2008, Kim et al., 2009), while the process design has been studied with case studies in which operating conditions are fixed at the experimental results of the reactor (Swanson et al., 2010). A more comprehensive analysis of the complete process is clearly

needed for selecting among different technologies and defining the operating conditions so as to optimize the process.

In this paper we focus on the conceptual design for the production of green diesel from lignocellulosic feedstock using the FT technology so as to make it competitive. To improve the design and the energy efficiency of lignocellulosic biodiesel, mathematical optimization techniques can be used (for optimal process synthesis problems see Grossmann et al., 1999). We propose a limited superstructure optimization approach where we first construct a flowsheet embedding the various process units involved in FT- diesel production, and then consider alternatives for some of the processes. These units are interconnected through network flows and other utility streams. The goal is to optimize the structure and the operating conditions to maximize FT-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 as well as design correlations. We then perform heat integration of the resulting process followed by an economic evaluation to select on the best technology (Grossmann and Martín 2010). Finally for the optimal solution we evaluate the water consumption using mathematical programming techniques (Ahmetovic et al. 2010)

2. Overall Process Description

The process consists of four different parts. The first one is the gasification of the biomass, switchgrass. Two different technologies have been considered: (1) Indirect gasification with steam where the combustion of char in a combustor heats up sand to provide energy for the gasification in a second chamber. (2) Direct gasification of the raw material with steam and oxygen, to avoid the dilution of the gas. The gas generated must be cleaned from solids as well as other compounds like hydrocarbons, NH_3, CO_2 or H_2S generated in the gasification. The hydrocarbons are partially removed in the tar where they are either reformed with steam or partially oxidized (Rand & Dell, 2008). In the case when high pressure is selected, solids are removed in a ceramic filter and next the gas is expanded generating energy. If the indirect lower pressure gasifier is used, the solids are removed together with NH_3 in a wet scrubber and the gas is compressed. The traces of hydrocarbons are removed in a PSA system with a bed of Silica gel. At this point 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) depending on the FT reactor.

Three alternatives are considered: Water Gas Shift reactor, bypass and hybrid membrane / PSA for H_2 (with a bed of oxides). The split fraction depends on the performance of the gasifier and the tar reformer.

The second part corresponds to the removal of sour gases, CO_2 and H_2S. According to the study by Martin & Grossmann (2011a) two technologies operating in sequence are considered for this task: the absorption of the sour gases in monoethanol amine (MEA) followed by a PSA system with a bed of Zeolite 5A .

Once the gas is purified, the syngas consisting of H_2 and CO follows the Fischer-Tropsch synthesis to produce liquid hydrocarbons using a catalyst of iron or cobalt. The operating conditions are to be optimized (ratio of H_2 and CO and operating temperature at the reactor). The synthetic diesel is produced in addition to gasoline, gas products and heavy fuels (Opdal & Skreiberg, 2006). The optimal operating pressure is assumed to be 30 atm according to experimental results (Wang 2008).
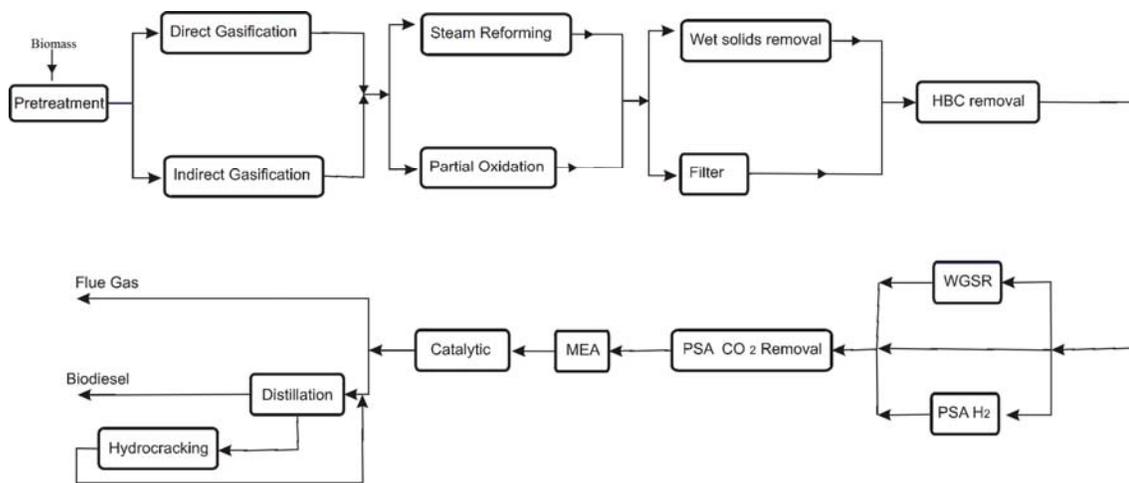
Figure 1.- Superstrcuture for the production of FT- Diesel

Finally, the FT liquids produced are separated using atmospheric distillation. The heavy products can be hydrotreated to increase the yield to diesel (Dry, 2002). The results from Bezergianni et al. (2009) are used to provide a model for the hydrocracking of the heavy oil. Figure 1 shows the superestructure embedding the different alternatives.

3.-Mathematical modelling.

All the unit operations in the production process of FT-diesel from the gasification of lignocellulosic raw materials are modeled using reduced order models for the reactors (FT, WGSR and Hidrocracking) mass and energy balances and design equations. The model is written in terms of the total mass flows, component mass flows, component mass fractions, and temperatures of the streams in the network that are the main variables whose values have to be determined from the optimization. The details for switchgrass gasification and gas clean up can be found in a previous paper by the authors (Martin & Grossmann 2011a). Here we only present a brief description. The components in the system include those present in the switchgrass, plus those produced during the process of liquid fuels production, and belong to the set $J = \{$ Wa, Met, But, Gasoline, Diesel, Wax, C_6H_6, MEA, Tars, CO_2, CO, O_2, N_2, H_2, H_2S, NH_3, CH_4, C_2H_2, C_2H_4, C_2H_6, SO_2, C, H, O, S, N, Olivine, Char, Ash $\}$.

3.1.-Pretreatment

The pre-treatment stage consists of washing the incoming feed of switchgrass with a stream of freshwater with no contaminants inside a washing unit. This step removes dirt and dust from the grass. A small amount of the wash water (1%) is assumed to stay with the feed. The spent washing water is treated and then reused in other processes in the plant, although this option is not considered in the model. It is assumed that 0.5 kg of washing water is needed to wash 1 kg of switchgrass. The washing step does not consume any heat because it takes place at room temperature. Then, the grass is partially dried by means of a mechanical press being able to remove 90% of the water that goes with the switchgrass. In order for the gasification to be effective, a reduction in the size of the grass is needed. However, the size required is bigger, around 10 mm, than in case of chemical pretreatment. Thus the energy needed is comparatively smaller, 30kWh/t (Mani et al., 2004).

3.2.-Gasification

Many different alternatives can be found in the literature for gasification (Bridgwater 2003). In this paper we consider the two most popular ones, indirect gasification and direct gasification. The first technology generates more hydrocarbons but operates at low pressure and can use air for the combustion of the char. The

direct gasifier requires pure oxygen so as to avoid diluting the gas generated and produces less hydrocarbons. Further details can be seen in Martin and Grossmann (2011a).

Indirect gasification (Ferco based gasifier): For this technology the switchgrass from the grinding stage enters the gasifier together with steam and a type of sand, olivine, that provides the energy. The gas generated is separated from the solids, mainly char and olivine, in a cyclone. The gas is cleaned in further steps. The solids go to a second chamber, the combustor, where the char is burned to provide the energy to reheat the sand. Due to the fact that the combustion takes place in a different chamber, air can be used. A make-up of sand due to the losses must also be provided. The solids, mainly olivine, are separated from the gases in a cyclone and recycled to the gasifier. The combustion gas is cleaned from ash and cooled down from where energy can be obtained for the process.

The model for this system is based on the experimental results presented in Phillips et al., (2007) that assumes an equilibrium between the gasifier and the combustor takes place when the gasifier works at 890 °C and 1.6 bar and the combustor works at 995 °C.

Direct (Renugas based gasifier): The design of the direct gasifier is simpler than the indirect one. In this case the switchgrass is fed to the gasifier together with pure oxygen and steam. We consider that only steam and no nitrogen is used to pressurize and fluidize the gasifier, thereby avoiding the dilution of the syngas generated. The experimental values for a pilot plant gasifier are used to calculate the gas generated (Gissy et al., 1992). The basic equations for determining the composition of the char and the gases are similar as for the low pressure indirect gasifier but using the new composition of the gas and the oxygen and steam specified by (Gissy et al. 1992). The gas exiting the direct gasifier is cleaned from char in Cyclon 3. All the ash in the biomass is assumed to be in the char. Cyclon 3 removes most of the char before the gas is set to the reforming stage.

3.3.-Hydrocarbon removal

There are two main alternatives for decomposing the hydrocarbons generated during the gasification process, steam reforming and partial oxidation. The first one produces more hydrogen but is endothermic, reducing the energy available within the process for heat integration but generates more hydrogen. Partial oxidation is exothermic, which provides energy for the system but the yield to hydrogen is lower. Other processes

that are not considered are dry reforming, by using CO_2 instead of steam or oxygen or auto-thermal reforming (Rand & Dell, 2008).

Steam reforming: The reactions taking place are of the form given by eq. (1)-(2). Thus, the mass balances for the different species are given based on the stoichometric relationships derived from them. We assume the conversions of the hydrocarbons are given as (Conv_CH4 = 0.8, Conv_C6H6 = 1, Conv_Tar = 1, Conv_C2H6 = 0.99, Conv_C2H2 = 0.90, Conv_C2H4 = 0.90) and that of the ammonia (Conv_NH3 = 0.90) as proposed by Philips et al. (2007). The reactions are endothermic. We assume that the reactor works adiabatically and that the final temperature is reduced to provide energy for the reactions.

$$C_nH_m + nH_2O \longrightarrow nCO + (\frac{m}{2} + n)H_2 \tag{1}$$

$$NH_3 \longrightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2 \tag{2}$$
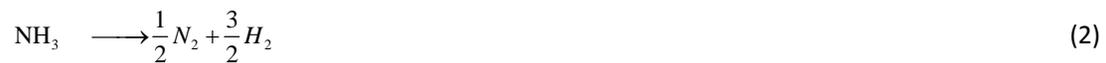
Partial Oxidation: For partial oxidation, pure oxygen is provided to eliminate the hydrocarbons generated during the gasification process generating more CO and hydrogen. The oxygen injected is calculated from the stoichiometry. Thus, the inlet temperature to the HX4 is be calculated assuming adiabatic mixing of the streams from the gasifier and that provide oxygen. The HX4 will only be used in case of using low pressure indirect gasifier since otherwise the process of heating up this stream is too expensive and no energy is available for it. The tar reformer can work at low or high pressure (Brenes, 2006). Thus, the equations are unchanged if the feed comes from cyclon 1 (low pressure indirect gasifier) or 3 (high pressure direct gasifier). Thus, the mass balances of the species in the tar are calculated based on the conversions of the hydrocarbons and the ammonia following the stoichiometric relationships given by eqs (2-3):

$$C_nH_m + \frac{n}{2}O_2 \longrightarrow nCO + \frac{m}{2}H_2 \tag{3}$$
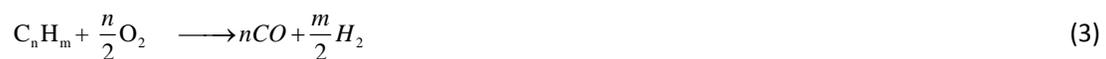
The conversions of the different hydrocarbons (Conv_i) are taken to be the same as in the report by Philip et al. (2007) based on the results by Vernon et al. (1990) and Deutschmann & Schmidt (1998). The process is exothermic and we assume that it is able to generate steam in order to cool down the equipment.

3.4.-Clean up

We consider two different possibilities to remove the solids from the gas; the so called hot and cold cleaning (Olofsson et al., 2005). In case of operating at high pressure, hot cleaning is used. If we operate at low pressure, cold cleaning is considered

Hot cleaning. The steam coming from the high pressure from the reformer is cooled to 500 ºC and is treated at a ceramic filter to remove the solids. In the filter only the solids (Char, Olivine) are eliminated. The gases leaving the filter are expanded to obtain energy before entering the PSA system. The expansion is assumed to be polytropic to calculate the final temperature of the gas and the energy that is obtained. Next, the stream is fed to the hydrocarbon trace removal.

Cold cleaning: If the indirect gasifier is used, the gas stream is cleaned at low pressure. Then, the gas is cooled down to 40 ºC, and as a result water condenses. The amount of condensed water is calculated based on the saturation humidity at the operating conditions of the scrubber (1.2 bar and 40ºC). Then, the stream is fed to the scrubber. The amount of water needed for the scrubber is given by rules of thumb in the literature (0.25 kg per m^3 of gas (Martelli et al., 2009)). The inlet water is at atmospheric temperature, 20 ºC. In the scrubber, solids (Ash, Char and Olivine) and NH_3 are be eliminated while the gas exits the scrubber with a humidity calculated assuming saturated conditions for the gas exiting the equipment. The final temperature at the scrubber is calculated assuming adiabatic behaviour. The stream coming out of the scrubber is saturated with water and is compressed to the working conditions of the PSA system, 4.5 bar (Olofsson et al., 2005) in Compressor 1. The final temperature and the energy required are calculated assuming polytopic behavior. The stream is fed to the PSA system.

PSA - HBC: The traces of hydrocarbons that have not been eliminated in the reformer are withdrawn from the gas stream using a PSA system. The typical working conditions for PSA systems are ambient 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). Due to the low temperature, more water condenses before the PSA adsorption beds and it is discharged. 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 and the nitrogen.

3.5.-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. In order to perform such adjustment we consider three technologies. The first one is the use of water gas shift to reduce the amount of CO by producing more H_2. The second is a simple bypass where the composition remains unchanged. Finally, a hybrid membrane/PSA system with a bed of Zeolite 13X is proposed to remove hydrogen (Neves & Schvartzman, 2005, Choi et al. 2010).

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

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

Its conversion depends on the molar ratio of steam to CO and the working temperature. Thus, using the experimental data by Choi et al. (2003), we developed a correlation (Martin & Grossmann, 2011c) to predict the conversion as function of both parameters so that the model can be solved in steady state. The optimization determines the addition of water as well as the temperature and the conversion of the reaction to minimize the energy consumption while maximizing the FT-diesel production.

Bypass: It may be possible that the stream does not need any adjustment in the CO:H_2 ratio due to the cost of that or simply because the composition is already suitable for the synthesis. 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 hydrogen (http://www.ist-world.org) has to be adjusted in terms of temperature, 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 behavior to determine the final temperature and energy required. As a result of the cooling, 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 100%. The other gases pass though. Finally, all the streams are mixed adiabatically. The ratio CO and H_2 is determined by the needs of the reactor to maximize the FT diesel production.

3.6.-CO_2 removal

The removal of CO_2 and H_2S is the last cleaning stage for the preparation of the syngas. Two different technologies that can work in sequence or in parallel are as follows:

CO_2 removal by PSA system: 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). Fig. 2 shows a scheme of the process. The cycle is short and the absorption capacity is around 0.1kg of CO_2 per kg of zeolite. The system is modeled as two beds, one operating and the second one in regeneration to allow continuous operation of the plant. As it was mentioned before, the operating conditions are 25 ºC and 4.5 bar.
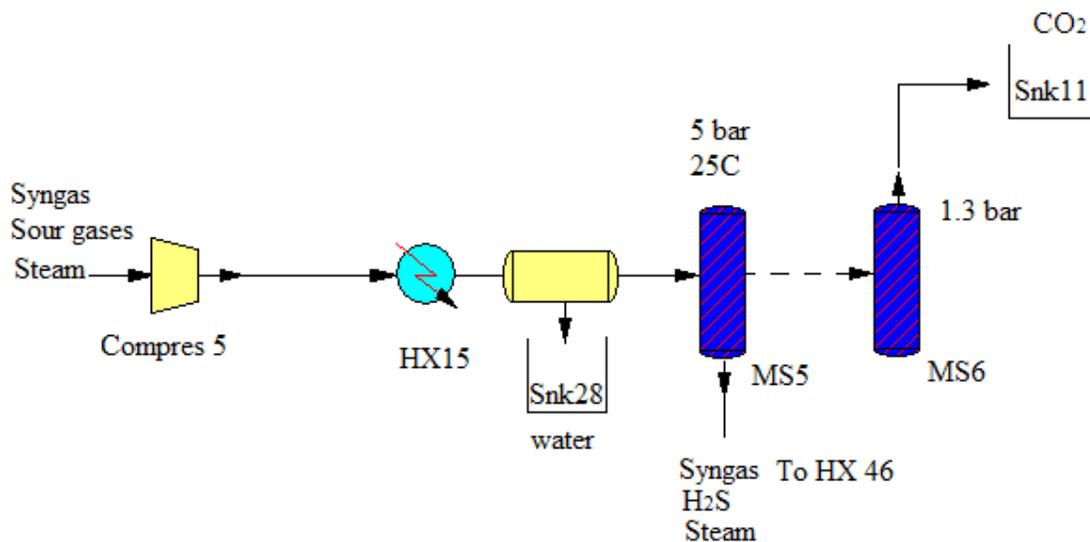
Figure 2.- PSA system for the removal of CO_2

Thus, a system comprised by a compressor and a heat exchanger are used to adjust the operating conditions. Once both streams are mixed at the working pressure they are cooled down to 25 ºC in HX15. In this process water condenses. The amount of water condensed is given by the saturation conditions of the exiting gas. The efficiency of the PSA system has an efficiency of 95% in CO_2 and 0 for any other gas of the mixture. However, the water vapor will accompany the CO_2 and is absorbed too. The outlet of the PSA system, once the majority of CO_2 has been removed, can be fed to the reaction system or recycled back to the MEA system, to mixer 2, for further treatment of H_2S.

CO_2 removal by MEA system: Typically MEA systems are used to further remove CO_2 and H_2S. These systems commonly operate at 29 ºC and elevated pressure, 29 bar (GPSA 2004, Philips et al. 2007, Nexant Inc.

(2006 a, b & c)). The sour gas in placed into contact with the MEA in a column adiabatically, see Figs. 3 and 4. The heat of reaction heats up the exiting streams. The liquid stream is treated to recover the amine in a distillation column, while the gas can be directed to synthesis, or fed to another process to continue the treatment in case the degree of purity is not achieved. Due to the required increase in the pressure, a two stage system with inter cooling is proposed. Thus, the temperature after each of the compressors and the energy required are calculated assuming adiabatic behavior with inter-cooling.

Once the gas is at the desired pressure, it has to be cooled down to 29 °C. Thus, condensation is likely. The water is eliminated to avoid the dilution of the solution of MEA. The main stream coming from mix 2 is treated in column 1 for the regeneration of the MEA. The characteristics of the solution of MEA needed to remove the CO_2 and H_2S are taken from GPSA (2004).
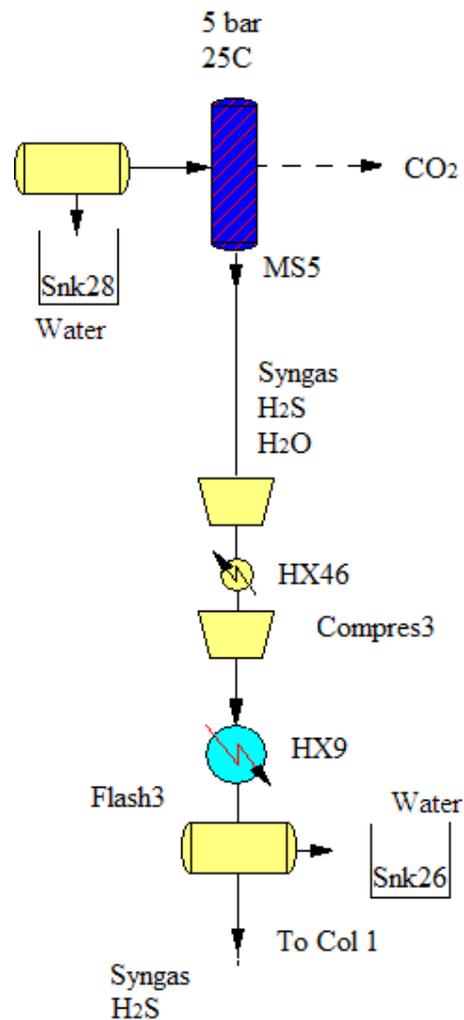
Figure 3.- Scheme for the removal of H_2S and CO_2

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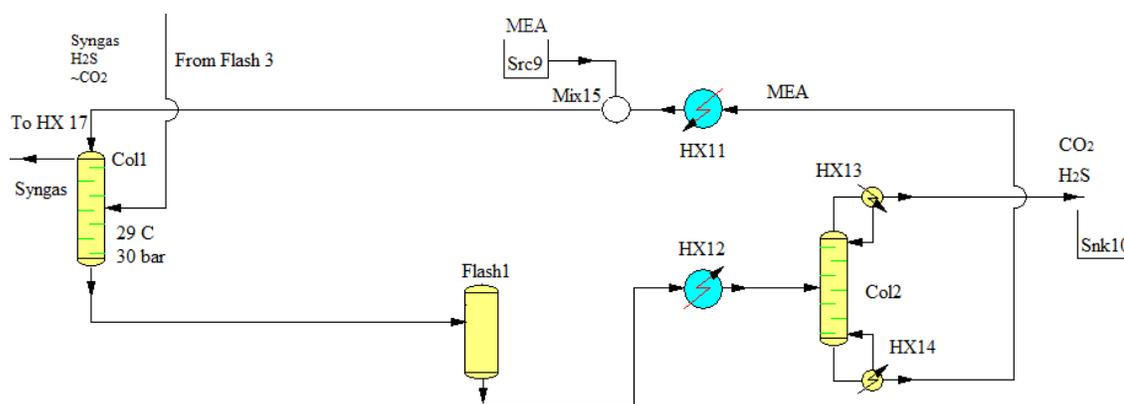
Figure 4.- Flowshee of the MEA regeneration

The MEA used in the column has two sources, fresh MEA and the one regenerated in a distillation column (Column 2). The final temperature of the mixture must be 29ºC, the operating temperature at the absorber column . HX 11 is used to cool down the MEA from the recovery column. The temperature of the streams exiting column 1 is calculated assuming adiabatic behavior of the column considering the heat of reaction due to the absorption of the sour gases on the MEA solution. The efficiencies for the recovery of sour gases are 0.9 and 1 for CO_2 and H_2S, respectively. The gas phase coming out of column 1 is calculated based on the separation efficiencies. The MEA with the sour gas is treated in a distillation column to regenerate the amine. The operation of this column is based on the experimental data and design conditions provided by GPSA (2004) and Nexant Inc. (2005), where the working temperatures as well as the energy required for regenerating the MEA are given. Thus , the energy balances are based on those recommendations (T_{Col2} = 93 ºC; T_{MEA_boil} =125 ºC; T_{MEA_ref} = 54 ºC). From the reboiler, the MEA regenerated is obtained and recycled to HX11. From the condenser, sour gases are produced, CO_2 and H_2S which carries MEA with them saturating the gases at P_{Col2} = 1.7 bar and 54 ºC. This is the MEA that must be fed to the system. The gas from Col1 is fed to the synthetic part of the plant.

Since the H_2S is toxic for the catalysts it has to be completely removed from the gas (Philips et al., 2007). The gas from treatment must be heated up to $T_{synthesis}$. The temperature and the ratio of CO and H_2 must be optimized for the correct distribution of fractions. According to the results by Wang et al (2008) the optimal pressure for diesel is 30bar (Wang et al., 2008). This fact, together with the toxicity of the H_2S for the catalytic and the results from the previous paper (Martin and Grossmann, 2011a), defines the clean-up of the gas as follows:

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the first stage is the PSA for the removal of CO_2, and next the MEA absorption which provides with the proper pressure for the Fischer Tropsch reactor.

3.7.-Synthesis

Figure 5 presents the scheme for the synthesis of liquid fuels from syngas.

Figure 5.- FT Reactor

Figure 6.- Polymerization scheme for the synthesis of high hydrocarbons

The details on the elementary chemical steps occurring on the surface of the catalysts have always been a matter of controversy, but the general agreement is that a stepwise chain growth process is involved equivalent to the polymerization of monomers. The formation of higher hydrocarbons is believed to occur through the dissociation of carbon monoxide. Figure 6 shows the polymerization path. At each stage of the growth process, the surface species (at first, surface carbon) have the option of desorbing to produce an alkene, or to be hydrogenated to desorb as an alkane, or to continue the chain growth process by adding another CH_2. Fischer-Tropsch liquids can be refined to various amounts of renewable (green) gasoline, diesel fuel, and aviation fuel depending upon process conditions.

The main reactions can be seen in eqs. (5)-(6). The first reaction in eq. (5) corresponds to methanation, the second is the water gas shift (WGS) reaction and the third reaction is the Boudouard reaction. The methanation reaction and the Boudouard reaction are undesirable.

$$CO + 3H_2 \longrightarrow CH_4 + H_2O; \qquad \Delta H_{298} = 247 kJ/mol$$
$$CO + H_2O \longrightarrow CO_2 + H_2; \qquad \Delta H_{298} = -41 kJ/mol \tag{5}$$
$$2CO \longrightarrow C + CO_2; \qquad \Delta H_{298} = -172 kJ/mol$$
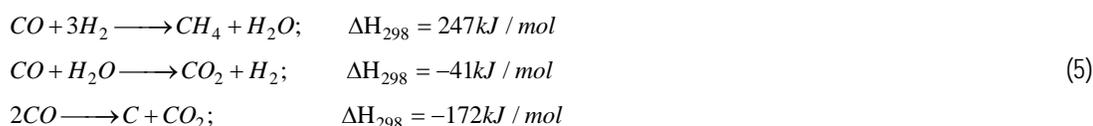
The reaction given in eq. (6) is desired and is the most dominant reaction when applying cobalt-based FT catalyst. When using iron-based catalyst, the WGS reaction also readily occurs enabling the operation at a lower temperature.

$$nCO + \left(n + \frac{m}{2}\right)H_2 \longrightarrow C_nH_m + nH_2O \tag{6}$$
$$CO + 2H_2 \longrightarrow -CH_2- + H_2O; \qquad \Delta H_{FT} = -165 kJ/mol$$
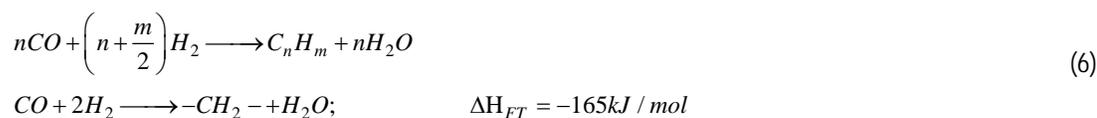
The operating conditions depend on the types and quantities of Fischer-Tropsch products desired, ranging from either low (200–240 °C) or high (300–350 °C) temperatures, and pressures from 10 to 40 bar employing either cobalt or iron based catalysts. However, the iron catalyst provides high selectivity in interval between $C_{10} – C_{18}$, which means a high yield of diesel. Moreover, the reactions with iron catalyst are usually conducted at 30 bars, which is convenient due to the fact that the MEA treatment is already operating at that pressure, and thus, is the catalysts of choice. 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).
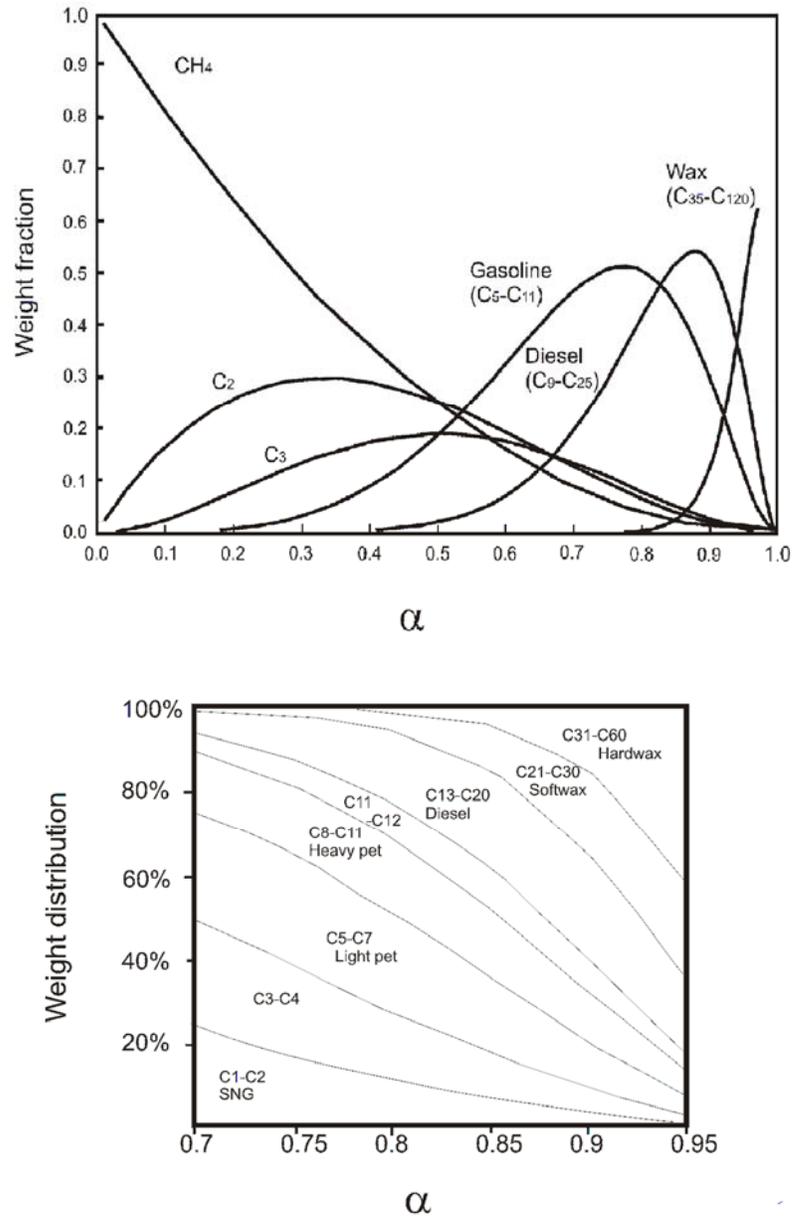
Figure 7.- Distribution of products from FT reaction

To determine the operating conditions we propose a model for the FT-reactor based on the Anderson-Schulz-Flory (ASF) distribution (Schulz, 1999) assuming that the Fischer - Tropsch reactor works as a polymerization reactor (Fürnsinn et al., 2005). The fraction of mass of the hydrocarbons i = number of C, w_i,

depends on the probability of chain growth, α. A conversion of 0.9 in CO is considered (Park & Norbeck, 2009). According to the studies by Song (2004), α is a function of the temperature, and the ratio CO to H_2 through eqs. (7-8) determine w_i. Figure 7 shows the effect of the value of alpha on the distribution of products obtained in the reaction. The distribution is to be optimized for the production of FT-diesel.

$$w_i = \alpha^{i-1}(1-\alpha)^2 \cdot i \tag{7}$$

$$\alpha = \left(0.2332 * \left(\frac{y_{co}}{y_{H_2} + y_{co}}\right) + 0.633\right) * \left(1 - 0.0039 * \left((T\_Synthesis + 273) - 533\right)\right) \tag{8}$$

The distribution of the different fractions is calculated by numerical integration. Thus, the following expressions are proposed for calculating the fraction of the different products as a function of α:

$$fracCH4 = (1-\alpha)^2 + (\alpha)*(1-\alpha)^2 *2 \tag{9}$$

$$fracC3C4 = \alpha^2 (1-\alpha)^2 \cdot 3 + (\alpha)^3 *(1-\alpha)^2 *4 \tag{10}$$

$$fracgasolina = 3(\alpha^4 (1-\alpha)^2 \cdot 5 + (\alpha)^9 *(1-\alpha)^2 *10) \tag{11}$$

$$fracdiesel = 5(\alpha^{10} (1-\alpha)^2 \cdot 11 + (\alpha)^{19} *(1-\alpha)^2 *20) \tag{12}$$

$$fracwax = 1 - fracCH4 - fracC3C4 - fracgasolina - fracdiesel; \tag{13}$$

$$fc(j,'Spl3','HX17') = fc(j,'HX17','Reactor2'); \qquad \forall j \notin J \tag{14}$$

Thus, the mass balances in the reactor are simplified to eqs. (15) – (24) using the values calculated for the different fractions of the products.

$$fc('Wa','Reactor2','HX21') = fc('Wa','HX17','Reactor2') + \left(\frac{MW_{Wa}}{MW_{CO}}\right) * Convr\_CO * fc('CO','HX17','Reactor2');$$

$$\tag{15}$$

$$fc('CO','Reactor2','HX21') = (1\text{-}Convr\_CO) * fc('CO','HX17','Reactor2'); \tag{16}$$

$$fc('H2','Reactor2','HX21') = (1\text{-}Convr\_CO) * fc('H2','HX17','Reactor2'); \tag{17}$$

$$fc('CO2','Reactor2','HX21') = fc('CO2','HX17','Reactor2'); \tag{18}$$

$$Massproduct = Convr\_CO * \left(fc('H2','HX17','Reactor2') + (1 - \frac{MW_{Wa}}{MW_{CO}}) \cdot fc('CO','HX17','Reactor2') \right) \tag{19}$$

$$fc('Met','Reactor2','HX21') = fracCH4 * Massproduct \tag{20}$$

$$fc('But','Reactor2','HX21') = fracC3C4 * Massproduct \tag{21}$$

$$fc('Gasoline','Reactor2','HX21') = fracgasolina * Massproduct \tag{22}$$

$$fc(\text{'Diesel'},\text{'Reactor2'},\text{'HX21'}) = fracdiesel * Massproduct; \tag{23}$$

$$fc(\text{'Wax'},\text{'Reactor2'},\text{'HX21'}) = fracwax * Massproduct; \tag{24}$$

3.8.-Separation and hydrotreatment.

The separation of the hydrocarbons is common in the petrochemical industry. The most important problem is the fact that we are dealing with a mixture of compounds instead of single species. 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 the mixture is cooled down to 30ºC in HX21. See figure 5 for the Flowsheet of the separation

The vapor recovery of the flash is assumed to be 1 for the gases and small 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 as flue gas to produce energy. Figure 8 shows the scheme of the separation of the C1-C2 fraction from C3-C4 fractions. The efficiency of the flash 5 is considered to be 1 for the gases C3 and C4, and 0 for the methane and ethane, H_2 and others. From the expansion of the gases energy can be obtained. These gases can be used later as flue gas or recycled to the process.
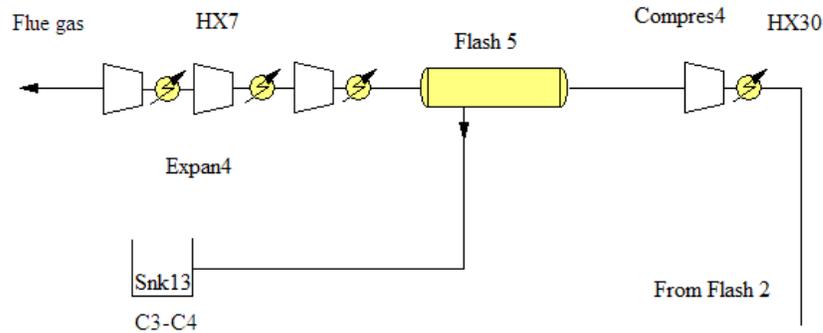
Figure 8. Gas treatment and separation
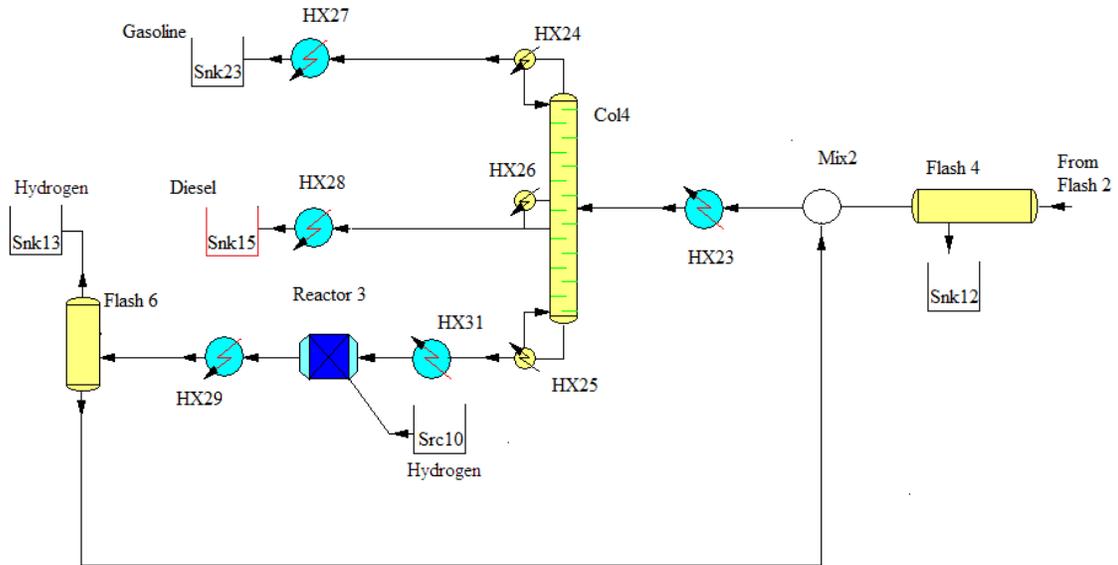
Figure 9.- Diesel and gasoline fractionation

The three liquid fractions are separated as in any crude distillation system as shown in Figure 9. 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 from the top mainly gasoline, form the middle diesel and from the bottom the heavy fraction. These kind of columns do not have a reboiler since steam is directly injected. In order to simplify the model, since the steam is considered inert in the column, the energy that must be provided to the column is simulated as heat exchanger 25.

The bottoms of the column can be treated to obtain more diesel. Hydrocracking is the best option in order to produce diesel virtually free from aromatics (Dry, 2002). The temperature of operation is selected so as to optimize the production of diesel.
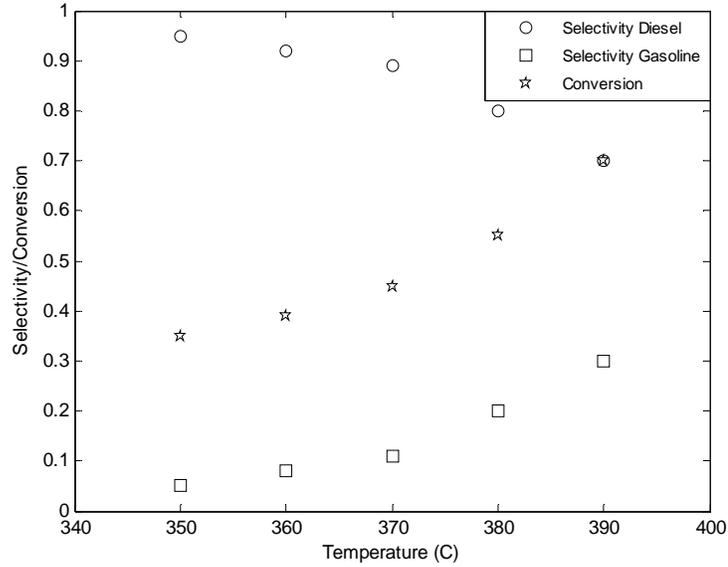
Figure 10.- Conversion profiles for the hydrocracking reactor

To model the hydrocracking reactor we use the experimental data for the conversion and selectivity as a function of the temperature from the paper presented by Bezergianni et al. (2009). Figure 10 shows the profiles of the conversion and selectivity to the main products. We correlate these profiles using polynomials to develop a reduced order model for the hydrocracking reactor, equations. (25)-(26).

$$X\_R3 = 0.000185714*\left(T\_reactor3\right)^2 - 0.128829*T\_reactor3 + 22.6931; \tag{25}$$

$$S\_diesel = -0.00014286*\left(T\_reactor3\right)^2 + 0.099514*T\_reactor3 - 16.383; \tag{26}$$

The reactor also requires a stream of 600 scft/bbl of hydrogen (Speight, 1991). Eq. (27) models the input of hydrogen and heavy fraction to the reactor.

$$masshydro = 1.01 \cdot fc\left('Heavy','HX23','Col4'\right) \tag{27}$$

Thus, the products from the reactor will be:

$$fc\left('Diesel','Reactor3','HX29'\right) = X\_R3*S\_diesel*masshydro; \tag{28}$$

$$fc\left('Gasoline','Reactor3','HX29'\right) = X\_R3*\left(1-S\_diesel\right)*masshydro; \tag{29}$$

$$fc\left('Heavy','Reactor3','HX29'\right) = \left(1-X\_R3\right)*masshydro; \tag{30}$$

$$fc\left('H2','Reactor3','HX29'\right) = 0.15*m\left('Heavy','HX23','Col4'\right); \tag{31}$$

These products will be separated by cooling them to 30 ºC in a flash so that the fraction of C3-C4 will be mixed with the one obtained in the reactor, while the gasoline and Diesel fractions are recycled to the column to be separated. The H_2 is separated so as to be recycled so that the make-up of hydrogen is small. Meanwhile, the liquids (Gasoline, Diesel and Heavy) are recycled to the column to be separated.

3.9.-Solution procedure.

A partial decomposition technique is used. The original MINLP problem is decomposed into 4 NLP's subproblems, whether the selected gasification is direct or indirect, and whether the reforming is partial oxidation or steam reforming. Figure 11 shows the tree resulting from the partial decomposition of the problem.
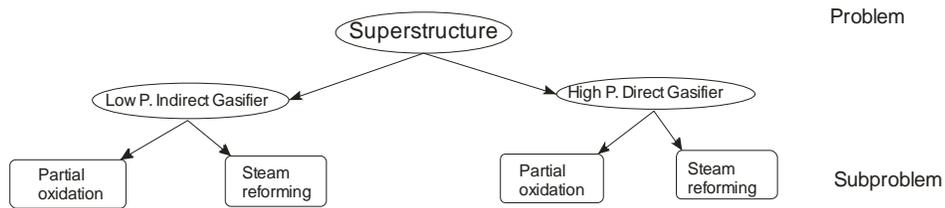
Figure 11.- Decomposition of the problem

The MINLP problem is then decomposed into subproblems, each consisting of around 5,500 equations and 6,200 variables, and each is solved as an NLP which optimizes the operation conditions, such as the ratio CO/H_2 to be used at the reactor, the operating temperature in the WGSR and the Fischer - Tropsch reactor and the operating conditions in the hydrocraking unit. The objective function to be maximized is given by a simplified manufacturing cost where the selling price of diesel is assumed to be 1 $/kg and the use of energy to prepare the feed for the WGSR and the FT reactor as well as the cost of hydrogen used in hydro cracking must be minimized.

$$Z = (m(Diesel, Col4, Snk15) \cdot 1) - 0.0005 \cdot 0.019 \cdot (Q(HX8) + Q(HX17) + Steam_{WGSR}) - 0.01 \cdot m(Wax, HX23, Col4) \cdot 1.6$$

$$(32)$$

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 amount of steam needed) the operating conditions in the Fischer-Tropsch reactor (temperature and CO/H_2 ratio), and the

hydrocracking conditions. Next, the heat integration within the process is performed to design the heat exchanger network and to reuse the excess of energy. Finally, a detailed economic evaluation is carried out to decide upon the different four subproblems.

4.-Results and discussion.

In order to compare this facility with bioethanol production plants and due to limitations in the availability of raw material, the production capacity of the liquid biofuel (biodiesel and green gasoline) is fixed to be 60 Mgal/yr. The optimization of each of the four subproblems results in three main operating features:

-The optimal ratio H_2/CO at the FT-reactor is the one generated after gasification and reforming without further composition adjustment because the values range from 1.5 to 2, which are the preferred ones for diesel production according to the literature (Wang et al., 2008: Swanson et al., 2010). So far the studies suggested adjusting the ratio H_2/CO to 2 due to the optimization of the process based on optimal operating conditions in the reactor (Wang et al., 2008; Teles and Fernandes, 2008; Kim et al., 2009; Swanson et al., 2010). As it is shown in this paper, a more comprehensive analysis is required to obtain a better solution to the problem.

-The main variable that determines the yield towards diesel is the temperature at the FT-reactor so that the probability for the chain growth reaches around 0.91 in all four subproblems, a value typically reported in the literature (Swanson et al., 2010). The optimal distribution of products from the FT-reactor can be seen in Figure 12
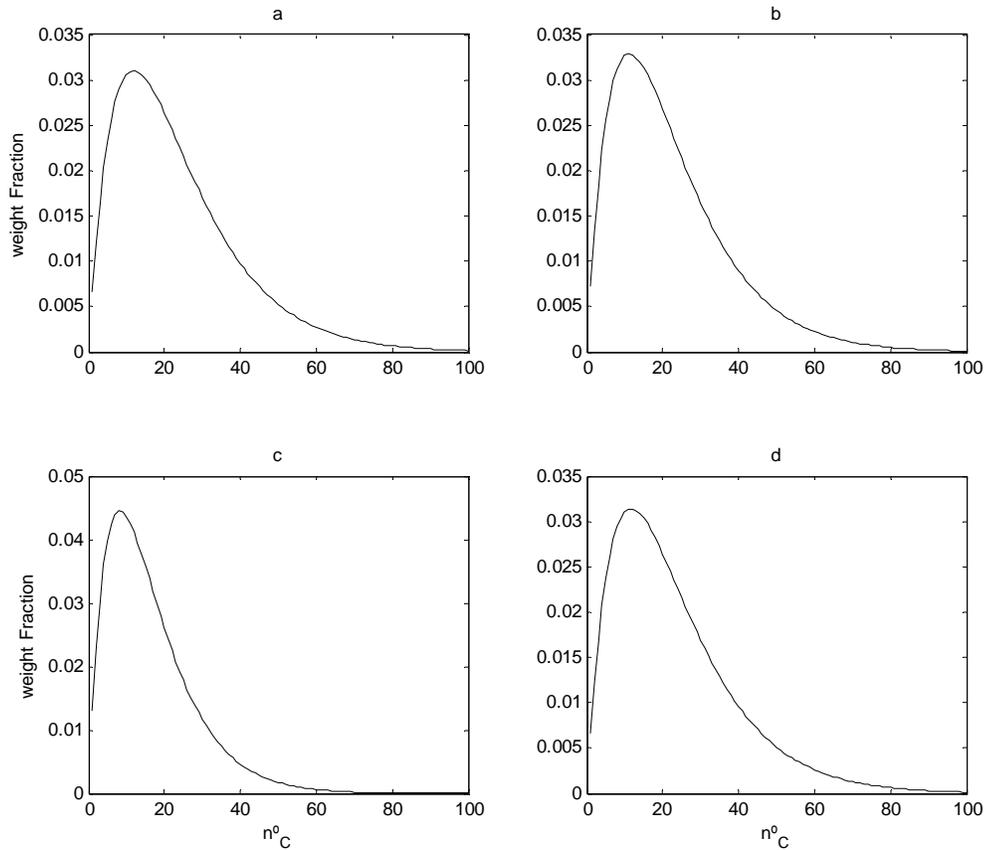
a) Ferco Gasifier, Partial Oxidation. b) Ferco Gasifier Steam Reforming c) Renugas gasifier, Partial Oxidation. d) Renugas gasifier. Steam Reforming.
Figure 12.- Optimized distribution of products

-The effect of the cost of hydrogen for hydrocracking is negligible in the operating conditions so long as the unreacted hydrogen is recycled. However, if there is no recycle of hydrogen the cost of hydrogen is so significant that the conditions in the FT reactor change in order to reduce the amount of heavy generated and thus reduce the consumption of hydrogen for hydrocracking. In general, this option is not further evaluated since the amount of hydrogen unreacted is so important that it makes perfect sense to recycle it

Figure 13 shows the net energy balance for the four subproblems. The high operating temperature at the F-T reactor, 200-225 ºC, and at the hydrocracking, at 350ºC, allow the generation of steam not only to satisfy the requirements of the gasifiers, but also for the purpose of generating a surplus of energy. Two features determine the results shown in Fig. 13, the consumption of steam by the gasifier and the of reaction at the reformer. The lower consumption of steam by the low pressure indirect gasifier (Ferco) give the processes

operating with this technology an advantage in terms of energy consumption. Furthermore, steam reforming is endothermic, and thus, the energy available is lower compared to partial oxidation.
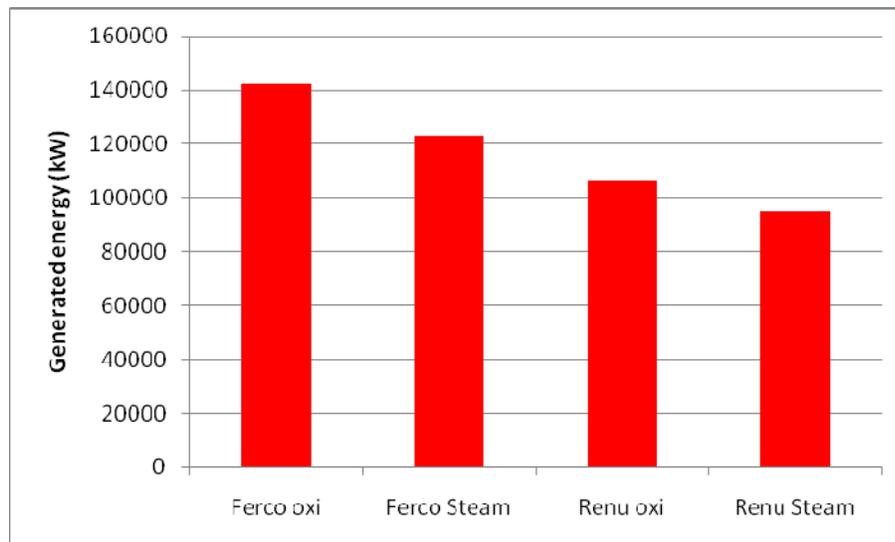
Figure 13.- Energy balance in the process.

In order to decide among the four alternatives (two gasifiers and two reforming processes) a detailed cost analysis is performed. 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 generation of an excess of steam is considered as a revenue of 0.0077$/kg$_{steam}$ (updated from Smith and Varbanov, 2005). The cost correlations for the different equipment can be found in supplementary material of Martin and Grossmann (2011a). Table 2 summarizes the results.

As it can be seen from the values presented in Table 2, the low yield towards biofuels, together with the high consumption of utilities in the direct gasifier (Renugas), (pure oxygen and large amount of steam) makes the processes involving this technology less attractive. On the other hand, among the processes that use indirect gasification, in spite of the excess of energy in case of using the partial oxidation as reforming alternative, the total yield towards biofuels and the fact that no pure oxygen is required, results in the fact that the most profitable alternative is the indirect gasification followed by steam reforming.

Table 2. Production cost for a 60Mgal/yr of Biofuel

	Ferco Gasifier	
	Partial Oxidation	Steam reforming
Raw material contribution (%)	52.4	52.9
Utilities contribution (%)	-8.5	-8.6
Biofuel yield (kg/kg$_{wet}$)	0.23	0.24
Selectivity to Diesel	0.81	0.75
Production cost ($/gal)	0.76	**0.72**

	Renugas Gassifier	
	Partial Oxidation	Steam reforming
Raw material contribution (%)	52.6	51.6
Utilities contribution (%)	-3.5	-0.2
Biofuel yield (kg/kg$_{wet}$)	0.19	0.18
Selectivity to Diesel	0.69	0.79
Production cost ($/gal)	0.91	0.98

Thus, the optimal flowsheet involves indirect low pressure gasification followed by steam reforming with no further composition adjustment, removal of sour gases, FT-synthesis and hydrocracking of the heavy products. Figure 14 shows the optimal flowsheet and the most relevant operating conditions. The manufacturing cost of the process is $44 millions/yr, where 52% corresponds to raw material followed and 36% annualized equipment as the main contribution as seen in Figure 15, using the method discussed in a previous paper by the authors (Martín and Grossmann, 2011a). Notice that, in order to keep production costs below 1 $/gal the raw material must be below 55 $/MT because of the high contribution of the raw material to the production cost.
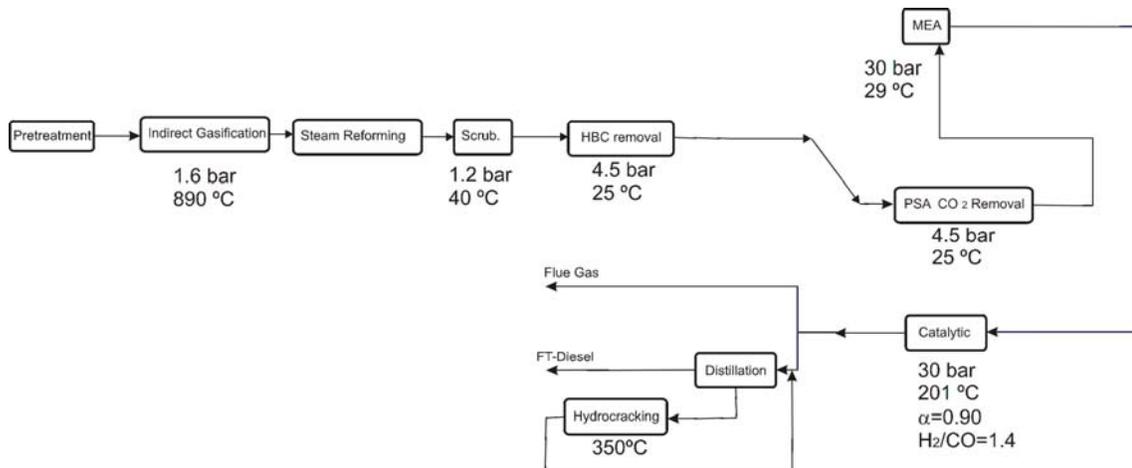
Figure 14. Optimal flowsheet

The investment cost of the plant (Sinnot, 1999) is $212 millions (based on the equipment cost of $47.9MM), 20% higher than the production of ethanol via hydrolysis (Martín & Grossmann, 2011b). However, it represents 2/3 of the investment required for the production of ethanol via gasification (Martín & Grossmann, 2011a). In Table 3 we summarize a more complete comparison of the economics of the production of different biofuels, (ethanol, hydrogen and FT-Diesel) from swichgrass using results from previous papers from the authors (Martin & Grossmann 2011 a,b,c). There is an obvious tradeoff between the production of ethanol via gasification and catalysis and the other technologies since it implies the highest investment and the lowest production cost. On the other hand, hydrogen production involves fewer pieces of equipment resulting in the lowest investment cost although we need to keep in mind that the switchgrass is not only a source of hydrogen but also a source of carbon. In between, we find FT –Diesel and other paths towards ethanol. The only process that requires energy is the production of ethanol via gasification and fermentation of the syngas due to the low concentration of ethanol in the fermentor, requiring energy intense dehydration technologies, together with the low operating temperature at this reactor which prevents from good energy integration. However, the FT-Diesel cost is the most sensitive to the cost of raw material since its production cost relies on up to more than 50% on the raw material cost in contrast to the 40% of the other production paths. Therefore, the decision on the optimal path for the production of biofuels is not obvious and further research is required. The use of mathematical programming techniques can be used to resolve the number of tradeoffs pointed out in table 3.
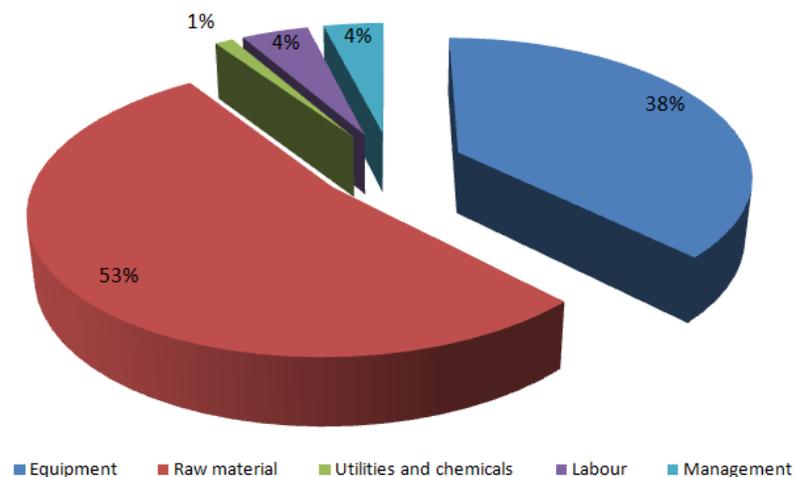
Figure 15.-Production cost distribution.

Table 3. Comparison of the production costs and investment for different biofuels from switchgrass (60MMgal /yr[*])

	Ethanol (Hydrolysis)	Ethanol (Gasification & Catalysis)	Ethanol (Gasification & Fermentation)	FT-Diesel	Hydrogen
Total investment ($MM)	161	335	260	212	148
Biofuel yield (kg/kg$_{wet}$)	0.28	0.20	0.33	0.24	0.11
Water consumption(gal/gal)	1.66	0.36	1.59	0.15	--
Energy consumption (MJ/gal)(*)	-10.2	-9.5	27.2	-63.0	-3.84
Production cost ($/gal) (*)	0.80	0.41	0.81	0.72	0.68
Byproduct	Energy CO$_2$	Hydrogen Energy CO$_2$	Hydrogen CO$_2$	Green Gasoline Energy CO$_2$	Energy CO$_2$

(*) when referring to hydrogen we focus on kg instead of gallons since the energy in 1 kg of hydrogen is equivalent to the energy of 1gal of gasoline

One of the main concerns in the production of ethanol is the consumption of water due to the elevated production rates to meet the mandates of the Energy Act 2007 and the availability of water in the areas where the raw material is produced (Martín et al., 2011). So far the production of green gasoline and diesel from biomass using FT processes has focused either on the optimization of the reactor performance (Wang et al., 2008) or the simulation of the process (Swanson et al., 2010) but to the best of our knowledge, no data related to water consumption has been reported. We can find some data related to water consumption in coal to liquids plants, also based on Fischer Tropsch technologies (Nowakowski 2008), reporting values from 1gal/gal to 5gal/gal depending on the processing technology used and whether the plants use air cooling or water cooling. Therefore, we believe that evaluating the water consumption for the production of a biofuel is also indicative of the environmental impact of the production process even though there is no such concern in the literature so far.

We use the approach presented by Martin et al. (2010) to calculate the water consumption for the optimal process resulting from this paper, which consists of the low pressure indirect gasifier, followed by steam reforming and FT synthesis of green diesel and gasoline. The base case considers the process designed after energy integration. Water is required in the gasifier (the steam required is produced using the excess of energy available within the process) and in the scrubber. There are three sources of water either as condensed water before the adsorption using PSA systems, as well as after the scrubbing process and the FT reactor. We assume that the sources of water contain mainly organics and that they can be properly treated in the waste treatment

facilities, which include secondary and tertiary treatment. Water is also needed for washing the raw material producing a stream that only contains suspended solids. Using the model proposed by Ahmetovic and Grossman to evaluate the minimum freshwater consumption, it results in 3.1 gal/gal$_{green fuel}$, which is a value in the range of those presented for the new corn based production plants (Ahmetovic et al 2010). However, as in the case for the production of ethanol, this process operates at high temperatures resulting from the gasification and catalytic reaction and air can be used instead of water as cooling agent. With this assumption, the cooling needs for water are reduced to only 15% of the original ones (8MW vs. 54MW) and only 0.15 gal/gal$_{green fuel}$ is required as long as the treatment methods are efficient enough to purify the contaminated water coming from the process so as to recycle it and the air cooling is used to cool the streams up to 60ºC. In Table 3 we also present the water consumption for all the processes with the exception of hydrogen since in that case water can be considered as a raw material for the process. It can be seen that the gasification and catalytic based processes required less consumption of cooling water as long as air cooling is implemented while those processes that rely on fermentation show higher values since the fermentations are not only exothermic but operate at low temperature so that it is not possible to efficiently reuse that energy within the process and cooling water is needed resulting in higher flow rates to the cooling tower, and thus, higher water losses due to evaporation.

The main uncertain parameter in this study is the ratio H_2/CO, therefore a sensitivity analysis is performed to evaluate the effect of the bounds on this paramenter. While some reviews, van der Laan & Beenkakers (1999), and recent experimental studies Mazzone & Fernandez (2006), Wang et al (2008) report that the production of gasoline and diesel is enhanced for H_2/CO ratios from 1 to 2 and for optimal production of the diesel fraction the ratio lies around 1.5, some other researchers report a minimum ratio of 1.7 for iron catalysts (Dry 2002). In our previous results the optimal ratio found Is the one obtained by gasification and reforming (around 1.5 for indirect gasification and direct gasification followed by partial oxidation) without further adjustment to save energy. However, in order to cope with this uncertainly we decide to impose as lower bound for the ratio H_2/CO equal to 1.7 and re-optimize the four subproblems. It turns out that only the Renugas based process followed by steam reforming reports the same values since the original ratio is already higher than 1.7. For the other three cases WGSR is needed to increase the hydrogen available in the stream. In order to reduce the energy consumption only a fraction of the total gas stream undertakes the WGSR at around 300ºC while the rest

is bypassed directly to the mixer. Due to the fact that energy is required to adjust the composition, the optimization yields a ratio H_2/CO set to be the lower bound of 1.7, while in order to get the optimal probability of chain growth for diesel fraction, close to 0.9 according to fig 7., the operating temperature at the reactor is approximately 200ºC. In table 4 we present the updated results enforcing the minimum ratio H_2/CO at the FT-reactor to be 1.7. The extra energy required together with the lower yield of the processes due to the consumption of CO to generate more H_2 losing C as CO_2 in the WGSR result in an increase in the production cost. However, the decision on the best alternative remains the same. The most economical process is based on the indirect gasification and steam reforming with a production cost slightly higher. The main operating conditions of the optimal flowsheet can be seen in figure 16.

Table 4. Production cost for a 60Mgal/yr of Biofuel ($H_2/CO_{min} = 1.7$)

	Ferco Gasifier	
	Partial Oxidation	Steam reforming
Raw material contribution (%)	57.7	56.1
Utilities contribution (%)	-11.2	-13.4
Biofuel yield (kg/kg$_{wet}$)	0.18	0.22
Selectivity to Diesel	0.71	0.71
Production cost ($/gal)	0.86	**0.73**

	Renugas Gassifier	
	Partial Oxidation	Steam reforming
Raw material contribution (%)	52.9	51.6
Utilities contribution (%)	-0.8	-0.2
Biofuel yield (kg/kg$_{wet}$)	0.16	0.18
Selectivity to Diesel	0.71	0.79
Production cost ($/gal)	1.02	0.98
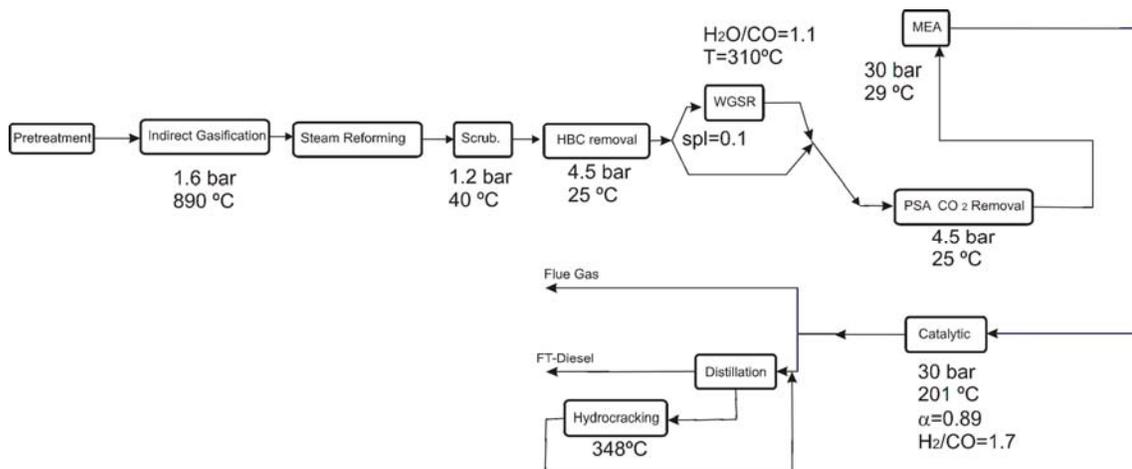
Figure 16. Optimal flowsheet($H_2/CO_{min} = 1.7$)

Finally, we may consider the production of green gasoline as main product, in this case we substitute in the objective function, eq, (32) by

Z =m(Gasoline,Col4,Snk23)-0.0005*0.019*(Q(HX8)+Q(HX17)+Steam$_{WGSR}$)-0.01*m(Wax,HX23,Col4)*1.6;

$$(33)$$

However, according to figure 7, when the fraction of gasoline increases the light products fraction also increases reducing the yield to liquid fuels which does not seem very promising due to the main aim of this technology. When optimizing the production of gasoline for the process based on the Ferco gasifier followed by steam reforming, assuming H$_2$/CO $_{min}$ =1.7, α turns out to be 0.83, and the operating temperature at the FT-reactor is 220ºC while the Hydrocraking needs to operate at 398ºC. For this process the yield to liquid fuels is 15% lower than when the diesel fraction is optimized due to the increase in the production of light products with a distribution of 50% green gasoline and 50% diesel. In the case of the renugas gasifier followed by steam reforming, assuming H$_2$/CO $_{min}$ =1.7, α turns out to be 0.83, and the operating temperature at the FT- reactor is 219ºC while the Hydrocraking needs to operate at 330ºC with a reduction of 10% in the yield to liquids with respect to the optimization of diesel production, see table 4, with 45% of green gasoline and 53% of diesel. In case of using partial oxidation and either ferco gasifier or renugas, similar decrease in liquid fuels yield is found.

5.-Conclusions

The advantages of the production of biofuels by using the FT technologies are obvious. The products are similar to the fuels produced by treating crude oil which allows their use in the current automobiles either gasoliene or diesel fuelled. However, the distribution of products reduces the specific production of each one. Thus, the production plant operates under the optimum conditions for the production of the one which cannot be obtained in other way. Basically, ethanol from lignocellusolic material partially substitutes gasoline. Thus, FT focuses on producing Diesel even though the production of gasoline is also important. The production of gasoline helps in the economy of the plant.

The superstructure for selecting the optimal flowsheet has been formulated as a MINLP. The problem is solved by decomposing the MINLP into four NLP's, one for each gasifier and reforming alternative. Each subproblem is optimized to determine the corresponding operating conditions. Due to the excess of hydrogen

produced, no further adjustment is provided by the optimization since it requires energy in terms of heating the stream entering the water gas shift reactor. However, the operating temperature of the FT reactor is adjusted to improve the yield towards diesel. Therefore, it is shown that a more comprehensive analysis of the production of any chemical is needed since focusing only on optimizing the reactor as recent studies lead to locally optimal solutions (Teles and Fernandes, 2008; Kim et al., 2009).

As a result of the study, the optimal process uses the indirect gasification followed by steam reforming while there is no further composition adjustment in terms of the ratio CO/H_2 obtained before the syngas is fed to the FT-reactor. The optimal operating conditions for the production of diesel requires a chain length of 0.91, 30 bar, 201ºC and hydrocracking of the heavy products providing an operating cost of 0.72 $/gallon of either FT-diesel or FT-gasoline. For this process consumes 0.15 gal/gal$_{green\ fuel}$ of freshwater water as long as the contaminated water generated in the process can be properly treated and air cooling is implemented. These are very promising values making this process competitive. Nevertheless, the optimal solution should be validated with pilot plant scale experiments due to the complex FT-reactor kinetics.

Finally, the FT technology reaches its aim for the production of FT-diesel since it generates higher yield of biomass to liquid fuels while the production of green gasoline is still reasonably high.

Acknowledgments

6.-Nomenclature.

Alpha   chain length
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.
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 from unit1 to unit2 (kg/s)
F(unit1,unit2)   mass flow rate from unit1 to unit2 (kg/s)
Mass_dry_j   Mass dry gas at equipment j   (Kg/s)
Massproduct   Mass flow of liquid products   (kg/s)
Masshydro   Mass flow of hydrogen   (kg/s)
MassGas   mass of gas generated   (kg)

MW_gas_j   Molecular weight in equipment j   (kg/kmol)
NonCondensed_j   Amount of water non condensed after equipment j (kg)
P_Synthesis   Working pressure at reactor   (bar)
P_flash2   Pressure at the flash   /760/   (mmHg)
S_diesel   Selectivity to diesel
S_gasoline   Selectivity to gasoline
T_cooldown   Cool down temperature /25/   (ºC)
T_flash2   /30/;   (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)
X_R3   Conversion of reactor 3 (Hydrocracking)
x(J,unit1,unit2)   mass fraction of stream from unit 1 to unit 2

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