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Petroleum Refinery Hydrogen Production Unit: Exergy and Production Cost Evaluation

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Abstract

Some specific processes are required to obtain pure hydrogen and the most usual one is natural gas reforming, where natural gas reacts with superheated steam producing H_2, CO, CO_2 and H_2O. This paper presents the exergy and production costs evaluation of a complete hydrogen production unit of a petroleum refinery. The hydrogen production unit analysed in this paper has to supply 550,000 Nm^3 of hydrogen per day to purify diesel oil. Based on a synthesis plant of the hydrogen production unit, the exergy efficiency of each component and of the overall plant are calculated. The hydrogen production cost is determined by means of a thermoeconomic analysis in which the equality cost partition method is employed, including capital and operational costs, in order to determine the production cost of hydrogen and other products of the plant.

Keywords: hydrogen production, exergy analysis, thermoeconomic analysis

1. Introduction

Hydrogen is normally found combined with other elements, such as oxygen in water and carbon in hydrocarbons and the majority of organic composites. Due to its great chemical activity and consequent easiness of reaction, pure hydrogen is often used in industrial processes and oil refineries to purify several products and fuels.

Annual world hydrogen production is currently around $5x10^{11}Nm^3$ corresponding to about 2% of primary energy demand. *Figure 1* shows the main production routes, indicating that 96% is produced from fossil fuels (Ewan and Allen, 2005).

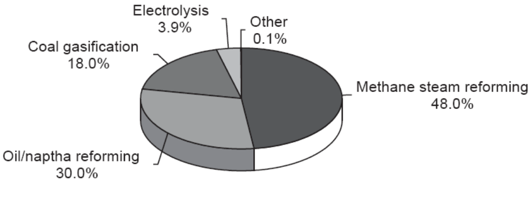

Figure 1 - Present distribution of primary energy sources for hydrogen production (Ewan and Allen, 2005)

The hydrogen production unit analysed in this paper has to supply 550,000 Nm^3 of hydrogen per day to purify diesel oil. Based on a synthesis plant of a petroleum refinery hydrogen production unit**,** the exergy efficiency of each component and of the overall plant are calculated. The hydrogen production cost is determined by means of a thermoeconomic analysis in which the equality cost partition method is employed, including capital and operational costs, in order to determine the production cost of hydrogen and other products of the plant.

2. Methane reforming process

Hydrogen can be obtained using the methane reforming process. In this process (Docekal, 1986), steam (H_2O) reacts with natural gas composed of a mixture of CH_4 (89%), C_2H_6, (9%), C_3H_8, C_4H_{10}, N_2 and CO_2. The product of this reaction is a mixture of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2) and steam (H_2O), according to Equation 1 (for each hydrocarbon):

$$\alpha C_mH_{2n} + \beta H_2O \rightarrow [(m+n)\alpha+\gamma]H_2 + (m\alpha-\gamma)CO + \gamma CO_2 + (\beta-m\alpha-\gamma)H_2O \quad (1)$$

where

$$0 \leq \gamma \leq m\alpha \quad (2)$$

The stoichiometric coefficient γ of Equation 1 depends on the chemical equilibrium of the reaction.

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The design of a hydrogen production plant is extremely complex. A great number of equipment, valves, pipes and connections are necessary to build the plant and guarantee its production. Due to this great number of information and variables, it is necessary to develop a synthesis plant to describe the main functions of the real process, as presented in *Figure 2*.

Before entering the Reformer, the feed (node 100) is compressed in the Feed Compressor (node 110). From the Feed Compressor, natural gas is heated in the Feed Preheater (from node 110 to node 141), mixed with recycled hydrogen (node 145) and sent to the Reformer Feed Preheat Coil (node 150). The gas leaving the Feed Preheat Coil (node 160) goes to the Desulphurizer.

The outlet flow from the Desulphurizer (node 170) is mixed with process steam (node 590) and sent to the Reformer Mix Feed Preheater Coil, located in the reformer convection section. Then it goes to the catalyst tubes (node 220) located in the Reformer at 2.8 MPa and 460°C.

Hydrogen is produced in the reforming section by the reaction of hydrocarbons with steam in the presence of a catalyst. As the reforming reaction is strongly endothermic and the heat required is at very high temperature, the reforming catalyst is placed in vertical tubes installed inside the Reformer radiant section.

The Reformer consists of a single top-fired radiant cell (the burners are located in the roof of radiant cell) and a vertical convection box. Flue gases leave the radiant bottom.

The combustion air is injected in the burners by the Forced Draft Fan (node 330) and is preheated in the Combustion Air Preheater located in the convection section of the Reformer. The fuel used by these burners comes from a second stream from the feed (node 310).

In the convection section the flue gas, in addition to preheating the air, exchanges heat in the following coils: Steam Generator Coil, Mix Feed Preheat Coil, Feed Preheat Coil and Steam Superheater Coil.

The reformed gas leaves the catalyst tubes (node 230) at 840°C and 2.58 MPa and goes to the Waste Heat Exchanger. The reformer effluent temperature is controlled by the burners' control system.

The reformer effluent is cooled in the Waste Heat Boiler and goes into the Shift Reactor (node 240). In the Shift Reactor CO reacts with steam to form hydrogen and CO_2, as shown in the equation below:

$$(m\alpha-\gamma)\,CO + (\beta-m\alpha-\gamma)\,H_2O \rightarrow (m\alpha-\gamma)\,H_2 + (m\alpha-\gamma)\,CO_2 + (\beta-2m\alpha)\,H_2O \qquad (3)$$

where $(\beta-2m\alpha)$ is the steam excess from Equation (1) and $(m\alpha-\gamma)$ is the number of mols of both molecular hydrogen and carbon dioxide formed in the Shift Reactor.

This reaction reduces CO and simultaneously increases the production of H_2. The shift reaction is exothermic and the effluent temperature depends on the CO concentration, the reactor inlet temperature and the reactor feed flow.

The boiler feed water to the steam generating system (node 480) is preheated in the Boiler Feed Water Heater (node 490), recovering heat from the Shift Reactor effluent, and goes into the Steam Drum.

From the Steam Drum the water is distributed by natural circulation to the Steam Generator Coils (node 540) and also to the Waste Heat Exchanger (node 510).

The generated steam is collected in the Steam Drum and flows to the Steam Superheater Coil (node 560). The superheated steam is divided in three streams: the first stream is the process steam and it is mixed with the feed (node 580), the second stream is used to exchange heat with the feed at the Feed Preheater (node 350) and the third stream is the exported steam (node 600). The exported steam follows to the refinery medium pressure steam header.

The Shift Reactor effluent is cooled in the following exchangers: Boiler Feed Water Heater (node 260), First PSA (Pressure Swing Adsorption) Feed Cooler (node 270) and Second PSA Feed Cooler (node 280).

The gas leaving the Second PSA Feed Cooler is sent to the Condensate Stripping Column, where the process condensate is removed (node 400), and then flows to the PSA System (node 290). The final hydrogen purification (99.90 % vol.) is done in the PSA system. The PSA System generates two streams: the purge gas, which is used as a fuel in the Reformer (node 900), and the hydrogen product (node 300).

The design, installation, maintenance and operation of every component of the plant and each chemical element that composes the process have a direct impact on the hydrogen production cost. Each is difficult to evaluate but proper evaluation during the design and construction of a new plant can mean the difference between profits and losses.

3. Exergy Analysis of the Plant

The exergy analysis of the natural gas reforming plant was developed using the synthesis plant shown in *Figure 2* considering the composition, mass flow rate, pressure and temperature indicated in each one of the sections of that figure assuming steady state operating

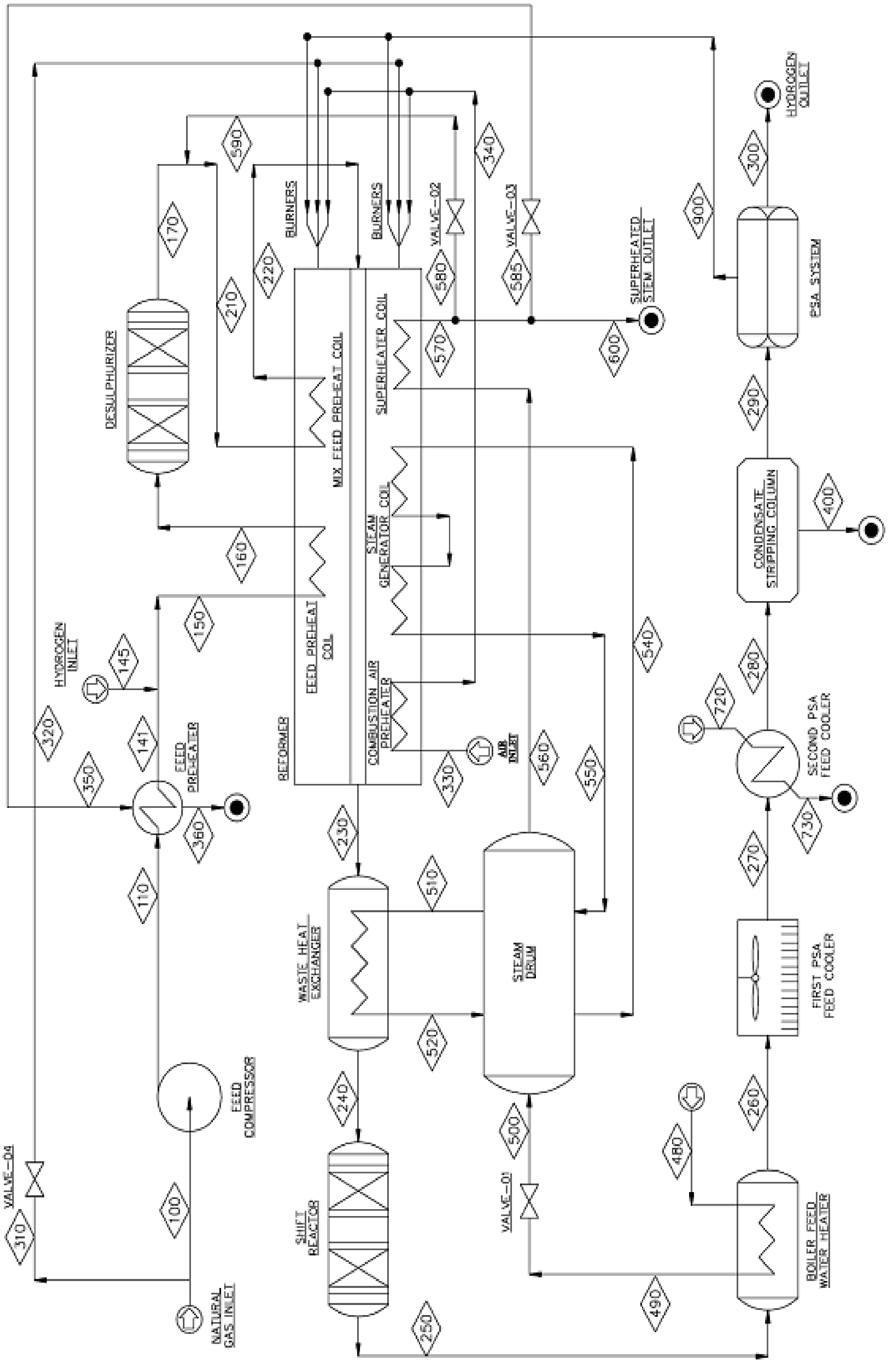

Figure 2 - Synthesis plant

TABLE I. MAIN INLET AND OUTLET FLUID CHARACTERISTICS

Section		Product	Mass Flow Rate (kg/h)	Temperature (°C)	Pressure (kPa)	Physical Exergy (MW)	Chemical Exergy (MW)	Total (MW)
INLET FLOWS	100	Natural Gas	7,910.00	40	2465.3	0.91	103.63	104.54
	145	Hydrogen	37.00	40	3085.9	0.03	0.96	0.99
	310	Natural Gas	662.00	40	2465.3	0.07	8.42	8.49
	330	Dry Air	78,564.0	25	101.3	0.00	0.09	0.09
	480	Compressed Water (8.4 MPa)	41,739.00	145	8473.8	1.08	0.61	1.69
	720	Compressed Water to Second PSA Feed Cooler	52,400.00	25	465.8	0.01	0.74	0.75
OUTLET FLOWS	300	Hydrogen	2,004.00	44	2091.1	2.17	68.05	70.22
	360	Saturated Water (1.3 Mpa)	1,223.00	192	1322.7	0.04	0.01	0.05
	400	Liquid Water from Stripping Column	13,177.00	40	2189.5	0.01	0.19	0.20
	600	Superheated Steam (3.1 MPa)	17,011.00	436	3056.3	6.11	0.25	6.36
	730	Compressed Water from Second PSA Feed Cooler	52,400.00	25	465.8	0.01	0.74	0.75
	920	Combustion Products	97,657.00	359	99.3	3.66	1.31	4.97

conditions. Thermodynamic and transport properties of every flow were determined by means of the software EES (Klein, 2006). TABLE I presents the main inlet and outlet fluid characteristics of the synthesis plant. All the gases and gas mixtures were treated as ideal gases because their compressibility factors are close to one (in node 100 the compressibility factor is 0.958; in node 145 it is 1.018 and in node 150 it is 0.995 (Cruz, 2004)).

Based on the synthesis plant and with the thermodynamic and transport properties of the fluids in each section, it is possible to develop calculations of mass, energy and exergy balances for each component of the synthesis plant, as well as its respective exergy efficiency. In these balances, it is assumed that there are no heat losses to the environment in any analysed component, and P_0 = 101.3 kPa and T_0 = 25°C were used as the reference environment pressure and temperature. The atmosphere composition was considered the same as proposed by Szargut et al. (1988). These conditions represent the real average values of pressure, temperature and atmosphere composition of the environment in which the studied hydrogen production unit will be installed. Based on these definitions and on the process data, the exergy flow rate in each point of the system was calculated and, consequently, it was possible to evaluate the exergy destruction rate in each component. These values are shown in TABLE II.

The exergy efficiencies for the main components and for the overall plant were calculated using the following equations:

- Feed Compressor:

$$\varepsilon = \frac{B_{110} - B_{100}}{W} \tag{4}$$

- Feed Preheater:

$$\varepsilon = \frac{B_{141} - B_{110}}{B_{350} - B_{360}} \tag{5}$$

- Waste Heat Exchanger:

$$\varepsilon = \frac{B_{520} - B_{510}}{B_{230} - B_{240}} \tag{6}$$

- Boiler Feed Water Heater:

$$\varepsilon = \frac{B_{490} - B_{480}}{B_{250} - B_{260}} \tag{7}$$

- Reformer:

$$\varepsilon = \frac{\begin{bmatrix} (B_{160} - B_{150}) + (B_{220} - B_{210}) + (B_{570} - B_{560}) + \\ + (B_{550} - B_{540}) + (B_{340} - B_{330}) + (B_{230} - B_{220}) \end{bmatrix}}{(B_{900} + B_{340} + B_{320})} \tag{8}$$

- Overall plant:

$$\varepsilon = \frac{\left(B_{300}+B_{360}+B_{400}+B_{600}+B_{730}\right)}{\left(B_{100}+B_{145}+B_{310}+B_{330}+B_{480}+B_{720}\right)} \quad (9)$$

The exergy efficiencies calculated for the main components are presented in TABLE III. The results shown in TABLE III indicate the influence of the reformer efficiency in the overall efficiency of the plant, due to reaction and heat transfer irreversibilities.

Using the same approach utilised in the exergy analysis, the energy efficiency of the plant was evaluated, giving an overall value of 81.7%. This value was calculated differently as proposed by Lutz et al (2003). It was calculated considering not only the hydrogen flow rate, but also every secondary flow like high-pressure steam and water, since these secondary products are used in another refinery production process.

4. Thermoeconomic Analysis

Thermoeconomic analysis combines exergy analysis and principles of economic analysis to provide information about the effective cost of the products of a plant or system (Bejan et. al., 1996).

TABLE II. EXERGY DESTRUCTION RATE IN EACH COMPONENT OF THE PROCESS

Component	Exergy Destruction Rate (kW)	(%)
Feed Compressor	20.55	0.06
Feed Preheater	110.10	0.30
Mixer-01	47.07	0.13
Mixer-02	1,024.07	2.77
Waste Heat Exchanger	2,885.86	7.82
Shift Reactor	197.68	0.54
Boiler Feed Water Heater	759.27	2.06
First PSA Feed Cooler	4,890.60	13.25
Second PSA Feed Cooler	410.08	1.11
PSA System	867.01	2.35
Valve-01	45.17	0.12
Valve-02	35.20	0.10
Valve-03	27.11	0.07
Valve-04	35.27	0.10
Steam Drum	3.62	0.01
Reformer	25,559.05	69.23
Overall	**36,917.70**	**100.00**

TABLE III. EXERGY EFFICIENCY OF THE MAIN COMPONENTS

Component	Exergy Efficiency (%)
Feed Compressor	84.95
Feed Preheater	51.85
Waste Heat Exchanger	63.05
Boiler Feed Water Heater	73.48
Reformer	46.40
Overall Plant	**66.60**

To initiate the analysis, beyond the data of the exergy flow rate at each point of the plant, it is also necessary to make an analysis of the economic data of the system and its equipment.

Data concerning equipment costs, engineering costs, construction and erection costs have been obtained through some commercial proposals and interviews with the professionals involved in the construction of the real hydrogen production plant (Cruz, 2004) and are presented in TABLE IV.

To continue the economic analysis it was necessary to distribute the equipment costs throughout time and, for this reason, several economic variables have been defined as follows:

- Annual operational and maintenance fixed cost factor (f_{omf}): 6% of the total investment;
- Annual operational and maintenance variable cost factor (f_{omv}): 2% of the total investment;
- Load factor (f_l): 100%
- Annual operation time: 8,400 hour/year
- Annual interest rate (i): 15%
- Capital recovery period (n): 20 years
- Capital recovery factor (f_a): 16%
- Natural gas cost: c_{100}= 2.20 US$/GJ
- Compressed water @85bar: c_{480}=1.10 US$/t

The levelized annual cost (C_{aeq}) for each component of the plant (TABLE V) were determined using Equation 10:

$$C_{aeq} = I_{eq}\left(f_a + f_{omf} + f_l\, f_{omv}\right) \quad (10)$$

The combination of the costs balances of the main components of the synthesis plant gives Equation 11

$$c_{100}B_{100}+c_{145}B_{145}+c_{310}B_{310}+c_{330}B_{330}+c_{480}B_{480} + c_{720}B_{720}+\sum C_{eq}= c_{300}B_{300}+c_{360}B_{360}+c_{400}B_{400} + c_{600}B_{600}+c_{730}B_{730}+c_{920}B_{920} \quad (11)$$

In order to determine the production costs for every one of the outlet flows the following assumptions were taken:

TABLE IV. DIRECT AND INDIRECT COSTS BY EQUIPMENT AND ANNUAL LEVELIZED COSTS

Component	I_{eq} (US\$) (2003)	C_{aeq} (US\$/year)
Feed Compressor	11,200,000.00	2,688,000.00
Feed Preheater	142,000.00	34,080.00
Mixer-01	5,000.00	1,200.00
Desulphurizer	3,570,000.00	856,800.00
Mixer-02	5,000.00	1,200.00
Waste Heat Exchanger	715,000.00	171,600.00
Shift Reactor	1,785,000.00	428,400.00
Boiler Feed Water Heater	2,143,000.00	514,320.00
First PSA Feed Cooler	1,650,000.00	396,000.00
Second PSA Feed Cooler	640,000.00	153,600.00
Condensate Stripping Column	22,800.00	5,472.00
PSA System	6,411,000.00	1,538,640.00
Valve-01	13,000.00	3,120.00
Valve-02	13,000.00	3,120.00
Valve-03	13,000.00	3,120.00
Valve-04	13,000.00	3,120.00
Demixer	5,000.00	1,200.00
Steam Drum	85,000.00	20,400.00
Reformer	32,140,000.00	7,713,600.00
Total	**60,570,800.00**	**14,536,992.00**

a) As the flue gases are discharged into the atmosphere they do not have any value:

$$c_{920} = 0 \text{ US\$/kJ} \qquad (12)$$

b) As the combustion air is taken from the atmosphere, its cost is zero:

$$c_{330} = 0 \text{ US\$/kJ} \qquad (13)$$

c) Hydrogen that is added to process (node 145) comes from an external reservoir that is not connected to the steam reforming plant. Its cost was evaluated taking into account a correction factor that considers transportation, storage and compression costs:

$$c_{145} = 1.5c_{300} \qquad (14)$$

Although this estimation can be criticized, its influence on the products' cost determination is small because the flow rate in node 145 is about 1% of the produced hydrogen flowrate.

d) Compressed liquid water cost in section 720 is considered equal to compressed liquid water @ 85 bar:

$$c_{480} = c_{720} = 1.10 \text{ US\$/t} \qquad (15)$$

As the flows in sections 300, 360, 400, 600 and 730 are utilized in other refinery processes, the equality cost partition criterion (Kotas, 1995) is taken as an auxiliary relation to determine the production costs of these five mass flows:

$$c_{300} = c_{360} = c_{400} = c_{600} = c_{730} = c_{prod} \qquad (16)$$

With the aforementioned assumptions it is possible to determine the value of c_{prod}.

TABLE V shows the calculated costs of the products of the studied plant on an exergy basis (c_{bb}), mass basis (c_{mb}) and time basis (c_{tb}).

If the flue gases were used to preheat any refinery flow, the hydrogen production cost would be improved. In the conventional process, they are sent to the atmosphere at 359 °C with a significant amount of exergy. For example, if an additional heater was considered in the system with a similar cost to the first PSA cooler that uses the combustion gas flow with an exergy efficiency of 70% and 10% pressure loss between inlet and outlet, the new exergetic cost of hydrogen would be 9.67 US\$/GJ, or 2,443.39 US\$/h. This simplified calculus shows that it is possible to obtain a reduction of 0.82% in the hydrogen production cost, or an economy of 169,800.00 US\$/year. In this evaluation, it was considered that the gases leave the heater at 120°C.

Other improved hydrogen production processes as proposed by Aitani (1996) could reduce the production costs even more.

5. Concluding Remarks

An exergy analysis and the production cost evaluation of the products of a petroleum refinery hydrogen production unit were used to determine the overall exergy efficiency of the plant as well as the hydrogen production cost. The hydrogen production cost was determined using the equality partition method because, in the analyzed process, hydrogen is produced to purify diesel oil, and the secondary products of the reforming process are used in other areas and processes in the petroleum refinery.

TABLE V. COSTS OF THE PRODUCTS OF THE PLANT

Product	c_{bb} (US$/GJ)	c_{mb} (US$/t)	c_{tb} (US$/h)
Hydrogen	9.75	1,185.86	2,463.61
Superheated Steam (3,1 MPa)	9.75	12.39	223.19
Saturated Water (1,3 MPa)	9.75	1.95	1.67
Liquid Water from Condensate Stripping Column	9.75	0.52	7.27
Compressed Water from Second PSA Feed Cooler	9.75	0.52	27.53

Taking this analysis of the hydrogen production process in a larger context, the values of both the exergy efficiency for the overall plant (66.60%) and the hydrogen production cost (1.18 US$/kg), although obtained in a refinery plant, show clearly the thermodynamics performance limitations for reforming natural gas to produce hydrogen for fuel cells based systems.

Finally, it is important to observe that the values presented in TABLE V were obtained using several simplifications and approximations. Therefore these data are the result of a first approach to the problem and these values need to be further refined to obtain more accurate values. However, the applied methodology proved to be very useful in the determination of the hydrogen production cost. This approach can also be applied to other hydrogen production processes based on different primary energy sources (electrolysis, coal gasification and oil/nafta reforming) in order to perform a comparative production cost analysis.

Nomenclature

B_i:	Exergy rate / flow rate of a substance / product (kW)
c_i:	Exergy specific cost of a substance or product (US$/GJ)
C_i:	Cost rate of a substance, product or equipment (US$/year, US$/s)
f_a:	Capital recovery factor
f_l:	Load factor
f_{omf}:	Operational and maintenance fixed cost factor
f_{omv}:	Operational and maintenance variable cost factor
I:	Cost (US$)
PSA:	Pressure swing adsorption
p_0:	Environment pressure (kPa)
T_0:	Environment temperature (°C)
W:	Power (kW)

Greek letters

ε	Exergy efficiency
$\alpha, \beta, \gamma, \delta, \sigma$:	Stoichiometric coefficients

Subscripts

aeq	annual equipment cost
bb	exergy based
eq	equipment
m	number of carbon atoms
mb	mass based
n	number of hydrogen molecules
prod	product
bt	time based

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