

NATURAL GAS STEAM REFORMING FOR HYDROGEN PRODUCTION. AN ENERGETIC APPROACH

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Abstract. *The objective of the present work is to evaluate hydrogen production from natural gas using steam reforming as feedstock for use in fuel cells. A thermal system fuel by natural gas with 89.35 % of methane and 8.03 % of ethane is proposed. In order to reduce the destroyed exergy, the heat recovery processes are included and its benefits discussed. Mass and energy balances in the steam reforming process have been carried out, making use of a simulation program developed for this purpose. The mass flow diagram is presented as well as an energy diagram according to Sankey, which defines the energy flows in the reformer under different operation conditions.*

Keywords. *natural gas reforming, hydrogen, thermodynamic analysis, energy balance.*

1. Introduction

Hydrogen represents a clean source of energy, though not available as primary source, it can be obtained by different technologies using fossil fuels, such as hydrocarbons, or non-fossil fuels, such as biomass or water. Hydrogen can be transported and stored, having the benefit, that several current energy systems may be adapted for its use. Its major advantage yields in that the controlled combustion of hydrogen produces water as mean reaction product, with no damage effects on local environment. Due to the low emission of pollutants, such as carbon monoxide CO or nitrogen oxides NO_x, the use of hydrogen in combustion engines and in fuel cells plays an important role in mobile as well as in stationary applications (p.ex. electricity generation). At the present time, our society is looking forward to developing clean energy sources and due to these benefits; its demand increases constantly worldwide. Natural gas has a great potential for hydrogen production; several technologies have been developing and new ones are all the time being investigated. Though it is predicted that natural gas reserves will not reach to cover the worldwide demand during the entire actual century, natural gas reforming represents nowadays a viable technology that will allow in the coming years to develop quickly hydrogen based energy systems (Sosa et al, 2000).

In this work, a thermodynamic analysis of a natural gas steam reformer is presented with the goal to determine operating conditions of the reactor units comprising the proposed system. The steam reforming is modeled, considering an endothermic reaction mechanism. Mass and energy balances allow the determination of the required heat in the process, as well as the mass amount of natural gas to run a phosphoric acid fuel cell (PAFC).

2. Nomenclature

T	Temperature, K	max.	Maximum	α	Extent of reaction
t	Temperature, °C	NG	Natural gas	x	Number of carbon atoms
H	Enthalpy, kJ	vol%	Volume percent, vol %	y	Number of hydrogen atoms
h	Specific enthalpy, kJ/kg	m%	Mass percent, m %	C _x H _y	Generic hydrocarbon
ΔH	Reaction enthalpy difference, kJ/kg	m	Mass, kg	LHV	Low heating value, kJ/kg
Q	Reaction heat, kJ	\dot{m}	Mass flow, kg/s	FC	Fuel cell

Subscripts

i	Chemical compound	CO	Carbon monoxide	H ₂ O	Steam
H ₂	Hydrogen	CO ₂	Carbon dioxide	CH ₄	Methane

Superscripts

* Exhaust gas

3. Fuel cell

To meet the energetic needs of our industrialized society and taking account of reserves reduction of non-renewable resources, environment contamination, rate of global warming, greenhouse effect, ecosystems alterations and sea level rise, in the last decade industries and technologists have accelerated worldwide the fuel cell development for vehicles, buildings as well as electric generation. Nevertheless, the statistics shows that non-renewable energies contribute with less than 1% to total world installed power generation (Dunn, 2000; World bank, 1999).

Furthermore, among alternative energy generation devices, fuel cell systems have emerged as one of the most promising energy conversion technologies. Disadvantages are the levels of capital investment and operational costs. The major markets are power generation and transport. Fuel cells are used in stationary applications that range from large central power stations, to distributed-power generators in urban areas, to small systems in remote areas. Their high energy-efficiency and low environment effects will contribute to reduce carbon dioxide emissions and will lower atmospheric pollutants as well. In distributed-power generation they can also reduce transmission and distribution costs and on the other hand, they are able to provide simultaneously heat and electricity.

A fuel cell is an electrochemical device that transforms chemical energy directly into electric and thermal power. It works in similar form to a battery, but using only hydrogen and oxygen to feed the electrodes. By oxidizing hydrogen without combustion, converts the chemical energy directly in electricity, in direct current power, which can be transformed in alternating current power by means of an inverter. If not only electricity but also heat is produced, the system constitutes a cogeneration system with the associated technical, economical and environment benefits.

4. Fuel for fuel cell

Different fuel cells have been developed and can be classified by different ways, fuel reforming, operation temperature (Hirschenhofer et al, 1998). The most common one is by the type of electrolyte used in the fuel cell and includes:

Alkaline Fuel Cell	AFC
Protonic Exchange Membrane Fuel Cell	PEMFC
Solid Oxide Fuel Cell	SOFC
Molten Carbonate Fuel Cell	MCFC
Phosphoric Acid Fuel Cell	PAFC

Oxygen in air is the most common used oxidizer. The different types have quite different fueling requirements. All fuel cells run with at their most efficient on pure hydrogen and oxygen, but this is too expensive. Fossil fuels can also be used, if an adequate fuel reformer extracts from the hydrocarbon fuel a hydrogen-rich gas to run the fuel cell. Natural gas, ethanol and methanol are appropriate for this purpose. Among liquid fuels, ethanol is a promising source of hydrogen, belonging to the well-known renewable sources. In all these cases, the rich-hydrogen stream contains only traces of carbon monoxide in order to avoid poisoning of fuel cell electrocatalyst. Nowadays, natural gas is probably the most common fossil fuel used to produce hydrogen.

Fuel cells FC can be also classified by the form hydrogen is feed to the fuel cell, as pure or as reformed gas, as shown in Tab. (1). AFC and PEMFC operate at low temperatures (80°C) and use only fuel with pure hydrogen. If the operating temperature is higher enough, over 200°C (Costa &Oliveira, 2000), reforming must take place. PAFC, MCFC and SOFC can be feed directly with natural gas; however reforming will be internal or external depending on FC operating temperature. Above 600°C the process must be done externally, since the reaction heat is not able to supply the required heat for the reforming reaction. Cogeneration systems can only be developed with high temperature systems, MFCF and SOFC. Nevertheless, in some cases it is possible to obtain electricity and hot water production in cogeneration PAFC systems.

Table 1. Fuel, operating temperature, electrolyte and oxidizer according to fuel cell type

Fuel	Type	Operating temperature (°C)	Electrolyte	Oxidizer
Pure hydrogen	AFC	80	KOH	Oxygen/ Air
	PEMFC	80	Solid polymer	Oxygen/ Air
Reformed Fuel gas	externally PAFC	200	H ₃ PO ₄	Air
	internally MCFC	650	Li ₂ CO ₃ + K ₂ CO ₃	Air
	internally SOFC	1000	ZrO ₂	Air

5. Hydrogen production

In the last decade new conversion technologies have been developed, attempting to produce hydrogen from non-renewable sources. Wind power has a great potential as energy source and plays an important role among renewable

technologies. At present government and German industries, looking forward to use electrolysis to generate hydrogen via wind power, are analyzing a project for Patagonia, a region in the south of Argentina.

Most hydrogen for commercial sale is obtained from hydrocarbons, being natural gas its major producer. Composition depends widely on extraction place. Table (2) shows the natural gas NG composition according to data obtained by COMGAS in Campos Basin (Brazil), informed by Silveira et al, 1999.

Table 2. Natural gas low heating value LHV, volume (vol %) and mass (m %) composition (Silveira et al, 1999)

Chemical compounds in NG		Volume composition (vol %)	Mass composition (m %)	LHV (kJ/kg)
Methane	CH ₄	89.35	80.92	50 144
Ethane	C ₂ H ₆	8.03	13.64	47 593
Propane	C ₃ H ₈	0.78	1.94	46 455
n-Butane	C ₄ H ₁₀	0.07	0.23	45 810
n-Pentane	C ₅ H ₁₂	0.01	0.04	45 446
Carbon dioxide	CO ₂	0.48	1.20	-
Nitrogen	N ₂	1.28	2.03	-
Total		100%	100%	48 093

Methane and ethane can be considered as the only compounds responsible for the hydrocarbon transformation in hydrogen, since heavier hydrocarbons do not contribute significantly to natural gas composition. It is not possible to oxidize methane directly, since at temperatures above 800°C it breaks up and carbon deposition takes place. To avoid this, it should be mixed with steam and the well-known *steam reforming SR* process takes place, perhaps one of the major and most used techniques to obtain hydrogen from fossil fuels (Ragonha, 2000).

Two other major techniques are *partial oxidation POX* and *autothermal reforming ATR* (Seo et al, 2002). Though SR yields the highest efficiency, POX method has a smaller start-up-time and ATR is more energy-efficient (Ahmed et al, 2001; Pulgar et al, 2002).

6. Proposed fuel cell technical data

The BHKW B 200, developed by ONSI, is one of the earlier commercially available PAFC fuel cells. This power plant is a packaged factory assembled which provides an electrical rating of 200 kW_e and produces more than 204 kW_{th} of useful heat at rated power conditions, able to heat a customer water stream up to 60° C. The nominal design technical data is shown in Tab. (3).

Table 3. Nominal technical data of ONSI- PAFC-BHKW B 200 at rated power

Fuel cell type	PAFC	Modell	BHKW B 200
Rated power output (kW _e)	200	Heat-up time (hours)	3 (from 0 to 200 kW)
Output frequency (Hz)	50	Overall dimensions:	
Power generating efficiency (at LHV)	40 %	Power module (m)	5.5 x 3 x 3
Thermal power (kW _{th})	204	Cooling module (m)	4 x 1.2 x 1.2
Water output temperature (°C)	max. 85	Unit weight:	
Rated natural gas consumption (Nm ³ /h)	54	Power module (tons)	18
Power per natural gas demand (kWh/Nm ³)	9.3	Cooling module (tons)	0.7
Operating pressure (MPa)	0.101	Operating temperature (°C)	205

Table 4. Maximum allowable volume percent of chemical compounds in fuel gas

Chemical compound	Maximum allowable volume (%)	Chemical Compound	Maximum allowable volume (%)	Chemical Compound	Maximum allowable volume (ppmv)
Methane	100	n-Pentane	0.5	Sulphur	30
Ethane	10	Carbon dioxide	3	Chlorine	0.06
Propane	5	Nitrogen	4	Ammonia	1
n-Butane	1.25				

Working the fuel cell at rated load, the ONSI BHKW B 200 consumes 54 Nm³/h of inlet fuel gas. Its electrical generation efficiency at full load is 40% on a natural gas lower heating value LHV basis, remaining below at lower loads. The fuel cell runs on pipeline natural gas with fuel composition limits shown in Tab. (4).

An ONSI BHKW B 200 has been considered in this work. The reforming system proposed here should be able to fuel this 200 kW_e phosphoric acid fuel cell, being calculated the hydrogen production in terms of a 54 Nm³/h pipeline natural gas inlet and the simulated reformer is being contrasted with actual operating values.

7. Steam reforming

In presence of a catalyst, when a fossil hydrocarbon based fuel reacts endothermically with steam H₂O, produces hydrogen H₂ and as byproduct a gas mixture, carbon dioxide CO₂ and carbon monoxide CO in a high content. High temperatures and low pressures thermodynamically favor steam reforming, i.e. NG is reformed above 560°C.

The hydrocarbon conversion in hydrogen follows Eq. (1), being x the number of carbon C atoms and y the number of hydrogen H atoms present in a generic hydrocarbon C_xH_y.

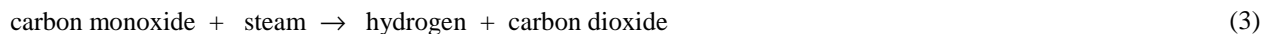


where the positive value of the reaction enthalpy ΔH denotes the endothermic condition. The hydrogen content in the generic hydrocarbon depends on the number of hydrogen atoms per carbon atom, i.e. y/x. On the other hand, the hydrocarbon conversion ratio H:C can be defined as shown by Eq. (2) as the amount of hydrogen produced from each carbon.

$$\text{conversion ratio H : C} = \frac{\text{moles of hydrogen}}{\text{moles of carbon}} = \frac{x + 1/2 y}{x} \quad (2)$$

The efficiency of the conversion depends strongly on hydrocarbon H: C ratio. Keeping in mind the natural gas composition given in Tab. (2), methane CH₄ is the hydrocarbon with the highest hydrogen content with a ratio of 4: 1 and a conversion ratio of 3: 1. On the other hand, ethane has a 3: 1 H:C ratio and a conversion ratio of 2.5: 1. Higher hydrocarbons in NG have smaller H:C and conversion ratios, and do not contribute to production of hydrogen due to its low percentage in the natural gas composition (Sosa et al, 2002).

Steam reforming carries the need of carbon monoxide removal from the reformed gas stream, since fuel cell catalyst can be poisoned. Table (4) shows for example that the maximum carbon dioxide allowable percent in NG is 3% to fuel a PAFC. Several techniques have been developed, such as, water gas shift reaction, methanation, dioxide absorption, etc. (Clarke et al, 2000). Adopting the water gas shift reaction technique, carbon monoxide reacts with steam and carbon dioxide and additional hydrogen are produced, as shown by Eq. (3).



As reaction rates are very fast, the reactor design depends actually on heat transfer for high operating temperatures. Steam reformers are suitable for long periods of steady-state operation and deliver high hydrogen concentrations (>70% on a dry basis) (Ahmed et al, 2001). Both reactions are reversible and endothermic and are normally at equilibrium, since the reaction rates have high values. Thermodynamics can be applied in order to analyze methane and ethane conversion.

A schematic diagram of steam reformer is shown in Fig. (1). In the *reforming* primary section occurs the reforming reaction with evolution of hydrogen and carbon oxides. The *shift* secondary section is responsible for the removal of carbon monoxide by shifting process.

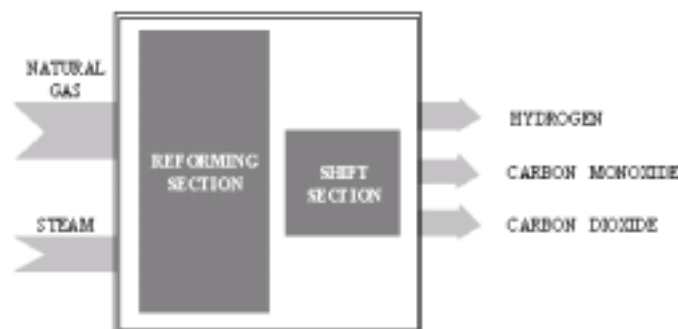


Figure 1. Schematic layout of the proposed steam reforming system

8. Natural gas steam reforming process description

The proposed layout to produce hydrogen from natural gas NG feedstocks is shown in Fig. (2) and consists basically of a preheater, a reformer, a vaporizer and three mixers.

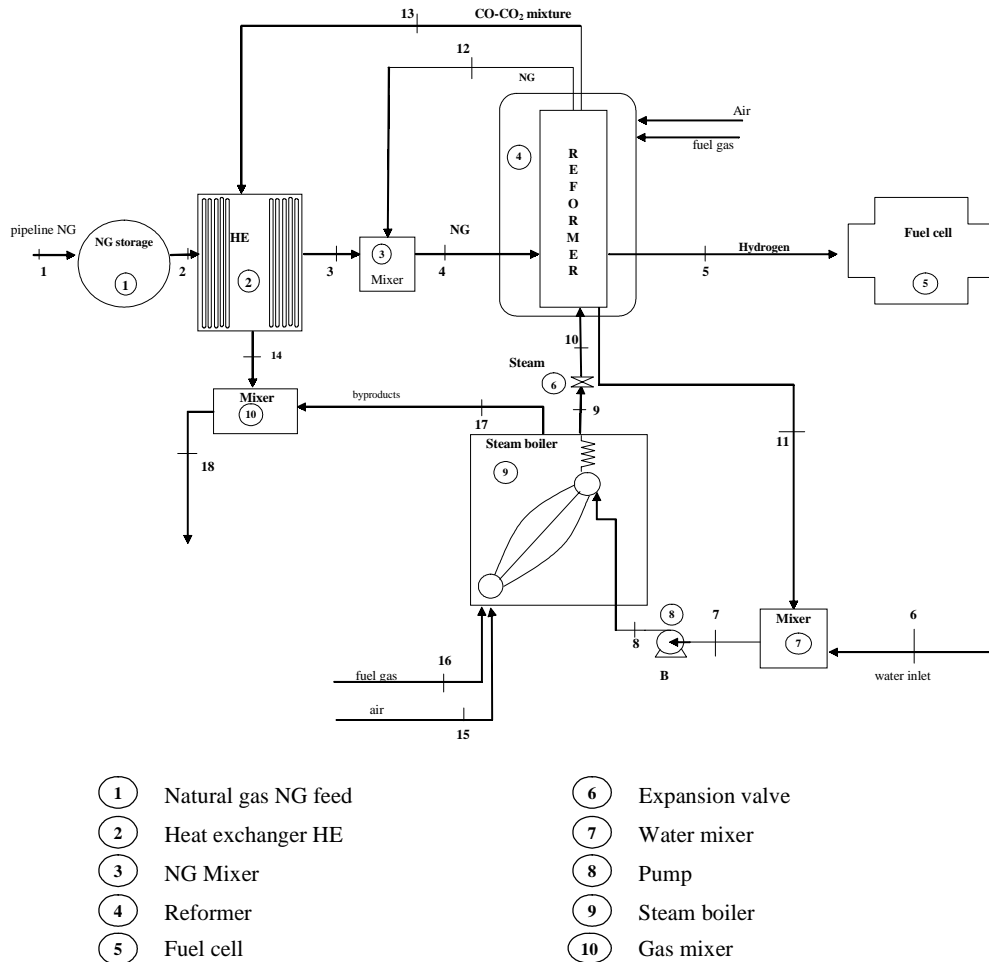


Figure 2. Schematic layout of the proposed steam reforming system

Pipeline natural gas flows into the system (1); next it is heated (2) by means of a heat exchanger HE, mixed with exhaust natural stream (3), then mixed with steam and reformed over nickel catalyst (4). This produces a synthesis gas containing hydrogen and carbon oxides. The synthesis gas passes through the shift conversion section, where carbon monoxide reacts with steam to form carbon dioxide with an additional hydrogen production. The carbon oxide exhaust stream is sent to the preheater HE (2) the exhaust natural gas is re-utilized, by mixing it with the input feed in a gas mixer (3). Hydrogen product is used as feedstock for a fuel cell system (5). If a PAFC is used, the operating temperature is 200°C and a cooler must be placed previous to the fuel cell.

Heat is required for the global endothermic reaction schema and it is supplied externally by combustion of fuel gas and air. Due to the high operating temperatures, a heat recovery unit is proposed, consisting of a heat exchanger (2), whose advantage is to reduce fuel costs in the preheating, as well as investment and operating costs. Besides, it allows diminishing the destroyed exergy.

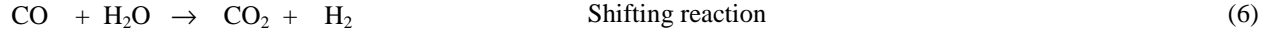
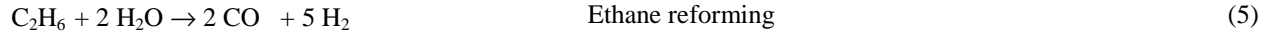
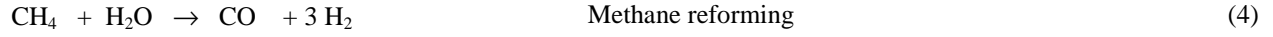
In the present work an energetic approach to the reforming process is presented, the irreversibilities taken place in the thermal units are not taken into account. Neither economic, nor thermoeconomic considerations are presented here, but they are included in future investigations (Sosa et al, 2003).

9. Computational program for the steam reforming system

A simulation program has been developed to evaluate the proposed steam reformer unit. The thermodynamic system has been represented by a flowsheet that considers units and interconnecting streams, that allows determining mass and molar composition as well as enthalpy, entropy and exergy values in each state of the proposed system. A spreadsheet has been used for this simulation.

10. Chemical equilibrium reactions

This reformer converts natural gas essentially to hydrogen in a two-steps-mechanism with the primary reforming reaction of the two major hydrocarbons in natural gas, methane CH_4 (Eq. (4)) and ethane C_2H_6 (Eq. (5)) and the secondary shifting reaction (Eq. (6)), carried out over a nickel catalyst at high temperature.



Hydrocarbons with more than two carbons (propane, n-butane, n-pentane) contribute only to hydrogen production with the hydrocracking process.

Equilibrium constants and the extent of reaction α were calculated for the above reactions as a function of the operating temperature, ranging from 600°-800°C and at different pressures in the range 0.101 - 0.303 MPa. Table (5) shows the values of the extent of reaction at 800°C and atmospheric pressure.

Table 5. Extent of reaction α at 800°C and atmospheric pressure for reforming reactions

	Reaction	α
Methane	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2$	0.9108
Ethane	$\text{C}_2\text{H}_6 + 2 \text{H}_2\text{O} \rightarrow 2 \text{CO} + 5 \text{H}_2$	0.9998
Shift	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	0.6196

The amount of hydrogen produced can be calculated in terms of the extent of the reforming reactions by means of the following equations.

$$m_{\text{H}_2} = \frac{PM_{\text{H}_2}}{PM_{\text{NG}}} \frac{3 \alpha_{\text{CH}_4}}{2(1 + \alpha_{\text{CH}_4})} 0.894 m_{\text{NG}} \quad \text{Methane reforming} \quad (7)$$

$$m_{\text{H}_2} = \frac{PM_{\text{H}_2}}{PM_{\text{NG}}} \frac{5 \alpha_{\text{C}_2\text{H}_6}}{3 + 4 \alpha_{\text{C}_2\text{H}_6}} 0.0803 m_{\text{NG}} \quad \text{Ethane reforming} \quad (8)$$

$$m_{\text{H}_2} = 1/2 \frac{PM_{\text{H}_2}}{PM_{\text{NG}}} \frac{3 \alpha_{\text{CH}_4}}{2(1 + \alpha_{\text{CH}_4})} 0.894 \frac{5 \alpha_{\text{C}_2\text{H}_6}}{3 + 4 \alpha_{\text{C}_2\text{H}_6}} 0.0803 \alpha_{\text{shift}} m_{\text{NG}} \quad \text{Shift reaction} \quad (9)$$

being PM_{H_2} the molecular weight of hydrogen, PM_{NG} of natural gas, m_{NG} the inlet mass amount of natural gas, α_{CH_4} , $\alpha_{\text{C}_2\text{H}_6}$, α_{shift} the extent of the methane, ethane and shift reactions.

11. Mass balance in natural gas steam reforming

Mass-balance has been carried out. The extent of reaction α shown in Tab. (5) allows calculating the mass flow of reformed gases, hydrogen, steam, methane, ethane and carbon oxides in equilibrium conditions, knowing the reformer inlet flow. For a given amount of natural gas, the flow sheet solves the outlet streams (mass amount and mole fraction), computed from the inlet streams, taking into account the mass-balance condition (Eq. (10)),

$$m_{\text{NG}} + m_{\text{H}_2\text{O}} = m_{\text{H}_2} + m_{\text{CO}} + m_{\text{CO}_2} + m_{\text{NG}}^* \quad (10)$$

being m_{NG} , $m_{\text{H}_2\text{O}}$, m_{H_2} , m_{CO} , m_{CO_2} and m_{NG}^* the mass amount m_i in kg for each chemical compound i, namely natural gas, steam, hydrogen, carbon monoxide, carbon dioxide and exhaust natural gas (Sosa et al, 2002). Since reforming reactions depend on temperature and pressure, the operating conditions fix the extent of reaction and therefore the mass amount of outgoing streams.

12. Energy balance in natural gas steam reforming

Energy-balance has been also carried out, as shown in Eq. (11).

$$H_{NG} + H_{H_2O} + Q = H_{H_2} + H_{CO} + H_{CO_2} + H_{NG^*} \quad (11)$$

being Q the required reaction heat and H_{NG} , H_{H_2O} , H_{H_2} , H_{CO} , H_{CO_2} and H_{NG^*} the total enthalpy values H_i in kJ for each chemical compound i , namely natural gas, steam, hydrogen, carbon monoxide, carbon dioxide and exhaust natural gas. The simulation program allows calculating the specific enthalpy h_i in kJ/kg for the each chemical compound i for each thermodynamic system state in equilibrium conditions, knowing mass amount m_i in the reformer-inlet and -outlet streams.

The specific enthalpy value $h_i(T)$ for the each chemical compound i in KJ/kg was calculated as a function of temperature T using Eq. (12), being T the temperature in grads Kelvin. the specific heat capacity at constant pressure in kJ/K.kg and $h_i^\circ(298K)$ the standard specific enthalpy at 298 K in kJ/kg, according to data informed by Kubachieski et all, 1979.

$$h_i(T) = h_i^\circ(298K) + \int_{298K}^T c_p(T') \cdot dT' \quad (12)$$

13. Discussion

Equation (13) defines the amount of methane in the outlet stream divided the corresponding amount in the inlet stream for methane reforming.

$$\% \text{ methane} = \frac{\text{outlet methane}}{\text{inlet methane}} 100\% = \frac{1 - \alpha_{CH_4}}{2(1 + \alpha_{CH_4})} 100\% \quad (13)$$

where α_{CH_4} is the extent of ethane reforming reaction. Figure (3) shows this percentage that depends strongly on temperature, remaining at temperatures above 750° C less than 20% of the inlet methane stream.

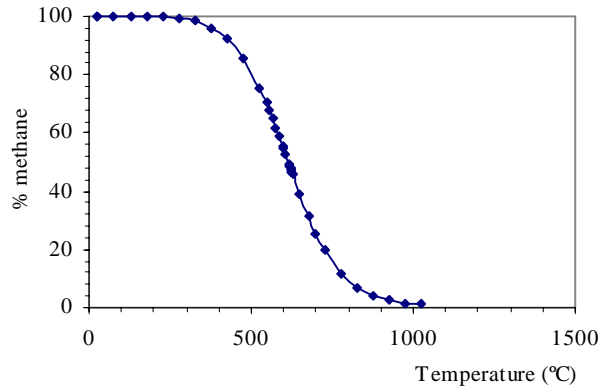


Figure 3. Methane percent (% methane) as a function of temperature (°C)

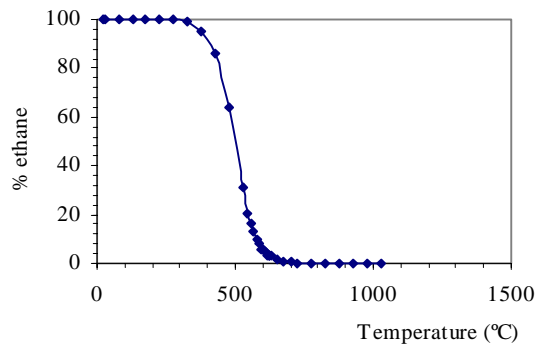


Figure 4. Ethane percent (% ethane) as a function of temperature (°C)

The hydrocarbon conversion in hydrogen depends can be defined by Eq. (14) for methane. Complete conversion is achieved at temperatures above 1000°C.

$$\text{methane conversion efficiency} = \frac{\text{inlet methane}}{\text{outlet methane}} 100\% = \frac{1}{\% \text{ methane}} \quad (14)$$

Equation (15) indicates the remaining ethane percent in the outlet stream, being $\alpha_{C_2H_6}$ the extent of the ethane reforming reaction. Figure (4) shows this percentage as function of temperature.

$$\% \text{ ethane} = \frac{\text{outlet ethane}}{\text{inlet ethane}} 100\% = \frac{1 - \alpha_{C_2H_6}}{3 + 4 \alpha_{C_2H_6}} 100\% \quad (15)$$

The ethane conversion in hydrogen depends can be defined by Eq. (16). Complete conversion is only achieved at temperatures above 600°C.

$$\text{ethane conversion efficiency} = \frac{\text{inlet ethane}}{\text{outlet ethane}} 100\% = \frac{1}{\% \text{ ethane}} \quad (16)$$

This shows that the hydrocarbon conversion efficiency depends on the extent of reaction values. It is desired a value as high as possible, so as to maximize the amount of hydrogen produced, reducing irreversibilities and the destroyed exergy as well. Nevertheless, a complete reforming approach is not realistic, since it can be only achieved at high temperatures, which should be avoided, because they favor carbon deposition. On the other hand, heat requirements limit as well the extent of reaction. Usual operating temperatures range over 800°C. Table (6) compares the input and output volume and mass percentage of the reformer products.

Table 6. Chemical compounds composition in volume (vol %) and mass percent (m %) at 800°C and at atmospheric pressure (0.101 MPa) for the reforming products

Chemical compounds in natural gas NG		Volume percentage (vol %)		Mass percentage (m %)	
		inlet	outlet	inlet	outlet
Hydrogen	H ₂	0	52.66	0	10.45
Methane	CH ₄	34.06	12.82	37.52	20.25
Ethane	C ₂ H ₆	3.06	0.04	6.32	0.12
Steam	H ₂ O	61.88	18.66	53.65	10.20
Carbon monoxide	CO	0	5.75	0	15.86
Carbon dioxide	CO ₂	0.13	9.50	0.55	41.15

Mass flow defining reformer streams were calculated for the reformer under different operating temperature and pressure conditions. High temperatures will favor the conversion efficiency. Calculations were carried out calculations for temperatures ranging between 600°C and 900°C. For all the analyzed pressures the hydrogen production increases with temperature.

The hydrogen production decreases when the pressure is increased. Calculations were carried out calculations for pressures ranging between 0.101 MPa and 0.303 MPa. Increasing the operating pressure above the atmospheric one, the conversion efficiency is smaller and should be avoided. Both methane and ethane reforming reactions indicate an increase of volume, since the mole difference Δn has a positive value.



On the other hand, the shift reaction has a zero Δn value, signifying that pressure has no effect on the shift reaction.



Figure (5) shows the flow diagram in mass % for 800°C and 0.101MPa, assuming a total mass inlet of 1 kmol (17.71 kg/kmol NG) of natural gas. The amount of steam was calculated in terms of the mass amount of natural gas requiring 1.15 kg steam/ kg NG. The figure shows that if the reformer operates at 800°C, 10.4 kg of hydrogen will be produced from 46.4 kg of natural gas with 22.4 m % conversion efficiency and 65 % vol efficiency.

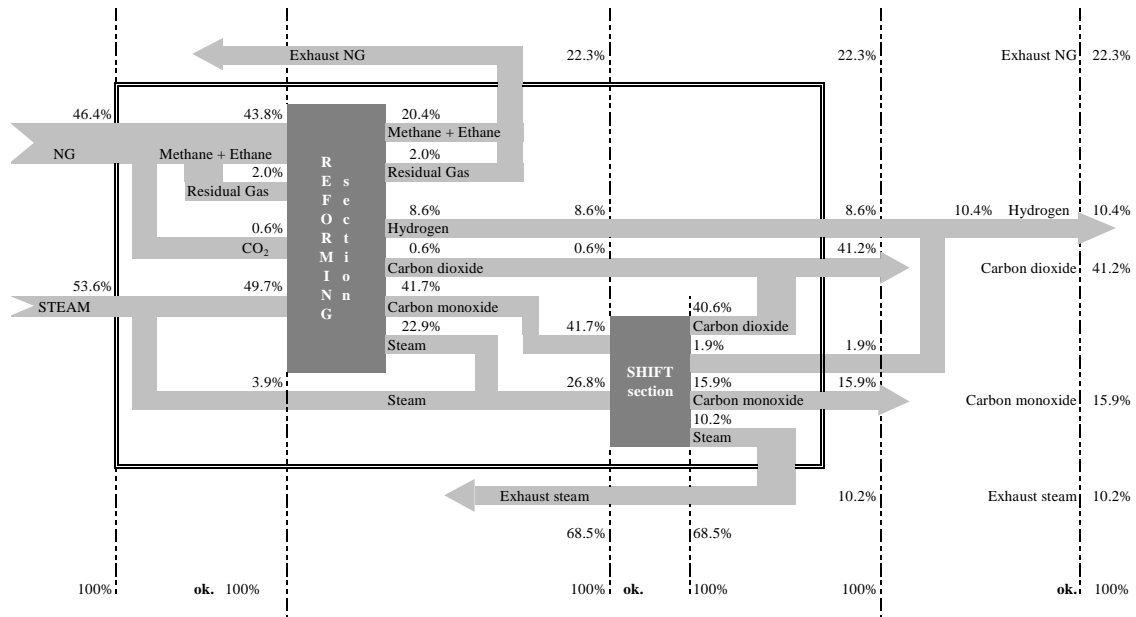


Figure 5. Mass flow diagram in m% at 800°C and 0.101 MPa

Figure (6) shows the different enthalpy of the inlet and outlet streams, calculated in terms of a mol of inlet NG. Since the reforming process is endothermic, 6271 kJ/kg N heat is required according to Eq. (11).

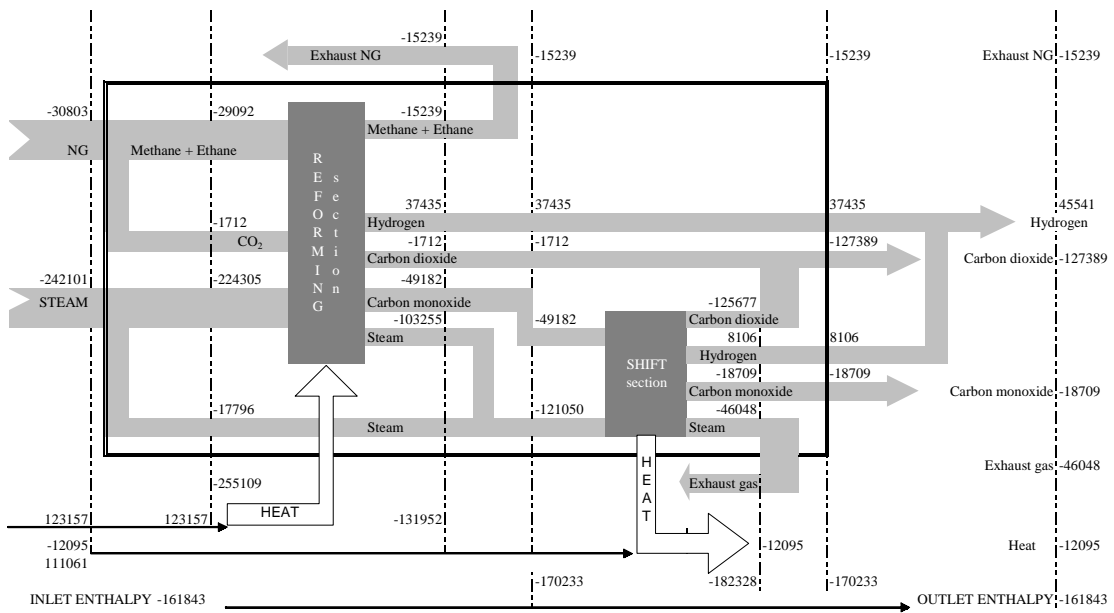


Figure 6. Enthalpy flow diagram in kJ at 800°C and 0.101 MPa

Figure (7) shows a schematic diagram presenting the energy balance in terms of an amount of mass of 1 kg inlet natural gas. The efficiency of the conversion of hydrogen from natural gas gives a value of 23%.

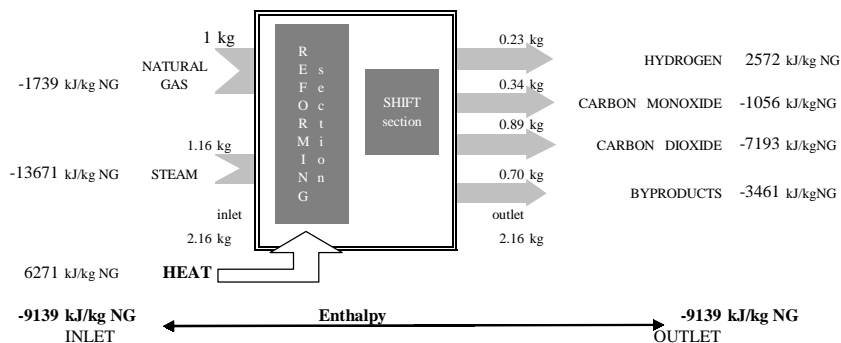


Figure 7. Enthalpy schema in kJ/kg GN at 800°C and 0.101 MPa.

14. Conclusions

The proposed model simulates the hydrogen production from natural gas using steam reforming as feedstock for use in fuel cells. The advantages of the method are that temperature and pressure dependence can be easily analysed and the model solves the determination of the thermodynamic functions in every point of the reformer. Thermodynamic analysis gives fundamental information about the equilibrium conversion of the hydrocarbons involved.

The mass flow diagram is presented and the benefits of the proposed thermal system are discussed. The mass flow diagram is presented as well as an Sankey type energy diagram, which defines the energy flows in the reformer under different operating conditions of temperature, ranging from 600°C to 800°C and of pressure between 0.101 and 0.303 MPa. In the case of PAFC-BHKW B 200, the conversion efficiency of natural gas into hydrogen is about 23 %. In next papers we will be analysed in terms of exergy and economy the proposed reformer system to run the PAFC device.

15. References

- Ahmed S. and Krumpelt M., 2001, "Hydrogen from Hydrocarbon Fuels for Fuel Cells", *Int.J.Hydrogen Energy*, Vol. 26, pp. 291-301.
- Clarke S.H., Dicks A.L., Pointon K., Smith T. and Swann A., 1997, "Catalytic Aspects of the Steam Reforming of Hydrocarbons in Internal Reforming Fuel Cells", *Catalysis Today*, 38, pp. 411-423.
- Costa, G.J. and Oliveira, E.A., 2000, "Produção de Hidrogênio associado à Cogeração: o Uso de Células de Combustível", *Monografia de Graduação em Engenharia Mecânica, Universidade Estadual Paulista, Faculdade de Engenharia, Guaratinguetá.*
- Cobem
- Dunn, S., 2000, "Micropower: The Next Electrical Era", ed. J.A. Peterson, Worldwatch Institute, USA, Worldwatch Paper 151.
- Hirschenhofer, J.H., Stauffer, D.B., Engeleman, R.E. and Klett, M.G., 1998, "Fuel Cell Handbook, 4th Edition", DOE/FETC-99/1076, ed. Parsons Corporation, U.S. Department of Energy, Morgantown, WV, USA.
- Kubachski, O. and Alcock, C.B., 1979, "Metallurgical Thermochemistry", Pergamon Press, 5th edition, ed. Wheaton & Co., Ltd, Exeter, U.K.
- Pulgar R.G., Matelli J.A. and Martins Oliveira Jr. A.A., 2002, "Influence of Natural Gas Reforming Processes on the Performance of a Fuel Cell", *Proceedings of the ENCIT 2002, 9th Brazilian Congress of Engineering and Thermal Sciences, Caxambu, Brazil, Paper CIT02-0666, pp.1-11 (CD ROM)*
- Ragonha Jr.L.F., 2000, "Análise Energética e Econômica de Células de Combustível Comercialmente Disponíveis", *Monografia de Graduação em Engenharia Mecânica, Universidade Estadual Paulista, Faculdade de Engenharia, Guaratinguetá.*
- Seo, Y.-S., Shirley, A. and Kolaczowski, S.T., 2002, "Evaluation of Thermodynamically Favourable Conditions for Production of Hydrogen in Three Different Reforming Technologies", *J. of Power Sources*, Vol. 108, pp. 213-255.
- Silveira, J. L., Leal, E.M. and Ragonha, L.F., 1999, "Estudo Termoeconômico da Implantação de um Sistema de Cogeração utilizando Célula de Combustível", *Proceedings of the 4th Iberoamerican Congress of Mechanical Engineering CIDIM'99, Vol.1, pp. 45-51.*
- Sosa, M. I. and Fushimi, A., 2000, "La Cogeneración en el Contexto de las Tecnologías de Conversión Energética del Futuro", *AVERMA, Avances en Energías Renovables y Medio Ambiente, Vol. 4, Resistencia, Argentina, N° II, pp. 07.01- 07.06.*
- Sosa, M. I., Silveira, J.L. and Fushimi, A., 2003, "Natural Gas Steam Reforming for Hydrogen Production- An Exergetic Approach", to be presented at 5th Latin-American Congress: Electricity Generation and Transmission CLAGTEE 2003, São Pedro, Brazil, 16-20 November, 2003.
- Sosa, M. I., Silveira, J.L. and Fushimi, A., 2002, "Thermodynamic Balance in Fuel Cell Hydrogen Production from Natural Gas Reforming", *Proceedings of the 9th Brazilian Congress of Engineering and Thermal Sciences ENCIT 2002, Caxambu, Brazil, Paper CIT02-0386, pp.1-12 (CD ROM)*
- World Bank, 1999, "World Development Indicators", Washington DC, USA.

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