

Energy optimization of Hydrogen production from biomass

Mariano Martín, Ignacio E. Grossmann¹

Chemical Engineering Department. Carnegie Mellon University

Pittsburgh PA 15213

Abstract.

In this paper we address the conceptual design for the production of hydrogen from lignocellulosic raw materials. The process is modeled as an MINLP using short-cut models and empirical correlations for a superstructure embedding two different gasification technologies, direct and indirect gasification, and two reforming modes, partial oxidation or steam reforming. A water gas shift reactor (WGSR) with membrane separation is used to obtain pure hydrogen. The MINLP problem is solved by fixing the binary variables so as to select each gasifier and reforming mode yielding four NLP's. Next, the energy is integrated, and an economic evaluation is performed to determine the production cost of each of the four alternatives. It is shown that indirect gasification with steam reforming is the preferred technology providing higher production yields than the ones reported in the literature for hydrogen from natural gas and at a potentially lower and promising production cost 0.67 \$/kg.

Keywords: Energy, Biofuels, Alternative fuels, Fuel cells, Water

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

1.-Introduccion

The early history of hydrogen as a clean and abundant form of energy dates back to 1820 when William Cecil proposed the idea of replacing steam engines by hydrogen based ones (Cecil, 1820). The use of hydrogen would also overcome some disadvantages of the steam engine like the long start-up in cold weather.

It was not until the 1930's and 1940's when Rudolf Erren modified internal combustion engines to run on fuel - hydrogen mixtures or even on pure hydrogen. The tragedy of the Hindenburgh stopped any further development, even though the fire was due to the material of the fabric that covered the airship. In 1950's the first practical fuel cell was presented by Francis T. Bacon. Current developments on fuel cell technology for both stationary generation of electricity and for road transportation represent an important step towards energy security. However, as any other alternative fuel, the availability and low cost of fossil fuels has slowed down their development (Cole, 2007; Rand and Dell, 2008)

Hydrogen has become one of the most promising fuel alternatives in terms of emissions and engine efficiency (Cole, 2007) but its deployment in the market is not ready due to the strength and convenience of the liquid fuels industry (the energy per unit mass of liquid fuels is much higher) as well as the lack in the development of the hydrogen-based technology, which makes it more expensive. Hydrogen is difficult to handle and store, and the particular characteristics of the automobiles will increase their final price (Cole, 2007). Some car makers are working on the optimization of the performance of hydrogen fuelled cars, and BMW presented the first version of the BMW 750hL in the Expo 2000. A scheme of the internal structure in a new series 7 can be seen in Figure 1. BMW is preparing to launch the BMW hydrogen Series 7 with the aim of be capable of selling 140,000 cars per year starting in 2020.(BMW 2000)<http://www.madrimasd.org>

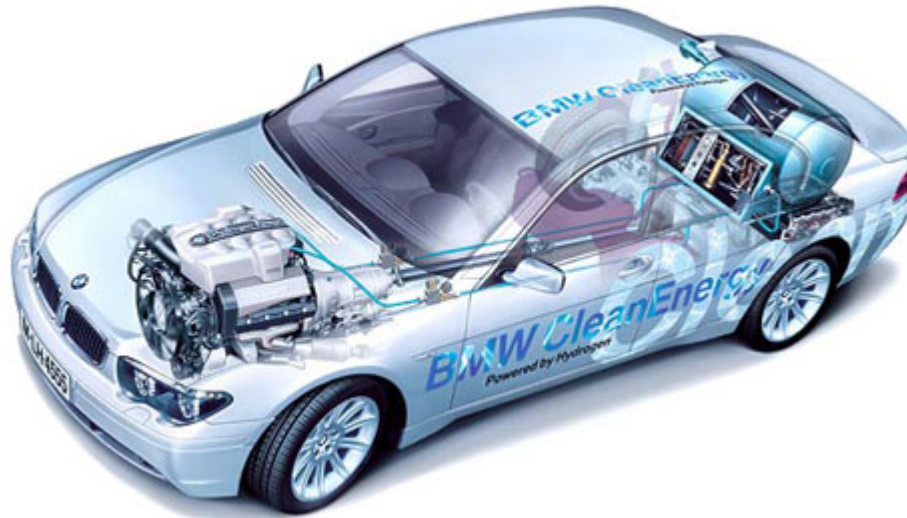


Figure 1.- Hydrogen fueled car (With permission)

The key issue to transform hydrogen into an alternative fuel is to optimize the production process and making it attractive using renewable raw materials instead of the more traditional processes such as electrolysis of water or natural gas reforming (Rand and Dell, 2008). Gasification of biomass generates a fair amount of H_2 which has to be purified and/or separated from the other gases resulting from the gasification (Tanksale et al., 2010) Recent studies have evaluated the production of hydrogen from gasification with good perspectives in terms of yield and energy consumption (Lau et al., 2002; Hamelinck and Faaij, 2002; Mueller-Langer, 2007; Feng et al., 2009; Gao, et al., 2009; Ji et al., 2009a&b; Li et al 2010).

To improve the design and energy efficiency of hydrogen production plants from biomass, process synthesis and mathematical optimization techniques can be used (Grossmann et al., 1999). We propose a conceptual design based on the optimization of a superstructure embedding the various process units involved in hydrogen production and considering alternatives for some of the processes. These units are interconnected to each other through network flows and other utility streams. The aim is to optimize the structure and the operating conditions minimizing the production cost. The optimization of the superstructure 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.

This particular problem is solved by partial enumeration fixing the binary variables to the various choices, reducing the problem into nonlinear programming (NLP) subproblems where the optimum operating conditions at the gasifier and the WGSR are determined. We then perform a heat integration analysis of the resulting process. Finally, an economic evaluation is performed to determine the production cost. The reported optimal design requires further experimental validation.

2. Overall Process Description

The biomass is first preprocessed to eliminate solids and water. Later, gasification produces gas from the biomass. Gasification can be atmospheric or pressurized, direct or indirect, resulting in very different gas compositions. Next, different options are available for gas cleaning, processing and purification; generation of power is optional. Figure 2 shows the superstructure proposed for the process.

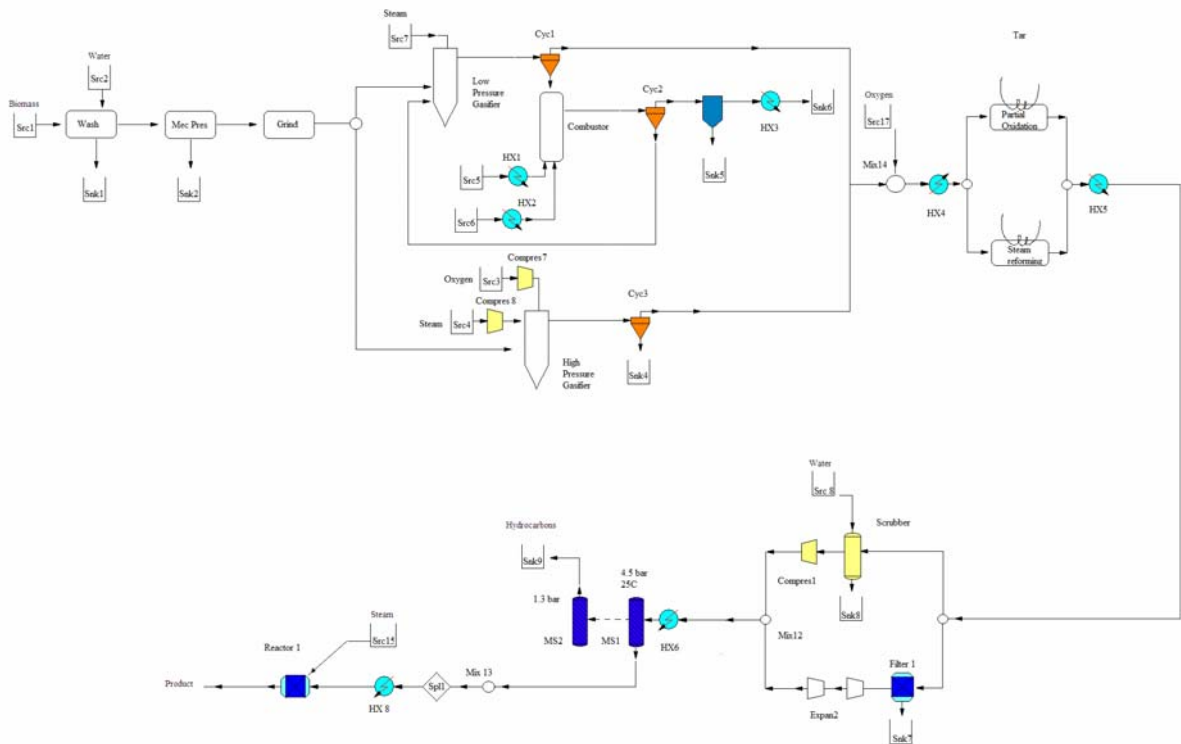


Figure 2.- Superstructure flowsheet

As it can be seen in Figure 2, two typical gasifier configurations are considered: the Institute of Gas Technology (IGT: Renugas) pressurised direct oxygen fired gasifier, and the BCL (Battelle Columbus: Ferco) atmospheric indirectly fired gasifier.

According to the literature (Hamelinek et al., 2002), it is possible to operate the Renugas gasifier at maximum hydrogen production mode, by increasing the steam input. The Renugas gasifier produces a gas rich in CO_2 , while the fraction of CH_4 can be further reformed to hydrogen. Gasification at high pressure allows a large throughput per reactor volume and reduces the need for pressurization downstream, so less overall power is needed. The maximum hydrogen mode is not only useful for hydrogen production, but it is also possible to use it for the production of methanol with good yield due to the ratio of $\text{H}_2:\text{CO}$ that is obtained. However, the gasifier efficiency is lower and much more steam is needed. The Renugas gasifier uses oxygen to reduce downstream equipment size.

The low pressure gasifier is indirectly heated so it is possible to use air to combust the char obtaining energy since there is no risk of nitrogen dilution. It produces a gas with a low CO_2 content, but contains heavier hydrocarbons. Therefore, reforming is required to maximize the production of H_2 even if the operating conditions are optimized for hydrogen production. The reactor is fast fluidized, allowing throughputs equal to the bubbling fluidized Renugas gasifier, despite the nearly atmospheric operation. Working at lower pressure decreases the operating cost.

Reforming of the gas is the next step to increase the yield towards hydrogen. The reforming of the gas can be performed following either, (1) steam reforming, or (2) partial oxidation (Rand and Dell, 2008; Hamelink et al., 2002). The use of autoreforming or dry - reforming will not be evaluated since for the production of hydrogen, the yield is increased by the decomposition of water by steam reforming, while a surplus of energy can be obtained by partial oxidation which may be sold to improve the profitability of the process. Nevertheless, the amount of hydrocarbons to be reformed is not expected to be large due to the optimization of the gasifier conditions towards hydrogen production.

Next, the gas must be cleaned. Conventional available technologies are either cold or hot cleaning. In cold cleaning, the gas is cooled down and water scrubber is used to remove the solids and other species. Alternatively, hot gas cleaning can be considered using ceramic filters and reagents at 500 °C. In case of working at high pressure, the hot cleaning is selected meanwhile for low pressure, the cold cleaning process will be considered.

The water gas shift reaction (WGSR) is a widely known operation to shift the energy value of the CO to H₂, which can then be separated using pressure swing adsorption, membranes. The equilibrium constant for the WGSR increases as temperature decreases. Hence, to increase the production to H₂ from CO, it is desirable to conduct the reaction at lower temperatures, which is also preferred in view of steam economy. However, to achieve the necessary conversion, higher temperatures are required. A newly design of the reactor, capable of separating the hydrogen produced through a permeable membrane is considered (Doong, et al., 2005; Fu and Wu, 2007; Ji et al., 2009; Adrover, et al., 2009; Sa et al., 2009).

There are a number of trade – offs in the gasifier as well as in the yield of the water gas shift reactor that can be systematically studied by means of an MINLP formulation of the model to optimize the production of hydrogen from biomass. The MINLP is decomposed into four NLP's using a partially enumeration technique, obtaining one subproblem for each gasifier and reforming mode. Finally, heat integration and an economic evaluation will provide the operating costs for the different alternatives.

3. Process model.

The different options involved in the production of hydrogen are modelled using short-cut models that consist primarily of mass and energy balances, design equations and reduced order models. 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. These are the main variables whose values have to be determined from the optimization. In the model, $F(\text{unit1}, \text{unit2})$ denotes the total mass flow from *unit1* to

unit2 in the system in kg/s. The variable $fc(j,unit1,unit2)$ stands for the mass flow of component j from *unit1* to *unit2* in the system in kg/s. The term $x(j,unit1,unit2)$ is the mass fraction of component j in the stream from *unit1* to *unit2* in the system, while $T(unit1,unit2)$ represents the temperature (in °C) of the stream flowing from *unit1* and *unit2* in the network. The components in the system include those present in the corn, plus those produced during the process of ethanol production, and belong to the set $J = \{ Wa, C_6H_6, MEA, Tars, CO_2, CO, O_2, N_2, H_2, H_2S, NH_3, CH_4, C_2H_2, C_2H_4, C_2H_6, SO_2, C, H, O, S, N, Olivine, Char, Ash \}$.

The set of equations that relate the component flows, total flows and component fractions in all the streams in the network are:

$$fc(j,unit1,unit2) = x(j,unit1,unit2) * F(unit1,unit2) \quad \forall j \in J \quad (1)$$

$$F(unit1,unit2) = \sum_j fc(j,unit1,unit2) \quad (2)$$

The different units in the superstructure are modelled as described below.

Figure 3 shows a detail of the superstructure for the pretreatment stage accounting for washing, switchgrass drying and size reduction in sequence.

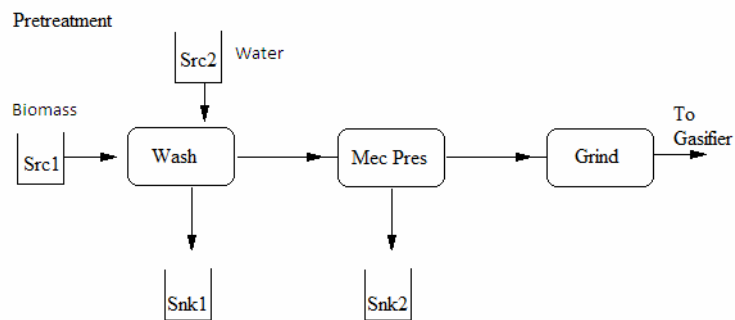


Figure 3.- Detail of the pretreatment stage

The incoming feed of switchgrass (from source *Src1*) is washed with a stream of freshwater with no contaminants inside a washing unit (*Wash*). This step removes dirt and dust from the grass. Part of the

washing water (from source *Src2*) will remain with the grass. Therefore, a small amount (1%) of the wash water is assumed to stay. 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. Eqs. (3-7) model the feedstock washing stage:

$$fc(j, Src1, Wash) = x_o(j) * F(Src1, Wash); \quad \forall j \in J \quad (3)$$

$$fc(Wa, Src2, Wash) = \min_{wash} * F(Src1, Wash); \quad (4)$$

$$fc(Wa, Wash, MecSep1) = fc(Wa, Src1, Wash) + \text{frac}_{wash} * fc(Wa, Src2, Wash); \quad (5)$$

$$fc(Wa, Wash, Snk1) = (1 - \text{frac}_{wash}) * fc(Wa, Src2, Wash); \quad (6)$$

$$fc(j, Src1, Wash) = fc(j, Wash, MecSep1) \quad \forall j \in J, j \neq \{water\} \quad (7)$$

In the above equations, \min_{wash} stands for the minimum amount of washing water required per kg of grass while frac_{wash} is the fraction of washing water that stays with the grass. $x_o(j)$ is the composition of the grass feedstock on a wet basis.

Then, the grass is partially dried by means of a mechanical press being able to remove 90% of the water that goes with the grass ($\text{frac}_{dried} = 0.9$). The short-cut model is given by eqs. (8-10)

$$fc(Wa, MecSep1, Grind) = (1 - \text{frac}_{dried}) * fc(Wa, Wash, MecSep1); \quad (8)$$

$$fc(j, MecSep1, Grind) = fc(j, Wash, MecSep1); \quad \forall j \in J, j \neq \{water\} \quad (9)$$

$$fc(Wa, MecSep1, Snk2) = (\text{frac}_{dried}) * fc(Wa, Wash, MecSep1); \quad (10)$$

In order for the gasification to be effective, a reduction in the size of the grass is needed. However, the required size is moderately large, around 10 mm, and so the energy needed is low, 30kWh/t (Mani et al 2004). The model for the grinding stage is as follows:

$$fc(j, 'MecSep1', 'Grind') = fc(j, Grind, Gasifier1); \quad \forall j \in J, j \neq \{water\} \quad (11)$$

$$W(Grind) = 30 * F(MecSep1, Grind) * 3.6 \quad (12)$$

3.1.-Gasification.

The two most common alternatives for gasification, indirect gasification and direct gasification, are considered (Bridgwater, 2003). Figure 4 shows a detail of the flowsheet.

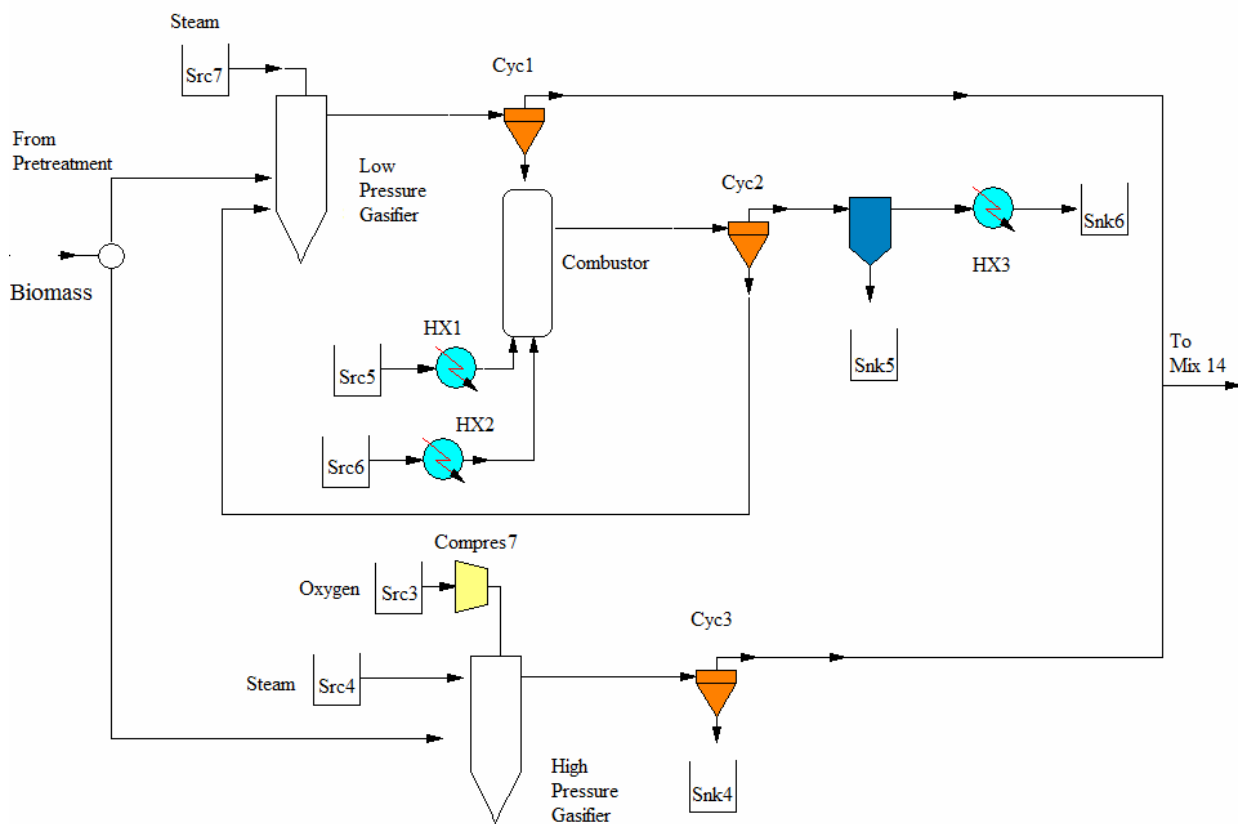


Figure 4.- Detail of the superstructure for the gasification of lignocellulosic materials

3.1.1.-Indirect gasification.

For indirect gasification, the switchgrass from the grind enters the gasifier where steam is also injected (Src 7 in the figure). The energy for the gasification is provided by a type of sand, olivine, coming from the combustor. The gases generated in the gasifier are separated from the solids, mainly char and

olivine, in a cyclone (Cyc 1). The gas is cleaned in further steps. The solids go to the combustor where the combustion of char provides the energy to heat up the sand again. Due to the fact that the combustion takes place in a different chamber, the combustor, air can be used (Src 5 in the figure). Make-up of sand due to the losses must be provided (Src 6). The solids, mainly olivine, are separated from the gases in a cyclone (Cyc 2) and recycled to the gasifier. The combustion gas is cleaned from ash and cooled down from where energy can be obtained for the process.

Together with biomass, steam and olivine are fed to the gasifier:

$$fc(Wa, Src7, Gasifier1) = Ratio_steam * (DryMass); \quad (13)$$

$$fc(Olivine, Cyc2, Gasifier1) = Ratio_olivine * (DryMass); \quad (14)$$

The Ratio_steam and Ratio_olivine are taken from the literature Phillips et al 2007 to be 0.4 and 27. In order to determine the composition of the gas and the char, the procedure presented in the same report by Phillips et al. (2007) will be used.

The mass of gas generated at the gasifier as well as its composition depends on the temperature. The experimental results and correlations presented in Phillips et al (2007), eqs (15-30) are used to determine both.

$$DryMass = \sum_{j \neq \{water\}} fc(j, Src1, Wash) \quad (15)$$

$$Massgas = \left(28.993 - 0.043325 \cdot (T_{Fercogas}) + 0.000020966 \cdot (T_{Fercogas})^2 \right) * (DryMass / 0.454) * \rho_{gas} \quad (16)$$

where $T_{Fercogas}$ must be in Fahrenheit .

$$\rho_{gas} = (101325 * MW_{gas} / (8314 * 273)) * (0.3048^3) \quad (17)$$

$$y_Syngasferco(C6H6) = 0.001; \quad (18)$$

$$y_Syngasferco(Tars) = 0.002; \quad (19)$$

$$fc(\text{Tars, Gasifier1, Cyc1}) = (0.045494 - 0.000019759 * (T_Fercogas * 1.8 + 32)) * \text{DryMass}; \quad (20)$$

$$y_Syngasferco(\text{CO}_2) = 0.01 * \left(-9.5251 + 0.0377889 * (T_Fercogas * 1.8 + 32) - 0.000014927 * (T_Fercogas * 1.8 + 32)^2 \right); \quad (21)$$

$$y_Syngasferco(\text{CO}) = 0.01 * \left(133.46 - 0.1029 * (T_Fercogas * 1.8 + 32) + 0.000028792 * (T_Fercogas * 1.8 + 32)^2 \right); \quad (22)$$

$$y_Syngasferco(\text{H}_2) = 0.01 * \left(17.996 - 0.026448 * (T_Fercogas * 1.8 + 32) + 0.00001893 * (T_Fercogas * 1.8 + 32)^2 \right); \quad (23)$$

$$y_Syngasferco(\text{H}_2\text{S}) = 0.0007; \quad (24)$$

$$y_Syngasferco(\text{NH}_3) = 0.003; \quad (25)$$

$$y_Syngasferco(\text{CH}_4) = 0.01 * \left(-13.82 + 0.044179 * (T_Fercogas * 1.8 + 32) - 0.000016167 * (T_Fercogas * 1.8 + 32)^2 \right); \quad (26)$$

$$y_Syngasferco(\text{C}_2\text{H}_2) = 0.01 * \left(-4.3114 + 0.0054499 * (T_Fercogas * 1.8 + 32) - 0.000001561 * (T_Fercogas * 1.8 + 32)^2 \right); \quad (27)$$

$$y_Syngasferco(\text{C}_2\text{H}_4) = 0.01 * \left(-38.258 + 0.058435 * (T_Fercogas * 1.8 + 32) - 0.000019868 * (T_Fercogas * 1.8 + 32)^2 \right); \quad (28)$$

$$y_Syngasferco(\text{C}_2\text{H}_6) = 0.01 * \left(11.114 - 0.011667 * (T_Fercogas * 1.8 + 32) + 0.000003064 * (T_Fercogas * 1.8 + 32)^2 \right); \quad (29)$$

Thus, the molar mass of the gas generated is calculated as eq. (30)

$$MW_{gas} = \sum_{j \neq \{water\}} y_{Syngasferco}(j) * MW(j) \quad (30)$$

In order to determine the composition of the gas and the char, the procedure presented in the same report by Phillips et al. (2007) is used:

-The amount of char produced contains the carbon that is left after the production of the gases.

$$\begin{aligned}
mc_char = & fc(C, Grind, Gasifier1) - \left(\frac{MW_C}{MW_{CO}}\right) * fc(CO, Gasifier1, Cyc1) + \\
& \left(\frac{MW_C}{MW_{CO_2}}\right) * fc(CO_2, Gasifier1, Cyc1) + \left(\frac{MW_C}{MW_{CH_4}}\right) * fc(CH_4, Gasifier1, Cyc1) + \\
& \left(2 * \frac{MW_C}{MW_{C_2H_2}}\right) * fc(C_2H_2, Gasifier1, Cyc1) + \left(2 * \frac{MW_C}{MW_{C_2H_4}}\right) * fc(C_2H_4, Gasifier1, Cyc1) + \\
& \left(2 * \frac{MW_C}{MW_{C_2H_6}}\right) * fc(C_2H_6, Gasifier1, Cyc1) + \left(6 * \frac{MW_C}{MW_{C_6H_6}}\right) * fc(C_6H_6, Gasifier1, Cyc1) + \\
& \left(10 * \frac{MW_C}{MW_{Tars}}\right) * fc(Tars, Gasifier1, Cyc1);
\end{aligned} \tag{31}$$

- Char is generated containing at least 0.04% of the oxygen from the biomass.

$$mo_char \geq 0.04 * m(O, Grind, Gasifier1); \tag{32}$$

$$mo_char \leq 0.1 * m(O, Grind, Gasifier1); \tag{33}$$

$$\begin{aligned}
mo_char = & m(O, Grind, Gasifier1) + Waterdecomp * \left(1/2 * \frac{MW_{O_2}}{MW_{Wa}}\right) \\
& - \left(\frac{MW_O}{MW_{CO}}\right) * m(CO, Gasifier1, Cyc1) - \left(2 * \frac{MW_O}{MW_{CO_2}}\right) * m(CO_2, Gasifier1, Cyc1);
\end{aligned} \tag{34}$$

-If there is not enough oxygen, steam decomposes to provide it according to equation (35) (Waterdecomp in eq. (34)):

$$fc(Wa, Gasifier1, Cyc1) = fc(Wa, Src7, Gasifier1) + fc(Wa, Grind, Gasifier1) - Waterdecomp; \tag{35}$$

-H₂S and NH₃ are generated proportionally to the amount of S and N in the biomass. A small percentage of both elements (8.3% and 6.6% respectively) remains in the char.

$$ms_char = 0.083 * fc(S, Grind, Gasifier1); \tag{36}$$

$$fc(H_2S, Gasifier1, Cyc1) = \left(\frac{MW_{H_2S}}{MW_S}\right) * (1 - 0.083) * fc(S, Grind, Gasifier1); \tag{37}$$

$$mn_char = 0.066 * fc(N, Grind, Gasifier1); \tag{38}$$

$$fc(\text{NH}_3, \text{Gasifier1}, \text{Cyc1}) = \left(\frac{MW_{\text{NH}_3}}{MW_{\text{N}}} \right) * (1 - 0.066) * fc(\text{N}, \text{Grind}, \text{Gasifier1}); \quad (39)$$

-The ash in the biomass goes to the char.

$$\text{mash_char} = fc(\text{Ash}, \text{Grind}, \text{Gasifier1}); \quad (40)$$

$$fc(\text{Char}, \text{Gasifier1}, \text{Cyc1}) = \text{ms_char} + \text{mn_char} + \text{mash_char} + \text{mo_char}; \quad (41)$$

-The hydrogen generated results from the mass balance of the compounds generated (Water decomposed, H₂S, NH₃ and Hydrocarbons formed)

$$\begin{aligned} fc(\text{H}_2, \text{Gasifier1}, \text{Cyc1}) = & fc(\text{H}, \text{Grind}, \text{Gasifier1}) + \text{Waterdecomp} * \left(\frac{MW_{\text{H}_2}}{MW_{\text{wa}}} \right) - \\ & \left(\frac{MW_{\text{H}_2}}{MW_{\text{H}_2\text{S}}} \right) * fc(\text{H}_2\text{S}, \text{Gasifier1}, \text{Cyc1}) - \left(\frac{3 * MW_{\text{H}_2}}{2 * MW_{\text{NH}_3}} \right) * fc(\text{NH}_3, \text{Gasifier1}, \text{Cyc1}) - \\ & \left(2 * \frac{MW_{\text{H}_2}}{MW_{\text{CH}_4}} \right) * fc(\text{CH}_4, \text{Gasifier1}, \text{Cyc1}) - \left(\frac{MW_{\text{H}_2}}{MW_{\text{C}_2\text{H}_2}} \right) * fc(\text{C}_2\text{H}_2, \text{Gasifier1}, \text{Cyc1}) - \\ & \left(2 * \frac{MW_{\text{H}_2}}{MW_{\text{C}_2\text{H}_4}} \right) * fc(\text{C}_2\text{H}_4, \text{Gasifier1}, \text{Cyc1}) - \left(3 * \frac{MW_{\text{H}_2}}{MW_{\text{C}_2\text{H}_6}} \right) * fc(\text{C}_2\text{H}_6, \text{Gasifier1}, \text{Cyc1}) - \\ & \left(3 * \frac{MW_{\text{H}_2}}{MW_{\text{C}_6\text{H}_6}} \right) * fc(\text{C}_6\text{H}_6, \text{Gasifier1}, \text{Cyc1}) - \left(4 * \frac{MW_{\text{H}_2}}{MW_{\text{Tars}}} \right) * m(\text{Tars}, \text{Gasifier1}, \text{Cyc1}); \end{aligned} \quad (42)$$

-The composition of the gas in terms of H₂S, H₂, and NH₃ is recalculated based on these mass balances instead of the one resulting from eqs. (23) – (25), while for the rest of the gases the outlet compositions are calculated using the equations (16-27, 43-44).

$$x_{\text{GasFerro}}(j) * MW_{\text{gas}} = y_{\text{Syngasferco}}(j) * MW(j) \quad (43)$$

$$fc(j, \text{Gasifier1}, \text{Cyc1}) = x_{\text{GasFerro}}(j) * \text{MassGas}; \forall j = \{ \text{CO}_2, \text{O}_2, \text{Tar}, \text{C}_6\text{H}_6, \text{CH}_4, \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6 \} \quad (44)$$

The energy for the gasification is given by the Olivine coming from the combustor:

$$fc(\text{Olivine}, \text{Gasifier1}, \text{Cyc1}) = fc(\text{Olivine}, \text{Cyc2}, \text{Gasifier1}); \quad (45)$$

$$Q(\text{Gasifier1}) = fc(\text{Olivine}, \text{Cyc2}, \text{Gasifier1}) * c_p_ind(\text{Olivine}) * (T_{\text{Combustor}} - T_{\text{Fercogas}}); \quad (46)$$

The stream coming out of the gasifier is separated. The solids go back to the combustor while the gas is fed to the tar removal. The short-cut model for the cyclone is given by eqs. (47-48):

$$fc(j, \text{Cyc1}, \text{Mix14}) = \text{Cyclon_1_eff}(j) * fc(j, \text{Gasifier1}, \text{Cyc1}); \quad \forall j \in J \quad (47)$$

$$fc(J, \text{Cyc1}, \text{Combustor}) = (1 - \text{Cyclon_1_eff}(j)) * fc(j, \text{Gasifier1}, \text{Cyc1}); \quad \forall j \in J \quad (48)$$

The olivine is heated up again in the combustor meanwhile the make-up of olivine is heated up in HX2 before it is fed to the combustor. Only olivine is present in the streams from Src6 to Combustor.

$$fc(\text{Olivine}, \text{Src6}, \text{HX2}) = fc(\text{Olivine}, \text{Cyc1}, \text{Mix14}) + (fc(\text{Olivine}, \text{Cyc2}, \text{Gasifier1}) * (1 - \text{Cyclon_eff_Olivine}) / \text{Cyclon_eff_Olivine}); \quad (49)$$

$$fc(\text{Olivine}, \text{Combustor}, \text{Cyc2}) * \text{Cyclon_eff_Olivine} = fc(\text{Olivine}, \text{Cyc2}, \text{Gasifier1}); \quad (50)$$

$$fc(\text{Olivine}, \text{HX2}, \text{Combustor}) = fc(\text{Olivine}, \text{Src6}, \text{HX2}); \quad (51)$$

$$Q(\text{HX2}) = fc(\text{Olivine}, \text{Src6}, \text{HX2}) * c_p_ind(\text{Olivine}) * (T_{\text{Combustor}} - T_{\text{amb}}); \quad (52)$$

In the combustor, char is burned with air (which is preheated to 200°C in HX1) to obtain energy to reheat up the olivine. The air injected in the combustor is in 20% of excess compared to the stoichiometric quantity,

$$fc(\text{Wa}, \text{Combustor}, \text{Cyc2}) = fc(\text{Wa}, \text{Src5}, \text{HX1}) + (3/2) * \left(\frac{MW_{\text{Wa}}}{MW_{\text{N}}} \right) * 0.99999 * mn_char; \quad (53)$$

$$fc(\text{O2}, \text{Src5}, \text{HX1}) = 1.2 * \left(\frac{MW_{\text{O2}}}{MW_{\text{CO2}}} \right) * fc(\text{CO2}, \text{Combustor}, \text{Cyc2}); \quad (54)$$

$$fc(\text{N2}, \text{Src5}, \text{HX1}) = (79/21) * \left(\frac{MW_{\text{N2}}}{MW_{\text{O2}}} \right) * fc(\text{O2}, \text{Src5}, \text{HX1}); \quad (55)$$

and its humidity is calculated through:

$$p_{\text{sat_atm}} = \text{Exp} \left(\text{coef_p}(\text{Wa},1) - \frac{\text{coef_p}(\text{Wa},2)}{(\text{coef_p}(\text{Wa},3) + T_{\text{amb}})} \right); \quad (56)$$

$$p_{\text{v_atm}} = \text{re_hum_atm} * p_{\text{sat_atm}}; \quad (57)$$

$$\text{spec_hum_atm} = 0.622 * \frac{p_{\text{v_atm}}}{(p_{\text{air}} - p_{\text{v_atm}})}; \quad (58)$$

$$\text{fc}(\text{Wa}, \text{Src5}, \text{HX1}) = (\text{fc}(\text{O2}, \text{Src5}, \text{HX1}) + \text{fc}(\text{N2}, \text{Src5}, \text{HX1})) * \text{spec_hum_atm} \quad (59)$$

$$\text{fc}(\text{O2}, \text{HX1}, \text{Combustor}) = \text{fc}(\text{O2}, \text{Src5}, \text{HX1}); \quad (60)$$

$$\text{fc}(\text{N2}, \text{HX1}, \text{Combustor}) = \text{fc}(\text{N2}, \text{Src5}, \text{HX1}); \quad (61)$$

$$\text{fc}(\text{Wa}, \text{HX1}, \text{Combustor}) = \text{fc}(\text{Wa}, \text{Src5}, \text{HX1}); \quad (62)$$

The air is preheated in HX 1 to 200°C before entering the combustor.

$$Q(\text{HX1}) = \sum_j \int_{T_{\text{amb}}}^{473} c_{p_v}(j) \cdot dT \cdot \text{fc}(j, \text{Src5}, \text{HX1}) \quad (63)$$

$$Q(\text{Combustor}) = \Delta H_f(\text{CO}_2) \Big|_{T_{\text{Combustor}}} \quad (64)$$

The model for the combustor is as follows. The char is decomposed liberating the ash, while the sulfur and the carbon are oxidized. Nitrogen is also generated from the nitrogen in the char.

$$\text{fc}(\text{Ash}, \text{Combustor}, \text{Cyc2}) = 0.99999 * \text{mash_char}; \quad (65)$$

$$\text{fc}(\text{N2}, \text{Combustor}, \text{Cyc2}) = \text{fc}(\text{N2}, \text{Src5}, \text{HX1}) + 0.99999 * \text{mn_char} \quad (66)$$

$$\text{fc}(\text{SO2}, \text{Combustor}, \text{Cyc2}) = \left(\frac{MW_{\text{SO}_2}}{MW_{\text{S}}} \right) * 0.99999 * \text{ms_char}; \quad (67)$$

$$\text{fc}(\text{CO2}, \text{Combustor}, \text{Cyc2}) = \left(\frac{MW_{\text{CO}_2}}{MW_{\text{C}}} \right) * 0.99999 * \text{mc_char}; \quad (68)$$

$$\begin{aligned}
fc(O_2, Combustor, Cyc2) &= fc(O_2, Src5, HX1) + mo_char * 0.99999 - \\
&\left(\frac{MW_{O_2}}{MW_{SO_2}}\right) * fc(SO_2, Combustor, Cyc2) - \\
&\left(\frac{MW_{O_2}}{MW_{CO_2}}\right) * fc(CO_2, Combustor, Cyc2) - (3/2) * (MW(O_2) / MW(N_2)) * mn_char;
\end{aligned} \tag{69}$$

The gases from the combustor are separated from the solids in cyclon 2 so that the olivine is recycled to the gasifier, while the rest of the gases are sent to the electrostatic precipitator to remove the ash before the stream can be used to provide energy to the process.

$$fc(j, Cyc2, PrecElectro) = fc(j, Combustor, Cyc2); \quad \forall j \neq \{ash, olivine\} \tag{70}$$

$$fc(Olivine, Cyc2, PrecElectro) = fc(Olivine, Combustor, Cyc2) * (1 - Cyclon_eff_Olivine); \tag{71}$$

$$fc(Ash, Cyc2, PrecElectro) = fc(Ash, Combustor, Cyc2); \tag{72}$$

In the electrostatic precipitator 99% of the ash is removed as well as all the olivine that has been dragged by that stream. The balances for the electrostatic precipitator are as follows:

$$fc(j, Cyc2, PrecElectro) = fc(j, PrecElectro, HX3); \quad \forall j \neq \{ash, olivine\} \tag{73}$$

$$fc(Olivine, PrecElectro, Snk5) = fc(Olivine, Cyc2, PrecElectro); \tag{74}$$

$$fc(Ash, PrecElectro, Snk5) = eff_{Precipitator} * fc(Ash, Cyc2, PrecElectro); \tag{75}$$

$$fc(Ash, PrecElectro, HX3) = (1 - eff_{Precipitator}) * fc(Ash, Cyc2, PrecElectro); \tag{76}$$

$$Q(HX3) = \sum_j \int_{T_{Combustor}}^{T_{Cooldown}} c_{p-v}(j) \cdot dT \cdot fc(j, PrecElectro, HX3) \tag{77}$$

According to the literature (Di Blasi, 2004), the energy generated by the combustion of char is approximately :

$$Q_{combustor} = 25000 * fc(Char, Gasifier1, Cyc1); \tag{78}$$

Thus, the energy generated at the combustor is the one available for the olivine to perform the gasification

$$Q(\text{'Combustor'}) = Q(\text{'Gasifier1'}); \quad (79)$$

$$Q(\text{'Combustor'}) \geq Q_{\text{- combustor}}; \quad (80)$$

3.1.2.-Direct Gasification

The design of the direct gasifier is simpler than the indirect one as in can be seen in Figure 3. For the production of hydrogen, the optimized operating conditions of a direct gasifier are presented in Table 1 (Hamelinck et al., 2002). The ratio of steam to biomass seems to have a small effect on the composition according to experimental results (Gao et al., 2009) and thus, is not considered in the optimization. Table (1) shows the composition and the operating conditions:

Table 1.- High pressure direct gasifier: Optimal conditions for Hydrogen production

| | |
|------------------|--------------|
| T (°C) | 920 |
| P(bar) | 25 |
| Gas Composition | (molar frac) |
| H ₂ O | 0.48 |
| H ₂ | 0.24 |
| CO | 0.115 |
| CO ₂ | 0.16 |
| CH ₄ | 0.005 |

The total mass of gas generated is a function of the biomass injected as given by eq. (81):

$$Mass_{gas} = 0.121 \cdot DryMass \cdot MW_{gas} \quad (81)$$

The steam injected is given by,

$$fc(Wa, Src3, Gasifier2) = 0.8 * (F(Grind, Gasifier2)); \quad (82)$$

while the oxygen is given by:

$$fc(O2, Src4, Gasifier2) = 0.38 * (F(Grind, Gasifier2)); \quad (83)$$

Recent studies (Eggeman, 2005; Zhu et al., 2009) also present correlations for the composition of the gases as function of the operating conditions. We use the optimized data provided in the literature since it has experimental validation. The basic equations for determining the composition of the char and the gases are similar as for the low pressure gasifier, see eqs. (31-44), but using the new composition of the gas (Table 1).

In the cyclone, Cyc 3, the char generated from the rests of the combustion is removed

$$fc(j, \text{Gasifier2}, \text{Cyc3}) = fc(j, \text{Cyc3}, \text{Mix14}); \quad \forall j \neq \{char\} \quad (84)$$

$$(1 - \text{Cyclon}_{eff_char}) * fc('Char', 'Gasifier2', 'Cyc3') = fc(\text{Char}, \text{Cyc3}, \text{Mix14}); \quad (85)$$

$$(\text{Cyclon}_{eff_char}) * fc(\text{Char}, \text{Gasifier2}, \text{Cyc3}) = fc(\text{Char}, \text{Cyc3}, \text{Snk4}); \quad (86)$$

3.2.-Gas clean-up.

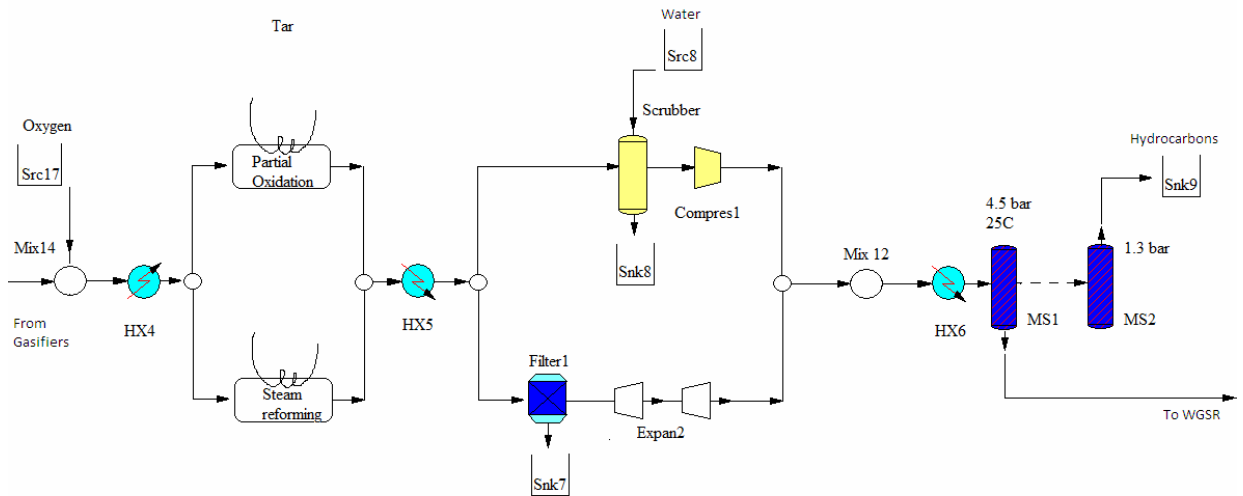


Figure 5.- Detail of the superstructure for gas clean up

Figure 5 shows the scheme of the gas clean up technologies. In this paper we consider two alternatives to decompose the hydrocarbons generated during the gasification process: steam reforming and partial oxidation. In this section we model the removal of hydrocarbons using both. Other processes

that are not considered are the dry reforming, by using CO₂ instead of steam or oxygen or autothermal reforming (Rand & Dell, 2008)

3.2.1.-Tar.

Partial oxidation. For partial oxidation, pure oxygen is provided (from Src 17 in Figure 5) to eliminate the hydrocarbons generated during the gasification process generating more CO and Hydrogen,

$$fc(j, \text{Cyc1 or Cyc3, Mix14}) + fc(j, \text{Src17, Mix14}) = fc(j, \text{Mix14, HX4}) \quad \forall j \in J \quad (87)$$

The oxygen injected is calculated assuming stoichiometric ratio . The conversions of the different hydrocarbons (Conv_i) are taken to be the same as in the report by Philip et al. (2007) and based on the experimental results by Vernon et al. (1990), Deutschmann & Schmidt (1998). In particular, 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)

$$\begin{aligned} fc(O_2, \text{Cyc3, Mix14}) + fc(O_2, \text{Src17, Mix14}) &= \left(\frac{1}{2} \frac{MW_{O_2}}{MW_{CH_4}} \right) * Conv_{CH_4} * fc(CH_4, \text{Mix14, HX4}) + \\ &\left(\frac{MW_{O_2}}{MW_{C_2H_6}} \right) * Conv_{C_2H_6} * fc(C_2H_6, \text{Mix14, HX4}) + \left(\frac{MW_{O_2}}{MW_{C_2H_4}} \right) * Conv_{C_2H_4} * fc(C_2H_4, \text{Mix14, HX4}) + \\ &\left(\frac{MW_{O_2}}{MW_{C_2H_2}} \right) * Conv_{C_2H_2} * fc(C_2H_2, \text{Mix14, HX4}) + \left(3 \frac{MW_{O_2}}{MW_{C_6H_6}} \right) * Conv_{C_6H_6} * fc(C_6H_6, \text{Mix14, HX4}) + \\ &\left(5 \frac{MW_{O_2}}{MW_{Tar}} \right) * Conv_{tar} * fc(Tars, \text{Mix14, HX4}); \end{aligned} \quad (88)$$

Thus, the inlet temperature to the HX4 is calculated as follows

$$\begin{aligned} \sum_j \int_{T(\text{Cyc1, Mix14})}^{T(\text{Mix4, HX4})} c_{p_v}(j) dT \cdot fc(j, \text{Cyc1, HX4}) + \\ \sum_j \int_{T_{amb}}^{T(\text{Mix4, HX4})} c_{p_v}(j) dT \cdot fc(j, \text{Src17, HX4}) = 0 \end{aligned} \quad (89)$$

The HX4 is only used in case of using low pressure gasifier since otherwise the process to heat up this heat exchanger is too expensive and no energy is available for it.

$$fc(j, HX4, Tar) = fc(j, Mix14, HX4); \quad \forall j \in J \quad (90)$$

$$T(Mix14, HX4) = T(HX4, Tar); \quad (91)$$

$$Q(HX4) = \sum_j \int_{T(Mix14, HX4)}^{T_{FerroGas}} c_{p-v}(j) \cdot dT \cdot fc(j, Mix14, HX4) \quad (92)$$

The tar reformer can work at low or high temperature (Brenes, 2006). Thus there is no change in the equations if the feed is coming from cyclon 1 (low pressure gasifier indirect gasifier) or 3 (high pressure direct gasifier). Thus, the mass balances for the species in the tar are calculated based on the conversions and stoichometric relationships of the hydrocarbons and the ammonia according to eqs. (93-100)



$$fc(j, Tar, HX5) = fc(j, HX4, Tar); \quad j = \{Wa, H_2S, CO_2, Char, Ash, Olivine\} \quad (95)$$

$$\begin{aligned} fc(H_2, Tar, HX5) = & fc(H_2, HX4, Tar) + \left(2 \frac{MW_{H_2}}{MW_{CH_4}}\right) * Conv_CH4 * fc(CH_4, HX4, Tar) + \\ & \left(3 \frac{MW_{H_2}}{MW_{C_2H_6}}\right) * Conv_C2H6 * fc(C_2H_6, HX4, Tar) + \left(2 \frac{MW_{H_2}}{MW_{C_2H_4}}\right) * Conv_C2H4 * fc(C_2H_4, HX4, Tar) + \\ & \left(\frac{MW_{H_2}}{MW_{C_2H_2}}\right) * Conv_C2H2 * fc(C_2H_2, HX4, Tar) + \left(3 \frac{MW_{H_2}}{MW_{C_6H_6}}\right) * Conv_C6H6 * fc(C_6H_6, HX4, Tar) + \\ & \left(4 \frac{MW_{H_2}}{MW_{tars}}\right) * Conv_tar * fc(Tars, HX4, Tar) + \\ & \left(\frac{3}{2} \frac{MW_{H_2}}{MW_{NH_3}}\right) * Conv_NH3 * fc(NH_3, HX4, Tar); \end{aligned} \quad (96)$$

$$\begin{aligned}
fc(\text{CO}, \text{Tar}, \text{HX5}) &= fc(\text{CO}, \text{HX4}, \text{Tar}) + \left(\frac{MW_{CO}}{MW_{CH_4}} \right) * \text{Conv}_{CH_4} * fc(\text{CH}_4, \text{HX4}, \text{Tar}) + \\
2 \frac{MW_{CO}}{MW_{C_2H_6}} * \text{Conv}_{C_2H_6} * fc(\text{C}_2\text{H}_6, \text{HX4}, \text{Tar}) &+ \left(2 \frac{MW_{CO}}{MW_{C_2H_4}} \right) * \text{Conv}_{C_2H_4} * fc(\text{C}_2\text{H}_4, \text{HX4}, \text{Tar}) + \\
\left(2 \frac{MW_{CO}}{MW_{C_2H_2}} \right) * \text{Conv}_{C_2H_2} * fc(\text{C}_2\text{H}_2, \text{HX4}, \text{Tar}) &+ \left(6 \frac{MW_{CO}}{MW_{C_6H_6}} \right) * \text{Conv}_{C_6H_6} * fc(\text{C}_6\text{H}_6, \text{HX4}, \text{Tar}) + \\
\left(10 \frac{MW_{CO}}{MW_{Tars}} \right) * \text{Conv}_{tar} * fc(\text{Tars}, \text{HX4}, \text{Tar}); &
\end{aligned} \tag{97}$$

$$fc(\text{N}_2, \text{Tar}, \text{HX5}) = fc(\text{N}_2, \text{HX4}, \text{Tar}) + \left(\frac{1}{2} \frac{MW_{N_2}}{MW_{NH_3}} \right) * \text{Conv}_{NH_3} * fc(\text{NH}_3, \text{HX4}, \text{Tar}); \tag{98}$$

$$\begin{aligned}
fc(j, \text{Tar}, \text{HX5}) &= (1 - \text{Conv}_j) * fc(j, \text{HX4}, \text{Tar}); \\
j &= \{NH_3, CH_4, C_2H_6, C_2H_4, C_2H_2, C_6H_6, Tar\}
\end{aligned} \tag{99}$$

$$\begin{aligned}
fc(\text{O}_2, \text{Tar}, \text{HX5}) &= fc(\text{O}_2, \text{HX4}, \text{Tar}) - \left(\frac{1}{2} \frac{MW_{O_2}}{MW_{CH_4}} \right) * \text{Conv}_{CH_4} * fc(\text{CH}_4, \text{HX4}, \text{Tar}) + \\
\left(\frac{MW_{O_2}}{MW_{C_2H_6}} \right) * \text{Conv}_{C_2H_6} * fc(\text{C}_2\text{H}_6, \text{HX4}, \text{Tar}) &+ \left(\frac{MW_{O_2}}{MW_{C_2H_4}} \right) * \text{Conv}_{C_2H_4} * fc(\text{C}_2\text{H}_4, \text{HX4}, \text{Tar}) + \\
\frac{MW_{O_2}}{MW_{C_2H_2}} * \text{Conv}_{C_2H_2} * fc(\text{C}_2\text{H}_2, \text{HX4}, \text{Tar}) &+ \left(3 \frac{MW_{O_2}}{MW_{C_6H_6}} \right) * \text{Conv}_{C_6H_6} * fc(\text{C}_6\text{H}_6, \text{HX4}, \text{Tar}) + \\
\left(5 \frac{MW_{O_2}}{MW_{Tars}} \right) * \text{Conv}_{tar} * fc(\text{Tars}, \text{HX4}, \text{Tar}) &
\end{aligned} \tag{100}$$

The process is exothermic and is able to generate steam in order to cool down the equipment

$$Q(\text{Tar}) = \sum_j \Delta H_f(j) \Big|_{T(\text{HX4}, \text{Tar})} \Big|_{(\text{Tar}, \text{HX5})} - \sum_j \Delta H_f(j) \Big|_{T(\text{HX4}, \text{Tar})} \Big|_{(\text{HX4}, \text{Tar})} \tag{101}$$

Steam reforming. The stream coming from the gasifiers is fed to the reformer:

$$fc(j, \text{Cyc}(1\text{or}3), \text{Mix}14) = fc(j, \text{Mix}14, \text{HX4}) ; \forall j \in J \tag{102}$$

$$T(\text{Mix}14, \text{HX4}) = T(\text{Cyc}3, \text{Mix}14) \tag{103}$$

$$T(\text{Mix}14, \text{HX4}) = T(\text{HX4}, \text{Tar}); \tag{104}$$

In this case the heat exchanger 4 is not needed.

$$Q(\text{HX4}) = 0; \tag{105}$$

The chemical reactions taking place in steam reforming are of the form given by eq, (106)



The decomposition of nitrogen is the same as in the previous case, eq. 94. Thus, the mass balances for the different species are given based on the stoichiometric relationships derived from eq. (106). We assume the same values for the conversions as before (Conv_CH4 = 0.8, Conv_C6H6 = 1, Conv_Tar = 1, Conv_C2H6 = 0.99, Conv_C2H2 = 0.90, Conv_C2H4 = 0.90, Conv_NH3 = 0.90), Philip et al. (2007). The mass balances are given by eq. (107)

$$fc(j, Tar, HX5) = (1 - Conv_j) \cdot fc(j, HX4, Tar); \quad (107)$$

$$j = \{NH_3, CH_4, C_2H_6, C_2H_4, C_2H_2, C_6H_6, Tar\}$$

In the case of steam reforming of the hydrocarbons, the reactions are endothermic. We consider that the reactor operates adiabatically and that the final temperature is reduced to provide energy for the reactions due to the complexity in providing energy directly to the catalytic bed.

3.2.2.-Gas clean-up.

Two different possibilities are evaluated to clean the gas from solids, cold cleaning and hot cleaning. In the case of high pressure operation a ceramic filter is used operating at 500 °C. If we operate at low pressure, a wet scrubber is implemented at 40 °C to help in the removal of NH₃ too (Olofsson et al 2005)²⁵.

Cold cleaning. The stream coming from the low pressure indirect gasifier is cooled down in HX5 to 40 °C. As a result water condenses:

$$fc(j, Tar, HX5) = fc(j, HX5, Scrubber); \quad \forall j \in J \quad (108)$$

$$T(HX4, Tar) = T(Tar, HX5); \quad (109)$$

$$Q(HX5) = \sum_j \int_{T(Tar, HX5)}^{T(HX5, Scrubber)} c_{p_v}(j) dT \cdot fc(j, Tar, HX5) - \text{Condensed}_{Scrubber} \cdot \lambda_{Wa}(T(HX5, Scrubber)) \quad (110)$$

Where

$$\lambda_{Wa}(T(HX5, Scrubber)) = \lambda_{Wa,0} \left(\frac{Tc_{Wa} - T(HX5, Scrubber)}{Tc_{Wa} - Tb_{Wa}} \right)^{0.38} \quad (111)$$

In order to determine the amount of water that condenses in HX5, the specific humidity is calculated at the pressure of the Scrubber (1.2 bar) and its operating temperature (40°C)

$$p_{sat_HX5} = \text{Exp} \left(\text{coef_p}(Wa,1) - \frac{\text{coef_p}(Wa,2)}{(\text{coef_p}(Wa,3) + T_{Scrubber})} \right); \quad (112)$$

$$p_{v_HX5} = \text{re_hum_atm} * p_{sat_HX5}; \quad (113)$$

$$\text{spec_hum_HX5} = \frac{MW_{Wa}}{MW_{gas(HX5, Scrubber)}} * \frac{p_{v_HX5}}{(p_{scrubber} - p_{v_HX5})}; \quad (114)$$

$$\text{Condensed}_{Scrubber} = fc(Wa, HX5, Scrubber) - \text{spec_hum_HX5} \cdot \sum_{j \neq Wa} fc(j, HX5, Scrubber) \quad (115)$$

The amount of water needed for the process (L/G) is given by the literature. (L/G = 0.25 kg per m³ of gas) (Martelli et al., 2009)

$$fc(Wa, Src8, Scrubber) = (L/G) \cdot \frac{1}{\rho_{gas(HX5, Scrubber)}} \cdot \sum_{j \neq Wa, Char, Olivine, Ash} (1 + \text{spec_hum_HX5}) * fc(j, HX5, Scrubber) \quad (116)$$

In the scrubber solids and NH₃ are eliminated (the model is given by eqs 117-122) while the gas exits the scrubber with a humidity calculated according to eq. (120-122)

$$fc(j, Scrubber, Snk8) = fc(j, HX5, Scrubber); \quad \forall j = \{NH_3, Ash, Char, Olivine\} \quad (117)$$

$$fc(j, Scrubber, Compres1) = fc(j, HX5, Scrubber); \quad \forall j \neq \{Wa, NH_3, Ash, Char, Olivine\} \quad (118)$$

$$fc(Wa, Scrubber, Compres1) = \text{spec_hum_scrub} \cdot \sum_{j \neq \{Wa, Char, Ash, Olivine\}} fc(j, HX5, Scrubber) \quad (119)$$

$$p_{\text{sat_scrubber}} = \text{Exp} \left(\text{coef_p}(\text{Wa},1) - \frac{\text{coef_p}(\text{Wa},2)}{(\text{coef_p}(\text{Wa},3) + T_{(\text{Scrubber,Compres1})})} \right); \quad (120)$$

$$p_{\text{v_scrubber}} = \text{re_hum_atm} * p_{\text{sat_scrubber}}; \quad (121)$$

$$\text{spec_hum_scrubber} = \frac{MW_{\text{Wa}}}{MW_{\text{gas}(\text{HX5,Scrubber})}} * \frac{p_{\text{v_scrubber}}}{(p_{\text{scrubber}} - p_{\text{v_scrubber}})}; \quad (122)$$

$$\text{fc}(\text{Wa},\text{Scrubber},\text{Snk8}) = \text{fc}(\text{Wa},\text{Src8},\text{Scrubber}) + (\text{fc}(\text{Wa},\text{HX5},\text{Scrubber}) - \text{fc}(\text{Wa},\text{Scrubber},\text{Compres1})) \quad (123)$$

An energy balance, assuming adiabatic operation in the scrubber, determines the outlet temperature,

$$0 = \sum_j \int_{T_{\text{Scrubber}}}^{T(\text{Scrubber,Compres1})} c_{\text{p_v}}(j) dT \cdot \text{fc}(j,\text{Scrubber},\text{Compres1}) - \text{Condensed}_{\text{Scrubber}} \cdot \lambda_{\text{Wa}}(T(\text{Scrubber,Compres1})) \quad (124)$$

where λ_{Wa} is defined as in eq (111). Compressor 1 will increase the pressure to the working conditions of the PSA system, 4.5 bar

$$\text{fc}(j,\text{Scrubber},\text{Compres1}) = \text{fc}(j,\text{Compres1},\text{Mix12}); \quad \forall j \in \text{J} \quad (125)$$

$$T(\text{Compres1},\text{HX6}) = \left((T(\text{Scrubber},\text{Compres1}) + 273) + (T(\text{Scrubber},\text{Compres1}) + 273) * \left(\left(\frac{P_{\text{PSA}}}{P_{\text{Scrubber}}} \right)^{0.4/1.4} - 1 \right) \right) - 273 \quad (126)$$

and the energy required

$$W(\text{Compres1}) = (F(\text{Scrubber},\text{Compres1})) * \frac{8.314 * 1.4 * (T(\text{Scrubber},\text{Compres1}) + 273)}{((MW_{\text{gas_Compres1}} + \text{eps1}) * (1.4 - 1))} \left(\left(\frac{P_{\text{PSA}}}{P_{\text{Scrubber}}} \right)^{0.4/1.4} - 1 \right); \quad (127)$$

Hot cleaning. The stream coming from the reformer is cleaned to remove the solids. In order to use the filter, the temperature is adjusted to 500 °C by means of heat exchanger 5 (HX5):

$$\text{fc}(j,\text{Tar},\text{HX5}) = \text{fc}(j,\text{HX5},\text{Filter}); \quad \forall j \in \text{J} \quad (128)$$

$$T(\text{HX4}, \text{Tar}) = T(\text{Tar}, \text{HX5}); \quad (119)$$

$$Q(\text{HX5}) = \sum_j \int_{T(\text{Tar}, \text{HX5})}^{T_{\text{HotCleaning}}} c_{p-v}(j) \cdot dT \cdot fc(j, \text{Tar}, \text{HX5}) \quad (130)$$

In the filter the solids (Char, Olivine) are eliminated. The mass balances for the filter are as follows:

$$\text{recovery}(j) * fc(j, \text{HX5}, \text{Filter}) = fc(j, \text{Filter}, \text{Snk7}) ; \quad \forall j \in J \quad (131)$$

$$fc(j, \text{Filter}, \text{Expan2}) = (1 - \text{recovery}(j)) * fc(j, \text{HX5}, \text{Filter}) ; \quad \forall j \in J \quad (132)$$

$$fc(j, \text{Filter}, \text{Expan2}) = fc(j, \text{Expan2}, \text{Mix12}); \quad \forall j \in J \quad (133)$$

The high pressure provides energy in the expansion of the gas stream previous to feed it to the PSA system. The expansion is modeled as polytropic to determine the final temperature $T(\text{Expan2}, \text{Mix12})$ and the energy $W(\text{Expan2})$:

3.2.3.-Final HBC elimination

The hydrocarbons that are not eliminated at the reformer are withdrawn from the gas stream using a PSA system. The typical working conditions for PSA systems are low temperature (25 °C) 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 all of the hydrocarbons left in the gas stream as well as the ammonia. Water is discharged. Thus, Eff_PSA_HBC is 1 for hydrocarbons, ammonia and nitrogen. Due to the low temperature, more water condenses in HX6. The model for the PSA is given as follows:

$$fc(j, \text{Mix12}, \text{HX6}) = fc(j, \text{HX6}, \text{MS1}) ; \quad \forall j \in J \quad (134)$$

$$NonCondensed_{MS1} = spec_hum_MS1 \cdot \sum_{j \neq \{Wa\}} fc(j, Mix12, HX6) \quad (135)$$

$$P_{sat_PSA} = \text{Exp} \left(\text{coef_p}(Wa,1) - \frac{\text{coef_p}(Wa,2)}{(\text{coef_p}(Wa,3) + T_{PSA})} \right); \quad (136)$$

$$P_{v_PSA} = P_{sat_PSA}; \quad (137)$$

$$spec_hum_MS1 = \frac{MW_{Wa}}{MW_{gas(Mix12, HX6)}} * \frac{P_{v_MS1}}{(P_{PSA} - P_{v_MS1})}; \quad (138)$$

$$Q(HX6) = \sum_j \int_{T(Mix12, HX6)}^{T_{PSA}} c_{p_v}(j) \cdot dT \cdot fc(j, HX6, MS1) - (fc(Wa, Mix12, HX6) - NonCondensed_{MS1}) \cdot \lambda_{Wa}(T_{PSA}) \quad (139)$$

$$fc(j, MS1, MS2) = \text{Eff_PSA_HBC}(j) * fc(j, HX6, MS1); \quad \forall j \in J \quad (140)$$

$$fc(j, MS1, Mix13) = (1 - \text{Eff_PSA_HBC}(j)) * fc(j, HX6, MS1); \quad \forall j \neq 1 \quad (141)$$

$$fc(Wa, MS1, Mix13) = NonCondensed_{MS1}; \quad (142)$$

$$fc(Wa, MS1, MS2) = fc(Wa, HX6, MS1) - NonCondensed_{MS1}; \quad (143)$$

$$fc(j, MS1, MS2) = fc(j, MS2, Snk9); \quad \forall j \in J \quad (144)$$

3.3.-Water shift.

Figure 6 shows the scheme of the reactor system. The reaction taking place in the water shift reactor is widely known:



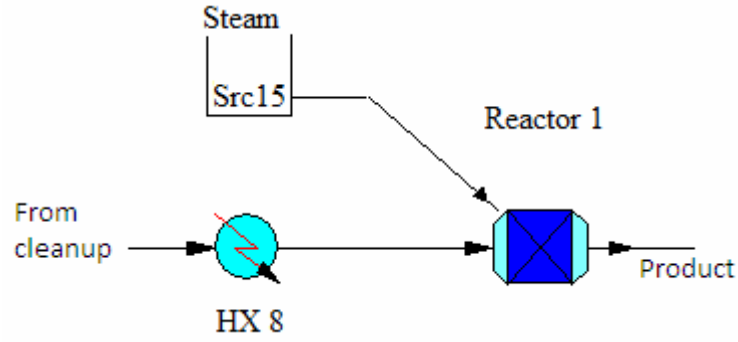


Figure 6.- Detail of the reaction zone.

However, its kinetics and conversion depend on the molar ratio of water to CO (H₂O to CO) and the operating temperature. Thus, using the experimental data presented by Choi et al (2003) we have developed a reduced order model to predict the conversion as function of both parameters so that the model can be solved in steady state. Based on the profiles shown in Choi et al (2003), we propose a model for the conversion of CO, see eq. (150). Thus, we solve a small parameter estimation problem to adjust 3 adjustable parameters. The model for the conversion is given by eqs. (146-150) The optimization determines the addition of water as well as the temperature of the reaction to minimize the energy consumption.

$$fc(j, HX8, Reactor1) = fc(j, Spl1, HX8); \quad \forall j \in J \quad (146)$$

$$T(\text{Mix13}, \text{Spl1}) = T(\text{Spl1}, \text{HX8}); \quad (147)$$

$$Q(\text{HX8}) = \sum_j \int_{T(\text{Spl1}, \text{HX8})}^{T(\text{HX8}, \text{Reactor1})} c_{p,v}(j) \cdot dT \cdot fc(j, \text{Spl1}, \text{HX8}) \quad (148)$$

$$fc(\text{Wa}, \text{Src15}, \text{Reactor1}) \geq 0; \quad (149)$$

$$\text{CO_shift_conv} = \frac{(0.0044 \cdot T(\text{HX8}, \text{Reactor1}) + 0.0924) \cdot \text{H2OtoCO}}{\left(\text{H2OtoCO} + \frac{46815}{T(\text{HX8}, \text{Reactor1})^2} \right)}; \quad (150)$$

Thus the products of the reactor will be:

$$fc(j, \text{Reactor1}, \text{Mix1}) = fc(j, \text{HX8}, \text{Reactor1}); \quad j \neq \{\text{Wa}, \text{CO}, \text{CO}_2, \text{H}_2\} \quad (151)$$

$$fc(Wa, Reactor1, Mix1) = fc(Wa, HX8, Reactor1) + fc(Wa, Src15, Reactor1) - fc(CO, HX8, Reactor1) * \left(\frac{MW_{Wa}}{MW_{CO}} \right) * CO_shift_conv \quad (152)$$

$$fc(CO, Reactor1, Mix1) = fc(CO, HX8, Reactor1) * (1 - CO_shift_conv); \quad (153)$$

$$fc(CO_2, Reactor1, Mix1) = fc(CO_2, HX8, Reactor1) + fc(CO, HX8, Reactor1) * \left(\frac{MW_{CO_2}}{MW_{CO}} \right) * CO_shift_conv \quad (154)$$

$$fc(H_2, Reactor1, Mix1) = fc(H_2, HX8, Reactor1) + fc(CO, HX8, Reactor1) * \left(\frac{MW_{H_2}}{MW_{CO}} \right) * CO_shift_conv \quad (155)$$

$$Q(Reactor1) = dH_shift_reac * fc(CO, HX8, Reactor1) * (CO_shift_conv) / MW_{CO} \quad (156)$$

A new reactor design is used in order to separate the hydrogen in the same reactor. It consists of membrane reactor that is porous to hydrogen as shown in Figure 7. According to recent results by (Killmeyer, 2003; Ji et al 2009a&b) the membrane allows directly the recovery of hydrogen from the reactor :



Figure 7.- Water shift reactor with membrane separation of H₂

4.-Solution procedure.

In order to optimize the superstructure, the partial enumeration technique described in a previous paper by the authors (Martín and Grossmann, 2010) has been applied. First, the MINLP is decomposed

into four subproblems, one per each gasifier and one per each reforming mode. Figure 8 shows the tree for the partial decomposition of the problem.

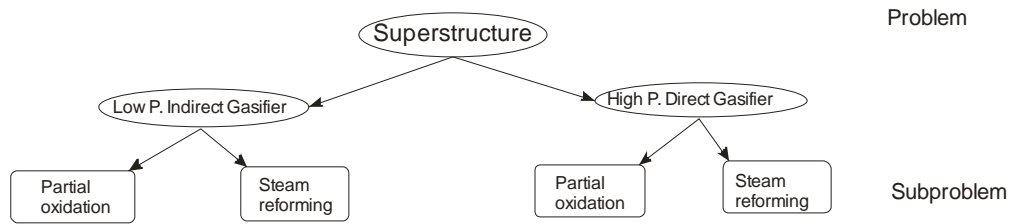


Figure 8.- Partial decomposition of the problem

For each one of the subproblems, the optimization of the operating conditions is obtained by solving an NLP. This yields the operating temperatures of the combustor and gasifier, in case of the indirect gasifier, as well as the working temperature and the steam injected into the water shift reactor. The objective function of each of the subproblems is given by eq. (157), which is a simplified economic optimization considering the production of hydrogen and the cost of energy and raw material to determine the operating conditions.

$$Z = fc(H_2, \text{Reactor1}, \text{Mix}') * 2.5 - 0.019 * (Q(\text{HX8}) / 2254 + fc(W_a, \text{Src15}, \text{Reactor1})) - 0.03 * F(\text{Src1}, \text{Wash}); \quad (157)$$

Next, heat integration within the process is carried out not only to determine the minimum amount of energy required in the process, but to produce the steam required for the operation of the gasifiers and that demanded by the water gas shift reactor. Finally, a detailed economic evaluation of the different subproblems is performed to decide upon the most economical process.

5.-Results.

Figure 9 shows the net energy produced and the cooling needs in the production of hydrogen for the 4 subproblems after the optimization of the operating conditions and heat integration. It can be seen that the steam reforming to eliminate the hydrocarbons generated in the gasification being endothermic, reduces the energy available in the process, while in case of partial oxidation, a larger surplus of energy

is generated. However, the large amount of steam that must be fed in the direct high pressure gasifier uses the excess of energy generated in the process. Thus, low pressure gasification is promising at this point.

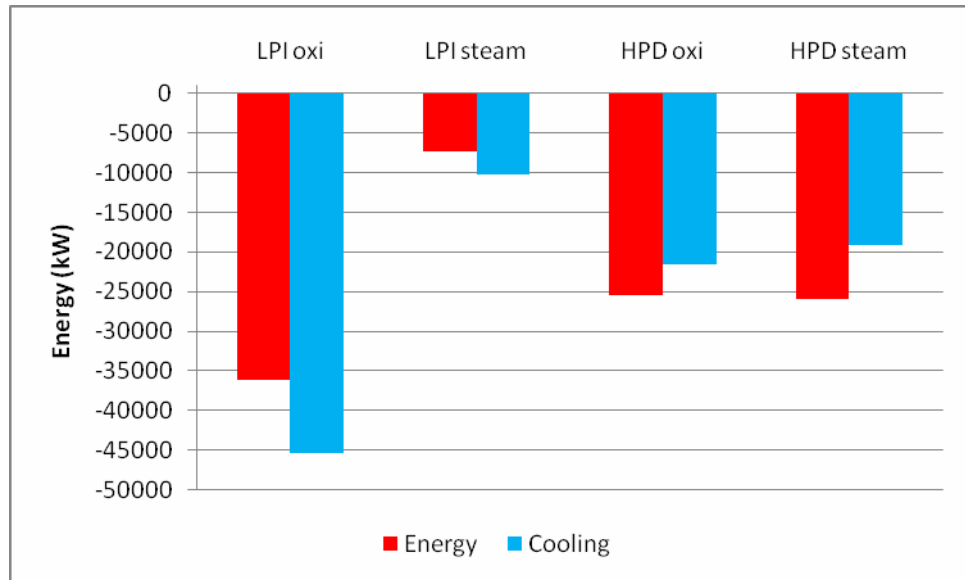


Figure 9.-Energy balance in the production of hydrogen

The contribution of the byproducts in the form of energy also plays an important role in the final decision on the process when performing the detailed economic evaluation. It is important to highlight that after the heat integration and steam production for the process, there is an excess of steam produced at a revenue of 0.0077\$/kg_{steam} (updated from Smith and Varbanov 2005)³⁰. The cost of the different utilities is taken 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)). The annualized cost of equipment is calculated updating the values from www.matche.com³⁴ web page, while the cost of salaries, administration and maintenance are based on those for a lignocellulosic ethanol plant which processes the same consumption of raw material. All hydrogen cost results in this report are shown in terms of dollars per kilogram (\$/kg) of hydrogen because a kilogram of hydrogen has roughly the same

energy content as a gallon of gasoline (Levene et al., 2006). Table 2 shows the yield and production cost using the four technologies evaluated after heat integration.

Table 2. Production cost for a 62Mkg /yr of hydrogen

| | Partial Oxidation | |
|----------------------------------------|-----------------------|----------------------|
| | Low pressure indirect | High pressure Direct |
| Raw material contribution (%) | 43.6 | 46.0 |
| Utilities contribution (%) | 1.7 | 0.0 |
| Hydrogen yield (kg/kg _{wet}) | 0.094 | 0.081 |
| Production cost (\$/kg) | 0.73 | 0.80 |
| | Steam reforming | |
| | Low pressure indirect | High pressure Direct |
| Raw material contribution (%) | 39.7 | 48.8 |
| Utilities contribution (%) | 4.4 | -4.0 |
| Hydrogen yield (kg/kg _{wet}) | 0.110 | 0.080 |
| Production cost (\$/kg) | 0.68 | 0.78 |

The optimal process with the lowest production cost is given by the low pressure gasifier and the steam reforming. The combustor operates at 984°C and the gasifier at 908°C, while the WGSR works at 314°C with an excess of steam to drive the conversion. The production cost is \$0.67/kg and the yield to hydrogen, 0.11kg/kg. Fig 10 shows the optimal flowsheet.

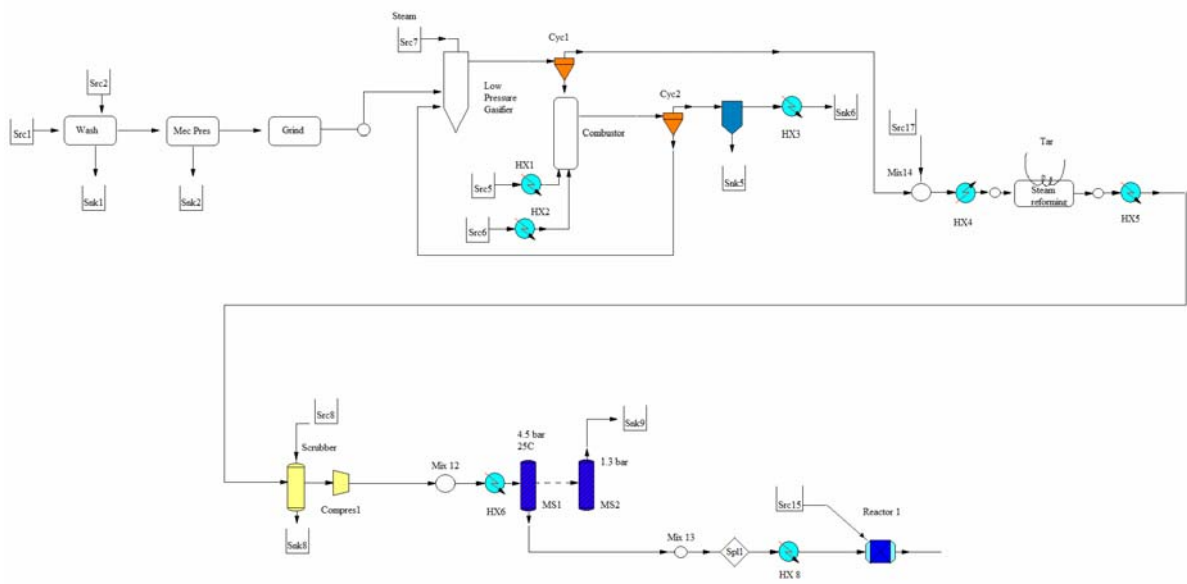


Figure 10.- Optimal flowsheet

If we compare steam reforming and partial oxidation for a fixed gasification technology (see Table 2) both show similar production costs. This is due to the fact that the partial oxidation process generates energy that can be used to alleviate the costs or the reduced production due to smaller yields towards hydrogen. In the case of steam reforming, the yield obtained is higher, but the endothermic nature of the reforming process reduces the energy available, and thus, the cost of the utilities increases. Another important fact to highlight from the results in Table 2 is that the conversion to H₂ reported in the literature is 0.084 kg/kg dry or 0.075 kg/kg dry (Lau et al., 2002; Bowen, 2003) which are values smaller than the ones obtained in this study (0.11 kg/kg wet Biomass or 0.13 kg/kg dry biomass). Furthermore, the production costs presented in this study are also lower than the ones reported in the literature; i.e.. the cost of production of hydrogen from whole tree forest biomass in Western Canada from a 2000 dry tonnes per day plant is \$1.14/kg of H₂ (Sarkar & Kumar, 2007). As a result it would be possible to meet the values required by the DOE who suggests a price of \$1.58 /kg (Bain, 2009) while the NERL obtained values in the range of \$1.18 –\$ 1.78 /kg (Spath et al., 2005). The only value they obtained below \$1/kg resulted from assuming zero cost for the raw material. Currently the selling price for Hydrogen is \$2.47/kg, meanwhile conservative scenarios suggest \$ 2.6 /kg when hydrogen is produced from reforming of natural gas in situ. The production cost other process alternatives are always higher. In the case of electrolysis of water, the price the values are (\$2.6 – \$4.2 /kg), while hydrogen produced by wind energy will cost from \$5.55/kg in the near term to \$2.27/kg in the long term (Levene et al., 2006).

Finally, an important issue to point out is the fact that this process generates CO₂, 1.2 kg/kg_{Biomass} together with 0.11 kg_{H₂}/kg_{Biomass}. It has recently been reported that the production of biodiesel from algae is a promising technology with a yield to biodiesel 10 to 100 times higher than using the current raw materials like soy bean or rapeedseed (Yusuf, 2007). However, it needs plenty of CO₂. This process could be a source for growing the algae. Biodiesel production requires in the range of 3.6kg of CO₂ per kg of biodiesel (Pate, 2008; Sazdanoff, 2006). Thus on a kg of biomass basis it would be possible to obtain 0.33kg_{Biodiesel}/kg_{Biomass} together with the hydrogen produced which provides full use of the biomass while

producing short – term and long term biofuels with good integration of different processes. According to the US DOE using algae for the production of biodiesel, it would be possible to meet the demand for biodiesel with 2-5% of the current cropland and with no consumption of water, since salt water can also be used.

6.-Conclusions.

A superstructure for the production process of hydrogen via gasification of switchgrass has been proposed embedding two technologies for the gasification (direct and indirect), two more for gas reforming (steam reforming and partial oxidation) and WGSR. The solution of the MINLP is performed by partial enumeration for the different technologies in terms of gasification and reforming. The 4 subproblems generated can be solved as NLP's to determine the operating conditions in the gasifier and in the WGSR that maximize the production of hydrogen.

The production process with lowest cost (\$0.68/kg of H₂) involves the use of indirect gasification with steam reforming of the hydrocarbon generated in the syngas. The cost of oxygen and the high consumption of steam penalize the direct gasification and partial oxidation alternatives. The solution also reveals that steam should be added to the water gas shift reactor to drive the conversion towards 1. Finally, the use of membrane separation combined with the WGSR, as proposed by Ji et al. (2009) reduces the equipment cost avoiding expensive gas separation for H₂ from CO₂ or H₂S. While the results presented in this paper are encouraging, further experimental validation is required to prove the conceptual design.

Acknowledgments

The authors acknowledge NSF Grant CBET0966524, the financial support of the industrial members of the CAPD and Dr. M. Martin also acknowledges the financial support from the Ministry of Education and Science of Spain and Fulbright commission providing a MICINN – Fulbright Postdoctoral fellowship.

7.-Nomenclature.

| | |
|-------------------------------|------------------------------------------------------------------------|
| Cyclon_1_eff(J) | Efficiency of separation in the cyclone 1 = 0.9999 solids |
| Cyclon_eff_Olivine | Efficiency of separation /0.9999/ |
| Cyclon_eff_Char | Efficiency of separation /0.9999/ |
| CO_shift_conv | Conversion of CO in the water shift reactor |
| COtoH2 | Molar ratio CO and H2 at mix1 |
| Conv_CH4 | Conversion of CH4 in tar /0.8/ |
| Conv_C2H6 | Conversion of C2H6 in tar /0.99/ |
| Conv_C2H2 | Conversion of C2H2 in tar /0.90/ |
| Conv_C2H4 | Conversion of C2H4 in tar /0.90/ |
| Conv_C6H6 | Conversion of C2H4 in tar /1/ |
| Conv_tar | Conversion of C2H4 in tar /1/ |
| Conv_NH3 | Conversion of NH3 in tar /0.90/ |
| 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 (kJperkmol) /-41200/ |
| Eff_PSA_HBC (J) = 1 | J={ C6H6, Tar, N2, NH3, CH4, C2H2, C2H4, C2H6} |
| eff _{precipitator} : | Efficiency of the electrostatic precipitator |
| Ferco_Pressure | Presure at Ferco gasifier bar /1.6/ |
| frac_wash | fraction of washing water that stays with the biomass /0.01/ |
| fraC _{dried} | Fraction of water removed in the drying step. |
| fc(j,unit1, unit2) | individual mass flow rate (kg/s) |
| F(unit1,unit2) | mass flow rate (kg/s) |
| H2OtoCO | Molar ratio H2o and Co |
| L/G | Ratio of water needed in the scrubber /0.25/ (kg/m ³) |
| MassGas | mass of gas generated (kg) |
| min_wash | min amount of washing water (kg per kg biomass) /0.5/; |
| mc_char | Mass of C in Char (kg) |
| mo_char | Mass of O in char (kg) |
| mn_char | Mass of N in char (kg) |
| ms_char | mass of S in char (kg) |
| mash_char | Mass of ash in char (kg) |
| MW_gas | Molar mass of syngas (kg/kmol) |
| MW_gas_Exp2 | Molar mass of gas in exp 2 (kg/kmol) |
| MW_gas_MS1_dry | Molar mass (kg/kmol) |
| NonCondensed_MS1 | Amount of water non condensed after HX6 (kg/s) |
| NonCondensed_MS3 | Amount of water non condensed after HX10 (kg/s) |
| P_Renugas | Pressure at Ferco gasifier /25/ (bar) |
| P_PSA | Presure required for PSA /4.5/ (bar) |
| P_PSA_d | Desorption presssure for PSA /1.3/ (bar) |
| P_scrubber | Pressure at scrubber /1.2/; (bar) |
| p_sat_atm | saturation pressure at 20 C (mmHg) |
| p_v_atm | actual vapor pressure of water in inlet (mmHg) |
| p_sat_MS1 | saturation pressure a (mmHg) |
| Q_combustor | Q generated at the combustor (kJ/s) |
| recovery (J) | J ={ Olivone, Char, Ash} |
| Ratio_olivine | Flow of olivine per mass of Biomass /27/ |
| Ratio_steam | Flow of steam required per mass of Biomass /0.4/ |
| re_hum_atm | rel humidity of air before regeneration at 20 C /0.7/ |
| Ratio_steam_renu | Flow of steam required per mass of Biomass /0.91/ |
| spec_hum_gas_MS1 | spec humidity (kg/kg) |
| spec_hum_atm | spec humidity of air before regeneration at 20 C (kg/kg) |
| T(unit1,unit2) | Temperature of the stream from unit 1 to unit 2 (°C) |

| | | | | | |
|-----------------|------------------------------------------------------|----------|-----------|-----------|--------|
| Waterdecomp | Water decomposition to adjust O concentration (kg/s) | | | | |
| x_Gasrenu | Mass fraction of gas in Renu | | | | |
| x_GasFerro | Mass fraction of gas in ferro | | | | |
| y_gas_Exp2 | Molar fraction in expansor 2 | | | | |
| y_gas_MS1_dry | Molar fraction in MS1 | | | | |
| y_Syngasrenu(J) | molar fraction of gas components in syngas dry | | | | |
| /Wa | 0.48; CO2 | 0.16; CO | 0.115; H2 | 0.24; CH4 | 0.005/ |

8.-References.

Adrover, M.E., López, E., Borio, D.O., Pedernera, M.N. (2009) Simulation of a membrane reactor for the WGS reaction: Pressure and thermal effects. Chem. Eng. J. 154, 1-3, 15 196-202

Bain, R. (2009) Indirectly Heated Gasification of Biomass to Produce Hydrogen http://www.hydrogen.energy.gov/pdfs/progress09/ii_b_1_bain.pdf

Balat, M. Havva Balat, H. and Öz, C. (2008) Progress in bioethanol processing Progress in Energy and Combustion Science, 34, 5, 551-573

BMW (2000) <http://www.madrimasd.org/informacionidi/noticias/noticia.asp?id=28723&sec=2&tipo=g>

Bowen, D.A. (2003) A Techno-Economic Assessment of Hydrogen Production by Gasification of Biomass GTI ; Berkeley, California May 19-22, 2003
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/merit03/30_gti_david_bowen.pdf

Brenes, M. D. (2006) Biomass and bioenergy Nova Science Publishers, Incorporated ISBN-13: 9781594548659

Bridgwater, A.V. (2003) Renewable fuels and chemicals by thermal processing of biomass. Chemical Engineering Journal 91 (2003) 87–102

Cecil, 1820 <http://www.eng.cam.ac.uk/DesignOffice/projects/cecil/cecil.pdf> accessed July 2010

Choi, Y. Stenger, H. G. (2003) Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen Journal of Power Sources 124 (2003) 432–439

Cole, D. E. (2007) Issues facing the Auto Industry: Alternative Fuels, Technologies, and Policies ACP Meeting Eagle Crest Conference Center June 20, 2007

Deutschmann, O., Schmidt, L.D. (1998) Two-dimensional modeling of partial oxidation of methane on rhodium in a short contact time reactor Twenty-Seventh Symposium (International) on Combustion/The Combustion Institute, 1998/pp. 2283–2291

Di Blasi, C.,(2004) Modeling wood gasification in a countercurrent fixed-bed reactor *AIChE J.*, 50, 9, 2306-2319

Doong, S., Roberts, M., Lau, F., (2005) Direct hydrogen production from biomass gasifier using hydrogen selective membrane. GTI Presentation to Minnesota Renewable Hydrogen Initiative Forum. May 27, 2005

Eggeman T. 2005. "Updated Correlations for GTI Gasifier – WDYLD8." Technical memorandum for Pam Spath, National Renewable Energy Laboratory, Golden, Colorado. June 27, 2005.

Feng, X., Wang, L., Min, S. (2009) Industrial energy evaluation for hydrogen production system from biomass and natural gas. Applied Energy, 86, 1767-1773

- Forsberg, C. W. Gorenssek, M.B. (2007) Relative Economic Incentives for Hydrogen from Nuclear, Renewable, and Fossil Energy Sources American Institute of Chemical Engineers Annual Meeting Salt Lake City; November 4–9, 2007
- Franceschin, G., Zamboni, A., Bezzo, F., Bertucco, A., (2008) Ethanol from corn: a technical and economical assessment based on different scenarios *Chemical Engineering Research and Design*, 86, 5, 488-498
- Fu, C-H, Wu, J.C.S.J. (2007) Mathematical simulation of hydrogen production via methanol steam reforming using double-jacketed membrane reactor *International Journal of Hydrogen Energy*, 32, 4830-4839
- Gao, N., Li, Aimin, Quan, C. (2009) A novel reforming method for hydrogen production from biomass steam gasification. *Bioresource Technology*, 100, 4271-4277
- Grossmann, I. E.; Caballero, J. A.; Yeomans, H. (1999) Mathematical Programming Approaches to the Synthesis of Chemical Process Systems, *Korean J Chem Eng*, 16, 407-426.
- Hamelinck, C.N., Faaij, A.P.C. (2002) Future prospects for production of methanol and hydrogen from biomass *Journal of Power Sources* 111, 1–22
- Ji, P., Feng, W., Chen, B., (2009) Production of ultrapure hydrogen from biomass gasification with air *Chemical Engineering Science* 64, 582 – 592
- Ji, P., Feng, W., Chen, B., (2009) Comprehensive Simulation of an Intensified Process for H₂ Production from Steam Gasification of Biomass *Ind. Eng. Chem. Res.* 2009, 48, 3909–3920
- Killmeyer, R., Rothenberger, K., Howard, B., Ciocco, M., Morreale, B., Enick, R., Bustamante, F. (2003) Water-Gas Shift Membrane Reactor Studies Hydrogen, Fuel Cells, and Infrastructure Technologies FY 2003 Progress Report*
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/ia9_killmeyer.pdf
- Lau, F.S. Bowen, D.A., Dihu, R., Doong, S., Hughes, E.E., Remick, R., Slimane, R., Turn, S. Q., Zabransky, R. (2002) Techno-Economic Analysis of Hydrogen Production by Gasification of Biomass Final Technical Report Work Performed Under DOE Contract Number: DE-FC36-01GO11089
- Levene, J., Kroposki, B., and Sverdrup, G., (2006) *Conference Paper* NREL/CP-560-39534 March 2006
<http://www.mwcog.org/uploads/committeedocuments/vVldW1k20060524150018.ppt>.
- Li, F.; Zeng, L., Fan, L.S. (2010) Techno-Economic Analysis of Coal-Based Hydrogen and Electricity Cogeneration Processes with CO₂ Capture *Ind. Eng. Chem. Res.* DOI: 10.1021/ie100568z
- Mani, S., Tabil, L.G., Sokhansanj, S. (2004) Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass *Biomass and Bioenergy* 27 (2004) 339 – 352
- Martín & Grossmann (2010) Energy optimization of bioethanol Submitted *Aiche J.*
- Martelli, E., Kreutz, T., Consonni, S., (2009) Comparison of coal IGCC with and without CO₂ capture and storage: Shell gasification with standard vs. partial water quench *Energy Procedia* 1, 607-614
- Matche (2009) www.matche.com
- Mueller_langer, F., Tzimas, E., Kalschmitt, M., Petevs, S. (2007) Techno-economic assessment of hydrogen production process for the hydrogen economy for the short and medium term *International Journal of Hydrogen Energy*, 32, 3797-3810

Olofsson, I., Nordin, A., and Söderlind, U., (2005) Initial Review and Evaluation of Process Technologies and Systems Suitable for Cost-Efficient Medium-Scale Gasification for Biomass to Liquid Fuels Ingemar ISSN 1653-0551 ETPC Report 05-02

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

Phillips, S.; A. Aden, J. Jechura, and D. Dayton T. Eggeman (2007) Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass *Technical Report*, NREL/TP-510-41168, April 2007

Rand, D.A.J., Dell, R.M. (2008) Hydrogen Energy Challenges and Prospects The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK ISBN: 978-0-85404-597-6

Sa, S., Silva, H., Sousa, J.M., and Mendes, A. (2009) Hydrogen production by methanol steam reforming in a membrane reactor: Palladium vs carbon molecular sieve membranes *Journal of Membrane Science*, 339, 160-170

Sarkar, S., Kumar, A., (2007) A Review of Techno-economics of Bio-hydrogen Production Technologies 2007 ASAE Annual Meeting 071649.

Sazdanoff, N. 2006 Modeling and Simulation of the Algae to Biodiesel Fuel Cycle Honors Undergraduate Thesis The Ohio State University

Smith, R., Varbanov, P. (2005) What's the price of Steam? CEP July 29-33

P. Spath, A. Aden, T. Eggeman, M. Ringer, B. Wallace, and J. Jechura (2005) Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier. *Technical Report NREL/TP-510-37408* May 2005

Tanksale, A., Beltramini, J.N., Lu, G. M (2010) A review of catalytic hydrogen production processes from biomass *Renewable and Sustainable Energy Reviews* 14 (2010) 166–182

Vernon P.D.F.; Green, M.L.H.; Cheetham, A.K.; Ashcroft, A.T. (1990) Partial oxidation of methane to synthesis gas *Catalysis Letters*, 6,2, 181-186

Yusuf, C., (2007) "Biodiesel from microalgae." *Biotechnology Advances* 25: 294-306.

Zhu, Y., Gerber, M.A., Jones, S.B., Stevens, D.J. (2009) Analysis of the effects of compositional and configurational assumptions on product costs for the thermochemical conversion of lignocellulosic biomass to mixed alcohols- FY 2007 Progress Report. U.S. DOE. PNNL 17949

<http://www.madrimasd.org/informacionidi/noticias/noticia.asp?id=28723&sec=2&tipo=g>