

# Effects of Catalyst Tubes Characteristics on a Steam Reforming Process in Ammonia

M.Boumaza

**Abstract**—The tubes in an Ammonia primary reformer furnace operate close to the limits of materials technology in terms of the stress induced as a result of very high temperatures, combined with large differential pressures across the tube wall. Operation at tube wall temperatures significantly above design can result in a rapid increase in the number of tube failures, since tube life is very sensitive to the absolute operating temperature of the tube. Clearly it is important to measure tube wall temperatures accurately in order to prevent premature tube failure by overheating. In the present study, the catalyst tubes in an Ammonia primary reformer has been modeled taking into consideration heat, mass and momentum transfer as well as reformer characteristics. The investigations concern the effects of tube characteristics and superficial tube wall temperatures on of the percentage of heat flux, unconverted methane and production of Hydrogen for various values of steam to carbon ratios. The results show the impact of catalyst tubes length and diameters on the performance of operating parameters in ammonia primary reformers.

**Keywords**—Catalyst, tubes, reformer, performance

## I. INTRODUCTION

THE tubes in a primary reformer furnace operate close to the limits of materials technology in terms of the stress induced as a result of very high temperatures, combined with large differential pressures across the tube wall. Metal temperatures, typically around 850°C for top fired reformers and up to 900°C for side fired or terraced wall reformers, mean that the tubes undergo irreversible creep and therefore only have a limited life before they fail. Operation at tube wall temperatures significantly above design can result in a rapid increase in the number of tube failures, since tube life is very sensitive to the absolute operating temperature of the tube. An increase of only 20°C in the tube metal temperature can reduce the life of the tube by over 50%. Clearly it is important to measure tube wall temperatures accurately in order to prevent premature tube failure by overheating. At the same time, an operator wants to avoid operating a furnace with tube temperatures so conservative that the full capacity of the furnace is not realized. The optimization of these parameters requires a finite and precise investigation of the catalyst tube including process and conversion parameters.

In the present study, the catalyst tube in an Ammonia primary reformer has been modeled taking into consideration heat, mass and momentum transfer as well as reformer characteristics. The investigations concern the effects of tube characteristics and superficial tube wall temperatures on the percentage of heat flux, unconverted methane and production of Hydrogen for various values of steam to carbon ratios.

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## II. PRIMARY REFORMER

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<sub>2</sub> 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 primary reformer is basically a furnace containing burners and tubes packed with supported nickel catalyst. 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<sub>2</sub>, Nitrogen N<sub>2</sub>, carbon monoxide CO, carbon dioxide CO<sub>2</sub>, water vapor H<sub>2</sub>O and inert gases (argon). A high ratio of steam to hydrocarbon (Z) and a low pressure generally produce higher rate of hydrogen and carbon monoxide [4].

## III. PRIMARY REFORMER MODELING

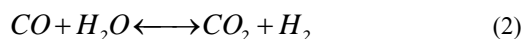
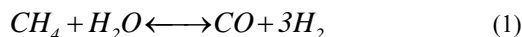
In order to develop the model, several assumptions are required :

The performance of one tube is assumed to represent the performance of all the tubes.

The radial variation of the process parameters are considered negligible.

The primary reformer is modeled using one homogeneous uni dimensional model.

Only the following chemical reactions are considered :



The catalyst tube is divided into elements having a length ΔZ (fig. 1)

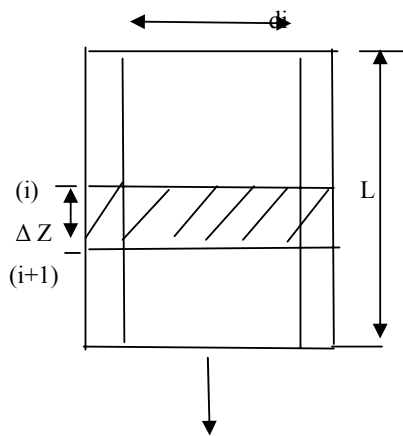
Gas Mixture inlet at  $T_e, P$ Exit Gas Mixture at  $T_s, P$ 

Fig. 1 Primary reformer catalytic tube

**A. Mass balances**

The mass balance for the different constituents along an element is as follows [5]:

$$\frac{d}{dZ}(\dot{m}_{CH_4}) = -r_{CH_4} \cdot A \cdot \rho_{cat} \quad (3)$$

$$\frac{d}{dZ}(\dot{m}_{H_2O}) = -r_{CH_4} \cdot A \cdot \rho_{cat} - r_{CO} \cdot A \cdot \rho_{cat} \quad (4)$$

$$\frac{d}{dZ}(\dot{m}_{CO_2}) = r_{CO} \cdot A \cdot \rho_{cat} \quad (5)$$

$$\frac{d}{dZ}(\dot{m}_{CO}) = r_{CH_4} \cdot A \cdot \rho_{cat} - r_{CO} \cdot A \cdot \rho_{cat} \quad (6)$$

$$\frac{d}{dZ}(\dot{m}_{H_2}) = 3r_{CH_4} \cdot A \cdot \rho_{cat} + r_{CO} \cdot A \cdot \rho_{cat} \quad (7)$$

$$\frac{d}{dZ}(\dot{m}_{N_{H_2}}) = 0 \quad (8)$$

**B Energy balance**

Energy balance along an element of the tube with a length  $dZ$  is as follows ;

$$(\dot{m}_g \cdot C_{pg})dT = Q_{dz} + [(-\Delta H_{CH_4})r_{CH_4} \cdot A \cdot \rho_{cat} + (-\Delta H_{CO})r_{CO} \cdot A \cdot \rho_{cat}]dZ \quad (9)$$

Where

$A$  : cross sectional area of the inside tube [ $m^2$ ]

$\rho_{cat}$  : density of the catalyst bed [ $Kg_{cat}/m^3$ ]

$Z$  : Tube length [ $m$ ]

$\dot{m}_g$  : Mole flow rate of the gas mixture [ $Kmol/s$ ]

$C_{pg}$  : Specific heat of the gas mixture [ $KJ/Kmol.K$ ]

$r_{CH_4}$  et  $r_{CO}$  : reactions rates of 1 and 2 (conversions rates of  $CH_4$  and  $CO$ ) [ $Kmol/Kg_{cat}.s$ ].

$\Delta H_i$  : Heat of reaction "i" at temperature  $T_i$  [ $KJ/mol$ ]

$Q_{dz}$  : Heat required to heat a tube element «  $dZ$  » [ $KJ/s$ ]

**C. Momentum balance**

The pressure drop through a catalytic bed is determined from Ergun Equation, as follows (6)

$$\frac{dP}{dZ} = \frac{G_m \cdot (1-\epsilon) \cdot 10^{-5}}{D_p \cdot \rho_g \cdot \epsilon^3} \left[ \frac{150 \mu_g \cdot (1-\epsilon)}{D_p} + 1.75 G_m \right] \quad (10)$$

$D_p$  : Equivalent diameter of a particle catalyst (m)

$G_m$  : Superficial mass velocity ( $Kg/m^2.S$ )

$$G_m = \frac{\dot{m}_g}{A_i} \quad (11)$$

$$A_i = \frac{\pi \cdot d_i^2}{4} \quad (12)$$

$\mu_g$  : Viscosité dynamique du mélange gazeux (Pa.s)

$\rho_g$  : Masse volumique du mélange gazeux à l'intérieur du tube ( $Kg/m^3$ )

$\epsilon$  : La porosité du lit catalytique.

**D. Heat Transfer Analysis**

Heat transferred through a tube element  $dZ$  is;

Conduction (from  $T_{pe}$  to  $T_{pi}$ ) :

$$Q = \frac{2\pi \lambda_p \cdot \Delta Z}{\ln\left(\frac{d_e}{d_i}\right)} (T_{pe} - T_{pi}) \quad (13)$$

- Convection (Inside gas mixture at  $T_g$  - Inside wall tube at  $T_{pi}$ ) :

$$Q = \pi \cdot d_i \cdot h_i \cdot (T_{pi} - T_g) \quad (14)$$

$h_i$  : Convection heat transfer coefficient ( $W/m^2.K$ )

$T_{pe}$  : Outside tube wall superficial temperature (K)

$T_{pi}$  : Inside tube wall superficial (K)

$T_g$  : Gas mixture temperature inside the tube (K)

$\lambda_p$  : Tube thermal conductivity ( $W/m.K$ )

$d_i$  : Inside tube diameter (m)

$d_e$  : Outside tube diameter (m)

Arranging (13) and (14) give

$$Q = \left[ \frac{1}{\frac{1}{2\pi \lambda_p \Delta Z} \ln\left(\frac{d_e}{d_i}\right) + \frac{1}{\pi d_i \Delta Z h_i}} \right] (T_{pe} - T_g) \quad (15)$$

Heat flux based on the outside tube wall is ;

$$q_i = \left[ \frac{1}{\frac{d_i}{2\lambda_p} \cdot \ln\left(\frac{d_e}{d_i}\right) + \frac{1}{h_i}} \right] (T_{pe} - T_g) \quad (16)$$

The convection heat transfer coefficient is obtained from the relation proposed by Ravi et al [3] :

$$h_i = 0.40 \frac{\lambda_g}{D_p} \left[ 258 \left( \frac{D_p G_m}{\mu_g} \right)^{1/3} \left( \frac{C_{pg} \mu_g}{\lambda_g} \right)^{1/3} + 0.094 \left( \frac{D_p G_m}{\mu_g} \right)^{0.8} \left( \frac{C_{pg} \mu_g}{\lambda_g} \right)^{0.4} \right] \quad (17)$$

$\lambda_p$  : Thermal conductivity of the gas mixture (W/m.K)

#### E. Heat of Reaction

The heat of reaction at temperature T is calculated as follows [7]

$$\Delta H_T = \Delta H_{298}^0 + \sum_j \left( \int_{298}^T C_{pj} dT \right)_{\text{produits}} - \sum_i \left( \int_{298}^T C_{pj} dT \right)_{\text{réactifs}} \quad (18)$$

$C_{pj}$ : Specific heat of constituent "j" [KJ/mol.K]

#### F. Kinetic Model

The kinetic model used in this study has been proposed by Singh and Saraf [8] :

$$r_{CH_4} = 457210^{+4} \cdot P^{-0.5} \cdot e^{\left( \frac{-92500}{R \cdot T_g} \right)} \cdot \left( p_{CH_4} - \frac{p_{H_2} \cdot p_{CO}}{K_{pCH_4} \cdot p_{H_2O}} \right) \quad (19)$$

$$r_{CO} = 1094410^{+3} \cdot P^{-0.5} \cdot e^{\left( \frac{-66100}{R \cdot T_g} \right)} \cdot \left( p_{CO} - \frac{p_{H_2} \cdot p_{CO_2}}{K_{pCO} \cdot p_{H_2O}} \right) \quad (20)$$

$p_j$  : Partial pressure of different constituents (Bar).

$R$  : Universal constant of ideal gas (KJ/Kmol.K)

$K_{pCH_4}$  : Equilibrium Constant for methane conversion

$K_{pCO}$  : Equilibrium Constant for CO conversion

#### G. Superficial Tube Wall

Data from published literature (13) has enabled to develop a model which can calculate the tube wall temperature « $T_p$ » along the tube length. This model uses a combination of two expressions. The first expression is in the form of polynomial, while the second is linear (variable profile)

$$\text{If } X < 3 : \quad T_p = 15x^2 + b_1x + c_1 \quad (21)$$

Such that : at  $x=0$ ,  $T_p=T_{pE}$  et à  $x=3$ ,  $T_p=T_{pS}+10$

$$\text{Otherwise} \quad T_p = a_2x + b_2 \quad (22)$$

Such that : à  $x=3$ ,  $T_p=T_{pS}+10$  et à  $X=L_g$ ,  $T_p=T_{pS}$

$T_{pE}$  : Initial outside tube wall temperature (°C)

$T_{pS}$  : Final outside tube wall temperature (°C)

$L_g$  : Tube length (m)

$x$  : distance (m)

$a_1, b_1, b_2, c_2$  constants which vary with  $T_{pE}$  et  $T_{pS}$ .

#### IV. RESOLUTION PROCEDURES

Primary reformer tube model is composed of a series of ordinary differential equation. An iterative method has been used to solve this series of equations. (3-7) through (7-10) are transformed into the following equations:

$$\Delta \dot{m}_{CH_4} = (-r_{CH_4} \cdot A \cdot \rho_{cat}) \cdot \Delta Z \quad (23)$$

$$\Delta \dot{m}_{H_2O} = (-r_{CH_4} \cdot A \cdot \rho_{cat} - r_{CO} \cdot A \cdot \rho_{cat}) \cdot \Delta Z \quad (24)$$

$$\Delta \dot{m}_{CO_2} = (r_{CO} \cdot A \cdot \rho_{cat}) \cdot \Delta Z \quad (25)$$

$$\Delta \dot{m}_{CO} = (r_{CH_4} \cdot A \cdot \rho_{cat} - r_{CO} \cdot A \cdot \rho_{cat}) \cdot \Delta Z \quad (26)$$

$$\Delta \dot{m}_{H_2} = (3r_{CH_4} \cdot A \cdot \rho_{cat} + r_{CO} \cdot A \cdot \rho_{cat}) \cdot \Delta Z \quad (27)$$

$$\Delta \dot{m}_{N_2} = 0 \quad (28)$$

$$\Delta T = \frac{[\pi d_i q_i + (-\Delta H_{CH_4}) r_{CH_4} A \rho_{cat} + (-\Delta H_{CO}) r_{CO} A \rho_{cat}]}{(\dot{m}_g \cdot C_{pg})} \Delta Z \quad (29)$$

Such that

$$\Delta T = (T_{i+1} - T_i) \quad (30)$$

$$\Delta P = (P_{i+1} - P_i) \quad (31)$$

$T_i$ : Inside temperature at the tube element [K]

$T_{i+1}$ : Outside temperature at the tube element [K]

$P_i$ : Total pressure at inlet of the tube element [bar]

$P_{i+1}$ : Total pressure at the exit of the tube element [bar]

The model developed follows the following steps:

1. Initializing temperature, pressure and composition of gas mixture entering the tube.
2. Fix tube length, inside and outside tube diameters.
3. Fix tube element « $\Delta Z$ »
4. Fix catalyst characteristics.
5. Determine the rate of conversion of  $CH_4$  and  $CO$  using (19) and (32).
6. Calculate the number of moles of each constituents leaving the tube element using (24) through (29).
7. Determine  $\Delta T$  using (30)
8. Calculate  $\Delta P$  using (31)

9. Steps 6 through 9 are repeated until the total length of the tube is reached.

## V. RESULTS AND DISCUSSIONS

The developed model has enabled to investigate the effect of catalyst tube characteristics (length, diameter), tube wall superficial temperature and steam to carbon ratio on the heat fluxes, the percentage of unconverted methane and the production of Hydrogen.

### A. Effects of Tube Wall Temperature on Heat Flux Profiles.

Figs 2 and 3 show the variation of the heat flux with respect to the tube length for three different catalyst tube temperatures, two different values of  $Z$  equal to 3 and 5, and inlet ( $T_i$ ) and exit gas temperatures ( $T_e$ ) respectively equal to  $740^\circ\text{C}$  and  $810^\circ\text{C}$ .

These figures show that

- The heat flux varies inversely proportional with the tube length in most case studied except in the beginning of the flow.
- A constant tube temperature  $T_p$  results with high heat flux at the entrance of the catalyst tube. This high flux can produce a thermal constraint for the tube material. This phenomenon becomes more important as  $Z$  increases. On the other hand this high heat flux enables to produce the same rate of methane conversion as the other variable  $T_p$ .
- A linear variation of the temperature tube wall enables to obtain a low constant heat flux along the tube. However, in this case a high percentage of unconverted methane is obtained at the exit of the tube. In order to reduce this fraction of unconverted methane, it is required to increase the catalyst tube length, which leads to further cost.

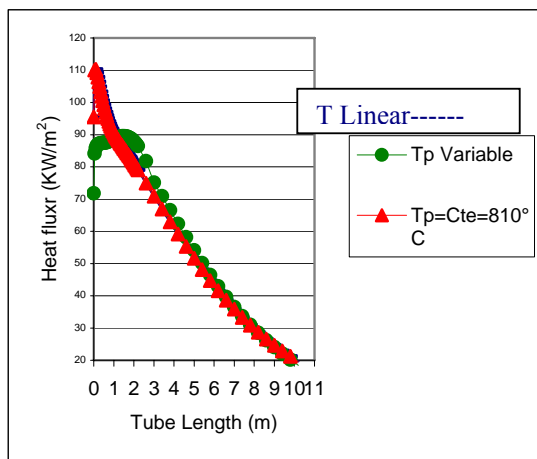


Fig. 2: Variation of heat flux with tube length ( $Z=3$ ,  $T_i=740^\circ\text{C}$ ,  $T_e=810^\circ\text{C}$ )

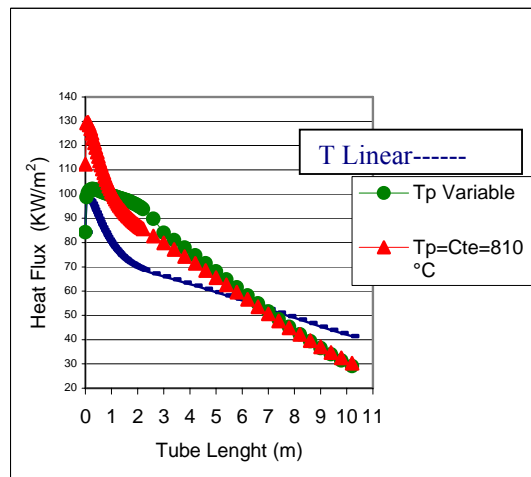


Fig. 3: Variation of heat flux with tube length ( $Z=5$ ,  $T_i=740^\circ\text{C}$ ,  $T_e=810^\circ\text{C}$ )

### B. Effects of the Unconverted methane fractions.

Figs 4 and 5 show the variation of the production of the percentage of unconverted methane ( $X_{\text{CH}_4}$ ) flux with respect to the tube length length for three different catalyst tube temperatures, two different values of  $Z$  equal to 3 and 5, and inlet ( $T_i$ ) and exit gas temperatures ( $T_e$ ) respectively equal to  $740^\circ\text{C}$  and  $810^\circ\text{C}$ .

It can be seen from these figures that the variation of  $X_{\text{CH}_4}$  is inversely proportional with the tube length for all values of both values of  $Z$ . The best possible conversion of Methane appears in the range of the tube length between 9m and 13m. A length of the catalyst tube below 9 meters reduces considerably the conversion of methane, while a tube length below 6 meters produces the lowest fraction of the conversion of methane. A tube length above 13 meters does not increase the conversion of methane, as this fraction remains constant above this length.

The fraction of unconverted methane appears higher in the case of the linear tube wall temperature than the variable tube wall temperature or the constant tube wall temperature. Also, it is clear from these results, as  $Z$  increases the conversion of methane increases. Finally the exit gas temperature has an important impact on the percentage of the unconverted fraction of methane, as When  $T_e$  increases,  $X_{\text{CH}_4}$  decreases.

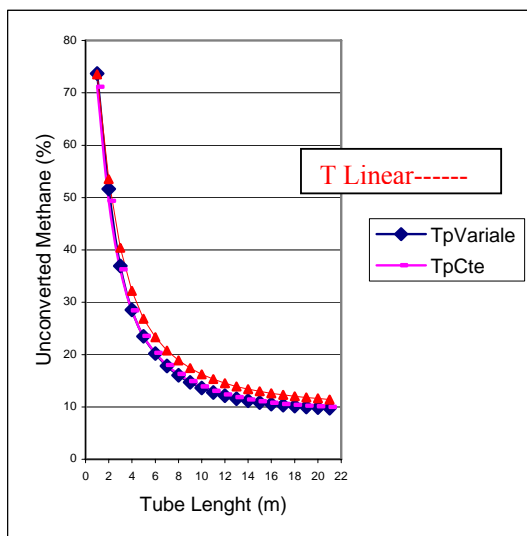


Fig. 4 : Variation of unconverted methane with tube length ( $Z=3$ ,  $T_i=740^\circ\text{C}$ ,  $T_e=810^\circ\text{C}$ )

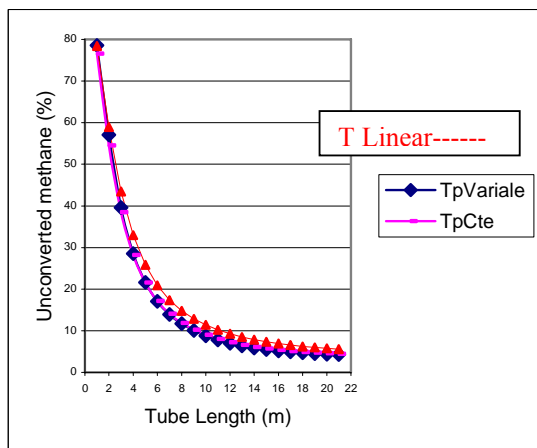


Fig. 5 : Variation of unconverted methane with tube length ( $Z=5$ ,  $T_i=740^\circ\text{C}$ ,  $T_e=810^\circ\text{C}$ )

### C. Effects on the production of the Hydrogen.

Figs 6 and 7 show the variation of the production of Hydrogen ( $M_{H_2}$ ) with respect to the tube length for three different catalyst tube temperatures, two different values of  $Z$  equal to 3 and 5, and inlet ( $T_i$ ) and exit gas temperatures ( $T_e$ ) respectively equal to  $740^\circ\text{C}$  and  $810^\circ\text{C}$ .

It can be seen from these figures that the variation of  $M_{H_2}$  is proportional with the tube length for all values of both values of  $Z$ , and  $T_s$ , and the three Temperatures tube wall profiles. Unlike the conversion of methane which becomes constant beyond a tube length of 13m, the production of hydrogen increases beyond this length. These results show also that the production of Hydrogen increases with both  $Z$  and  $T_e$ .

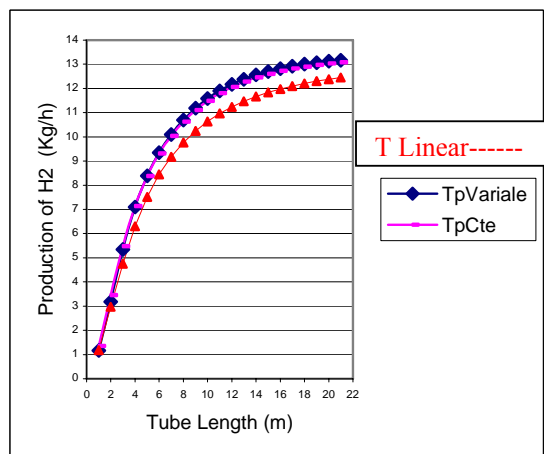


Fig. 6: Variation of the production of  $H_2$  with Tube length ( $Z=3$ ,  $T_i=740^\circ\text{C}$ ,  $T_e=810^\circ\text{C}$ )

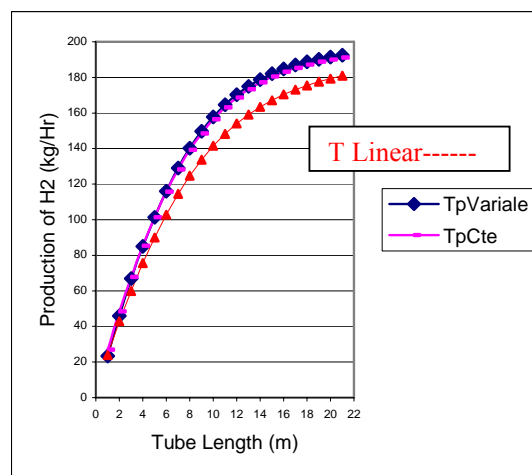


Fig. 7 : Variation of the production of  $H_2$  with Tube length ( $Z=5$ ,  $T_i=740^\circ\text{C}$ ,  $T_e=810^\circ\text{C}$ )

## V. CONCLUSIONS

The study enables to determine the effect of the catalyst tube characteristics used in ammonia primary reformer on the performance of operating parameters represented by the percentage of unconverted methane, the production rate of hydrogen and the heat fluxes required in the reformer. The results show 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 (8, 9), and finally increases the heat load required in the primary reformer.

- The energy consumed by the reformer decreases with an increase of the operating pressure. Moreover higher pressure will produce higher rate of methane non converted, which will require more supply of heat.

- Higher exit temperature  $T_s$ , reduces the amount of unconverted methane, however, it is recommended to limit this temperature to 900C in order to avoid the melting of the catalyst, reduce the energy load as well as CO<sub>2</sub> emission.
- An assumed tube wall temperature enables to produce higher heat fluxes at the entry of the tube, which can be the source of thermal constraint for the tube material. This phenomena becomes more important as  $Z$  increases. This temperature produces the same conversion of methane as when the tube temperature is assumed variable
- The unconverted methane is higher for the case of the constant wall temperature compared to the linear variation of this temperature.
- It appears that for most of the case studied higher performance of the reaction can be obtained when the tube length varies between 3 and 13m.
- The production of Hydrogen decreases with an increase of the operating pressure. Moreover higher pressure will produce higher rate of methane non converted (10).

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#### NOMENCLATURE

$C_{pi}$  : Specific heat of component 'i' (J/mole.K)  
 $E_{tot}$  : Total energy of the system (J/Kg)  
 $E_p$  : Potential energy (J/Kg)  
 $E_k$  : Kinetic energy (J/Kg)  
 $H$ : Specific enthalpy (J/kg)  
 $m$  : Mass flow rate (Kg/sec).  
 $n$ : molar flow rate (mole/sec)  
 $R_i$ : rate of reaction (moles/moles)  
 $v$  : Fluid velocity (m/sec)  
 $P$  : Fluid pressure (Bar)  
 $P_i$ : Partial gas pressure (Bar)  
 $V$  : Fluid volume (m<sup>3</sup>)  
 $U$  : Internal energy of the fluid (j/mole)  
 $x_i$ : Mole fraction  
 $T_e$  : Inlet gas temperature (°C)  
 $T_s$  : Outlet gas temperature (°C)  
 $X_{CH_4}$ : Percentage of unconverted methane

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