PROCESS SIMULATION TO OBTAIN A SYNTHESIS GAS WITH HIGH CONCENTRATION OF HYDROGEN

Sorin Ioan VLĂDAN[1], Gabriela ISOPENCU[2], Cosmin JINESCU[3], Monica Alina MAREŞ[4]

A fost realizată simularea procesului de obținere a gazului de sinteză cu un conținut ridicat de hidrogen. S-a utilizat ca software specializat programul de simulare Aspen HYSYS Version 2006. Procesul de simulare s-a realizat utilizând cinci reactoare legate în serie: un reactor de reformare, un reactor de ardere și trei reactoare de echilibru. Gazul natural pentru producerea hidrogenului se utilizează ca materie primă. Agenții utilizați pentru reformarea și, respectiv, arderea, materiei prime sunt aburul și aerul cu diferite concentrații de oxigen. Realizarea procesului de simulare a urmărit în special producerea uni gaz combustibil bogat în hidrogen, cu un consum minim de gaz natural și agenți de reformare și ardere, precum și reducerea procentului de gaze reziduale, rezultate în urma procesului de reformare catalitică, care pot afecta sistemul de pile de combustie și totodată pot avea un impact nedorit asupra mediului înconjurator.

A process simulation was conducted to obtain synthesis gas with a high content of hydrogen. Specialized software Aspen HYSYS Version 2006 was used as the simulation software. Process simulation was performed using five reactors in series: a reforming reactor, a reactor of steady burning and three equilibrium reactors. It uses natural gas as a feedstock for hydrogen production. The agents used for reforming and raw materials burning are steam and air with different concentrations of oxygen. The simulation process aimed mainly the production of combustible gas rich in hydrogen with a minimum consumption of natural gas and agents of reforming and burning, and either to reduce the percentage of residual gas, resulting from the catalytic reforming process, which may affect the fuel cells and also may have an undesirable impact on the environment.

Keywords: hydrogen, synthesis gas, reforming, methane

1. Introduction

Global economic development, especially in the last five decades led to a significant decrease in non-renewable resources of raw materials for technological

---

[1] Eng., SNAMPROGETTI Romania, e-mail: Vladan.Sorin.Guest@saipem.eni.it.

[2] Lecturer, PhD. eng., Dept. of Chemical Engineering, University POLITEHNICA of Bucharest, Romania

[3] Reader, PhD. eng., Dept. of Mechanical Engineering, University POLITEHNICA of Bucharest, Romania

[4] PhD. eng., Dept. of Chemical Engineering, University POLITEHNICA of Bucharest, Romania

industries and energetically industry (coal, oil, natural gas, ferrous and nonferrous mineral deposits, salt, etc.) [1].

Because the resources are diminishing, another effect is the environmental pollution (air, water and soil) to a level that seriously affects life on the planet.

Steam methane reforming is the process which currently produces a synthesis gas with the highest content of hydrogen on an industrial scale. This provides simulation of methane reforming process with purpose to determine the maximum concentration of hydrogen produced at industrial scale. A comparison was made based on the values of hydrogen content in the synthesis gas produced by reforming of natural gas, with the values of hydrogen content in the synthesis gas obtained from biomass gasification [2-4].

Reforming natural gas is an efficient process of hydrogen production, economical and widely used and provides for short and medium - term energy security and benefits for the environment. Varying the composition of reforming agent (especially air) it is obtain a high concentration of hydrogen in the synthesis gas [5-7].

Hydrogen is considered the "*fuel of the future*" because it is applicable to the technologies which are relating to fuel cells [8, 9].

Thus, one of the advantages of these simulations is to produce hydrogen-rich fuel gas and reducing the percentage of unwanted gas for fuel cell system and environment.

2. Process Description

In a typical process of synthesis gas production four reactors are needed [3]. The proposed simulation model requires five reactors, because the conversion and equilibrium reactions cannot be placed in the same reaction chain and thus cannot be placed in the same reactor. The combustor reactor is separated into a conversion reactor and an equilibrium reactor.

The proposed architecture of the model and the flow sheets of the feedstock, intermediary or final products are shown in figure 1. This conceptual model was realized in HYSIS software [10] according with the existing technologies.

The natural gas is reformed in a conversion reactor (Reformer) when it is combined with steam. Air is added to the second reactor for combustion. The oxygen from the air is consumed in an exothermic combustion reaction while the inert nitrogen passes through the system.

If the content of oxygen in the air is raised, the effect is the increasing of hydrogen content in the synthesis gas and the decreasing the nitrogen content. These effects are desirable because the hydrogen is the final product and nitrogen is a useless inert gas.

The addition of steam in the second reactor serves to the dual purpose of maintaining the reactor temperature and either to ensure that the excess of methane from the natural gas stream is consumed.

In the last two reactors equilibrium reaction takes place and consecutively with the water-gas shift, the temperature of the stream is successively lowered.
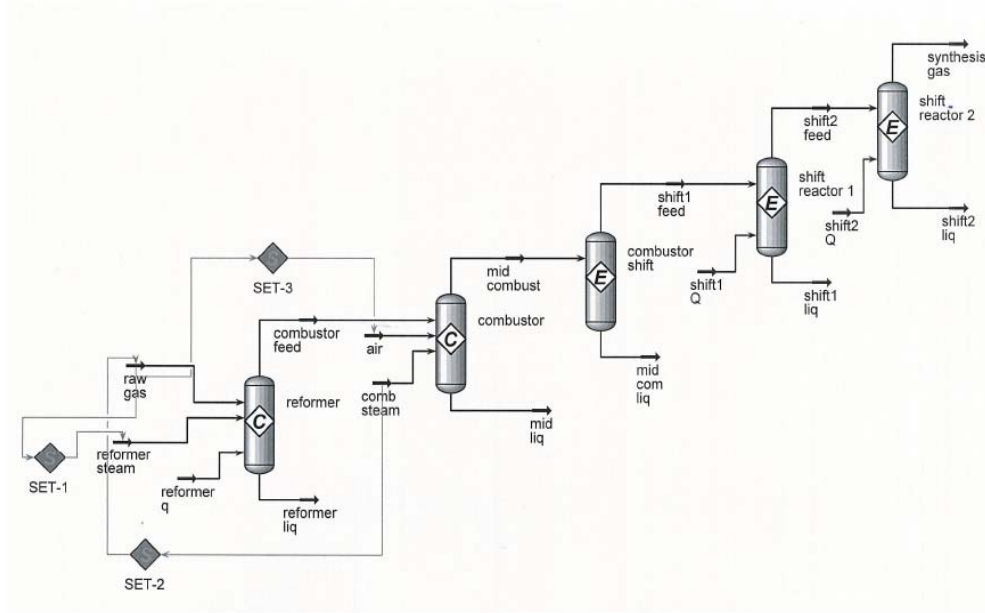

Fig. 1. Simulation stages of the process with the adequate equipments and streams

In the process simulation of the natural gas reforming and burning for hydrogen obtaining in higher concentration, are running two basic stages:

Setup. In this stage will be selected the fluid package (state equation, equilibrium equations), reaction sets and components (reactants and products of the reforming reaction). The reaction component list includes CH_4, H_2O, CO, CO_2, H_2, N_2 and O_2.

Steady State Simulation. The case will be setup in steady state with the following key unit operations:

- **Reformer**. A conversion reactor in which most of the methane is reacted with steam and it is produced hydrogen, carbon monoxide and carbon dioxide.
- **Combustor**. A second conversion reactor which has as a feeds stream the product of the reformer, air stream and combustion steam.

- **Shift Reactors**. A series of equilibrium reactors in which the water gas shift reaction occurs.

3. Simulator Setup

The simulation procedure of the reforming of natural gas is presented as following.

In HYSYS Simulation it is added a new component list which contain methane, water, carbon monoxide, carbon dioxide, hydrogen, nitrogen and oxygen as components. It is define the fluid package by choosing the Peng-Robinson equation of state and equilibrium. On the RXNS window it is add the Global RXN set and by clicking the Simulation Basis Mgr button to choose the fluid package view, the simulation process are running.

In the reforming process of the natural gas are three conversion reactions and one equilibrium reaction.

The reforming reactions, correlated with the proprieties package for the reformer equipment, are:

$$CH_4 + H_2O \rightarrow CO + 3 \cdot H_2 \tag{1}$$
$$CH_4 + 2 \cdot H_2O \rightarrow CO_2 + 4 \cdot H_2 \tag{2}$$
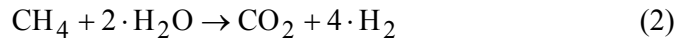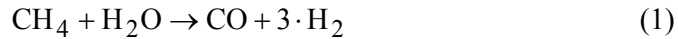
The combustion reaction, correlated with the proprieties package for the combustor equipment is:

$$CH_4 + 2 \cdot O \rightarrow CO_2 + 2 \cdot H_2O \tag{3}$$
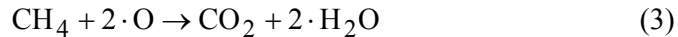
The equilibrium reaction, correlated with the proprieties package for the all three equilibrium reactors, is:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4}$$

In HYSYS the simulation of each reactor must have only one reaction set attached to it. However, a reaction may appear in multiple reaction sets. In this case it must provide 3 reaction sets for all 5 reactors.

In table 1 are presented thermodynamic characteristics of the reaction presented above [1]:

Table 1

Thermodynamic characteristics of the reactions

	Reaction heat at 25 °C [kJ/kgmol]	Equilibrium constants at 800 °C
Reaction (1)	2.1×10^5	0.0313
Reaction (2)	1.6×10^5	0.0166
Reaction (3)	-8×10^5	1.8×10^{17}
Reaction (4)	-4.2×10^4	4.063

4. Steady state simulation

In the first reactor are two feed streams: a natural gas stream and a reformer steam stream. To simulate the operating condition of this reactor it must define the combustion steam stream and the air stream

To identify the pressure of the steam and of the air (with different oxygen composition) it is use the SET operations.

To initialize the process and to can run the simulation, from specialty literature were chosen values for the proprieties of the gaseous phases implied in the reforming process.

In the table 2 are shown the initial condition of the streams, and the data subsequently optimized [3]:

Table 2

The initial conditions

name	Natural gas	Reformer steam	air	Combustion steam
Temperature [C]	24	500	350	400
Pressure [bar]	1	1	1	1
Mass flow [kg/h]	25	3	28.9	20
Comp.mole frac (CH_4)	1.0000	-	-	-
Comp.mole frac (H_2O)	-	1.0000	-	1.0000
Comp.mole frac (CO)	-	-	-	-
Comp.mole frac (CO_2)	-	-	-	-
Comp.mole frac (H_2)	-	-	-	-
Comp.mole frac (N_2)	-	-	0.7900	-
Comp.mole frac (O_2)	-	-	0.2100	-

Reformer: The reformer is a conversion reactor, in which most of the methane is reacted with steam to produce hydrogen, carbon monoxide and carbon dioxide. The outlet gas will also contain the un-reacted methane and excess water vapor from the steam. The conversion of the first reaction which produces carbon monoxide and hydrogen in the Reformer is 80% and the second reaction has a conversion of 70 %. The two reforming reactions are endothermic, so heat must be supplied to the reactor with purpose to maintain the reactor temperature. Thus the temperature of the combustor feed is set at 900°C, so that HYSYS will calculate the required duty.

Combustor: The combustor is the second conversion reactor. The feed streams for the combustor include the reformer product, an air stream and a combustion steam stream. The oxygen in the air is consumed in the combustion of methane. Depending of the content of oxygen in the air, the synthesis gas composition is changing. The concentration of 50% O_2 in the air ensure the highest content of hydrogen in produced synthesis gas.

Shift reactors: The three shift reactors are all equilibrium reactors within the water-gas shift reaction occurs. In the combustor shift reactor, the equilibrium shift reaction takes place and occurs with the reactions in the Combustor. A separate reactor must be used in the simulation because equilibrium and conversions reactions cannot be combined within a reaction set.

Set Operations: The set operations are used to specify the pressure of the steam and air streams. Depending of the set pressure of the natural gas we set the pressures of steam and air. The process takes place at atmospheric pressure.

5. Results

Using air with different content in O_2, the simulation process of the natural gas reforming gives the follow results for the properties of the produced synthesis gas (Table 3).

Table 3
Simulation results for synthesis gas for different O_2 concentration in the fed air

Parameters / *Reform. ag. composition*	T [°C]	P [bar]	F [kg/h]	CH_4 %	H_2O %	CO %	CO_2 %	H_2 %	N_2 %	O_2 %
Air with 21%O_2	400	1	76.9	7.5	2.8	12.04	7.04	57.12	13.48	0.00
Air with 30%O_2	400	1	76.9	5.57	3.08	12.66	7.81	59.19	11.7	0.00
Air with 50%O_2	400	1	76.9	1.55	3.62	13.94	9.41	63.49	7.99	0.00

The parameters followed during the simulation process are: T, ^{o}C – temperature (along the process cycle); P, bar, global pressure of the process; F, Kg/h, the flow rate of the reforming/combustion agent (mixture steam – air with different concentration of O_2); and the volumetric composition (% v/v) of the gases resulting from the reforming/combustion process of natural gas.

If is increased the concentration of O_2 in the air used in the second reactor, combustor reactor, the concentration of hydrogen in synthesis gas product increases. As secondary effect will decreased the concentration of nitrogen, which is an inert gas.

For a concentration of 50% O_2 it was obtained the best results of the simulation process: 61.5% H_2 and 8.5% N_2.

6. Conclusion

If it is increased the content of O_2 in the air used to the second reactor , the combustor, as reforming agent, the content of hydrogen in the produced synthesis gas is higher. Also the content of nitrogen which is an inert gas is decreased (7.99%).

The 50 % O_2 content in the air stream ensure the highest content of hydrogen (63.49%).

The synthesis gas obtained in these conditions has a better value of calorific power, higher than in the cases in which the content of O_2 in the combustion air is smaller.

Concerning the operating parameters for the reforming agent, those can be varied within technological ranges. Thus, the pressure of the process remains constant, while the temperature decreases from 900°C (in the combustor area) to 400°C (the temperature of the produced gas).

The natural gas is almost totally transformed in the process, so in the produced gas we have a small percent of CH_4 untransformed (1.55%), thus it can conclude that the process occurs with acceptable reformatting yield.

R E F E R E N C E S

[1]. *E. Rytter*, Method and reactor for reformation of natural gas and simultaneous production of hydrogen, 2001
[2]. *M.R. Beychok*, Process and environmental technology for producing SNG and liquid fuels, U.S. EPA report EPA-660/2-75-011, 1975
[3]. *A. Hartstein*, Hydrogen production from natural gas, 2003
[4]. *M. Feidt,* Energy efficiency and environment*,* U.P.B. Sci. Bull., Series C, **Vol. 72**, Iss. 1, 39-53, 2010
[5]. *C.E.G. Padro, V. Putsche*, Survey of the economics of hydrogen technologies, 1999
[6]. *A. Milne Thomas, C. Carolyn Elam, J. Robert Evans*, Hydrogen from Biomass – State of the Art and Research Challenges, 2001

[7]. *C. Basagianis, X.E. Verykos*, Production of Hydrogen from Biomass via Steam Reforming of Bio-oil, Proceedings International Hydrogen Energy Congress and Exhibition IHEC 2005, Istanbul

[8]. *S.C. Amendola, M. Binder, M.T. Kelly, P.J. Petillo, S.L. Sharp-Goldman*, Advances in Hydrogen Energy, 69–86, 2002.

[9]. *S. Gagnon*, Hydrogen. Jefferson Lab., 2008

[10]. ASPEN HYSYS Simulation, 2006.