Hydrogen production plants: emissions and thermal efficiency analysis

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Abstract

The rapid development of fuel cell technologies and their applications in fuel cells vehicles (FCVs) may soon require the establishment of new hydrogen production plants since hydrogen has been considered as the future fuel for transportation by many experts. Air quality and climate change have been the principal motivation for developing these new technologies, so the emissions and energy requirement at the fuel production plant become crucial in a life cycle analysis type for the FCVs.

A centralized plant based upon the natural gas (NG) steam reformation process has been suggested as the cheapest way to produce hydrogen. This paper presents the results of two months of data collection on an existing hydrogen plant with 35 mtpd (metric tons per day) capacity. The data collection was accomplished over the winter and summer seasons and involved consumption of NG, production of hydrogen and steam, levels of several pollutant emissions, etc. The paper also presents the results of discussions with an international expert advisory group about the process efficiency, equipment breakdown and emission rates of different plant size capacities, different emission control devices and steam production options for the year 2010. The discussion involved the existing plant and literature data and was done over multiple rounds. The anonymity of the comments was preserved. Uncertainty of future technology attributes and system designs, and also the unreliability of some data, were dealt by using probabilistic function calculations through Monte Carlo simulation technique. This effort is part of the Fuel Upstream Energy and Emissions Model (FUEEM) being developed as a complement to the larger fuel cell vehicle model project underway at UCDavis.

1 Introduction

To handle uncertainty in future technology attributes and system designs, as well as unreliability of some data, the model FUEEM (Fuel Upstream Energy and Emissions Model) uses probabilistic functions and relies on an international expert advisory panel to establish the major inputs. The FUEEM expert network is composed of 25 to 30 experts from more than one dozen organizations and they have been discussing the topics presented in this paper in the last couple of years. The information and results presented are the result of this effort and focus on the year 2010 as the time frame. The statistical attributes of the Monte Carlo technique such as Latin hypercube sampling and rank order correlations among variables are handled on the component model using @Risk $^{®}$ software.

Hydrogen has been extensively produced worldwide to serve basically two kinds of industry. The chemical industry consumes 53 % to 55 % of the total 31 to 32 billion of standard cubic feet of hydrogen produced per day (scf/d) and the majority of this hydrogen is used to produce ammonia for soil fertilization (Shanley and Ondrey, [1]). The refinery processing industry consumes 9.8 to 10 scf/d of this marketable hydrogen. Similar amount is internally produced in catalytic reformers and consumed by the refinery too but it is not accounted in the presented total figure. All the hydrogen in the refinery is utilized by the residuum hydrocracking process; residuum, heavy oil and distillate hydrotreating process; and naphtha hydrodesulfurization process (Radler, [2]). The FUEEM expert network expectation is that environmental concerns and pressure for low-sulfur fuels will increase the demand for hydrogen and new plants will be built over time. Eventual over demand due to the use of hydrogen fuel for fuel cell vehicles in the year 2010 is therefore assumed to be supplied by new plants also.

Hydrogen can be produced by different processes and feedstocks. Existing processes can be chemical such as steam reforming, partial oxidation, the composition of both called autothermal reforming and gasification, or electrochemical such as water electrolysis. Their main reactions are presented below:

- General steam reforming: $C_nH_m + n\,H_2O \leftrightarrows n\,CO + (n + m/2)\,H_2$ (1)
- Partial oxidation: $C_nH_m + n/2\,O_2 \leftrightarrows n\,CO + m/2\,H_2$ (2)
- Autothermal reforming: $C_nH_m + p\,O_2 + (n-2p)\,H_2O \leftrightarrows n\,CO + (n-2p+m/2)\,H_2$ (3)
- Gasification: $C + H_2O \leftrightarrows CO + H_2$ (4)
- Water electrolysis: $H_2O + e^- \leftrightarrows H_2 + \frac{1}{2}\,O_2$ (5)

According to the comments provided by the FUEEM expert network (FEN) steam reforming works very well for gaseous and light liquid hydrocarbons such as natural gas and naphtha. Compared with other hydrogen production processes it has a modest cost (around 1.90 to 2.70 \$/Mscf). Gasification is the preferred process for heavier liquid hydrocarbon feedstocks as well as for solid feedstock such as coal and biomass. Partial Oxidation (POX) has been considered for Fischer Tropsch fuel production due to its high syngas production rates for moderated plant size. Gasification, as well as POX can be utilized for gaseous, liquid and solid feedstock however their higher cost limit their application (3.00 to 4.30 \$/Mscf). Finally, water electrolysis produces oxygen (O_2) and hydrogen (H_2) by splitting the water molecule with electricity. Electricity can be produced from many different ways and the regional cost of the electricity associated with a moderate cost of the electrolyzer may limit the process use only for some market niches (12.00 to 20.00 \$/Mscf).

Basically the major cost for chemical hydrogen is a composition of the feedstock cost with the capital cost for the syngas production. Syngas is the primary gas produced by hydrocarbons that is mainly composed by percentages of H_2 and CO. In general, the syngas characteristic is expressed in terms of its H_2/CO ratio and the ratio requirement varies from one product to another (hydrogen, methanol, ammonia, etc.). In the hydrogen case the highest ratio is better. To increase the ratio a shift reaction is performed after the steam reformation reaction. Currently, steam methane reforming (SMR) is the most utilized process for hydrogen production. The price, abundance, availability, low-sulfur content of natural gas (methane) associated with its relatively and easily low cost processes and highest final H_2/CO ratio, drive this option. Based on all these characteristics the experts opinion (FEN) is that SMR will be the technology of choice in the following 20 years or so. The overall SMR reactions are presented below:

$CH_4 + H_2O \leftrightarrows CO + 3\,H_2$	reforming	(6)
$CO + H_2O \leftrightarrows CO_2 + H_2$	shift	(7)
$CH_4 + 2\,H_2O \leftrightarrows CO_2 + 4\,H_2$	overall	(8)

2 The plant design

A detailed understand of the overall process was required due to the level of discussion and data collection for the model. As stated before most of these information come directly from the expert panel, however to initiate and complement the discussion topics data from Patel et al. [3], Ogden et al. [4], Wang [5] and Spath and Mann [6] were used. A summary of the discussion result is presented here and the Figure 1 shows a simplified scheme of a typical plant configuration.

In general, natural gas (NG) is acquired by hydrogen plants at about 1 to 2.1 MPa (150 to 300 psi). Part of this NG is burned as fuel in the reformer furnace. The percentage of the NG utilized as fuel can vary from 3 % to 20 % depending on the plant design and operation parameters (see discussion below). The majority of the NG that is used as feed in the reformation process is then pressurized at about 3.1 to 4.1 MPa (450 to 600 psi) using single-stage reciprocating compressors powered by electric motors. Lower pressures favor the synthesis reactions increasing the efficiency of the plant. Also, higher pressures require ticker reformer catalyst tubes increasing the capital cost of the plant and provoking higher leakages. However, local situation such as the pressure of the feedstock gas and the desired product characteristics may change these economics. The typical reforming pressure is around 2.41 to 2.76 MPa (350 to 400 psi).

Basically, the steam methane reforming (SMR) technology accommodates the endothermic reforming reaction inside of high-alloy tubes filled primarily with nickel catalyst. Conventional catalysts are refractory like alumina containing 10 to 20 % of nickel. The tubes are fired heated inside of larger furnaces providing the necessary reaction energy. Since nickel is highly vulnerable to sulfur poisoning a desulphurisation process is added upstream. This process accomplish two steps, first organic sulfurs are hydrogenated to H_2S (hydrogen sulfide) by preheating the natural gas to about 360 to 380 °C (680 to 716 °F) and adding small amount of H_2 before the hydrogenation vessel. Then all the H_2S is removed in zinc oxide beds (ZnO) following the reaction below:

$$H_2S_{(g)} + ZnO_{(s)} \leftrightarrows ZnS_{(s)} + H_2O \qquad (9)$$

It is good to point out that zinc sulfide (ZnS) is a solid waste and therefore the only air SOx emitted is from the NG burned as fuel. This emission is calculated by mass balance in the FUEEM component model assuming that all H_2S is oxidized to SO_2.

$$H_2S + 3/2\ O_2 \leftrightarrows SO_2 + H_2O \tag{10}$$

Superheated steam at 265 to 280 °C (510 to 535 °F) and 2.41 to 2.65 MPa (350 to 385 psi) is added to the desulphurized feedstock on a steam-to-carbon ratio between 2.5 to 3.5. This amount of steam that is higher than the stoichiometric amount necessary (2.3 times) is used to minimize thermal cracking and coke formation. An optional pre-reformer may be installed to deal with the coke formation and also to produce an equilibrated mixture of carbon oxides, methane and hydrogen performing shift and reforming reactions simultaneously. Since the pre-reforming limits the extra-steam generation by using some of the waste heat other options for the coke formation have been developed like changing the catalyst composition at the end of the reforming tubes using "hydrotalcites" or adding potassium or uranium oxide (Bhattacharya, 1995). Before the pre-reformer the NG/steam mixture is pre-heated to 480 to 510 °C (900 to 950 °F) and after it the kind of syngas mixture (20 to 25 % of H_2, 65 to 70 % of CH_4 and traces of C_2H_6) is pre-heated again to 600 to 650 °C (1110 to 1200 °F) before it reaches the primary reformer.

After the reformer the hot syngas (870 to 950 °C or 1600 to 1740 °F) is cooled down to 340 to 360 °C (645 to 680 °F) preparing for the exothermic shift reaction. Higher reforming temperature increases conversion and accommodates better thermal recovering however the severity of the operations requires different reactor metallurgy. The cooling process is done in boilers generating steam from 1.72 to 4.8 MPa (250 to 700 psi) depending of the plant configuration. Extra steam for exportation can be an important co-product of the plant allowing for better integration in the plant design and increasing the overall thermal efficiency.

The next step of the syngas is the high temperature shift reactor (HTS) utilizing iron-based catalyst and operating around 350 °C (660 °F). The syngas is cooled down again and the final CO conversion is performed around 205 °C (400 °F) in a low temperature shift reactor (LTS) containing cooper-based catalyst. By this time 90 to 95 % of the CO has been "shifted" to CO_2 increasing the hydrogen concentration.

In modern plants the hydrogen purification has changed from CO_2 removal using chemical absorption and methanation process to pressure swing adsorption (PSA). PSA is a physical separation process based on the capacity of certain solid adsorbents to selectively remove certain components (CH_4, CO_2, CO, etc.) from multi-component gas streams. Activated carbon, carbon molecular sieves, silica gel, activated alumina and zeolites are normally used in the beds (Peramanu et al., [8]). PSA units work with coupled vessels up to 12 vessels. While one vessel is adsorbing the components from the hydrogen stream (syngas) the other one is desorbing the components and regenerating the bed by reducing the pressure to about 0.014 to 0.035 MPa (2 to 5 psi) and purging the desorbed gas with some hydrogen. This process generates a pure hydrogen stream (+ 99.8 %) at high
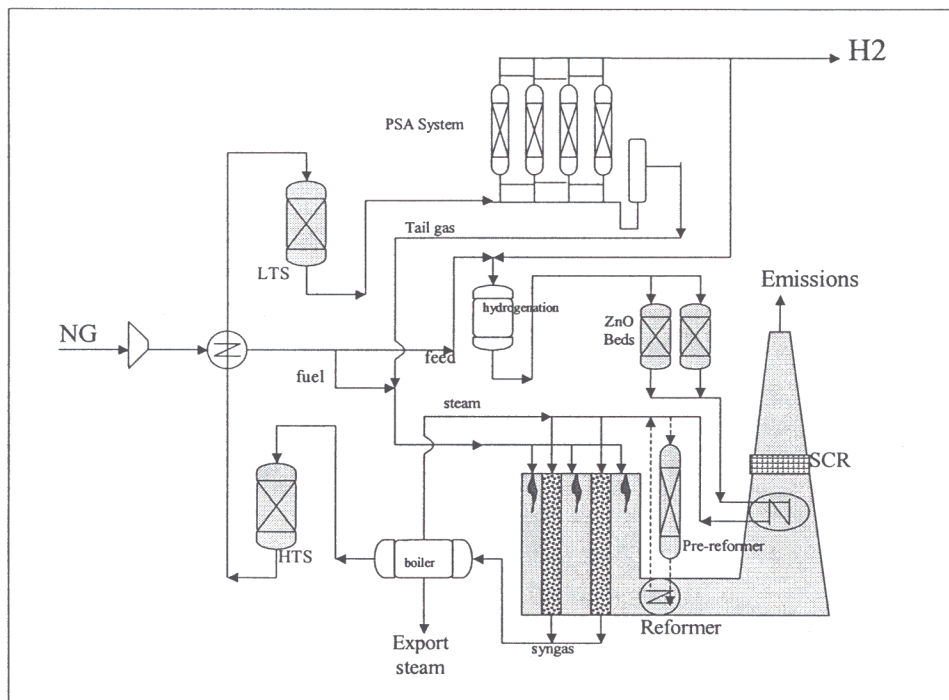

Figure 1: Simplified scheme of a typical new SMR hydrogen plant with steam exportation

pressure since the pressure drop in the system is around 0.07 MPa only. On the other hand, since hydrogen is necessary to regenerate the beds the recovery of it can vary from 65 to 90 % with small variations in the tail gas pressure making this variable the biggest operational controlling point (Peramanu et al., [8]). This high-energy content tail gas is burned in the reformer furnace providing most of the energy necessary to the reforming reactions. The composition of the tail gas varies a lot depending on the PSA operational sets. One example of this composition is presented by Spath and Mann [6]: H_2 (27 % mol), CH_4 (14 % mol), CO (3 % mol), N_2 (0.4 % mol) and some water vapor.

Finally, the burned gas (stack or flue gas) can be treated before vent at the gas waste-heat recovery session. The best available technology for air emissions control in this case is coupling a Selective Catalytic Reduction unit (SCR) with a Continuous Emission Monitoring System (CEMS) that continuously monitors the oxygen concentration, flow rate, temperatures and some emissions to adjust the process. The SCR unit contains catalytic layers including titanium dioxide, tungsten trioxide and others where the injected aqueous ammonia (NH_3) reacts with NO_x to generate inert gases. For example:

$$2/3 \; NH_3 \; + \; 1/5 \; NO_2 \; \leftrightarrows \; 7/12 \; N_2 \; + \; H_2O \tag{11}$$

Other costless options for NOx reduction are the Selective Non-Catalytic Reduction (SNCR) and low-NO_x burners. Even the tail gas recirculation (the uncontrolled situation) will generate less thermal NO_x than a natural gas furnace due to the presence of inert gases and hydrogen in the fuel composition (see Mark et al, [9] and Spath and Mann, [6]).

3 Literature survey

The expert discussion initiate over the existing data collected from the literature. Some proprietary data used as example for the mediator are not included in the paper. The following Tables 1, 2 and 3 summarize the survey result over the most comprehensive studies about gaseous hydrogen SMR production plants. Initially the idea was to understand the existing plants (and data) and later forecast the technology (and data) for the 2010 time frame. An identified source for disagreements over the future plants data was the size or production capacity of the new facilities. Some experts believe that new plants are going to be much bigger than the existing ones and others do not. According to Shahani et al [10] the majority of the existing SMR plant sizes are from 20 to 80 Mscf/d (million standard cubic feet per day) and the biggest ones are from 210 to 230 Mscf/d. The plant scale favors thermal efficiency and cost but requires a bigger hydrogen market and that, for certain regions, may not be the case considering the fuel cell vehicle's fuel demand in 2010 or so. Based on that the FEN decided to create two centralized plant size alternatives, a 27 metric tons per day (mtpd) and a 270 mtpd what is equivalent to a 30 and 300 mtpd (72 and 720 Mscf/d) operating at 90 % capacity (10 % of the time with operation zero for maintenance, etc.). The sizes were based on Moore and Raman [11] report. Also, a possible alternative for the introduction of the hydrogen fuel may be the installation of smaller units at the fuel station for decentralized hydrogen production. Studies done by Thomas et al [12], Ogden [13] and somehow used by Lipman [14] agree that this alternative can be competitive if the small units are mass-produced. The alternative takes advantage of using the existing NG infrastructure and the production volume of the units can be associated with similar reformers for small stationary fuel cells. There is still some concerns about safety and staff expertise to operate the "small chemical plant" in every fuel station but FUEEM is also considering this option with a flow rate of 2.7 mtpd.

Table 1: Existing values for centralized hydrogen plants using SMR and no extra-steam produced.

HYDROGEN PRODUCTION SMR – NO EXTRA STEAM	GREET 1.4 [a]	GREET 1.5 [16]	Acurex [b]	Ogden [c]	DTI [d]	Air Products [e]
Efficiency (%)	68	73	61.1	85/90	69	75 / 77.6
Input energy as electricity (%)	0.2	0.2	0	0	2.9	0.5 / 1.0
NG used as fuel (%)	100	17	52.8	17.6	17	10

a: Wang [15], only the combustion process is taken into account.
b: Unnasch et al [17] from Table 5-34, calculated using 100,000 Btu NG/lb H2 for feedstock, 52,830 Btu NG/lb H2 for combustion and 61,100 Btu/lb H2 (HHV). For fuel processing it gives the efficiency of 61.1 % that means 61,100 / 100,000. For the boiler (combustion) breakdown 52,830 / 100,000 = 52.8 %. In fact, these numbers do not appear on the report.
c) Ogden et al [4]. On page 11 they talk about 85 % efficiency. From the Table 6A-5 it can be calculated as 90 %. The other variables were calculated from the same table using 135 Btu-HHV per gram of H2 and 50.29 Btu-HHV per gram of NG. The number are closer to plants with extra-steam production (see Table 2) but no extra-steam appear in the table 6A-5. So far, the newest studies done at Princeton University are still using the same values.
d: From Table D-1 – Thomas et al [12].
e: Patel, Nitin [18]. Personal communication.

Table 2: Existing values for centralized hydrogen plants using SMR and producing extra steam for exportation.

Studies	Plant size (mtpd)	total effic. (%)	steam energ. (%)
Dybkjar [a]	23.81	85.86	23.78
Greet 1.5a [b]	-	83.0	14.46
Shahani-c1 [c]	120	80.9	6.66
Shahani-c2 [c]	120	85.1	24.27
Shahani-c3 [c]	120	86.8	30.44
Patel -H-N2 [d]	60	86.4	7.25
Patel - L-N2 [d]	60	85.2	7.28
NREL-2000 [e]	136.8	89.0	7.91

a: In Wang [5]
b: Wang [16] in low heating values.
c: Shahani et al [10]. c1 = basic case, c2 and C3 = case 2 and 3.
d: Patel et al. [3]. L-N2 = typical natural gas composition and H-N2 = high amount of nitrogen in the NG composition
e: Spath and Mann [6]. According to the authors 198.041 MBtu of exported steam per hour was used.

Table-3: Existing values for decentralized hydrogen plants (small units for fuel stations)

HYDROGEN PRODUCTION SMR – DECENTRALIZED	Air Products	Praxair	BOC	Praxair	BOC
Size (mtpd)	2.72	2.72	1.36	0.45	0.18
Efficiency (%)	66.6	70.5	64.3	69.3	77.6
Input energy as electricity (%)	0.7	2.4	0	3.4	0
NG used as fuel (%)	17.1	-	13.6	-	2.5

source: Thomas et al [12].

Table-4: Reformer Emission rates assumed by existing models to calculate the emissions of hydrogen production plants.

EMISSION RATE (g/MBtu-NG burned -HHV)	Acurex [a]	Mark et al [b]	Greet 1.4 [c]	Greet 1.5 [c]	NREL [d]
NO_x	45.44	31.75	23.339	35.19	58.6
CO	15.90	15.42	17.614	36.99	5.42
CH_4	1.33	-	0.128	0.99	0
NMOG	1.33	1.22	0.617	2.43	0
PM 10	-	-	1.321	3.33	1.48
SO_x	-	-	0.278	0.278	0
N_2O	-	-	0.189	0.99	0

a: From EFAC9.XLS (Unnasch et al [17]). The numbers were calculated using H2 density of 0.53 lb/100scf and energy content of 32,400 Btu/100scf (HHV). Process efficiency of 61.1 % and 52.8 % of energy share of NG combusted are used on the calculation also. The numbers in the report (grams of pollutant per lb of H2) are: NOx (2.4 g); CO (0.84 g); CH4 (0.07 g) and NMOG (0.07 g).
b: Mark et al [9] the original values are in terms of lb per MBtu of fuel burned. The values 0.07 (NO_x), 0.034 (CO) and 0.0027 (NMOG) are assumptions based on the 1993 version of the AP-42 [19] for NG combustion. The tail gas was considered to scale down the emission factors in terms of the amount of NG burned as fuel.
c: Wang ([15] and [16]). The emission factors are related to future devices and they are converted to HHV using the factor of 90%. The model considers industrial boiler emission factors in terms of NG burned as fuel.
d: Spath and Mann [6]. Apparently the plant only uses low NO_x burners as emission control device. The numbers in the report are 0.084 g of CO/Kg of H_2, 0.023 g of PM_{10}/Kg of H_2, 20 ppm of NO_x translated into 0.9072 g/Kg of H2 (Table 4), 8,892.2 g of CO_2/Kg of H_2 and zero for CH_4, N_2O, NMOG and SO_x (Table 4). The factors used in the transformation were 127 Mg of H_2/day and 82 MBtu of NG_{fuel}/hr.

The Environmental Protection Agency (EPA) is the American organization that has access to most of the equipment emission measurements and they provide a compilation of emission factors per level of equipment activity (EPA-AP42, [19]). Unfortunately, the report provides only the factor (perhaps the mean) and a letter rating the reliability, or robustness, of the factor that has no statistical meaning. Particularly, in the hydrogen

production case no emission factor is provided and what most of the studies did was to use the emission factors from natural gas boilers and somehow scale them down (mainly thermal NO_x) compensating for the inclusion of the PSA tail gas in the fuel composition. Van Der Drift [20] reports NO_x emissions from burners operating with a mixture of hydrogen and methane but the composition of the mixture has always-high content of hydrogen ($\sim$ 80 %). To complicate this lack of data the AP-42 report [19] provides burner emission factors for uncontrolled equipments only and special care must be taken to adjust the data for the inclusion of emission control devices such as low-NO_x burners or SCRs.

Agreements over the technologies assumed are very important and they are not always clearly stated in the reports for a future comparison purpose. FUEEM assumes three levels of air control technologies to be selected according to the area's air quality enforcement. A plant in a high controlled area may use SCR, CEMS and low-NO_x burners. For an intermediated controlled area the plant may only use SNCR and low-NO_x burners. Finally, an uncontrolled option is available for areas with lack of enforcement. The most controlled option was defined first and the others were scaled based on the expert experiences and in some values provided by the report EIIP [21]. The report presents the emission reduction level when a utility emission control is used. For a SCR(gas) NO_x is reduced by 80 % related to the uncontrolled equipment, CO 8 % and N_2O 60 %. The report also presents the efficiency loss as a percentage of the total efficiency due to the addition of the emission control technology. For the SCR the loss is 1 % and this idea has been incorporated into FUEEM energy requirement calculations.

4 Industry survey

The emission factors and equipment activities values such as efficiency must encompass the variations on the technologies that naturally occur in the reality even when some boundaries are delineated. Two plants very similar can operate at different PSA outlet pressure, different maintenance level, catalysts compositions, etc. Therefore, the establishment of these emission factors must be performed by organizations such as EPA that by mandatory reasons already has a great deal of data. One of the objectives of FUEEM project is also to sensitize such data-collector organizations for the importance and needs of better and more complete outputs. The FUEEM project has no enough resources to generate these factors properly even tough we decided to realize a survey in an industry to contribute for the general data collection process and to provide some inputs for the expert panel discussion. In the hydrogen case the main reasons for the industry survey were: the lack of emission data about hydrogen reformers and the rough and somehow subjective solution adopted so far; the necessity of investigating eventual correlations among variables since the FUEEM calculus is not deterministic; and the expert interest to investigate the shape of some probabilistic curves since this type of data discussion was new for most of them.

The investigated hydrogen plant has a production capacity close to the 27 mtpd alternative and extra-steam exportation. Data was collected in two different months. One month was in the winter season (December, 1999) and the other month was in the summer season (May, 2000). An existing continuous emission monitoring system (CEMS) reports the NO_x and CO emissions hourly and also information about the plant activities such as natural gas consumed, natural gas energy content (HHV), amount and energy content of the steam imported and exported, amount of hydrogen produced, etc. were collected daily.

One interesting occurrence was the variation of the NG composition between the two sets of data. In the winter time the plant used around 10 Mscf (Million standard cubic feet) per day of an available NG with high level of nitrogen and therefore lower energy content. Since the mean of the plant total efficiency (energy out/energy in) was a little bit different (83.37 % and 83.89 %) a graphical correlation study was done to generate an example of the envelop-method proposed by Vose [22]. The Figure 2 shows the study. The expert efficiency values for the 2010 plants alternatives were generated in terms of triangular distribution curves. The minimum, most probable and maximum values in the triangular curves are established in FUEEM calculus after the NG composition be sampled and the energy content of it be calculated. Lines having the same slope of the lines presented in the Figure 2 with the origins adjusted to match the expert efficiencies consensus define the input curves. The origins values assumed are presented on Table 5. The NG energy content is calculated according to the method proposed by Van der Lugt [23] considering non-ideal gas relations. The components summation factors necessary for the compressibility factor calculation in the method were assumed to be the same ones proposed by the author. A Natural Gas composition study was done to understand the variations of the gas in different regions and it will be a topic of a future paper however it is good to point out that from that study two NG gas composition curves were adopted in this component model. One called typical NG with the energy content mean of 37,738 KJ/m^3 (1013 Btu/scf) and standard deviation of 359.3 (9.64). The other one with higher content of N_2 has an energy content mean of 34,720 KJ/m^3 (931 Btu/scf) and standard deviation of 342.9 (9.20).
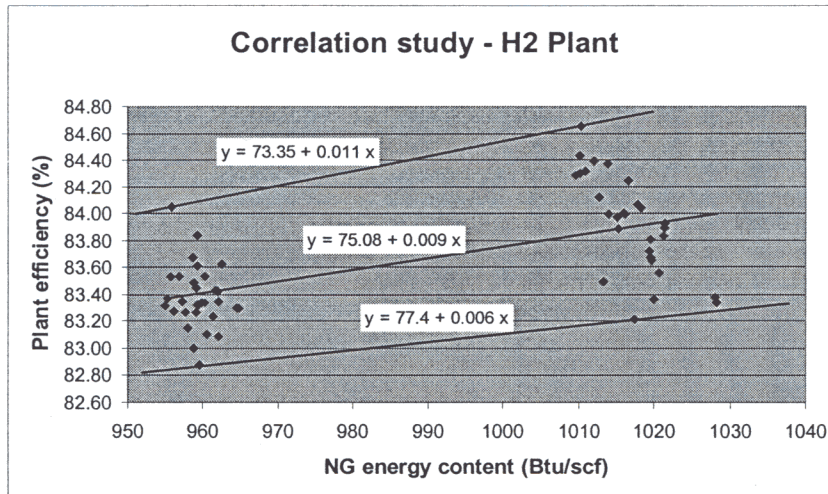
Figure 2: Correlation study between the hydrogen plant efficiency and the utilized NG energy content (HHV).

Another interesting occurrence was the modifications in the PSA operational parameters (among others parameters) to produce more or less steam. In the wintertime an average of 6 % of the total energy produced was steam while in the summer time this figure was 5.3 % in average. Based on that we decided to investigate the correlation between the extra-steam produced and the plant efficiency. After an interview with the engineers it was clear that not only the efficiency change manipulating the steam production but also, more important than that, the design of the plants are different for different steam production capacity because the manipulation of the operational parameters in a plant is, in general, limited. Spath and Mann [6] state, "The hydrogen plant efficiency changes if the excess steam can not be utilized by a nearby source. However, this does not change the amount of hydrogen produced by the plant.", but it is not correct. It assumes that first a plant is built and then the extra-steam is offered to the market but in reality if the market does not initially exist the plant design will be different. Shahani et al [10] are clear on this topic.

Trying to solve this correlation problem the Table 2 data, complemented with the industry survey results (seasons average data), were used to generate the Figure 4a. One first discussion is to accept the correlation and it is clear that much more data would be necessary for a reasonable level of confidence, however, based on the engineers position we decided to accept it. As an example we decided to use in this case the rank order correlation method developed by Iman and Conover [24] that is already developed into the software utilized. Based on that another discussion is to establish the right rank factor to use in the model since it is not an intuitive task. Several rank factors were tested and the graphics were analyzed by the experts to come up with the assumption of 0.6. The Figure 4b shows the sampling values of the first 2000 interactions.

(a)

(b)
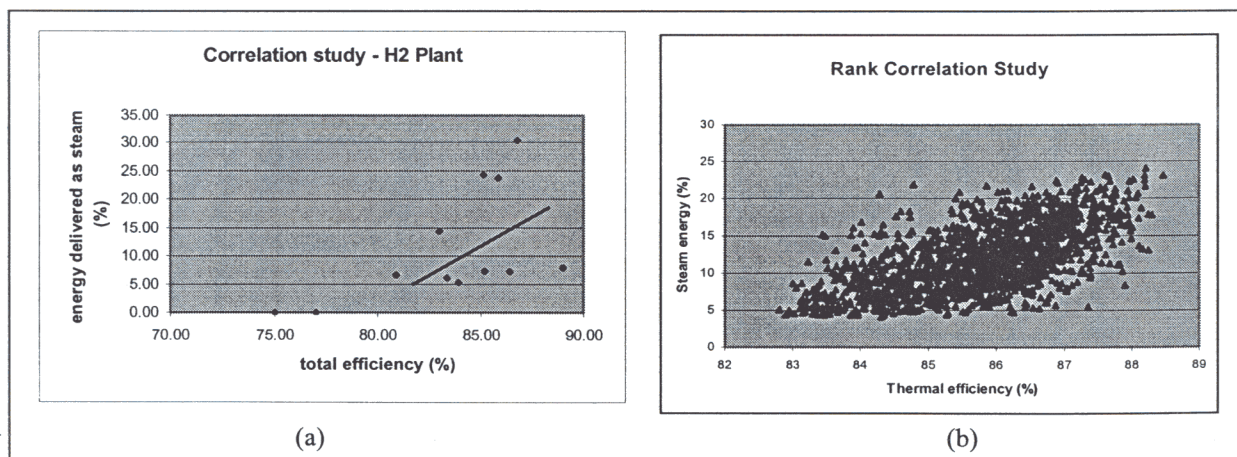
Figure 4: Rank order correlation study between the extra-steam produced by a hydrogen plant and its total thermal efficiency.

Changing the operational parameters of the PSA the tail gas composition varies and therefore the amount of NG necessary to be used as a fuel varies too. When the emission factors are based in the amount of NG burned as fuel such as in Wang [16] and Mark et al. [9] this variable become an important input. From the existing literature one can found values from 10 % to 18 % (Table 1) but in this industry survey values as low as 3 % were found and therefore to couple the emissions with the NG fuel variable was not a good solution because it would incorporate a huge uncertainty and a correlation with the efficiency through the extra-steam. The emissions were coupled with the amount of hydrogen produced and also some amount of the emissions was attributed to the extra-steam generated according to the energy content on both products. Since FUEEM is dealing mainly with fuels the co-products credits based on the energy content (HHV) were adopted as single method to use. Figure 5a shows the CO and NO_x emissions of the hydrogen plant in the survey and the data present no correlation with the plant efficiency. The Figure 5b shows one example of this.

Finally, most of the existing studies assume the fugitive emissions in the plant as natural gas or only methane sometimes. Trying to improve this assumption a little bit more some percentage of the fugitive emissions was assumed as syngas based on a study about the pipes length, valves, flanges, etc. carrying on syngas and NG. It was assumed a normal curve with a mean of 0.125 % of NG leaking per NG used (std. dv. = 0.065) and 0.291 % of syngas leaking per NG used (std. dv. = 0.15) assuming the conversion around 0.228 moles of syngas per mol of NG.

FUEEM inputs

Other major inputs are discussed in this session. The emission rates for the reformer in a high controlled area are presented in the results since they were assumed in terms of grams of pollutants per GigaJoule of hydrogen produced. For the intermediate air control enforcement area alternative NO_x is assumed to be reduced 50 % of the uncontrolled scenario, CO reduced 4 % of the uncontrolled scenario and N_2O reduced 30 %. For the small-decentralized plant there is some uncertainties related to the constant steady state operation of the plant. A CARB report (Unnasch and Drunert [25]) analyzes some vehicle reformer emissions and the majority of the emissions occur in the start up regime. Based on that and on the fact that there are some uncertainties about the kind of air control technology that should be used in the small-decentralized plants the intermediate scenario was assumed. $PM_{2.5}$ is still in a very low stage of understanding and data measurements. The great difficulty is to identify a way to forecasting these emissions since the majority of them comes from secondary formation involving complex atmospheric reactions. A roughly assumption was done based on EIIP [26]. FUEEM considers $PM_{2.5}$ as a composition of 20 % of the PM_{10} plus 25 % of the SO_x plus 25 % of the NO_x plus 20 % of the NMOG. This is assumed just to have an option of including this pollutant in the model but this should be revised as soon as better data is available.

The Table 5 presents the adjustments for the plant efficiencies explained above. The Table 6 presents the inputs related with the extra-steam produced and electricity share adopted.
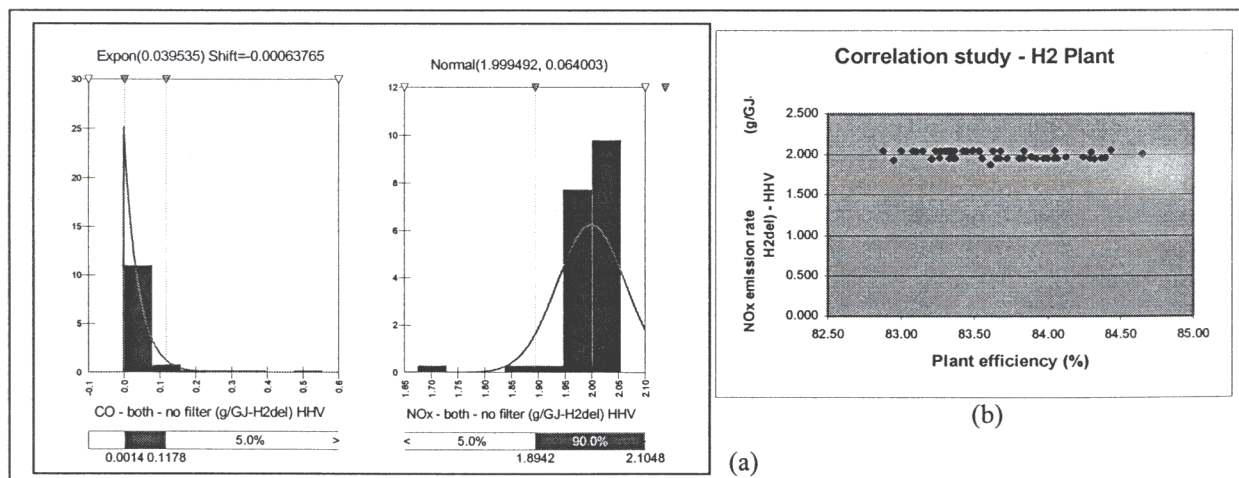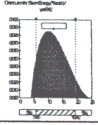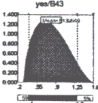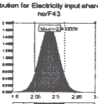

Figure 5: CO and NO_x emission rates from a hydrogen production plant (HHV).

Table 5: Origin of the lines used for the efficiency calculation

Plant configuration		Line origens		
size (mtpd)	extra-steam	minimum	most probable	maximum
270	yes	79.19	78.50	77.70
270	no	68.19	67.89	67.70
27	yes	76.71	77.08	79.19
27	no	66.19	65.99	65.70
2.7	no	59.19	58.09	58.70

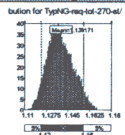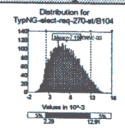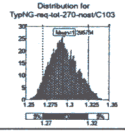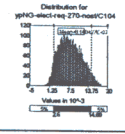Table 6: Other major FUEEM inputs for the energy requirement in hydrogen plants (HHV)
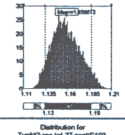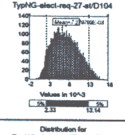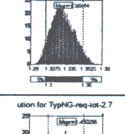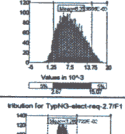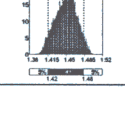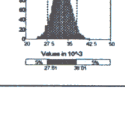
Variable	Units	Min/Max (90 % conf.)	Mode	Mean	Curve Shape
Extra-steam	%	5.66 / 19.42	9.88	11.88	
Electricity share Centralized Plants	%	0.4 / 1.3	0.69	0.81	
Electricity share Decentralized Plants	%	2.07 / 2.73	2.4	2.4	

Results

As stated before the objective of this study is to calculate the energy requirement and emissions generated by hydrogen plant alternatives. Table 7 presents the natural gas (NG) requirements and electricity requirements for all alternatives. On Table 8 the reformer and fugitive emissions are presented for the 27 mtpd plant, which produces extra-steam and uses a typical NG composition. Due to space limits we included the shape of the curves only on this two tables. Also, we decided not to present the other results such as the emissions for the 270 mtpd plants and all the scenarios using NG with high content of N_2. The reformer emissions of the 270 mtpd are similar to the 27 mtpd and the fugitive emissions are smaller since bigger capacity plants have higher efficiencies and therefore require less NG per H_2 produced.

At the component level the emission and energy requirement associated with the natural gas life cycle activities and with the electricity life cycle activities are not included yet. It makes the comparison with other studies a little bit more difficult because some reports present their numbers only at aggregated levels (including all activities from the "well to the plant"), especially the fugitive emissions. However, some conclusions can be made considering the plant efficiency, the amount of NG used as fuel, the emission factors used in each model (Greet 1.5a [16], Acurex [17] and NREL [6]) and the appropriated unit conversions by calculating a factor of 0.2389 MBtu of NG consumed as a fuel per MBtu of hydrogen produced by the plant (with steam exportation) in Greet 1.5a [16], a factor of 15.505 lb per GJ of hydrogen to transform Acurex [17] numbers and 142 MJ per kg of hydrogen in the NREL [6] data. First Acurex [17] overestimates a lot all the reformer emissions. It looks like that an external calculation was previously done, including the fugitive emissions in the reformer emission rates. However, checking the fugitive emission results (Table 8) we could see that this was not the case because NMOG and especially CH_4 emissions should be higher and not the NO_x and CO. Based on the industry survey this study assumes smaller emission rates for NO_x (1.9 to 2.1 g/GJ-H_2 in this study against 8.0 and 6.4 g/GJ-H_2 for Greet 1.5a [16] and NREL [6] respectively) indicating that more measurements would be necessary than just extrapolate the data from NG boilers. Similar conclusion can be done for CO where very few emissions were found in the industrial survey. We could check that while our maximum value is 0.12 g of CO/GJ-H_2 with a very small probability to occur NREL [6] value is 0.59 g/GJ-H_2 and the Greet [16] value is 8.4 g/GJ-H_2. On the other hand, for NMOG and especially for CH_4 the fugitive emissions are the most important parameter and unfortunately NREL [6] and Acurex [16] apparently neglected to consider it. The small differences on CO_2 emissions are mainly due to the differences on the assumed efficiencies.

Table 7: Fuel requirements of hydrogen plants using typical NG composition (GJ-$_{fuel}$ / GJ of H$_{2-produced}$ - HHV)

Plant Characteristics	Total NG requirement				Total Electricity requirement (x 10^{-3})			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
270 mtpd extra-steam	1.12 / 1.16	1.131	1.139		2.29 / 12.91	6.08	7.16	
270 mtpd no extra-steam	1.27 / 1.32	1.288	1.295		2.6 / 14.69	5.32	8.14	
27 mtpd extra-steam	1.13 / 1.19	1.129	1.159		2.33 / 13.14	3.44	7.28	
27 mtpd no extra-steam	1.30 / 1.36	1.299	1.330		2.67 / 15.07	8.16	8.35	
2.7 mtpd decentralized	1.42 / 1.48	1.437	1.450		27.6 / 38.0	29.23	32.83	

a: At 90 % of confidence.

Table 8: Calculated emissions for a 27 mtpd hydrogen plant with no extra steam exportation and typical NG used (grams / GJ-H$_{2-produced}$ - HHV)

Pollutants	Reformer emissions			Fugitive emissions		
	Min / Max	Mode	Mean	Min / Max	Mode	Mean
NO$_x$	2.07 / 2.43	2.11	2.24	-	-	-
CO	0.003 / 0.13	0.02	0.045	0.1 / 1.2 x 10^{-3}	0.36 x 10^{-3}	0.61 x 10^{-3}
NMOG	0.061 / 0.11	0.065	0.085	0.75 / 6.43	4.70	3.38
PM$_{10}$	0.172 / 0.225	0.178	0.198	-	-	-
PM$_{2.5}$	0.57 / 0.67	0.59	0.62	0.15 / 1.29	0.844	0.677
SO$_x$	10 / 54 x 10^{-3}	33.6 x 10^{-3}	30.5 x 10^{-3}	0.7 / 6.7 x10^{-4}	4.2 x 10^{-4}	3.5 x 10^{-4}
CH$_4$	0.145 / 0.187	0.154	0.166	6.26 / 48.8	23.71	26.72
N$_2$O	0.081 / 0.170	0.135	0.125	-	-	-
CO$_2$	65841 / 68784	66750	67223	0.11 / 0.86	0.336	0.427
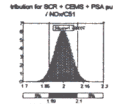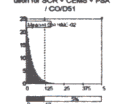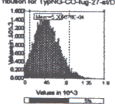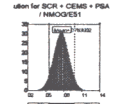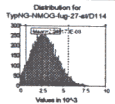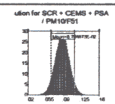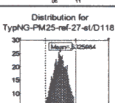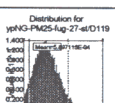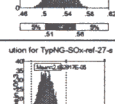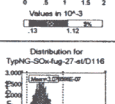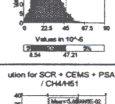
a: At 90 % of confidence.

Table 9: Calculated emissions for a 2.7 mtpd decentralized hydrogen plant using a typical natural gas (grams / GJ-H$_{2-produced}$ - HHV)

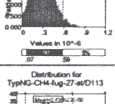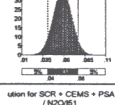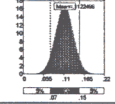| Pollutants	Reformer emissions			Fugitive emissions		
	Min / Max	Mode	Mean	Min / Max	Mode	Mean
NO$_x$	5.16 / 6.06	5.27	5.59	-	-	-
CO	0.003 / 0.140	0.021	0.047	0.2 / 1.3 x 10^{-3}	0.82 x 10^{-3}	0.66 x 10^{-3}
NMOG	0.061 / 0.110	0.064	0.085	0.82 / 7.00	0.95	3.69
PM$_{10}$	0.172 / 0.225	0.178	0.198	-	-	-
PM$_{2.5}$	1.355 / 1.584	1.387	1.483	0.16 / 1.40	1.04	0.74
SO$_x$	23 / 52 x 10^{-3}	26.9 x 10^{-3}	37 x 10^{-3}	0.9 / 7.3 x10^{-4}	1.9 x 10^{-4}	3.9 x 10^{-4}
CH$_4$	0.145 / 0.187	0.154	0.166	6.76 / 53.22	28.91	29.15
N$_2$O	0.143 / 0.298	0.245	0.220	-	-	-
CO$_2$	71524 / 75007	71465	73311	0.114 / 0.931	0.228	0.466

a: At 90 % of confidence.

Table 10: Calculated emissions for a 27 mtpd hydrogen plant with extra steam exportation and typical natural gas used (grams / GJ-$H_{2-produced}$ - HHV)

Pollutants	Reformer emissions				Fugitive emissions			
	Min / Max[a]	Mode	Mean	Shape	Min / Max[a]	Mode	Mean	Shape
NO_x	1.89 / 2.10	2.00	2.00		-	-	-	-
CO	0.003 / 0.12	0.004	0.0008		0.12 / 1.01 $\times 10^{-3}$	0.50 $\times 10^{-3}$	0.53 $\times 10^{-3}$	
NMOG	0.05 / 0.10	0.076	0.076		0.65 / 5.6	2.21	2.95	
PM_{10}	0.16 / 0.21	0.187	0.188		-	-	-	-
$PM_{2.5}$	0.53 / 0.58	0.558	0.553		0.13 / 1.12	0.38	0.59	
SO_x	8.5×10^{-3} / 47.2×10^{-3}	19×10^{-3}	26×10^{-3}		0.00007 / 0.00059	0.16 $\times 10^{-3}$	0.31 $\times 10^{-3}$	
CH_4	0.14 / 0.18	0.158	0.159		5.42 / 42.7	24.6	23.3	
N_2O	0.07 / 0.15	0.113	0.112		-	-	-	-
CO_2	57321 / 60015	58363	58577		0.09 / 0.74	0.32	0.37	

a: At 90 % of confidence.　　　　　　　　　　* To transform to lb/MBtu multiply by 2.326×10^{-3}

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