

Design of Process Plant for Producing Hydrogen from Steam Reforming of Natural Gas

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Abstract

Hydrogen has received increased attention as renewable and environmentally friendly option to help today's energy needs. We know well that the usage of hydrogen is enormous. The road leading to an understanding of hydrogen energy potential represents a fascinating tour through scientific discovery and industrial applications. Our goal is mainly to design a plant which is able to produce hydrogen economically. Though several methods of hydrogen production are there, steam reforming is the most economical means of converting fossil fuels to hydrogen at large scale especially from natural gas. We discussed clearly about the operation and design of a plant for producing hydrogen from natural gas with our engineering views. Eritrea has plentiful of natural gas reserves and thus this paper is aiming to introduce the process of producing hydrogen from natural gas.

Keywords: *pressure swing adsorption, reforming, shift conversion, space velocity.*

Introduction

Hydrogen is the most abundant element in the universe making up to 75% of the normal matter by mass and over 90% by number of atoms. Hydrogen can be used as a fuel for powering internal combustion engines or electric motors via hydrogen fuel cell (hydrogen gas vehicles). This has been suggested as one approach to shift economies of the world from the current states of almost complete dependence up on hydrocarbons for energy. Hydrogen can be used in major industries such as food, petrochemicals and explosives. Natural gas is a gas consisting primarily of methane. It is found associated with other fossil fuels, in coal beds, as methane clathrates, and is created by methanogenic organisms in marshes, bogs, and landfills. It is an important fuel source; a major feed stock for fertilizers and potent greenhouse gas. It was proved that there are more natural gas reserves. The following are the currently available processes for hydrogen production

- Electrolysis of water (sea water)
- Auto thermal reforming of hydrocarbons
- Direct conversion of natural gas (decomposition of natural gas)
- Reforming of refinery off gases
- Steam reforming of natural gas

The most economical and highly preferable process with the resources of Eritrea is steam reforming of natural gas. Thus we concentrated more on design of a complete process plant for hydrogen production from steam reforming of natural gas. Petroleum refineries are in need of hydrogen for majority of the processes such as hydrodesulphurization, hydro treating, hydro cracking etc.

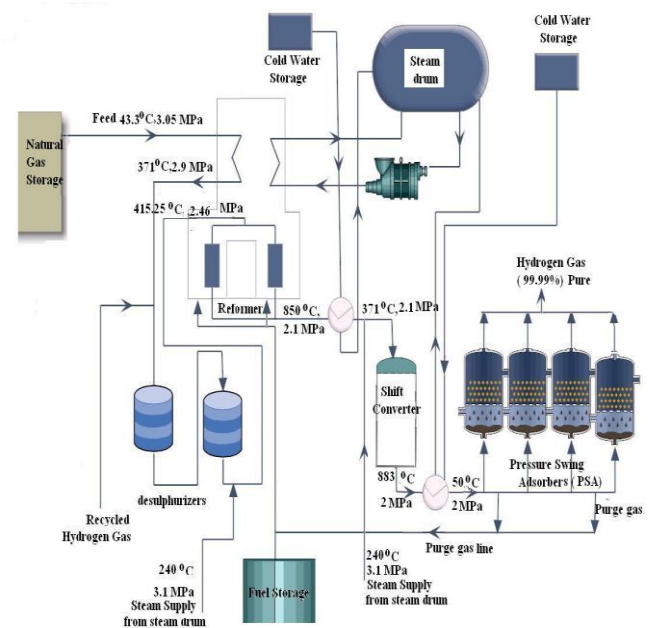


Fig : 1 – Overall Process Plant

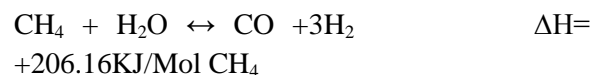
Process details:

STEAM REFORMING: We have chosen economically beneficial steam reforming of natural gas for hydrogen production. Here, steam reacts with methane to yield carbon monoxide and H_2 (g) at high temperature. $[CH_4 + H_2O \rightarrow CO + 3H_2]$ Additional hydrogen can be recovered from the steam by the use of carbon monoxide through the water gas shift reaction, especially with an iron oxide catalyst. $[CO + H_2O \rightarrow CO_2 + H_2]$. The product $CO_2 + H_2$ from the shift converter is sent to the pressure swing adsorption section at very high pressure. The best feed stocks for steam reforming are light, saturated, and low in sulphur; such as natural gas, refinery gas and light naphtha. Steam reforming is the dominant method for hydrogen production. This is usually combined with PSA to purify the hydrogen to greater than 99.99vol%. It has four main steps: Pre-treatment process, Reformer reactor, Shift reactor, Gas purification process.

PRETREATMENT (FEED PURIFICATION)

It is done by hydrogenating the feed, to convert the organic sulphur to hydrogen sulphide which is later adsorbed on zinc oxide.

STEAM REFORMING



It is an endothermic reaction carried out at pressure of 3-25 atm and temperatures of 900°C-1100°C. The external heat needed to drive the reaction is often provided by the combustion of a fraction of the incoming natural gas feed stock (up to 65%) or from burning waste gases, such as purge gas from the hydrogen purification system. Ni or magnesia can be used as catalyst. Alkalized catalyst allows the use of wide range of feed stocks and it reduces coking of catalyst, carbon formation as well as cracking.

SHIFT CONVERSION

The hot gas leaving the reformer tubes is cooled to 650 °F -700°F in waste heat boiler exchanger-

It enters at a shift converter. In this reactor the carbon monoxide is converted into carbon dioxide over an iron and chromium oxide catalyst. To slow down (but not eliminate) over reduction of catalyst into iron, steam: carbon ratio is maintained above 7 and the catalyst can be doped with copper, which acts by accelerating the conversion of carbon monoxide.

PURIFICATION (PSA)

PSA is a technology used to separate some gas species from a mixture of gases under pressure occurring to the species molecular characteristics and affinity for an adsorbent material. It operates near ambient temperature and so differs from cryogenic distillation techniques of gas separation. Special adsorptive materials (example zeolite) can be used as a molecular sieve, preferentially adsorbing the target gas species at high pressure points. The process then swings to low pressure to desorb the adsorbent material.

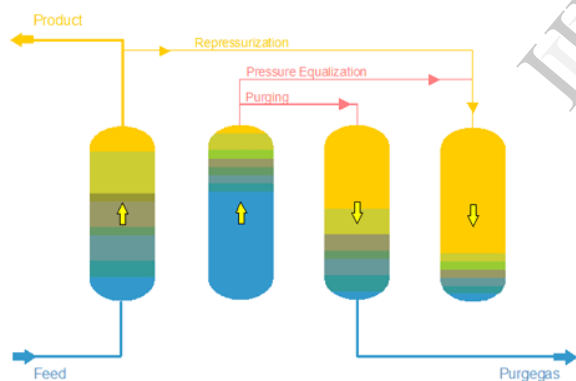


Fig 2 : PS Adsorber

When the gas leaves shift converter, it contains carbon monoxide, carbon dioxide and methane. As the gas is cooled down to ambient temperature, most of the water vapor is removed by condensation. The gas then enters one of the adsorption vessels, where all the carbon compounds; residual water vapor, any nitrogen,

and a small amount of hydrogen are adsorbed. Most of the hydrogen passes through, leaving as a very pure gas. After some time the molecular sieve adsorber becomes saturated, and the feed is switched to another vessel, containing a freshly regenerated molecular sieve. The saturated vessel is depressurized very slowly to a low pressure of approximately 3-5psi. The gas is then swept out using smallest possible quantity of hydrogen product. The vessel is then repressurized by hydrogen, and it is ready to be swung on line for its next period as absorber. Commercial systems have a minimum of three or four vessels to a smooth operation. But in our case using four vessels of PSA above 75% of hydrogen in the raw gas can be recovered. The purge gas flow is intermittent and of vary composition over the cycle. A surge vessel is required to ensure good mixing and even out flow. The purge gas is used as a fuel in the reforming furnace. The cost of the PSA system is relatively insensitive to capacity. This makes PSA more economic at larger capacities, while membrane units tend to be favored for smaller plants. PSA is generally the first choice for steam reforming plants because of its combination of high purity, moderate cost and ease of integration into the hydrogen plant. It is also often used for purification of refinery off gases, where it competes with membrane systems. Turn down is simple to about 30% of flow, where it is limited by the accuracy of low measurements. Systems can be designed to go somewhat lower by adding low range Transmitters. Reliability is very high.

A PSA installation consists of four major plants.

1. Adsorber vessels made from carbon steel and filled with adsorbents.
2. Valve and piping skid, including all valves and instrumentation must be prefabricated and tested in the work shop.

3. Control system, which is normally located in a remote control room and contains the cycle controls with distributed control system.

4. Mixing drum to minimize the composition variation the off gas.

BY-PRODUCT RECOVERY:

Carbon dioxide and steam is the major by products from hydrogen manufacture. Vacuum swing adsorption is preferred for recovery of carbon dioxide from tail gas.

Table 1: Operating Conditions of The Reformer

<i>Parameters</i>	<i>Unit</i>	<i>Amount</i>
Temperature in	°C	371.1
Temperature out	°C	857.22
Pressure in	Pa	24.65×10^5
Pressure out	Pa	21.228×10^5
space velocity [estimated H ₂]	Hr ⁻¹	2627

Table 2: Operating Conditions in the Shift Converter

<i>Temperature</i>	<i>Unit</i>	<i>Amount</i>
T inlet and outlet	°C	371.1 and 627.6
Feed inlet pressure	Pa	20.94×10^5
Reactor outlet pressure	Pa	20.84×10^5
Space velocity[dry gas theoretical]	Hr ⁻¹	1638

ESTIMATION OF THE PLANT CAPACITY

To produce 100 tons per day of hydrogen on 300 working days in a year as a basis, we can show the mass balance of the plant as follows.

Block Diagram of Mass Balance

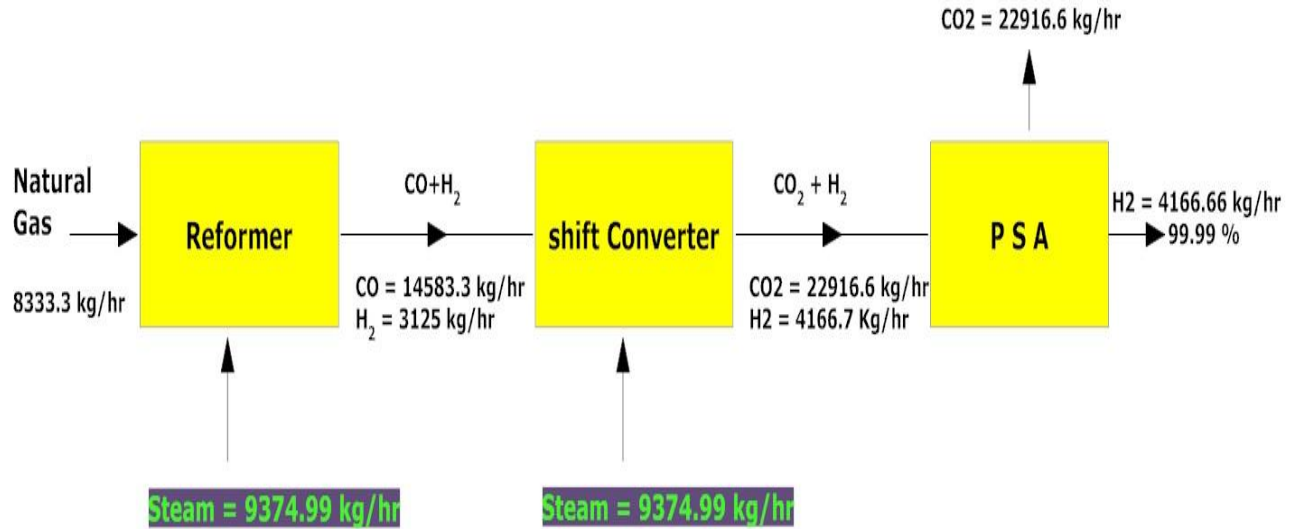
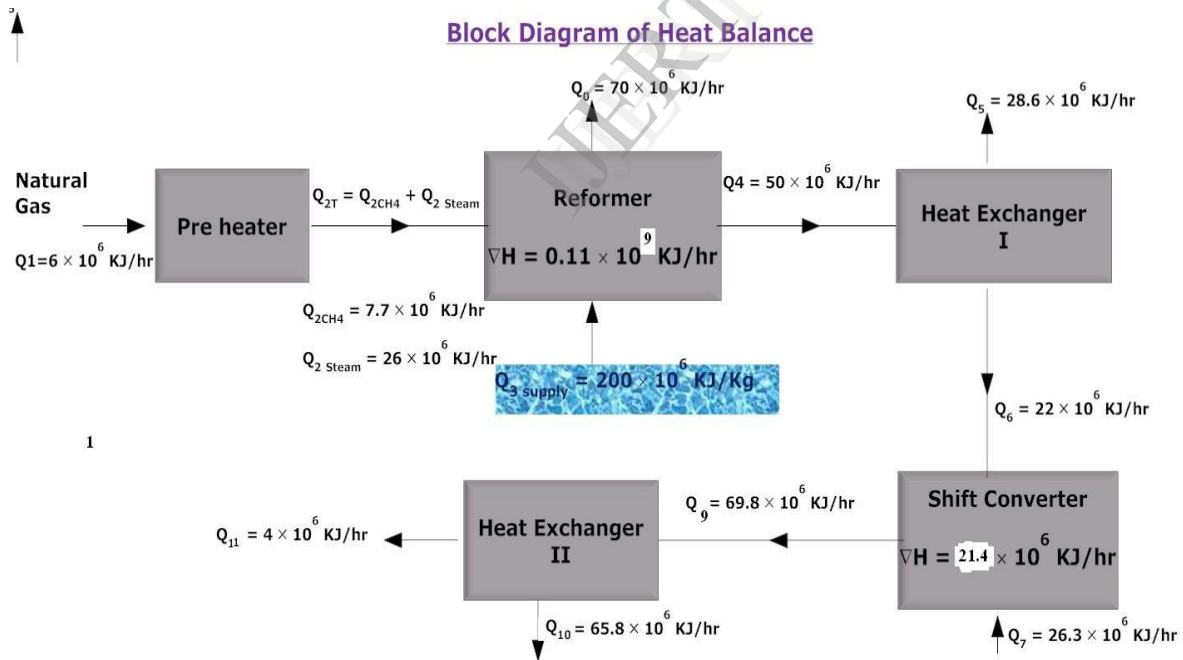


Fig 3:

Block Diagram of Heat Balance



REFORMER REACTORS DESIGN

Estimation volume of packing [catalyst]

Space velocity = Volumetric flow rate / volume of packing

Volumetric flow rate of feed = Mass flow rate of /density = 12207.7 m³/hr

Reasonable Assumptions:

Space velocity in the range of 500-600hr⁻¹

Void fraction = 0.45, Bulk density of a catalyst = 1123.6 Kg/m^3 , Volume of packing = **22.2m³**

Mass of catalyst = $22.2 \times 1123.6 = 24943.92 \text{ kg}$

Calculation volume of reactor:

$$\text{Void fraction}[\epsilon] = [V_R - V_p] / V_R$$

V_R = Volume of the reactor and V_p = Volume of packing

$$0.45 = [V_R - 22.2] / V_R$$

Calculation of the total number of tubes:

$$\text{Total volume of the reactor} = [n \pi D^2 L] / 4$$

n = number of tubes

Type = tubular reactor of diameter = 10cm

and $L = 7 \text{ m}$, $[n = 4 \times V_R / \pi D^2 L]$, $n = 4 \times 40.36 / \pi \times 0.12^2 \times 7$ we get $n = \mathbf{510 \text{ tubes}}$

PRESSURE SWING ADSORPTION (PSA)

DESIGN PROCEDURES

Estimation of volume packing:

Volume of packing = Volume flow rate of hydrogen / Space velocity = $50804.87 / 200 \text{ hr}^{-1} = \mathbf{254.02 \text{ m}^3}$

Estimation of the diameter of column (voids):

Assume hydrogen velocity through the pores = $1 \text{ m/sec} = 3600 \text{ m/hr}$

Total cross sectional area of PSA voids = Flow rate of hydrogen / $V = 50804.87 / 360 = \mathbf{14.11 \text{ m}^2}$

Cross sectional area of voids of single PSA = Total cross sectional area / 4 = $14.11 \text{ m}^2 / 4 = \mathbf{3.58 \text{ m}^2}$

Diameter of voids = $\sqrt{((C.A \times 4) / \pi)} = \sqrt{(3.58 \times 4 / \pi)} = \mathbf{2.1 \text{ m}}$

Estimation of the speed of feed through the voids:

Cross sectional area of void = volume of void / length

Volume of voids = Volume of the reactor – Volume of packing = $40.36 - 22.2 = \mathbf{18.16 \text{ m}^3}$

Cross sectional area of the voids = Volume of voids / length = $18.16 / 7 = \mathbf{2.59 \text{ m}^2}$

Speed of feed through the void = Volume flow rate of feed / Cross sectional area of voids = $12207.7 \text{ m}^3 / \text{hr} / 2.59 \text{ m}^2 = \mathbf{1.3094 \text{ m/sec}}$

Speed of the feed through the empty vessel:

$V = U_0 / \epsilon$ Where V = Speed through the voids and ϵ = void fraction, U_0 = Superficial velocity = $V \times \epsilon = 0.45 \times 1.3094 = \mathbf{0.59 \text{ m/sec}}$

Estimation of length of the PSA:

Length = Volume of packed (voids) / Cross sectional area = $254.02 \text{ m}^3 / 14.11 \text{ m}^2 = \mathbf{17.9 \text{ m}}$

Length of single column = $17.9 / 4 = \mathbf{4.49 \text{ m}}$

GENERAL DESCRIPTION OF PSA

PSA feed conditions

H_2 concentration = 25 %, Pressure = 0.3Mpa – 2.1Mpa, Temperature = $4^\circ \text{C} - 50^\circ \text{C}$

PSA product gas Flow range = $4166.66 \text{ Kg/hr} = 50804.87 \text{ m}^3 / \text{hr}$, Hydrogen concentration = 99.99% or higher, Pressure drop = $< 0.05 \text{ Mpa}$ Temperature = feed temp $\pm 10^\circ \text{C}$

PSA exhaust Pressure = 0.014Mpa for optimal performance.

Adsorber dimensions = 2.5m - 3.5m by 4.49m

Power = standard 220V - 110V / single phase / 50 or 60HZ or modified to suit local requirements.

Noise = less than 880dB at 1m.

Table 3: Design summary

Attributes of equipment design	Desuphurizer	Reformer	Heat exchanger one	Shift converter	Heat exchanger two	PSA
TYPE	Cylindrical tower	Tubular reactor	1 – 1 shell and tube heat exchanger	Cylindrical tower	1 – 1 shell and tube heat exchanger	Cylindrical tower
Diameter	6m	12cm	10cm	6m	10cm	2.1m
Length	12m	7m	2m	21.6m	2m	17.9m
Material of construction	Alloy steel	Alloy steel	Stainless steel	Alloy steel	Stainless steel	Alloy steel
Packed volume	187.48m ³	22.2m ³		335.7m ³		254.02m³
Volume of voids	153.3m ³	18.16m ³		274.72m ³		
Crosssectional area of voids	12.77m ²	2.59m ²		12.7m ²		14.11m²
Speed through the voids	0.0057m/s	1.3094m/s		1.1m/s		
Superficial velocity	0.00256m/s	0.59m/s		0.49m/s		
Number of tubes	-	734	85		463	
Total area	-	-	53.47m ²		290.98m ²	
Volume of reactor	340.8m ³	40.36m ³		610.49m ³		

Table 4: Selection of catalyst

Type	Co-Md on alumina support	Nickel on alumina support	Fe ₂ O ₃ on porous carbon support
Diameter	1.5mm	1.25mm	3.5mm
Length	4mm	6.25mm	5.2mm
Bulk density	660Kg/m ³	1123.6Kg/m ³	995.192Kg/m ³
Amount used	123,736.8Kg	24943.92Kg	334155.6Kg

PLANT OPERATION

It includes loading catalyst into former tubes, measuring tube metal temperature and pinching off catalyst tubes.

Spent Catalyst recovery

A spent reformer catalyst was treated with caustic soda solution of varying concentration at temperature 90-100°C for different times to dissolve aluminum as sodium aluminates. The recovery of aluminum was 97.4%. The recovery of nickel obtained 95-96% in the form of NiSO₄·7H₂O. They are generally supported on porous materials like alumina and silica through precipitation or impregnation process. In many of the cases the metals are in the form of oxides.

Hydrogen storage:

The liquefaction process, involving pressurizing and cooling steps is energy intensive. The liquefied hydrogen has low energy density by volume than gasoline by approximately a factor of four, because of the low density of liquid hydrogen. , hydrogen can be stored as a chemical hydride or in some other hydrogen containing compounds. Hydrogen gas is reacted with some other materials to produce the hydrogen storage material, which can be transported relatively easily. At the point of use the hydrogen storage material can be made to decompose yielding hydrogen gas. As well as the mass and volume density problems associated with molecular hydrogen storage, current barriers to practical storage schemes stem from the high pressure and temperature conditions needed for hydride formation and hydrogen release.

Conclusion

The hydrogen production technology in recent years has achieved great importance in purification system by applying the pressure swing adsorption. This has gained an advantage

in comparison with the older techniques in such a way that it has a simple construction. Attempts has been made to optimize designs in all the required equipments and proper mass and heat balance in the major sections of the plant, so that we can get about 99.99% pure hydrogen.

In Eritrea, hydrogen was being produced in Assab petroleum refining plant in the reforming step which is then supplied for the desulphurization, hydro treating and hydro cracking of the petroleum fractions but in the future as hydrogen application would gain more importance. We prepared a complete operational and design of plant for producing hydrogen by steam reforming of natural gas. We gave a suggestion of our production process is far better than the existing hydrogen production process using reforming and absorption system in the refinery. Recommending a state of the art technique of PSA system is our major goal in hydrogen production process.

Reference

- [1] APL study on process optimization to maximize H₂ production”, Technology Ventures, Chennai and India. By Dr.G.G.Rajan and associates, February 2002
- [2] Catalyst hydrogen carbon reformer with enhanced heat transfer mechanism,US patent No.5, 484,577. By Boswells. R, et al, (January 16, 1996).
- [3] Design and feasibility of a gaseous hydrogen refueling station based on small scale steam reforming of natural gas”. Princeton university senior thesis, Department of Chemical Engineering. By Dennis, E.B., May 1994.

- [4] Reforming of fuel fossil fuel: R and D at the Fraunhofer institute for solar Energy system,” 2000 Fuel cell Seminar Abstracts,October 30- November 2,2000,Portland,OR,pp.256-259. By Henizel, A.B. Vogel, T. Rampe, A. Haist, and P. Hubner (2000).
- [5] By product hydrogen sources and markets,” proceeding of the 5th National Hydrogen Association Meeting, March 23-25, 1994, Washington,DC,pp. 6-59 to6-80. By Heydorn, B. (1994).
- [6] Thermally enhanced compact reformer,”US Patent No.6, 183,703By HSU, M. and E.D.Hoag, (February 6, 2001).
- [7] Kvaerner based technologies for environmentally friendly energy and hydrogen production,” Proceeding of the 12th world Hydrogen Energy Conference, Buenos Aires,Argentina, June 21-26,1998,pp.637-645 By Lynum, S., R. Hildrum, K.Hox, and J.Hugdahl, (1998).
- [8] Refinery hydrogen management.By Towler, G.P., Mann, R.J.Serriere, A.J.L., Gabaude, C.M.D., (1996)