EXERGY ANALYSIS IN HYDROGEN PRODUCTION FROM STEAM REFORMING OF NATURAL GAS

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Abstract. *Steam Reforming of Natural Gas is the most economical process for producing Hydrogen. This work performs an exergy analysis in this process. The main steps in Steam Reforming are the reforming reaction, the shift reaction and the hydrogen purification. The final hydrogen has purity by about 99.999% and can be used in fuel cells. The catalyzed steam methane reforming is operated in a Nickel based catalyst on an oxide alumina support. The catalyst is active in temperatures above 600ºC. Synthesis Gas containing H_2, H_2O, CO_2, CO and residual CH_4 is formed inside reformer; its composition depends on the Steam-CH_4 ratio and the temperature-pressure conditions. Equilibrium conditions in the synthesis gas components are considered at reformer exit. After reforming, shift reaction converts CO and H_2O into CO_2 and H_2. Absorption in amine is used in order to separate CO_2 from the gas stream. CO_2 can be collected and sold as a sub-product. Molecular sieves are used in order to purify the hydrogen eliminating H_2O, CO_2 and CO and CH_4 residuals. Silica gel was used to separate H_2O, activated carbon to CO_2 and CH_4 and zeolite 4A to CO. An exergy analysis was performed in this process identifying the main sources of irreversibility and the results are discussed.*

Keywords*: Hydrogen Production; Exergy; Natural Gas; Steam Methane Reforming*

1. INTRODUCTION

Nowadys the society and the global market pressures the industries for more efficient and cleaner processes. To produce noble fuels from natural gas is a reply to this necessity.

Light hydrocarbons, especially methane, are the main source of hydrogen because they have a low production cost associated to large reserves all over the world (Armor, 1999). Steam reforming of natural gas SMR is the most economical way to produce hydrogen (Khotari *et al.*, 2004). The process is divided in three main steps: reforming, a highly endothermic reaction between H_2O and CH_4, shift reaction, an exothermic reaction between CO and H_2O producing H_2. The last step is the purification of hydrogen, where highly pure H_2 is produced. During purification, a large amount of CO_2 is produced as by product. In the simulation, natural gas was assumed as simply methane. In order to make the process more efficient a Pressure Swing Adsorption - PSA was introduced to improve a highly pure H_2 as main product.

Some authors have studied similar processes analysing energetic (Chouldhary & Goodman, 2000; and Anderson & Boudart 1981) and exergetic consumption (Rosen, 1986 and 1991). The H_2 production process here analyzed was based on the proposal of Rosen (1986) modified to incorporate an adsorption unit to produce highly pure H_2 that can directly be used in fuel cells. Hydrogen purification is performed through absorption followed by adsorption. Purity up to 99.999 % H_2, (in weight), can be achieved (Yang, 1997).

This work aims at contributing to improve the use of energy at the industrial hydrogen production through studying the evolution of the exergetic costs inside the process, identifying the main sources of irreversibility and evaluating the exergetic cost of each process stream. Also, as hydrogen is seeing as a new fuel, it is useful to calculate how much exergy is needed to produce a unit of exergy in the hydrogen current, considering the by-products production and the characteristics of the system.

This paper is part of a bigger work that performs an exergoeconomic analysis and optimization of the hydrogen production from methane. More details can be seen in Alves (2007).

2. THE SMR PROCESS

The process needs material and power inputs. The material inputs are methane (3 bar, 25ºC), air and water at environmental conditions (101.3 kPa and 25 °C). The power input is electrical energy to drive pumps and compressor. Water enters at environmental pressure and temperature. It is compressed up to 3 MPa, heated and evaporated in a boiler, HR2, and mixed with methane previously heated in a heat exchanger, HR3 (See Fig. 1).

The mixture of steam and methane goes to heat recovery HR1 and to reformer, where synthesis gas is produced. Synthesis gas passes through shift reactors to reduce CO producing additional H_2 and goes to purification. The main steps of the process are described bellow.

2.1. Reformer

During reforming, natural gas and steam react over a nickel catalyst producing synthesis gas at 2323 kPa and 950 °C, the source of heat is the same natural gas burnt in combustion chamber. The SMR process was performed using a stoichiometric steam to methane ratio of 2:1, coke deposition was neglected in this work.
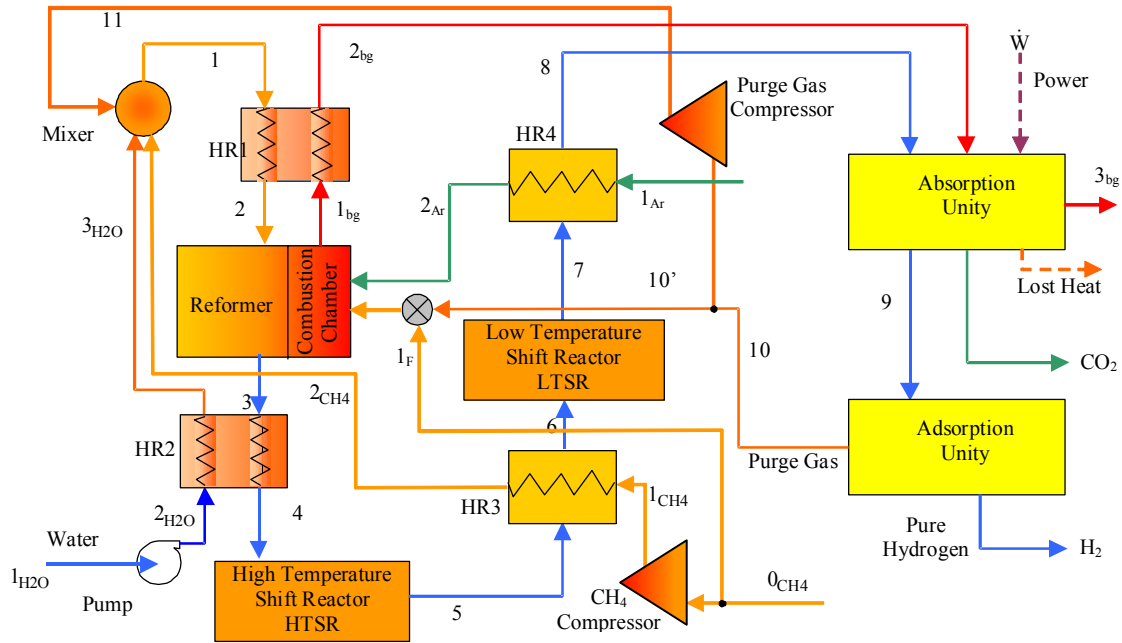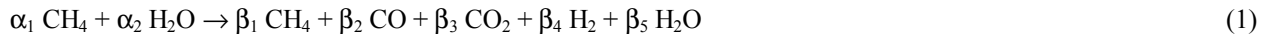

Figure 1. Schematic of SMR process.

The global reforming reaction between methane and steam can be represented generally as Equation (1), and the partial reactions as Equations (2) and (3):

$$\alpha_1 \, CH_4 + \alpha_2 \, H_2O \rightarrow \beta_1 \, CH_4 + \beta_2 \, CO + \beta_3 \, CO_2 + \beta_4 \, H_2 + \beta_5 \, H_2O \tag{1}$$

$$CH_4 + H_2O \rightarrow CO + 3 \, H_2 \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

Starting from an input of α_1 moles of methane and α_2 moles of steam, the β_s coefficients in Equation (1) are determined by the assumption that reactions (2) and (3) come to equilibrium, from the element balances.

The reforming step is composed of a heat recovery, HR1, the reformer and a boiler, HR2. HR1 heats the methane and steam mixture before reformer. HR2 produces superheated steam. The reformer is composed of a fixed bed with nickel catalyst. Inside reformer, synthesis gas rich in H_2 and CO is formed.

2.2. Shift Reaction

The shift reaction is a reaction between CO and H_2O that reduces CO and produces more H_2. To be more efficient, this reaction occurs in two steps: high temperature shift reaction, HTSR, and low temperature shift reaction, LTSR, both occur in a fixed bed with catalyst. Chemical equilibrium into shift reactions was assumed. Shift reaction is exothermic, and after each shift reactor a heat recovery is used to heat methane and air that go to combustion chamber. After HTSR, gas stream exits at 238 °C and after LTSR at 182 °C. Shift reduces the amount of CO from 15.1 % to 1.7 % in the HTSR and to 1.6 % in the LTSR.

2.3. Absorption Unity

A solution of DEA 30% in water was used as absorbent. Absorption of CO_2 in diethanolamine is of chemical absorption type. DEA is alkaline and CO_2 is an acid gas.

Absorption was modelled based on (Park *et al*. 2002 and Perry & Grenn, 1999), where was assumed that the concentration of CO_2 into DEA solution comes to equilibrium in absorption and desorption phases. The absorption unit was designed based on Ruthven description (Perry & Grenn, 1999). Figure 2 has a scheme of the absorption unit.
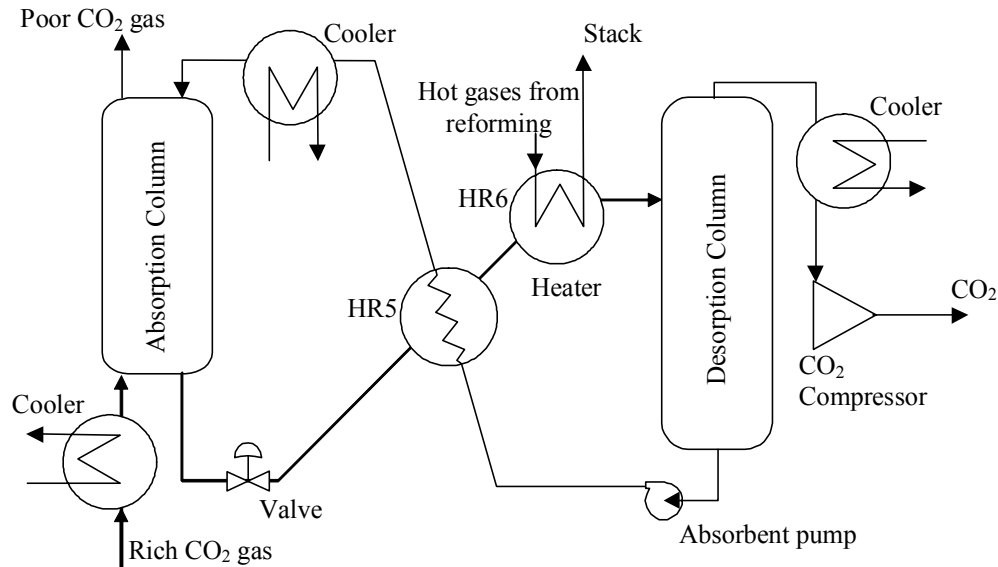
Figure 2. Process scheme of the DEA absorption unit.

The governing equations of phenomenon are described as (Kent and Eisenberg, 1976):

$$RNH3 \xleftarrow{\quad K_1 \quad} H+ + RNH_2 \tag{4}$$

$$RNHCOO^- + H_2O \xleftarrow{\quad K_2 \quad} RNH_2 + HCO_3 \tag{5}$$

$$CO_2 + H_2O \xleftarrow{\quad K_3 \quad} H^+ + HCO3^- \tag{6}$$

$$HCO3^- \xleftarrow{\quad K_{34} \quad} H^+ + CO3^{2-} \tag{7}$$

$$H_2O \xleftarrow{\quad K_5 \quad} H^+ + OH^- \tag{8}$$

where "R" Represents DEA radical. The dissolution of CO_2 into liquid phase was determined by Henry law contant:

$$H_{CO_2} = \frac{P_{CO_2}}{[CO_2]} \tag{9}$$

where P_{CO_2} is the partial pressure of CO_2 and $[CO_2]$ is the concentration of CO_2, (kmol/m^3) in liquid phase.

Before pass through absorption column, the gas is cooled until 40ºC to promote better absorption (see Figure 2). The absorbent and the gas flow in counter current along the absorption column, the CO_2 is carried out by the absorbent. To promote stripping, the absorbent is heated until 70 ºC and the pressure is reduced to 40 kPa. The CO_2 passes through a cooler that lower the temperature to 40ºC and a compressor to elevate the pressure to 101 kPa (see Figure 2). The heating limit of DEA solution is the bubble point. To heat the absorbent solution, the unit has two heat exchangers. The coolers are heat exchanges that dissipate heat into refrigeration water.

In this unit CO_2 is produced as a by-product at 101 kPa and 185 ºC. CO_2 molar ratio is reduced from 18% (71.81 % wt) to 0.62 % (6.82 % wt). After absorption unit H_2 mol ratio is of 89%.

2.4. Adsorption Unity

Adsorption is the last step in H_2 production. Its role is purifying H_2 up to 99.999 % (wt). This high purity is due to the elevated selectivity of hydrogen in the adsorbent bed related to CO_2, CO, N_2, CH_4 and H_2O. Silica gel, activated carbon and zeolites compose the adsorbent beds (Yang, 1997).

A system of valves improves adsorption and regeneration of beds in a Pressure Swing Adsorption, PSA. The PSA system can be assumed near to steady state if at least four beds are used. This system uses five beds that promote steady state and a high hydrogen recuperation ratio.

The valve system controls the absorption and regeneration phases. When a bed is saturated the valve system inverts the H_2 flow and lowers its pressure for the atmospheric pressure. Pure H_2 at atmospheric pressure passes through the bed regenerating it, no vacuum pump are needed, the driving force for desorption is the difference of pressure between the incoming gas (1856 kPa) and the purge gas at atmospheric pressure. While one bed is adsorbing, the others are regenerating, more details can be seeing at Yang (1997) and Ruthven (1984).

This system divides gas stream into two flows: pure hydrogen and purge gas. Purge gas is burnt in the combustion chamber. From its composition, for this purge gas a Low Heat Value of 25,400 kJ/kg was calculated. The purge stream saves 82 % of methane in the combustion chamber.

Due to PSA system, hydrogen exits at high pressure while purge gas, at atmospheric pressure.

Recuperation factor, understood as the amount of hydrogen presents in the stream that is separated after the adsorption cycle, was assumed as 82%. This value was based on Yang (1997) and Sircar *et al.* (1999).

Although adsorption process is exothermic, it can be approximated as an isothermal process. This hypothesis is applied to cyclic process with short duration adsorption phase (Yang, 1997 and Ruthven, 1984).

3. EXERGETIC ANALYSIS

In order to improve exergetic analysis, the process was divided into several control volumes CV and each performance relative to its function was determined. Some considerations were assumed:

- Environmental standard temperature and pressure conditions $T_0=25ºC$ and $P_0=101.3$ kPa to exergy calculus. The composition was assumed as that proposed by Szargut *et al.* (1988).
- Exergy efficiencies determined according to the definitions: Fuel F, Product P and Irreversibility I concept of Kotas (1985) ε; or input output method, ζ, for dissipative control volumes. These efficiencies are defined as:

$$\varepsilon = \frac{P}{F} \tag{9}$$

$$\zeta = \frac{Ex_{out}}{Ex_{in}} \tag{10}$$

The irreversibility in both definitions is determined as:

$$I = F - P \tag{11}$$

$$I = Ex_{in} - Ex_{out} \tag{12}$$

Where Ex_{in} and Ex_{out} are total exergies that enter and exit from CV respectively.

The exergy of a gas mixture is calculated as sum of each mixture component exergy plus the reversible isothermal work to compress (or decompress) from its partial pressure P_k to $P_{\infty,k}$ of the component in the environment (Szargut *et al.*, 1988). So, chemical exergy is calculated as:

$$\overline{ex}_{ch} = \sum_k x_k \overline{ex}_{ch,k} + RT_0 \sum_k x_k \ln(x_k) \tag{14}$$

Applying previous considerations to each CV according to figure 1:
Water pump:

$$F = \dot{W}_{pump} \tag{15}$$

$$P = Ex_{2,H_2O} - Ex_{1,H_2O} \tag{16}$$

Heat Exchanger 1 (HR1):

$$F = Ex_{1,bg} - Ex_{2,bg} \tag{17}$$

$$P = Ex_2 - Ex_1 \tag{18}$$

Heat Exchanger 2 (HR2):

$$F = Ex_3 - Ex_4 \tag{19}$$

$$P = Ex_{3,H_2O} - Ex_{2,H_2O} \tag{20}$$

Heat Exchanger 3 (HR3):

$$F = Ex_5 - Ex_6 \tag{21}$$

$$P = (Ex_{1,CH_4} + Ex_{1,F}) - Ex_{0,CH_4} \tag{22}$$

Heat Exchanger 4 (HR4):

$$F = Ex_7 - Ex_8 \tag{23}$$

$$P = Ex_{2,Air} - Ex_{1,Air} \tag{24}$$

Reformer:

$$F = (Ex_{1;F} + Ex_{10} + Ex_{2,Air}) - Ex_{1,bg} \tag{25}$$

$$P = Ex3 - Ex2 \tag{26}$$

High Temperature Shift Reactor (HTSR):

$$F = Ex_{ch,4} - Ex_{ch,5} \tag{27}$$

$$P = Exph,5 - Exph,4 \tag{28}$$

Low Temperature Shift Reactor (LTSR):

$$F = Ex_{ch,6} - Ex_{ch,7} \tag{29}$$

$$P = Ex_{ph,7} - Ex_{ph,6} \tag{30}$$

Mixer (dissipative CV):

$$Ex_{in} = Ex_{3,H_2O} + Ex_{1,CH_4} \tag{31}$$

$$Ex_{out} = Ex_1 \tag{32}$$

Absorption Unit (dissipative CV):

$$Ex_{in} = Ex_8 + Ex_{2,bg} + \dot{W}_{ABS,pump} + \dot{W}_{CO_2,Comp} \tag{33}$$

$$Ex_{out} = Ex_9 + Ex_{CO_2,Sold} \tag{34}$$

Adsorption Unit (dissipative CV):

$$Ex_{in} = Ex_9 \tag{35}$$

$$Ex_{out} = Ex_{10} + Ex_{H_2,Sold} \tag{36}$$

Where $\dot{W}_{pump}$ and $\dot{W}_{ABS,pump}$ (isentropic efficiencies 0.85) are the power required by water and absorbent solution pumps, respectively, $\dot{W}_{CO_2,Comp}$ (isentropic efficiency 0.85) is the power required by vacuum pump at stripping column; $Ex_{CO_2,Sold}$ and $Ex_{H_2,Sold}$ are the product exergies, CO_2 and H_2.

4. RESULTS AND DISCUSSIONS

All parameters were calculated related to 1 kmol/s of methane entering in the reformer. These parameters are shown in Table 1. EES® software was used to perform the calculations.

Table 1. Stream values of the SMR process.

Flow	T (K)	P (kPa)	$\dot{N}$ (kmol/s)
1_{H_2O}	298.2	101.3	2
2_{H_2O}	298.3	3300	2
3_{H_2O}	1016	3000	2
0_{CH_4}	298.2	3000	1.1038
1_{CH_4}	490.6	3000	1
1_{bg}	1273	101.3	4.843
2_{bg}	877.5	101.3	4.843
1_F	490.6	3000	0.1038
1_{Air}	298.2	101.3	4.001
2_{Air}	445.8	101.3	4.001
1	803.4	2867	3
2	1253	2581	3
3	1223	2323	4.78
4	338.3	2206	4.78
5	510.6	2140	4.78
6	455.1	2076	4.78
7	465.8	2014	4.78
8	352.2	1953	4.78
9	313	1856	3.958
10	313	101.3	1.072
$CO_{2.Sold}$	458.7	101.3	0.8219
$H_{2.Sold}$	313	1670	2.886

The molar fractions of main flows are shown in Table 2. The exergies total, physical and chemical of flows are shown in Table 3.

Table 2. Molar ratios of the main streams of the SMR process.

Flow	CH_4	CO	CO_2	H_2	H_2O
1	0.3330				0.6670
3	0.0230	0.1510	0.0348	0.593	0.1970
5	0.0230	0.0170	0.1690	0.728	0.0631
7	0.0230	0.0085	0.1780	0.736	0.0545
9	0.0278	0.0103	0.0062	0.890	0.0659
10	0.1030	0.0379	0.0229	0.593	0.2440

The exergetic balance identifying irreversibility along the cycle is made based on these previous values. Table 4 shows irreversibility of each CV and its exergetic efficiencies.

It can be observed that the main source of irreversibility is the reformer (combustion chamber comprised), 52.7% of net irreversibility. Although chemical exergy increases the effect of the combustion destroying exergy makes the reformer the main source of irreversibility, this effect was previously presented in Alves and Nebra (2003). Important note the high efficiencies of mixer and absorption unit. This high efficiency is due to chemical exergy in the streams at inlet and exit of the control volumes, although the high efficiency they have a considerable irreversibility over the process.

The second biggest source of irreversibility was the absorption unit, 26 % of total irreversibility. This result is due to the heat consumption, power to absorbent and CO_2 compressor and many heat exchangers wasting exergy to improve separation of CO_2 in this unit.

Table 3. Flow exergy values normalized to 1 kmol/s methane input.

Flow	Ex_{ph} (kW)	Ex_{ch} (kW)	Ex (kW)
1_{H_2O}	0	18980	18980
2_{H_2O}	115.5	18980	19096
3_{H_2O}	115183	18980	79249
0_{CH_4}	9270	917936	927207
1_{CH_4}	10239	831650	841889
$1F$	1062	86286	87349
1_{Air}	0	0	0
2_{Air}	3259	0	3259
1_{bg}	103194	10355	102915
2_{bg}	52133	10355	51993
1	65872	845896	911768
2	115183	845896	961079
3	118270	959221	1077491
4	36867	959221	996088
5	44120	943885	988005
6	40474	943885	984359
7	40702	943236	983938
8	35714	943236	978950
9	28571	932042	960614
10	11.89	252273	252284
$CO_{2.Sold}$	1089	16331	17419
$H_{2.Sold}$	20078	681388	701466
$\dot{W}_{pump}$	136	-	136
$\dot{W}_{ABS,pump}$	2202	-	2202
$\dot{W}_{CO_2,Comp}$	4869	-	4869

Table 4. Irreversibility and Exergy efficiencies of the different units of the SMR process.

CV	I (kW)	I (%)	ε	ζ
Water pump	20.37	0.009	0.8501	—
HR1	1611	0.687	0.9684	—
HR2	21250	9.061	0.739	—
HR3	1615	0.688	0.5572	—
HR4	1729	0.737	0.6534	—
HTSR	8083	3.447	0.473	—
LTSR	420.9	0.179	0.3514	—
Reformer	123566	52.690	0.4851	—
Mixer	9370	3.996	—	0.9898
Absorption unit	59981	25.580	—	0.9422
Adsorption unit	6863	2.927	—	0.9936

Adsorption unit produces only 3 % of total irreversibility. This low irreversibility generation has some reasons: isothermal process in ideal gases, in this condition, enthalpy of ideal gas remains unchanged; no heat and power consumption appear in this unit. The biggest reduction of pressure, source of irreversibility, happens in the purge gas that has lower exergy than hydrogen flow.

Considering the exergies of H_2 and CO_2 sold, the net process efficiency was 75.4 %. If CO_2 can not be used its exergy must be neglected. In this case the net efficiency diminishes to 73.6 %.

It can be observed the high efficiency of the dissipative CVs. The irreversibility is mainly related to physical exergy but the chemical exergy is much bigger than the physical. This effect is clear in mixer (99%) and adsorption unity (99%).

5. CONCLUSIONS

This work simulated SMR hydrogen production in order to perform the exergetic balance of process.

Some important considerations were assumed to perform the simulation: temperature of reformer, 950 ºC; recuperation factor of hydrogen in the adsorption unit as 82 %; ideal gas mixture in the flows.

The reference environment was adopted as that proposed in Szargut *et al.* (1988) as well as the methodology to determine chemical exergy.

Exergetic analysis showed that the main source of irreversibility is the combustion inside combustion chamber of reformer. This result is according to what can be expected. Methane reform is the main step in hydrogen production; the simulation showed that 80% of hydrogen produced along the process is in the reforming step and 20% in shift reaction.

The second biggest source of irreversibility was the absorption unit due to the heat and power consumption. The third biggest source of irreversibility is the Heat Exchange HR2 due to amount of heat exchanged and the difference of temperature between the streams.

Adsorption unit is not important in net irreversibility producing only 3 % of total irreversibility.

6. ACKNOWLEDGEMENTS

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