THERMOECONOMIC EVALUATION OF A PETROLEUM REFINERY HYDROGEN PRODUCTION UNIT

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Abstract. Pure hydrogen is an useful gas in chemical and petrochemical industries because it reacts easily with several other elements. In spite of its abundance, hydrogen is normally found associated with other chemichal components like water or hidrocarbons like methane or butane. Same especific process are required to obtain pure hydrogen, and the most usual process is the natural gas reforming, where natural gas reacts with superheated steam producing H_2, CO, CO_2 and H_2O. This paper presents the thermoeconomic analisys of a complete Hydrogen Production Unit of a petroleum refinery, including capital and operational costs, in order to determine de production cost of hydrogen and other products of the plant.

Keywords: thermoeconomic analysis, exergy analysis, hydrogen production

1. Introduction

Despite of its abundance in the nature, hydrogen is rarely found in its molecular form (H_2). Hydrogen is normally found combined with other elements, as the oxygen in the water, the carbon in the 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.

The hydrogen production unit analysed in this paper has to supply 500.000 Nm^3 of hydrogen per day to purify diesel oil. The hydrogen production cost is determined by means of a thermoeconomic analysis in which the equality cost partition method is employed.

2. Methane reforming process

Hydrogen can be obtained using the Methane reforming process. In this process, steam (H_2O) reacts with natural gas (essentially composed of methane - CH_4) and forming a mixture of hydrogen (H_2), carbon monoxides (CO), carbon dioxide (CO_2) and steam (H_2O), according to Eq.(1):

$$\alpha_1 \, CH_4 + \beta_1 \, H_2O \;\; \rightarrow \;\; \gamma_1 \, H_2 + \delta_1 \, CO + \varepsilon_1 \, CO_2 + \sigma_1 \, H_2Q \tag{1}$$
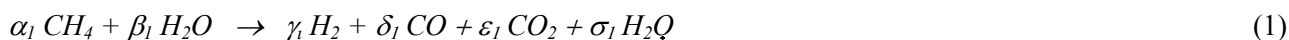
The stoichiometric coefficients of Eq. 1 depend on the chemical equilibrium and mass flow rate of the feed. Before entering in the Reformer (Fig. 1) the feed (node 100 of Fig. 2) is compressed in the Feed Compressor (node 110 of Fig. 2).

From the Feed Compressor the natural gas is heated in the Feed Preheater (from node 110 to node 141 of Fig. 2), mixed with recycled hydrogen (node 145 of Fig. 2) and sent to the Reformer Feed Preheat Coil (node 150 of Fig. 2). The gas leaving the Feed Preheater Coil (node 160 of Fig. 2) goes to the Desulphurizer.

The outlet flow from the Desulphurizer (node 170 of Fig. 2) is mixed with process steam (node 390 of Fig. 2) and sent to the Reformer Mix Feed Preheater Coil, located in the reformer convection section. Then it goes to the catalyst tubes (node 220 of Fig. 2) located in the Reformer at 2.88 MPa and 485°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 and is preheated in the Combustion Air Preheater located in the convection section of the Reformer. The fuel used by these burners came from a second stream from the feed (node 320 of Fig. 2).
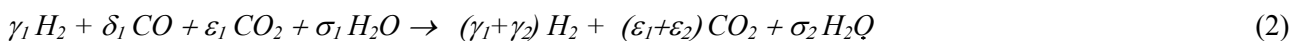
Figure 1. Reformer.

In the convection section the flue gas, besides 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 of Fig. 2) 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 to the Shift Reactor (node 240 of Fig. 2). In the Shift Reactor the CO reacts with steam to form hydrogen and CO_2, as showed in the equation below:

$$\gamma_1 H_2 + \delta_1 CO + \varepsilon_1 CO_2 + \sigma_1 H_2O \rightarrow (\gamma_1 + \gamma_2) H_2 + (\varepsilon_1 + \varepsilon_2) CO_2 + \sigma_2 H_2 Q \qquad (2)$$

Where σ_2 is the steam excess from the Eq. (1), γ_2 and ε_2 are the number of mols of molecular hydrogen and carbon dioxide formed in Shift Reactor.

This reaction reduces CO and simultaneously increases the global process efficiency. 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 of Fig. 2) is preheated in the Boiler Feed Water Heater (node 490 of Fig. 2), recovering heat from the Shift Reactor effluent, and goes to the Steam Drum.

From Steam Drum the water is distributed by natural circulation to the Steam Generator Coils (node 540 of Fig. 2) and also to the Waste Heat Exchanger (node 510 of Fig. 2).

The generated steam is collected in the Steam Drum and follows to the Steam Superheater Coil (node 560 of Fig. 2). The superheated steam is divided in three streams: the first stream is the process steam and it is mixed with the feed (node 210 of Fig. 2), the second stream is used to exchange heat with the feed at Feed Preheater (node 350 of Fig. 2) and the third stream is the exported steam (node 600 of Fig. 2). The exported steam goes to refinery medium pressure steam header.

The Shift Reactor effluent is cooled in the following exchangers: Boiler Feed Water Heater (node 260 of Fig. 2), First PSA Feed Cooler (node 270 of Fig. 2) and Second PSA Feed Cooler (node 280 of Fig. 2).

The gas leaving the and Second PSA Feed Cooler is sent to the Condensate Stripping Column, where the process condensate is removed (node 400 of Fig. 2), and then follows to the PSA System (node 290 of Fig. 2).

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 of Fig. 2) and the hydrogen product (Fig. 2 node 300).

Design, installation, maintance and operation of these equipments and each chemical element that composes the process are directly related with the hydrogen cost production and they are also hard to evaluate and can be the difference between profits and losses when it is designed and built a new plant.

3. Exergetic analysis of the system

The design of a hydrogen production plant is extremely complex. A great number of equipment, valves, pipes and connections are necessary to built the plant and guarantee its production. This great number of information and variable becomes impracticable the analysis of the process in each equipment. Therefore, it is necessary to develop a plant synthesis to describe the main function of the real process. With the information of the process in hands, it is possible to develop a plant that characterizes the studied system in a simpler way. The plant synthesis is presented in the Figure 2.

Finally, based on the synthesis plant and with the thermodynamic and transport properties of the fluids in each section, it is possible to initiate the calculations of mass flow rate, energy and exergy of each equipment and stream, as well as its respective exergetic efficiency. At this phase, it is assumed that there is not heat loss to the environment in any equipment analysed.

Table 1. Exergy destroyed in each equipment of the process.

| Equipment	Exergy Destroyed (kW)	(%)
Feed Compressor	20.55	0.06
Feed Preheater	110.10	0.30
Mixer-01	47.07	0.13
Desulphurizer	0.00	0.00
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
Condensate Stripping Column	0.00	0.00
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
Desmixer	0.00	0.00
Steam Drum	3.62	0.01
Reformer	25,559.05	69.23
Total	**36,917.70**	**100.00**
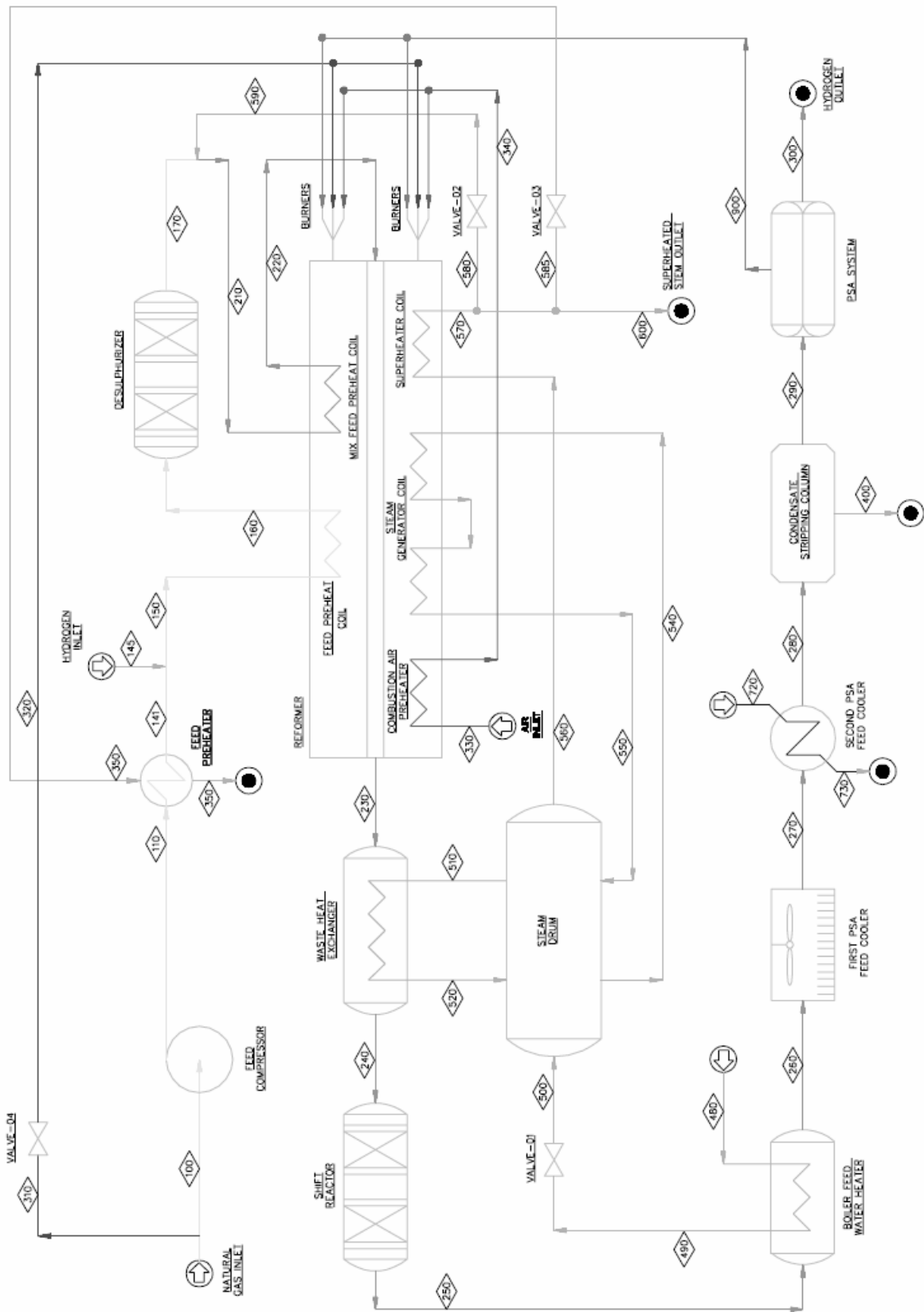
Figure 2. Synthesis Plant.

The values of 101.3 kPa and 25°C were used as the reference environment pressure and temperature.This hypothesis is reasonable since it represents the real average values of pressure and temperature of the environment in which it will be installed the unit of the studied hydrogen production plant. Based on these definitions and the information of the processes it was calculated the exergy flow rate (rate) in each point of the system and consequently it was possible to evaluate the exergy destroyed in each component. These values are shown in Tab. 1.

The exergy flows of the products of the plant are directly related with their costs (Kotas, 1985). Therefore the information about the exergy flow rates is necessary to develop the economic analysis. The calculated exergy flow rate for each fuel and products, determined using the software EES (2004), are presented in Tab. 2.

Table 2. Exergy flow rates for each fuel and product.

Flag	Product	Physical Exergy (MW)	Chemical Exergy (MW)	Total (MW)
100	Natural Gas (i)	0.91	103.63	104.54
145	Hydrogen (i)	0.03	0.96	1.00
310	Natural Gas (i)	0.07	8.42	8.50
330	Dry Air (i)	0.00	0.09	0.09
480	Compressed Water (8.4 Mpa) (i)	1.08	0.61	1.68
720	Compressed Water to Second PSA Feed Cooler (i)	0.01	0.74	0.75
300	Hydrogen (o)	2.17	68.05	70.22
360	Saturated Water (1.3 Mpa) (o)	0.04	0.01	0.05
400	Liquid Water from Stripping Column (o)	0.01	0.19	0.21
600	Superheated Steam (3.1 Mpa) (o)	6.11	0.25	6.36
730	Compressed Water to Second PSA Feed Cooler (o)	0.01	0.74	0.75
920	Combustion Products (o)	3.66	1.31	4.97

The exergetic efficiency for each component and for the overall plant was calculated using the follow equations (B is the exergy flow rate/rate and $\dot{W}$ is power):

Feed Compressor:
$$\varepsilon = \frac{B_{110} - B_{100}}{\dot{W}} \tag{3}$$

Feed Preheater:
$$\varepsilon = \frac{B_{141} - B_{110}}{B_{350} - B_{360}} \tag{4}$$

Mixer-01:
$$\varepsilon = \frac{B_{150}}{B_{141} + B_{145}} \tag{5}$$

Desulphurizer:
$$\varepsilon = \frac{B_{170}}{B_{160}} \tag{6}$$

Mixer-02:
$$\varepsilon = \frac{B_{210}}{B_{170} + B_{510}} \tag{7}$$

Waste Heat Exchanger:
$$\varepsilon = \frac{B_{520} - B_{510}}{B_{230} - B_{240}} \tag{8}$$

Shift Reactor:
$$\varepsilon = \frac{B_{240}}{B_{250}} \tag{9}$$

Boiler Feed Water Heater:
$$\varepsilon = \frac{B_{480} - B_{490}}{B_{260} - B_{250}} \tag{10}$$

First PSA Feed Cooler:
$$\varepsilon = \frac{B_{270}}{B_{260}} \tag{11}$$

Second PSA Feed Cooler:
$$\varepsilon = \frac{B_{720} - B_{730}}{B_{280} - B_{270}} \tag{12}$$

Condensate Stripping Column:
$$\varepsilon = \frac{B_{290} + B_{400}}{B_{280}} \tag{13}$$

PSA System:
$$\varepsilon = \frac{B_{900} + B_{300}}{B_{290}} \tag{14}$$

Valve-01:
$$\varepsilon = \frac{B_{500}}{B_{490}} \tag{15}$$

Valve-02:
$$\varepsilon = \frac{B_{590}}{B_{580}} \tag{16}$$

Valve-03:
$$\varepsilon = \frac{B_{350}}{B_{585}} \tag{17}$$

Valve-04:
$$\varepsilon = \frac{B_{320}}{B_{310}} \tag{18}$$

Demixer:
$$\varepsilon = \frac{\left(B_{580} + B_{585} + B_{600}\right)}{B_{570}} \tag{19}$$

Steam Drum:
$$\varepsilon = \frac{\left(B_{560} - B_{500}\right)}{\left(B_{520} - B_{510}\right) + \left(B_{550} - B_{540}\right)} \tag{20}$$

Reformer:
$$\varepsilon = \frac{\left[\begin{array}{c}\left(B_{160} - B_{150}\right) + \left(B_{220} - B_{210}\right) + \left(B_{570} - B_{560}\right) + \\ + \left(B_{550} - B_{540}\right) + \left(B_{340} - B_{330}\right) + \left(B_{230} - B_{220}\right)\end{array}\right]}{\left(B_{900} + B_{340} + B_{320} - B_{920}\right)} \tag{21}$$

Overall plant:
$$\varepsilon = \frac{\left(B_{300} + B_{360} + B_{400} + B_{600} + B_{730} + B_{920}\right)}{\left(B_{100} + B_{145} + B_{310} + B_{330} + B_{480} + B_{720}\right)} \tag{22}$$

The exergetic efficiency calculated for each component of the plant is presented in Tab. 3.

Table 3. Exergetic efficiency of each component of the plant.

Equipment	Exergetic Efficiency (%)
Feed Compressor	84.95
Feed Preheater	51.85
Mixer-01	99.96
Desulphurizer	100.00
Mixer-02	99.11
Waste Heat Exchanger	63.05
Shift Reactor	99.84
Boiler Feed Water Heater	73.48
First PSA Feed Cooler	98.30
Second PSA Feed Cooler	8.47
Condensate Stripping Column	100.00
PSA System	99.27
Valve-01	98.81
Valve-02	99.60
Valve-03	91.06
Valve-04	99.58
Demixer	100.00
Steam Drum	99.96
Reformer	50.84
Overall Plant	**70.86**

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). To initiate the analysis, beyond the data of the exergy flow rate in each point of the plant, it is also necessary to make an analysis of the economic data of the system and its equipment. The data concerning equipment costs, engineering costs, construction and erection costs had been obtained through some commercial proposals and interviews with the professionals involved in the construction of the real hydrogen production plant (Eduardo da Cruz, 2004) and are presented in Tab. 4.

Table 4. Direct and indirect costs by equipment (I_{eq}).

Equipment	I_{eq} (US$)(2003)
Feed Compressor	11,200,000.00
Feed Preheater	142,000.00
Mixer-01	5,000.00
Desulphurizer	3,570,000.00
Mixer-02	5,000.00
Waste Heat Exchanger	715,000.00
Shift Reactor	1,785,000.00
Boiler Feed Water Heater	2,143,000.00
First PSA Feed Cooler	1,650,000.00
Second PSA Feed Cooler	640,000.00
Condensate Stripping Column	22,800.00
PSA System	6,411,000.00
Valve-01	13,000.00
Valve-02	13,000.00
Valve-03	13,000.00
Valve-04	13,000.00
Demixer	5,000.00
Steam Drum	85,000.00
Reformer	32,140,000.00
Total	**60,570,800.00**

To continue the economic analysis, in order to write the costs balances, it is also necessary to define some economic variables as follow:

- Operation and maintenance fixed costs (f_{omf}): 6% of the total investment;
- Operation and maintenance variable costs (f_{omv}): 2% of the total investment;
- Annual operation time (T_o): 8,400 hour/year
- Annual interest rate (i): 15%
- Amortization time (n): 20 years

Based on these information it was calculated the amortization factor (f_a) using the Eq. (23):

$$f_a = \frac{i}{1 - (1+i)^{-n}}$$
(23)

And the levelized annual cost (C_{aeq}) and the cost rate (C_{eq}) for each equipment (Tab. 5) using Eq. (24) and Eq. (25):

$$C_{aeq} = I_{eq} \left(f_a + f_{omf} + f_c \, f_{omv} \right)$$
(24)

$$C_{eq} = \frac{C_{aeq}}{T_o \, 3600}$$
(25)

Eq. (26) defines the general cost balance (c_i are the inlet costs and c_o the outlet costs per exergy unit) for a given equipment or system with "n" inlet/outlet streams (Moran *at al.,* 2004):

$$\sum \left(c_i \, B_i \right)_n + C_{eq} = \sum \left(c_o \, B_o \right)_n$$
(26)

Table 5. Annual levelized costs and costs by second for each component of the plant.

Equipment	C_{aeq} (US$/year)	C_{eq} (US$/s)
Feed Compressor	2,688,000.00	320.00
Feed Preheater	34,080.00	4.06
Mixer-01	1,200.00	0.14
Desulphurizer	856,800.00	102.00
Mixer-02	1,200.00	0.14
Waste Heat Exchanger	171,600.00	20.43
Shift Reactor	428,400.00	51.00
Boiler Feed Water Heater	514,320.00	61.23
First PSA Feed Cooler	396,000.00	47.14
Second PSA Feed Cooler	153,600.00	18.29
Condensate Stripping Column	5,472.00	0.65
PSA System	1,538,640.00	183.17
Valve-01	3,120.00	0.37
Valve-02	3,120.00	0.37
Valve-03	3,120.00	0.37
Valve-04	3,120.00	0.37
Demixer	1,200.00	0.14
Steam Drum	20,400.00	2.43
Reformer	7,713,600.00	918.29
Total	**14,536,992.00**	**1,730.59**

The cost per second (US$/s) can be obtained using Eq. (27), where "*x*" can be any product of the system:

$$C_x = \frac{c_x}{B_x} \qquad\qquad (27)$$

For the studied systems, it was used the equality product cost partition criteria (Kotas, 1985), where every product of the plant has the same specific exergy cost.

To avoid distortions on the results, the economic value of the combustion products of the reformer was defined as zero. This assumption is justified by the fact that the combustion products are rejected directly to the atmosphere.

Table 6 brings the calculated costs of the products of the studied plant in exergy basis (c), mass basis (C_m) and time basis (C).

Table 6. Costs of the products of the plant.

Product	c (US$/GJ)	C_m (US$/t)	C (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
Combustion Products	0.00	0.00	0.00

5. Concluding Remarks

It must be pointed out that the cost of production of hydrogen is obtained through the equality partition method, where all the products have the same unitary exergetic cost. The application of this criterion can be questioned, since the main objective is to produce pure hydrogen and the other product flows have less commercial interest on this process. However, in the analyzed process, hydrogen is produced to purify diesel oil and the use of these secondary products by other areas and processes in the refinery can characterize these products as essential for those processes, reducing the uncertainty related to the application of this criterion.

Finally, it is important to observe that the values presented in Tab. 6 carry on themselves a several number of simplifications, considerations and hypothesis. It means that these data are the result of a first approach to the problem and they need to be more elaborated to obtain more accurate values. However, the methodology applied to obtain the costs of the products is useful in several problems of economic engineering.

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