International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:8, No:2, 2014

Simulation of the Performance of the Reforming of Methane in a Primary Reformer

A. Alkattib, M. Boumaza

Abstract**—**Steam reforming is industrially important as it is incorporated in several major chemical processes including the production of ammonia, methanol, hydrogen and ox alcohols. Due to the strongly endothermic nature of the process, a large amount of heat is supplied by fuel burning (commonly natural gas) in the furnace chamber. Reaction conversions, tube catalyst life, energy consumption and CO_2 emission represent the principal factors affecting the performance of this unit and are directly influenced by the high operating temperatures and pressures.

This study presents a simulation of the performance of the reforming of methane in a primary reformer, through a developed empirical relation which enables to investigate the effects of operating parameters such as the pressure, temperature, steam to carbon ratio on the production of hydrogen, as well as the fraction of non converted methane.

It appears from this analysis that the exit temperature T_e, the operating pressure as well the steam to carbon ratio has an important effect on the reforming of methane.

Keywords**—**Reforming, methane, performance, hydrogen, parameters.

I. Introduction

THE steam reformer is very important process equipment, used in the production of ammonia, via the production of hydrogen. The reformer is a major consumer of energy [1], [2], [3]) and the efficiency of the reformer section has a major bearing on the overall energy consumption of the plant. However due to the large amount of energy consumption by this unit on one hand, and due to the environment protection (reduction of CO_2 emission) on the other hand, most of the actual research is oriented in finding ways of reducing the energy consumption in the primary reformer, through an increase of methane reaction rates. The optimization of these parameters requires a finite and precise investigation of the catalyst tube including process and conversion parameters [4], [5].

The present paper presents various profiles of the percentage of hydrogen and unconverted methane with respect several to process parameters such as the temperatures, operating pressures, and steam flow rates, during the steam reforming of methane.

II. Primary Reformer Description

The primary reformer is basically a furnace containing burners and tubes packed with supported nickel catalyst.

A.Alkhatteb and M.Boumaza are with King Saud University, Dept of Chemical Engineering, Riyadh, Saudi Arabia, (Phone: + 96614679151, fax + 96614678770, e-mail: akhatteb@gccsg.org, muradbza@gmail.com).

Ammonia is synthesized by chemically combining hydrogen and nitrogen under pressure, in the presence of a catalyst. The Hydrogen requirement is met by, catalytically reacting a mixture of steam and hydrocarbons, usually methane at an elevated temperature to form a mixture of Hydrogen and oxides of Carbon.

Gas leaving the primary reformer contains a small fraction of methane as well as Hydrogen H_2,Nitrogen N_2, carbon monoxide CO, carbon dioxide CO_2, water vapor H_2O and inert gases (argon). This gas mixture flows to the secondary reformer reaction (A) is endothermic and proceeds at high temperatures (800 to 900°C). A high ratio of steam to hydrocarbon (Z) and a low pressure generally produce higher rate of hydrogen and carbon monoxide [6], [7].

III. Primary Reformer Modeling

A. Introduction

There exits two distinct sections in the primary reformer, the radiant zone and the convective zone. Therefore the modeling must consider both sections. The radiant zone represents the section where methane is converted to carbon monoxide and hydrogen inside the catalyst tube. The convective zone is used to collect the heat from the exhaust gas leaving the radiant zone.

In order to investigate the effects of operating parameters on the unconverted methane in the reformer, it is necessary to simulate the catalytic tube primary reformer [9]-[11]. The simulation is based on energy, mass and momentum balances along the tube.

In order to investigate the effects of operating parameters on the production of hydrogen, it is necessary to simulate the catalytic tube primary reformer. The simulation is based on mass, energy and momentum balances through the tube..

The simulation is based on the following assumptions;

- It is assumed that all the tubes are similar in the primary reformer, and therefore one tube can represent all the tubes...
- It is supposed that physical properties of the gas remain constant in the radial direction
- The fluid is considered to be a mixture of chemical species. And the composition changes as the reaction proceeds.

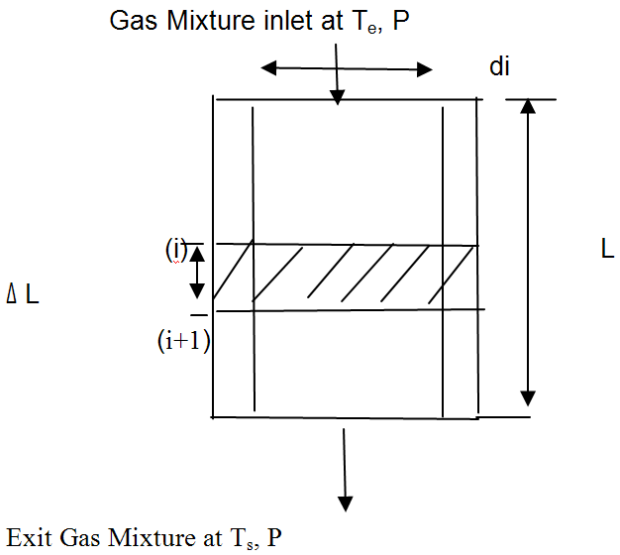


Fig. 1 Primary reformer catalytic tube

B. Energy Balance

The heat of reaction at temperature T is calculated as follows [5]:

$$\Delta H_T = \Delta H^0_{298} + \sum_j \left(\int_{298}^{T} C_{Pj}.dT \right)_{prods} - \sum_i \left(\int_{298}^{T} C_{Pj}.dT \right)_{reacts} \quad (1)$$

As the mixture undergoes a chemical reaction, then the enthalpy of component 'i' is given by [12]:

$$\hat{h}_{fi} = \Delta \hat{h}^0_{fi} + \int_{T0}^{T} C_{Pi}.dT \quad (2)$$

$\hat{h}^0_{fi}$: Standard heat of formation of component 'I'.

Standard heat of formations as well as specific heats of different fluids is available in the literature [15].

C. Mass Balance

Applying principles of mass conservation [8]

$$\frac{dm_{i,tot}}{dt} = \rho_1.v_1.S_1 - \rho_2.v_2.S_2 + m_{i,m} + R_{i,tot} \quad (3)$$

$R_{i,tot}$= Rate of reaction of 'I'

$m_{i,tot}$: Total mass of component 'i' within the reformer boundaries.

ρ_i : Density of component 'i'

Equation (3) can be arranged as follows;

$$\frac{dm_{i,tot}}{dt} = -\Delta m_i + m_{i,m} + R_{i,tot} \quad (4)$$

D. Equilibrium Constants, K.

The equilibrium constant is defined as follows [13], [14]:

$$K(T) = \pi_i \, a_{i,eq}^{vi} \quad (5)$$

v_i : stoechiometric coefficient

a_i : component activity coefficient.

Thus for the present reactions, the equilibrium constants can be determined as follows;

$$K_{PCH_4} = \frac{P_{CO}.(P_{H2})^3}{p_{CH4}.p_{H2O}} \quad (6)$$

The constant K_{PCH4} depends on temperatures, and can be calculated through the following relations [16], [17]:

$$K_{PCH_4} = 1.198\,10^{13} \exp\left(\frac{-26830}{T_S}\right) \quad (7)$$

An empirical correlation has been developed based on the least method square method to determine the effects of operating parameters such as the temperature, the pressure and the steam to carbon ratio on the percentage of unconverted methane (XCH_4) in the primary reformer reaction.

$$\Delta \dot{m}_{CH4} = (-r_{CH4}.A.\rho_{cat}).\Delta Z \quad (8)$$

$$XCH4 = M_{iCH4} - \Delta m_{CH4}$$

IV. Results and Discussions

This paper has investigated the effect of process parameters such steam to carbon ratio (Z), exit gas pressure (P), exit and inlet gas temperatures (Ts, Te) (Z) on the percentage of unconverted methane (XCH_4), as well as the production of hydrogen in a primary reformer process.

A. Effect of Pressures, P on Hydrogen Production, H_2

Figs. 2 (a)-(c) show the effect of exit gas pressures for various exit gas temperatures T_s and fixed inlet gas temperature (T_e=520°C) as well as 3 different values of Z, respectively equal to values 2, 2.5, 3.6 on the production of Hydrogen. It can be seen that the production of Hydrogen varies inversely proportional with the pressure for all the cases studied, while the amount of Hydrogen produced varies proportionally with the exit temperature and the steam to carbon ration (Z).

B. Effect of (Z) on X_{CH4}.

Figs. 3 (a)-(c) illustrate the effect of steam to carbon ratio (Z) for three different exit gas pressures (27, 33 and 39 Bars) and different exit temperatures T_s for an inlet gas temperature T_e (520°C)on the quantity of the unconverted fraction of methane, X_{CH4}.

These figures show that X_{CH4} varies inversely proportional with Z for any value of P, and also decreases as P increases, while it is proportional to T_s. The shape of this variation can be best represented by an exponential function

$$(XCH4 = aZ^b).$$

C. Effect of Z on H_2

Figs. 4 (a)-(c) show the effect of steam to carbon ratio (Z) for three different exit gas pressures (27, 33 and 39 Bars) and different exit temperatures T_s for an inlet gas temperature T_e(520°C) on the production of hydrogen.

It can be seen from these figures that the amount of H_2 increases by 8.2% for every increase in the steam/carbon ratio (Z) equal to 0.5 at low pressure (27 bar) and high exit Temperature (T_s). This amount is further increased to 12.4% for the same increase in Z (0.5) at low exit Temperature (T_s), for the same pressure (27 Bars).

At higher pressures and higher T_s, the amount of H_2 increases by 9.4% for an increase of 0.5 in S/C ratio. On the other hand, at high pressure and low T_s, the amount of H_2 increases by 12.7% for every 0.5 increase in S/C ratio. This can leads us that increasing Steam/carbon ration at high T_s does not affect the production of H_2significantly. However, the production of H_2 increase significantly as the exit temperature (T_S) rises from 740 to 900°C at low pressure and high Z.

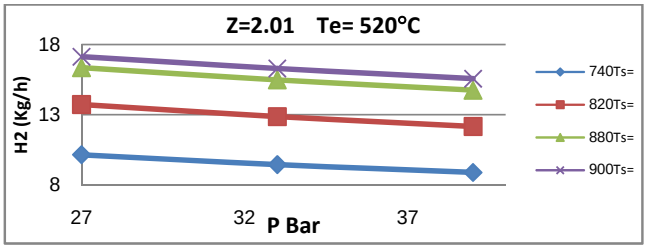
V. Conclusions

This paper enables to determine the effect of the operating parameters on the percentage of unconverted methane as well as the production of hydrogen in an ammonia primary reformer. Thus the present analysis shows that:

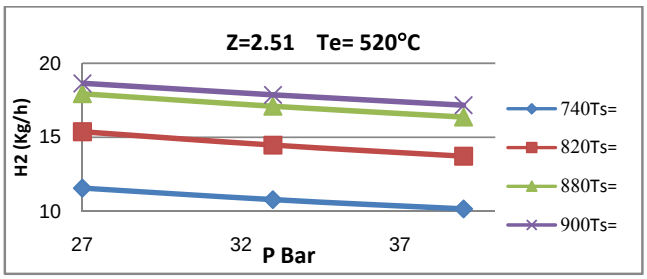
- Steam to carbon ratio (Z) is an important factor in the operation of the ammonia primary reformer and on the production of Hydrogen. A higher value of Z will produce higher production rate of Hydrogen, reduces the quantity of methane non converted as well as the formation of carbon which can reduce the efficiency of the catalyst [14], [15].
- Higher exit temperature T_s, reduces the amount of unconverted methane; however, it is recommended to limit this temperature to 900°C in order to avoid the melting of the catalyst, reduce the energy load as well as CO_2 emission.
- The inlet gas mixture temperature T_e does not have a direct impact of the amount of unconverted methane, but affects directly the energy consumed by the reformer.
- The operating pressure has impact on the production of hydrogen at high exit gas temperatures.

Nomenclature

C_{pi}:	Specific heat of component 'i' (J/mole.K)
H:	Specific enthalpy (J/kg)
m:	Mass flow rate (Kg/sec).
n:	molar flow rate (mole/sec)
Ri:	rate of reaction (moles/moles)
v:	Fluid velocity (m/sec)
P:	Fluid pressure (Bar)
P_i:	Partial gas pressure (Bar)
x:	Mole fraction
T_e:	Inlet gas temperature (°C)
T_s:	Outlet gas temperature (°C)
X_{CH4}:	Percentage of unconverted methane



(a)



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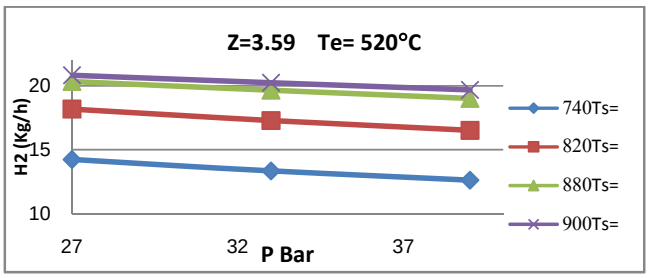
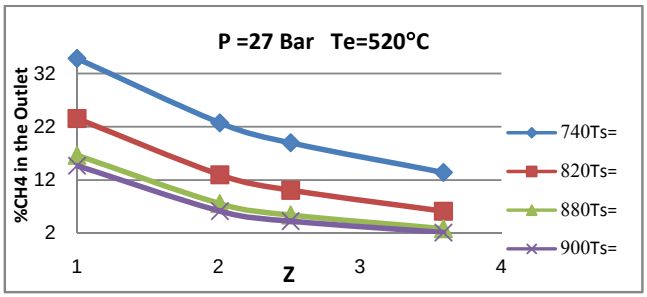
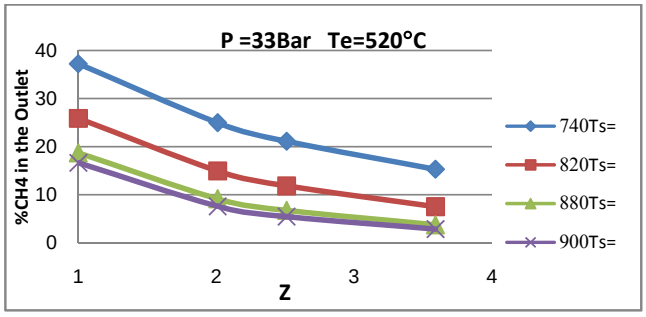


(c)

Fig. 2 Effect of the pressure on the production of Hydrogen for various exit Temperature and Z (a) Z= 2.1, (b) Z=2.51, (c) Z=3.59



(a)



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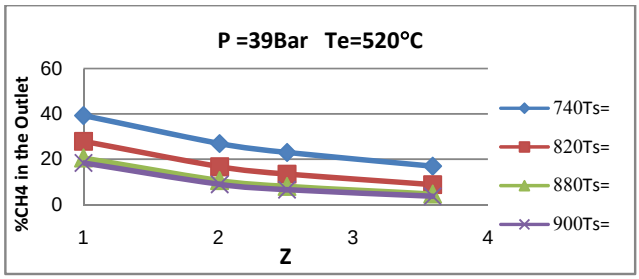
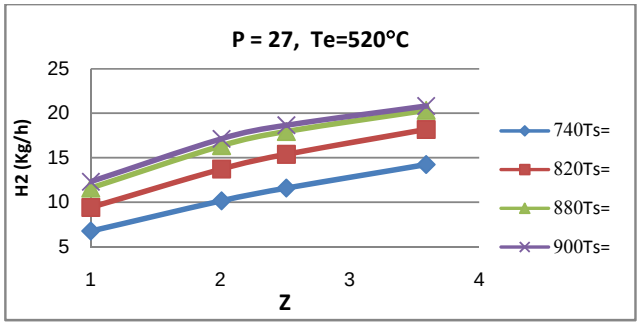
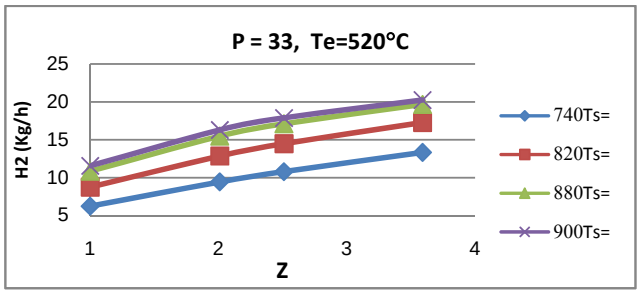


(c)

Fig. 3 Effect of steam to carbon ratio (Z) on the fraction of unconverted methane (XCH4) for various exit temperatures, Ts and pressure (P) (a) P= 27 bar, (b) P=33 bar, (c) P=39 bar



(a)



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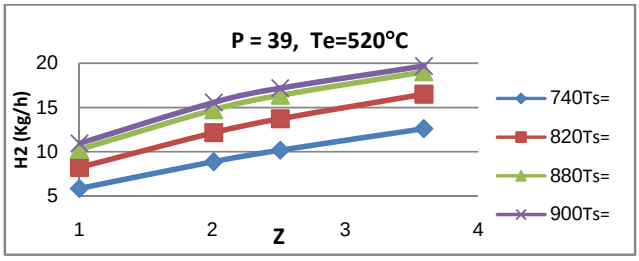

(c)

Fig. 4 Effect of steam to carbon ratio (Z) on the production of hydrogen (H_2) for various exit temperatures, Ts and pressure (P) (a) P= 27 bar, (b) P=33 bar, (c) P=39 bar

Acknowledgments

The author is very grateful and thankful to research centre of the college of engineering, King Saud University, Riyadh, Kingdom of Saudi Arabia for their help and which have enabled to conduct this present research.

References

[1] Appl. M.: *Ammonia Principles and Industrial Practice, 1999, Wiley-VCH Ed.*
[2] Dunn A.J, Yustos. J, Mujtaba. I. M: *Pap – 6th WCCE, Melbourne,2001*
[3] Ravi. K, Joshi. Y. K, Dhingra. S. C, Guha. B. K: *Chem.Eng.Tech 1989, 12, 358-364.*
[4] Singh. C. P, Saraf. D.N; *Ind. Eng. Chem, 1979, 12, 1-7.*
[5] Freemont *Ammonia Plant,*
[6] Numaguchi. T, Shoji. K, Yoshida. S: *Applied catalyst, 1995, 133, 241-262.*
[7] Heinzel. A, Vogel. B, Hubner. P*: J of Power Sources, **2002**, 105, 202-207.*
[8] Rostrup-Nielsen J.R*: Catalysis today, 2002, 71, 243-247.*
[9] J. M. Smith, H.C Van Ness, M. M. Abott: Introduction to Chemical Engineering Thermodynamics, 7th edition, McGraw-Hill, 2005.
[10] Levent. M, Gunn. D. J, ElBousiffi M.A*: I.J of Hydrogen Energy 2003, 28, 945-0959.*
[11] Krisha. G, Sievaminathan. J, S. Bangen: Reminant Life Assessment and Microstructural Studies on Service Exposed Primary Reformer Tubes of a Catalytic Converter of an Ammonia Plant, High Temperature Materials and Processing, Vol 31, pp759-767, 2012.
[12] Klaus. N.: Ammonia Plant Capacity Increased by Autothermal Reforming and Dual Pressure Synthesis, 35th Int Conference on Ammonia of Ammonia, Chicago, USA, Sept 2012.
[13] Lee. J. S., Seo. J., Kim, H. Y., Park. S., Lee. Y.; Effects of Geometries on Flow Characteristics and Reforming Performance of a Steam Methane Reformer, *Internal Conference on Renewable Energies and Quality Power, Bilbao*, Spain, March 2013.
[14] Labanowski. J.: Evaluation of Reformer Tubes Degradation after Long Term Operation, *Journal of Achievement in Materials and Manufacturing Engineering, Vol 34, 2010*
[15] M.de Jong, A. H. M. Reinders , J. B. Kok, Optimizing a Steam Methane Reformer for Hydrogen Production, *Int J Hydrogen Energy*, 2009, Vol 34, pp285-92.
[16] G Brun, J. Smyed: Numerical Modeling of Radiative Heat Transfer in an Internal Indirect Reforming Type SOFC, *j Power Sources 2008, Vol 181, pp 8-16.*
[17] Nist Chemistry Web Book,, http// *webbook.mist.gov/ chemistry fluid, Last Access dec 2012.*