

Investigation of Inert Gas Injection in Steam Reforming of Methane: Energy

Amjad Riaz, Ali Farsi, Gholamreza Zahedi, Zainuddin Abdul Manan

Abstract—Synthesis gas manufacturing by steam reforming of hydrocarbons is an important industrial process. High endothermic nature of the process makes it one of the most cost and heat intensive processes. In the present work, composite effect of different inert gases on synthesis gas yield, feed gas conversion and temperature distribution along the reactor length has been studied using a heterogeneous model. Mathematical model was developed as a first stage and validated against the existing process models. With the addition of inert gases, a higher yield of synthesis gas is observed. Simultaneously the reactor outlet temperature drops to as low as 810 K. It was found that Xenon gives the highest yield and conversion while Helium gives the lowest temperature. Using Xenon inert gas 20 percent reduction in outlet temperature was observed compared to traditional case.

Keywords—Energy savings, Inert gas, Methane, Modeling, Steam reforming

I. INTRODUCTION

ALTHOUGH partial oxidation, auto-thermal reforming, CO_2 reforming or a combination of these is in practice, but by far the most widely used process for generation of synthesis gas is steam reforming of natural gas [1]; commonly referred to as Methane Steam Reforming (MSR). Over the years, improvements in the practical efficiencies have been achieved by a combination of developments in engineering and catalyst. It has been estimated that in most applications of synthesis gas such as methanol, Fischer-Tropsch synthesis and ammonia about 60-70% [2, 3] of the overall process cost is associated with synthesis gas generation. The synthesis gas routes are highly efficient, but capital intensive because they involve exchange of energy in the reformers and heat recovery units. Reduction in synthesis gas generation costs can have a large and direct influence on the overall economics of this process.

Steam reforming has been known since 1924 [4]. Highly

Amjad Riaz is with Process Systems Engineering Centre (PROSPECT), Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, Skudai 81310, Johor Bahru (JB), Malaysia, on leave from Department of Chemical Engineering, COMSATS Institute of Information Technology, Lahore, Pakistan.

Ali Farsi is with Department of Chemical Engineering, Faculty of Engineering, ShahidBahonar University of Kerman, Jomhori Blvd, Kerman, Iran.

Gholamreza Zahedi and is Process Systems Engineering Centre (PROSPECT), Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, Skudai 81310, Johor Bahru (JB), Malaysia (e-mail: grzahedi@cheme.utm.my).

Zainuddin Abdul Manan is with Process Systems Engineering Centre (PROSPECT), Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, Skudai 81310, Johor Bahru (JB), Malaysia.

endothermic nature of the process requires large amount of heat input, usually provided by the combustion furnaces. The thermodynamics of the reactions demand high exit temperature resulting in thermal cracking, etc. and coke destroys the nickel based catalyst. Literature suggests a high steam to carbon ratio in order to suppress carbon formation and increase methane conversion. Extra steam accompanied by poor heat transfer increases energy requirement and makes MSR one of the most cost and energy intensive industrial processes [1, 5-8].

In a typical reformer natural gas is reacted with steam over $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst to produce synthesis gas by the two endothermic steam reforming reactions of methane and the parallel exothermic water gas shift reaction, respectively [9]:



As evident, the reaction is highly endothermic and is carried out in a natural gas fired multi-tubular furnace reactor at temperature of 900 °C and pressures of 15-30 atm. Steam to carbon ratio is kept in excess to the stoichiometric and equilibrium requirement in order to prevent carbon formation on the catalyst, good conversion and CO reforming to CO_2 . About 90 – 92 % of methane (CH_4) is converted to carbon dioxide (CO_2), carbon monoxide (CO), hydrogen (H_2), and water (H_2O) [2, 10].

Synthesis gas is therefore cooled by feed of the reformer and the high heat content is used to generate high-pressure steam. In this way, overall thermal efficiency of the fired duty approaches 90–97% as only 50% of the fired energy is directly transferred to reactor tubes [11]. Poor heat transfer to process makes MSR a cost and energy intensive process. Fuel firing, heating, cooling and excess steam contribute to large heat transfer duties and large investments [5, 10].

Usually, inert gas of nitrogen is used as carrier gas or standard criterion while its effect on the reaction process was seldom studied. Similar is the case with other noble/inert gases. Luo et al [12] studied the effect of Nitrogen on activity of $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Radovan et al [13] found an increase in equilibrium conversion in the presence of inert gases but emphasized on their optimal concentration as the reaction rate may be affected at larger flows. Mikhail et al [14] noted pronounced effect of inert gases on carbon selectivity in methane oxidation reaction. Lee et al [15] investigated the characteristic effect of inert gas addition on gas phase mass

transfer in molten carbonate fuel cells. The studies of this nature have been termed as Diluent gas effect and Inert gas step addition but their application to steam reforming is yet to be seen. The major objective of this study was to study the effects of injecting inert gases on reaction conversion, yield and savings in terms of energy. The present study may be regarded as novel as there was not any evidence of any research work done with perspective of energy benefit of using inert gases.

II. REACTOR MODELING

MSRs are modeled either as a whole or by choosing in between furnace side and process side. Model was developed based on the following assumptions:

- 1-One dimensional plug flow is considered.
- 2-Axial dispersion of heat is neglected compared to convection term.
- 3-There are no radial concentration and temperature gradients.

The model of Xu and Froment[16] was used in the present study.

$$r_1 = \frac{k_1}{P_{H_2}^{2.5}} \left[P_{CH_4} \cdot P_{H_2O} - \frac{P_{H_2}^3 \cdot P_{CO}}{K_1} \right] / (DEN)^2 \quad (4)$$

$$r_2 = \frac{k_2}{P_{H_2}} \left[P_{CO} \cdot P_{H_2O} - \frac{P_{H_2} \cdot P_{CO_2}}{K_2} \right] / (DEN)^2 \quad (5)$$

$$r_3 = \frac{k_3}{P_{H_2}^{3.5}} \left[P_{CH_4} \cdot P_{H_2O}^2 - \frac{P_{H_2}^4 \cdot P_{CO_2}}{K_3} \right] / (DEN)^2 \quad (6)$$

Where,

$$DEN = 1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{CH_4} \cdot P_{CH_4} + K_{H_2O} \cdot \frac{P_{H_2O}}{P_{H_2}} \quad (7)$$

Here, r_1 , r_2 and r_3 are reaction rates; P_i is partial pressure of component i ; k_1 , k_2 , and k_3 are the rate coefficient of reaction; K_1 , K_2 and K_3 equilibrium constant of reaction respectively. K_{CH_4} , K_{CO} , K_{H_2} are the adsorption constants and K_{H_2O} is the dissociative adsorption equilibrium constant.

The mass and energy balance for fluid phase are expressed by:

$$\varepsilon_b c_t \frac{\partial y_i}{\partial t} = -c_t \frac{\partial (u y_i)}{\partial z} - K_{gi} a_V c_t (y_i - y_{is}) \quad (8)$$

$$\varepsilon_b c_p c_t \frac{\partial T}{\partial t} = -c_p c_t \frac{\partial T}{\partial z} - h a_V (T - T_s) + \frac{4\pi U_{tube}}{D_{in}} (T_{tube} - T) \quad (9)$$

The following two conservations equations are written for the solid phase:

$$\varepsilon_s c_t (1 - \varepsilon_b) \frac{\partial y_{is}}{\partial t} = K_{gi} a_V c_t (y_i - y_{is}) - a r_i \eta_i \rho_b \quad (10)$$

$$c_p s \rho_b \frac{\partial T_s}{\partial t} = h a_V (T - T_s) + \sum_{i=1}^3 (-\Delta H_r) a r_i \eta_i \rho_b \quad (11)$$

Where y_{is} and T_s are the mole fraction and temperature on

the catalyst surface. y_i and T are the gas phase mole fraction and temperature. ε_b is bed void fraction, ε_s is catalyst porosity, u is superficial velocity, ρ_b density of the catalyst in bed, η_i is effectiveness factor, $c_p s$ is heat capacity of catalyst, h is inside film coefficient, ΔH_r is heat of reaction, U_{tube} is overall heat transfer coefficient and K_{gi} is mass transfer coefficient between gas and solid phase for component i .

The boundary conditions are as follows:

$$\text{At } z = 0 ; y_i = y_{i0} \text{ and } T = T_0 \quad (12)$$

The initial conditions are:

$$\text{At } t = 0; y_i = y_i^s, y_{is} = y_{is}^s, T = T^s, T_s = T_s^s, a=1 \quad (13)$$

Where y_i^s , y_{is}^s are steady state mole fractions, and T_s , T_s^s are temperature of fluid phase and solid phase, respectively.

To obtain the effectiveness factor the mass and energy balance inside the equivalent particle are expressed by:

$$\eta_i = \frac{\int_0^V r_i(p_{jr}, T_r) \frac{dV}{V}}{r_{is}}; \quad i = 1, 2, 3; \quad j = CH_4, CO, CO_2, H_2, H_2O \quad (14)$$

$$D_e c_t \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dx_{ir}}{dr} \right) = -r_{ir} \rho_b \quad (15)$$

$$k_e \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dT_r}{dr} \right) = -\sum_{i=1}^3 (-\Delta H_r) r_{ir} \rho_b \quad (16)$$

The boundary conditions are as follows:

$$r = 0 ; \frac{dx_{ir}}{dr} = 0, \frac{dT_r}{dr} = 0 \quad (17)$$

$$r = R_p ; D_e \frac{dx_{ir}}{dr} = K_{gi} (y_i - x_{ir}), k_e \frac{dT_r}{dr} = h(T - T_r) \quad (18)$$

Catalyst deactivation model for the commercial MSR (R67-7H) was adopted from[17].

$$\frac{d\left(\frac{D}{D_0}\right)}{dt} = -k_{Act} \exp(-E_{Act}/RT) \left(\frac{D}{D_0}\right)^n \quad (19)$$

Where n , D_0 , E_{Act} and k_{Act} are sintering order, initial dispersion, activation energy and deactivation constant of the catalyst; and their numerical calculated values are 0.82, 0.78 ($\frac{j}{mol}$), 0.01 ($\frac{1}{h}$) and 2 respectively.

III. RESULTS AND DISCUSSIONS

The set of differential (ordinary and partial) and algebraic equations were solved in Matlab software. As stated earlier, the study of such a scope has not been performed and the results obtained may serve as a basis for future research. Effect of six inert gases namely Helium, Neon, Argon, Krypton, Xenon and Nitrogen; have been studied on reaction yield, concentration, conversion and temperature at the reactor outlet. Input parametric values were as tabulated in Table 1.

TABLE I
 INPUT PARAMETRIC VALUES

Flow rate (F)	100 (cm ³ /min)
Reactor diameter (d)	6 x 10 ⁻³ (m)
Reactor Length	15 x 10 ⁻² (m)
Superficial Velocity (u)	5.895 x 10 ⁻² (m/s)
Porosity (ε)	0.1
Total Pressure (P _t)	1.0 atm
% Inert Gas	30

Each of the six inert gases mentioned above were injected with feed and outlet concentration of CO and H₂ were recorded. A continuous increase in the concentration of H₂ (in particular) and CO along the reactor length is noteworthy. The obtained results were used to calculate percentage yield and conversion of feed gas components (CH₄ and H₂O). The yield (Fig. 1) and conversion (Fig. 2) have shown an upward trend. The two figures are suggestive of the fact that by introducing noticeable amount of an inert gas, yield and conversion may be enhanced by some magnitude.

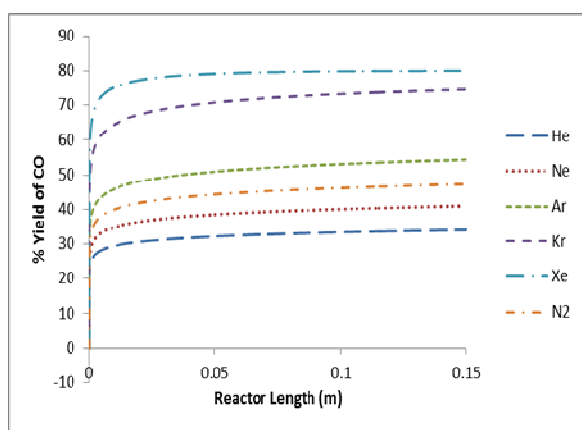
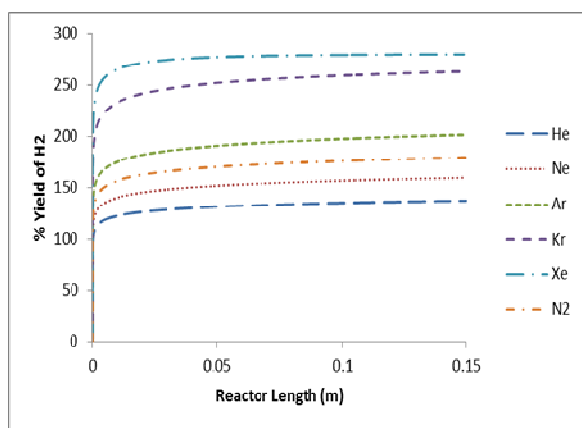


Fig. 1 Percent yield vs. Reactor length

Such results may be reasoned by 1) increased rate of adsorption/desorption due to collisions with inert gases, 2) mobility changes of reactant and product gases due to inert

gases adsorption on solid surface, or 3) changes in efficiency of heat removal from catalyst surface as detailed by S. Ahmed and M. H. Black [18]. Xenon (Xe) gives the highest increase in synthesis gas yield and feed gas conversion while helium (He) gives the lowest. Increase in conversion would mean lower recycle ratio and so noticeable energy quantities may be saved using this technique.

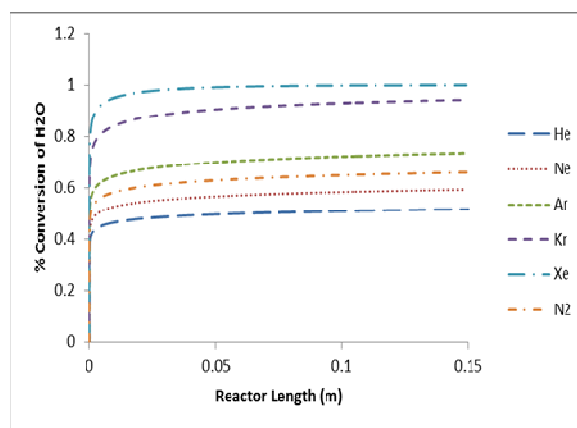
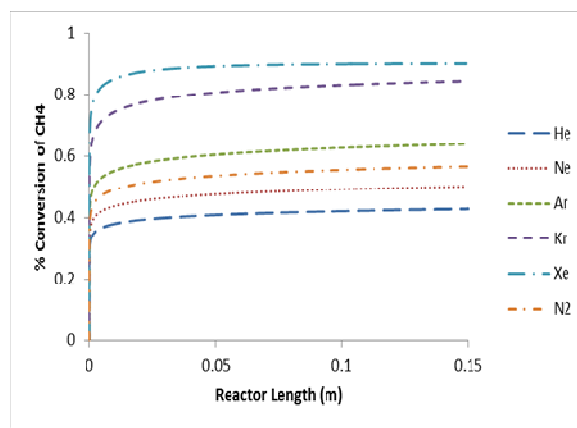


Fig. 2 Percent conversion vs. reactor length

A lower value of operating temperature has been observed during the study (Fig. 3). The outlet temperature has lowered to as low as ~810 K. In case of temperature the lower outlet

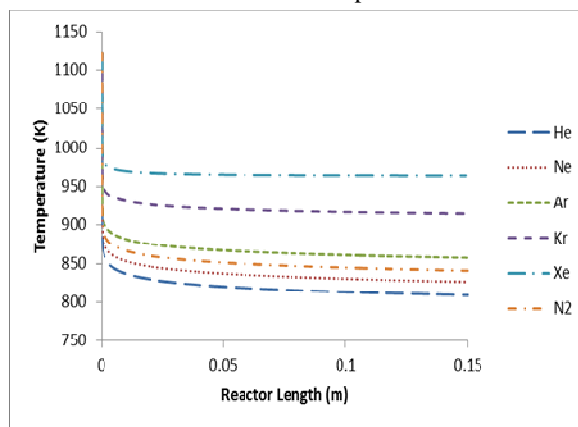


Fig. 3 Temperature Profile

value is attained by injecting helium (He) while for Xe the value stays roughly at 970 K. The lowered temperature suggests lesser heat requirement which currently is the major cost of production. In the normal circumstances, the outlet temperature may range from 1100 to 1200 K depending upon the type of feedstock and the end use for which synthesis gas is being produced. But if the temperature at the reactor outlet is reduced to 800-900 K (at least 20 % lower), one may find relief in terms of investments on high energy needs of the process.

The study of this stature was not performed earlier, so we need to go more into the details of the process and try finding the reasons for this energy saving technique. Fig. 4 gives a comparative of the above shown results and once again it is evident that higher percent conversion and yield can be achieved while simultaneously requiring lower temperature with the injection of inert gases. The results may serve as a breakthrough to the future energy demands.

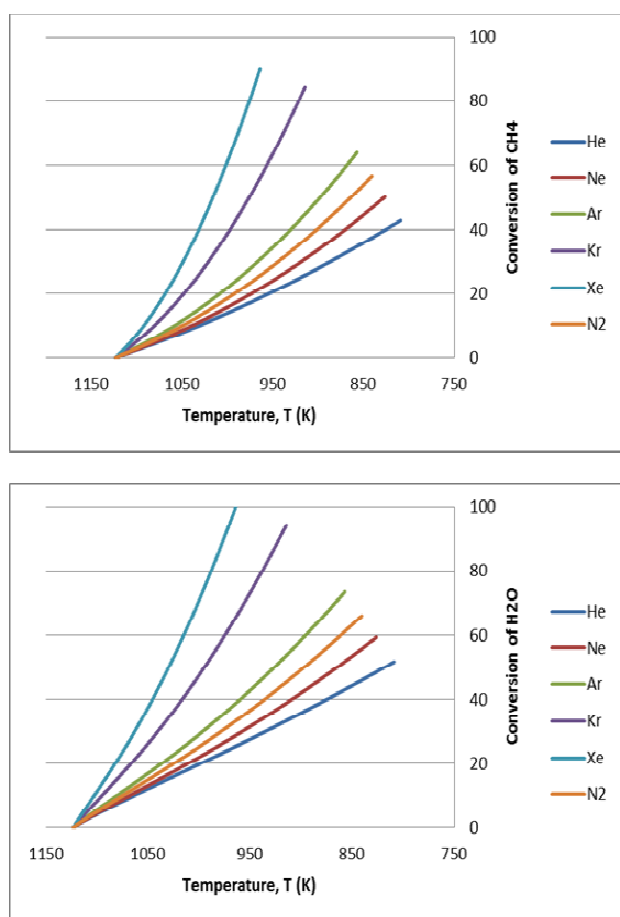


Fig. 4 Increase in percent conversion compared to decrease in temperature

IV. CONCLUSION

The initial results of injecting inert into the reforming reaction have shown considerable potential for detailed study and analysis. It is presumed that with the application of this technique there may be about 20% reduction in outlet

temperature that may result in significant savings in terms of process energy requirements only (compared to traditional process) concurrently to increase in conversion. It was found that Xenon gives the highest yield and conversion while Helium gives the lowest temperature. In the future work the process may be optimized to obtain even better results.

ACKNOWLEDGMENT

AmjadRiaz and Gholamreza Zahedi would like to acknowledge Universiti Teknologi Malaysia for financial support under grant No.Q.J130000.2525.00H81.

REFERENCES

- [1]. A. M. Adris, S.S.E.H.E., R. Hughes, A Fluidized Bed Membrane Reactor for the Steam Reforming of Methane. *The Canadian Journal of Chemical Engineering*, 1991 69: p. 1061-1070.
- [2]. S.S. Bharadwaj, L.D.S., Catalytic partial oxidation of natural gas to syngas. *Fuel Process. Technol.*, 1995. 42: p. 109-127.
- [3]. Song, X.P. and Z.C. Guo, Technologies for direct production of flexible H-2/CO synthesis gas. *Energy Convers. Manage.*, 2006. 47(5): p. 560-569.
- [4]. York, A.P.E., T.C. Xiao, M.L.H. Green, and J.B. Claridge, Methane oxyforming for synthesis gas production. *Catalysis Reviews-Science and Engineering*, 2007. 49(4): p. 511-560.
- [5]. Aasberg-Petersen, K., J.H.B. Hansen, T.S. Christensen, I. Dybkjaer, P.S. Christensen, C.S. Nielsen, *et al.*, Technologies for large-scale gas conversion. *Applied Catalysis A: General*, 2001. 221(1-2): p. 379-387.
- [6]. Hu, Y.H. and E. Ruckenstein, Binary MgO-based solid solution catalysts for methane conversion to syngas. *Catalysis Reviews-Science and Engineering*, 2002. 44(3): p. 423-453.
- [7]. Lucrecio, A.F., G.T. Filho, and E.M. Assaf, Co/Mg/Al hydrotalcite-type precursor, promoted with La and Ce, studied by XPS and applied to methane steam reforming reactions. *Appl. Surf. Sci.*, 2009. 255(11): p. 5851-5856.
- [8]. Tengfei Liu, H.T., Götz Vesper, Autothermal Reforming of Methane in a Reverse-Flow Reactor. *Chem. Eng. Technol.*, 2009. 32(9): p. 1358-1366.
- [9]. Ali Alizadeh, N.M., and Farhang Jalali-Farahani, Multiobjective Dynamic Optimization of an Industrial Steam Reformer with Genetic Algorithms. *International Journal of Chemical Reactor Engineering*, 2007. 5(A19): p. 1-16.
- [10]. Lange, J.P., Methanol synthesis: A short review of technology improvements. *Catal. Today*, 2001. 64(1-2): p. 3-8.
- [11]. Wesenberg, M.H., Gas Heated Steam Reformer Modelling. in *Department of Chemical Engineering* 2006, Norwegian University of Science and Technology.
- [12]. Luo, N.-J., J.-A. Wang, T.-C. Xiao, F.-H. Cao, and D.-Y. Fang, Influence of nitrogen on the catalytic behaviour of Pt/ γ -Al₂O₃ catalyst in glycerol reforming process. *Catal. Today*, 2010.
- [13]. Radovan, O.E., G.M. Ciric, M.N. Tekic, and R.N. Paunovic, Applicability of two-membrane reactors for reversible gas phase reaction. Effects of flow patterns and inerts. *J. Membr. Sci.*, 1997. 128: p. -221.
- [14]. Sinev, M.Y., Y.P. Tulenin, O.V. Kalashnikova, V.Y. Bychkov, and V.N. Korchak, Oxidation of methane in a wide range of pressures and effect of inert gases. *Catal. Today*, 1996. 32(1-4): p. 157-162.
- [15]. Lee, C.G., H.K. Ahn, K.S. Ahn, and H.C. Lim, Characteristics of a novel method, inert gas step addition, for the investigation of gas-phase mass-transfer effects in a molten carbonate fuel cell. *J. Electroanal. Chem.*, 2004. 568: p. 13-17.
- [16]. Xu, J. and G.F. Froment, Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics. *AIChE J.*, 1989. 35(1): p. 88-96.
- [17]. Bartholomew, C.H., Mechanisms of catalyst deactivation. *Applied Catalysis A: General*, 2001. 212: p. 17-60.
- [18]. Ahmed, S. and M.H. Back, The effect of water vapor and inert gases on the carbon-oxygen reaction. *Carbon*, 1987. 25(6): p. 783-789.