

## MASS BALANCE SIMULATION FOR STEAM REFORMER IN DIRECT REDUCTION OF IRON ORE BY HYL III PROCESS.

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### ABSTRACT

HYL direct reduction of iron ore process uses a reducing gas composed of a mixture of H<sub>2</sub> and CO in order to reduce iron oxide pellets to metallic iron (DRI). This process is mainly dependent on a reformer to supply the reducing gas. In the reformer, natural gas is catalytically converted into reducing gas by reaction with steam at a temperature of 800 to 850°C and pressure between 8 and 8.5 bars in the presence of Nickel based catalyst. In order to analyze the reformer operation, it is necessary to estimate the reformed gas composition for some specific process conditions.

The present work is based on the solution of a set of non-linear equations describing mass balances of carbon, hydrogen, oxygen and higher hydrocarbons, to enable the calculation of reformed gas composition for a steam reformer. The procedure can assist both process engineers tackling the problem of estimating output from a primary reformer at the design stage and plant operating engineers. The mass balance equations are solved by using the equilibrium constants for the reforming and water gas shift reactions. This includes simultaneously solving non-linear equations relating to the composition of reactants and other variables as temperature and pressure at which reactions take place. In addition, amount of carbon contained in natural gas compared to amount of steam used in steam reforming reaction is also considered during calculations. The basic requirements to establish the model are a set of reactions and values of equilibrium constants for the reforming and water gas shift reactions.

### Keywords

Reformer, hydrocarbons, steam, equilibrium.

### 1. INTRODUCTION

There are different methods of iron ore reduction and new technologies developed for steel making in electric arc furnace (EAF). The main goal of the process development has been to avoid coke utilization and reduce the operating costs. In general, in a direct reduction process, oxygen is removed from iron oxide, in a furnace by using a reducing gas composed of CO and H<sub>2</sub>, if the cooling zone in the furnace is eliminated, the direct reduced iron (DRI) can be immediately briquetted into hot briquetted iron (HBI). The reducing gas can be obtained by reforming of hydrocarbons such as natural gas in a reformer using Nickel based catalyst. Processes using this general procedure are mainly [1]:

- Midrex direct reduction technology (CO<sub>2</sub> reformer)
- HYL direct reduction technology (steam reformer)

- HYL direct reduction technology (zero reformer), the reforming process takes place by mixing natural gas and oxygen into the reduction furnace (in-situ reforming)

The HYL direct reduction process was the first direct reduction technology to operate successfully on industrial scale in the world (1957), proposing a technological concept that was a real solution to the iron needs of Hylsa in Mexico. Based on a fixed bed reactor concept, the results achieved with this technology were so attractive and innovative that other steelmaking companies acquired the HYL process license. Twenty-two reduction units were installed in different countries, with a total capacity of over 9 Million ton/year of DRI [2].

However, it was foreseen by HYL that the competitiveness of this technology would be limited due to its batch nature. For this reason, a research program was initiated in 1967 to develop a continuous (moving bed) process. The first industrial plant started producing in May 1980 in Hylsa Monterrey, Mexico. The new process concept led to higher plant productivity, superior DRI quality, lower energy consumption and a simpler plant operation [3].

One of the main advantages of the HYL [steam reforming] process is its configuration based on independent reducing gas generation and reduction sections. Under these conditions, the only requirement is an independent source to supply the  $H_2$  and  $CO$  needed for reduction. This is supplied from what is called a Steam Reformer which is fed with steam and NG at a certain condition of pressure and temperature to produce  $H_2$  and  $CO$  with no changes involved in the process scheme see figure 1 [3].

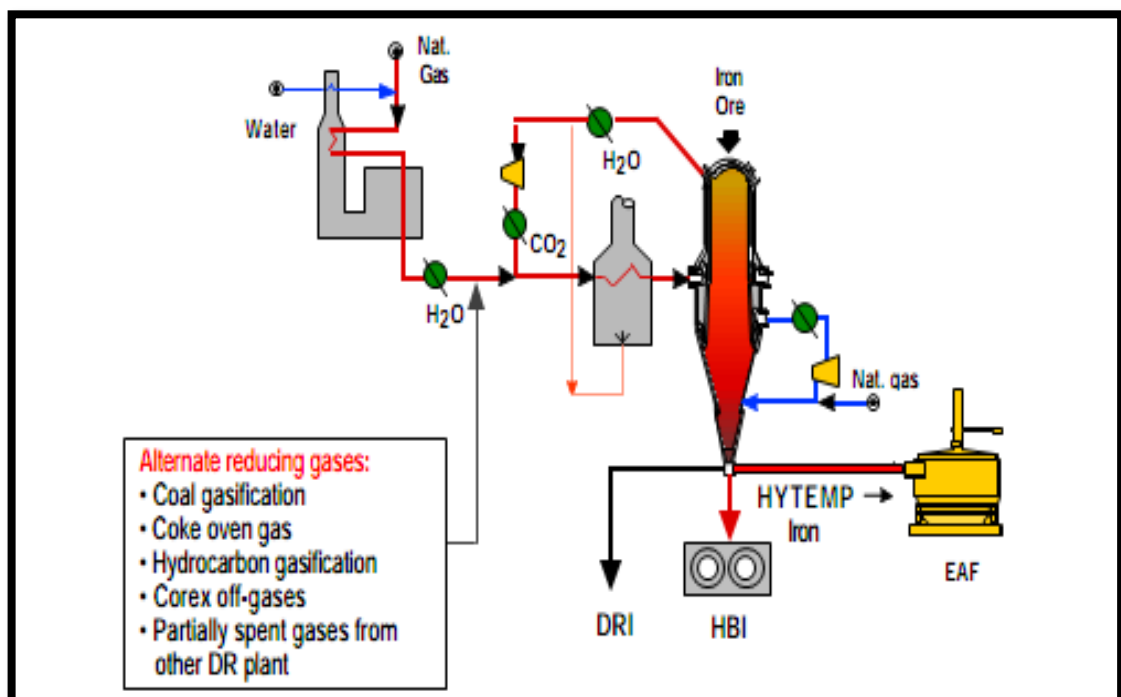


Fig. 1: HYL III (steam reforming) process scheme. [3]

The present work concentrates on the study of steam reforming of natural gas, which is normally used for the production of reducing gas [3]. Operators of steam reforming-based plants prefer feedstock options to minimize operating costs and maximize operational flexibility [4].

Its aim is to estimate the reformed gas composition by knowing the following parameters:

- Temperature at which reaction is proceeding
- Pressure at which reaction is taking place
- Ratio of Steam to carbon contained in natural gas in the reformer feed stock.

The model that will be produced to estimate reformed gas composition is very important to assist both process engineers tackling the problem of estimating output from a primary reformer at the design stage and plant operating personnel to further tune their plant parameters to get the best gas quality and optimum energy consumption.

### 1.1. Formulation of the Problem

The two main reactions governing the process of steam methane reforming are:



Reaction (1) is the reforming reaction while reaction (2) is the water gas shift reaction.

A comprehensive study was made on equilibrium conditions and other process parameters affecting the quality and condition of the gas produced by these reactions to better understand how steam reformer behavior can vary with varying these conditions.

As a general observation, only these two equations are necessary to represent the overall equilibrium process. In addition, when reforming higher saturated hydrocarbons and provided that contact time is long enough, the exit gas composition is that which approximately corresponds to the chemical equilibrium involving the methane-steam reforming and water gas shift reactions (equations 1 and 2).

Considering, as a first step, a reformer working at relatively high temperature and low pressure, in such a way that only CO, H<sub>2</sub> and water, besides N<sub>2</sub> are the products. CO<sub>2</sub> and CH<sub>4</sub> cannot coexist under these conditions.

Therefore, the products at this step will be:

CO = C (All carbon becomes CO)

Total hydrogen:

H<sub>2</sub> = H/2 – H<sub>2</sub>O =A (all hydrogen becomes H<sub>2</sub> except the Hydrogen combined as H<sub>2</sub>O).

$H_2O = O - CO = B$  ( $H_2O$  is equal to all the oxygen not combined as CO).

### 1.2. Definitions

$C_1 C_2 \dots; C_n$  “mole fractions of  $CH_4 \dots C_n H_{2n+2}$  in the natural gas fed to the reformer”.

$x_{CO_2}, x_{CO}, x_{H_2}, x_{N_2}, x_{H_2O}$ : “mole fractions of  $CO_2, CO, H_2, N_2$  and  $H_2O$  respectively in the natural gas fed”

$r$ : “Steam/carbon molar ratio fed to the reformer”

Then, the total carbon fed to the reformer will be:

$$C^* = \sum n C_n + X_{CO} + X_{CO_2}$$

By definition, the steam fed will be:

$$S = r * C$$

Consequently, the total oxygen fed to the reformer will be:

$$O = x_{CO} + 2x_{CO_2} + r * C + x_{H_2O}$$

Finally, the inert gas will be the Nitrogen:

$$I = x_{N_2}$$

Rearranging:

$$CO = C$$

$$H_2 = H/2 - O + C = A$$

$$H_2O = O - C = B$$

$$N_2 = I$$

As a second step, consider the actual conditions of temperature and pressure and the  $CH_4$  and  $CO_2$  in equilibrium at the stated conditions.

Methane and carbon dioxide will be produced according to equations (1) and (2):

The reforming reaction which will produce “W” moles of  $CH_4$  by reaction (1) and the water gas shift reaction producing “Z” moles of  $CO_2$  as a consequence of reaction (2). The actual reformer outlet will comply with the new mass balance:

$$CH_4 = W \text{ moles } CH_4 \text{ produced by reaction (1)}$$

$$CO_2 = Z \text{ moles } CO_2 \text{ produced by reaction (2)}$$

CO = C - W - Z (CO consumed to produce CH<sub>4</sub> and CO<sub>2</sub>).

H<sub>2</sub> = A - 3W + Z (H<sub>2</sub> consumed to produce CH<sub>4</sub> and H<sub>2</sub> as a result of CO<sub>2</sub> generation)

H<sub>2</sub>O = B + W - Z (H<sub>2</sub>O produced when generating CH<sub>4</sub> and that consumed to form CO<sub>2</sub>)

I = I (Inert gas does not react)

F<sub>t</sub> = (A + B + C + I) - 2W = F - 2W

If A + B + C + I = F; total flow.

### 1.3. Basic Equations

In this model, two main equations represent the equilibrium for steam methane reforming and water gas shift reaction. The equilibrium constant for reaction (1) is:

$$K_W = \frac{(P_{H_2})^3 (P_{CO})}{(P_{CH_4})(P_{H_2O})} = \frac{(H_2)^3 (CO)}{(CH_4)(H_2O)} \left(\frac{P_t}{F_t}\right)^2 \dots \dots \dots (3)$$

For reaction (2)

$$K_Z = \frac{(P_{CO_2})(P_{H_2})}{(P_{CO})(P_{H_2O})} = \frac{(CO_2)(H_2)}{(CO)(H_2O)} \dots \dots \dots (4)$$

Substituting the functions of “W” and “Z for results in Reaction (1)

$$K_W = \frac{(A - 3W + Z)^3 (C - W - Z)}{W(B + w - Z)} * \left(\frac{P_t}{F_t - 2W}\right) \dots \dots \dots (5)$$

And Reaction (2)

$$K_Z = \frac{Z(A - 3W + Z)}{(C - W - Z)(B + w - Z)} \dots \dots \dots (6)$$

The equilibrium constant K for each reaction can be obtained from the following equation [5]

$$\Delta G^\circ = -RT \ln K \dots \dots \dots (7)$$

Where ΔG° is the change of standard free energy accompanying the reaction, in Cal/mol, R is the universal gas constant in Cal/deg.mol and T is the absolute temperature in Kelvin.

The value of ΔG° at different temperature can be calculated using the data in table 1, and the equation ΔG° = ΔH° - TΔS° where ΔH° and ΔS° are the changes in the standard enthalpy in cal/mol and standard of entropy in cal/deg.mol

$$\Delta G^\circ (\text{Reaction}) = G^\circ (\text{products}) - G^\circ (\text{Reactants}) \dots\dots\dots (8)$$

$$K = \exp (-\Delta G^\circ / R.T) \dots\dots\dots (9)$$

**Table (1): Gibbs free energy for some compounds.**

Compound	$G^\circ = H^\circ - T.S^\circ$
CO <sub>2</sub>	-94200-0.2*T
CH <sub>4</sub>	-16520+(12.25*T*log(T)) - (15.62*T)
CO	-26700-20.95*T
H <sub>2</sub> O	-58800+13.1*T

All spontaneous reactions occur with a decrease in Gibbs free energy, while at equilibrium, Gibbs free energy change is zero. The products and reactants have the same Gibbs free energy and the reaction lacks a driving force in any direction. In an analogous way, a corresponding expression for the driving force for a process with constant volume can be derived [6].

There are two possibilities for solving for “W” and “Z”.

The solution is mainly dependent on equilibrium relationships for reactions (1) and (2).

It is directly based on the definition of chemical equilibrium for reactions (1) and (2).

$P_{N_2}, P_{CO} \dots P_i$  = Partial pressure of the component “i”

$P_t$  = total pressure or reformer working pressure.

$K_w$  = equilibrium constant for reaction (1), as a function of temperature.

$K_z$  = equilibrium constant for reaction (2), as a function of temperature.

$P_i = x_i \cdot P_t$

The solution requires solving those two nonlinear equations using solver functionality and visual basic programming inside Microsoft excel [7], to get W and Z then calculate a set equations to get  $x_{CH_4}, x_{CO_2}, x_{CO}, x_{H_2}, x_{N_2}, x_{H_2O}$  in reformed gas.

Actually using the program representing this model requires only entering reformed gas temperature, pressure, steam to carbon ratio, equilibrium approach and natural gas composition and the program automatically computes the reformed gas composition.

Then the difference between theoretical and actual data from the plant gives a complete picture about the status of the catalyst. Because, if the difference is too big and slip methane in the reformed gas is very high in the actual compared to the theoretical data

meaning that the catalyst is damaged and may need to be steamed or reduced or even completely changed to increase the efficiency of the reforming process [8].

The interface of the program was enhanced using VBA programming. [9]

## 2. EXPERIMENTAL DATA

In this article, data obtained on the steam reformer working at seven different cases at EZZ direct reduction plant (HYL III) are used. Table 2 shows the data of EZZ plant compared to the data obtained from the above-mentioned model in order to estimate the expected reformed gas composition by introducing the working pressure, temperature steam to carbon ratio fed in the reformer feed and the composition of natural gas entering the reformer.

**Table (2): Case 1, 2, 3, 4 regarding reformed gas composition variation with steam to carbon ratio and temperature.**

Case1			Case2			Case3			Case4		
Temp °C	STEAM TO CARBON	Pressure bar	Temp °C	STEAM TO CARBON	Pressure bar	Temp °C	STEAM TO CARBON	Pressure bar	Temp °C	STEAM TO CARBON	Pressure bar
810	2.5	8.1576	815.3	2.6	8.1576	750	2.58	8.116812	827.18	2.56	8.116812
Compound	Percentage %		Compound	Percentage %		Compound	Percentage %		Compound	Percentage %	
	Model	actual		Model	actual		Model	actual		Model	actual
CH <sub>4</sub>	3.220278	3.4	CH <sub>4</sub>	2.683599	3.2	CH <sub>4</sub>	7.489555	8.08	CH <sub>4</sub>	2.247432	2.74
CO <sub>2</sub>	8.070007	7.6	CO <sub>2</sub>	8.154994	7.8	CO <sub>2</sub>	10.07666	9.73	CO <sub>2</sub>	7.783985	7.58
CO	14.4569	14.3	CO	14.44707	14.2	CO	10.92351	10.72	CO	15.06429	14.55
H <sub>2</sub>	74.25281	74.7	H <sub>2</sub>	74.53979	74.8	H <sub>2</sub>	71.51027	71.44	H <sub>2</sub>	74.90429	75.13
N <sub>2</sub>	0	0	N <sub>2</sub>	0	0	N <sub>2</sub>	0	0	N <sub>2</sub>	0	0
H <sub>2</sub> O	0	0	H <sub>2</sub> O	0	0	H <sub>2</sub> O	0	0	H <sub>2</sub> O	0	0

**Table (3): Case 5, 6, 7 regarding reformed gas composition variation with steam to carbon ratio and temperature.**

Case5			Case6			Case7		
Temp °C	STEAM TO CARBON	Pressure bar	Temp °C	STEAM TO CARBON	Pressure bar	Temp °C	STEAM TO CARBON	Pressure bar
810	2.83	8.25957	815	3.07	8.167797	815.34	2.81	8.147403
Compound	Percentage %		Compound	Percentage %		Compound	Percentage %	
	Model	actual		Model	actual		Model	actual
CH <sub>4</sub>	2.48004202	2.71	CH <sub>4</sub>	2.211115	2.74	CH <sub>4</sub>	2.24521417	2.84
CO <sub>2</sub>	8.81526546	8.29	CO <sub>2</sub>	9.284175	7.58	CO <sub>2</sub>	8.63658443	7.97
CO	13.6874215	13.53	CO	13.14724	14.55	CO	13.9854327	13.76
H <sub>2</sub>	75.017271	75.49	H <sub>2</sub>	75.27052	75.13	H <sub>2</sub>	75.1327687	75.44
N <sub>2</sub>	0	0	N <sub>2</sub>	0	0	N <sub>2</sub>	0	0
H <sub>2</sub> O	0	0	H <sub>2</sub> O	0	0	H <sub>2</sub> O	0	0

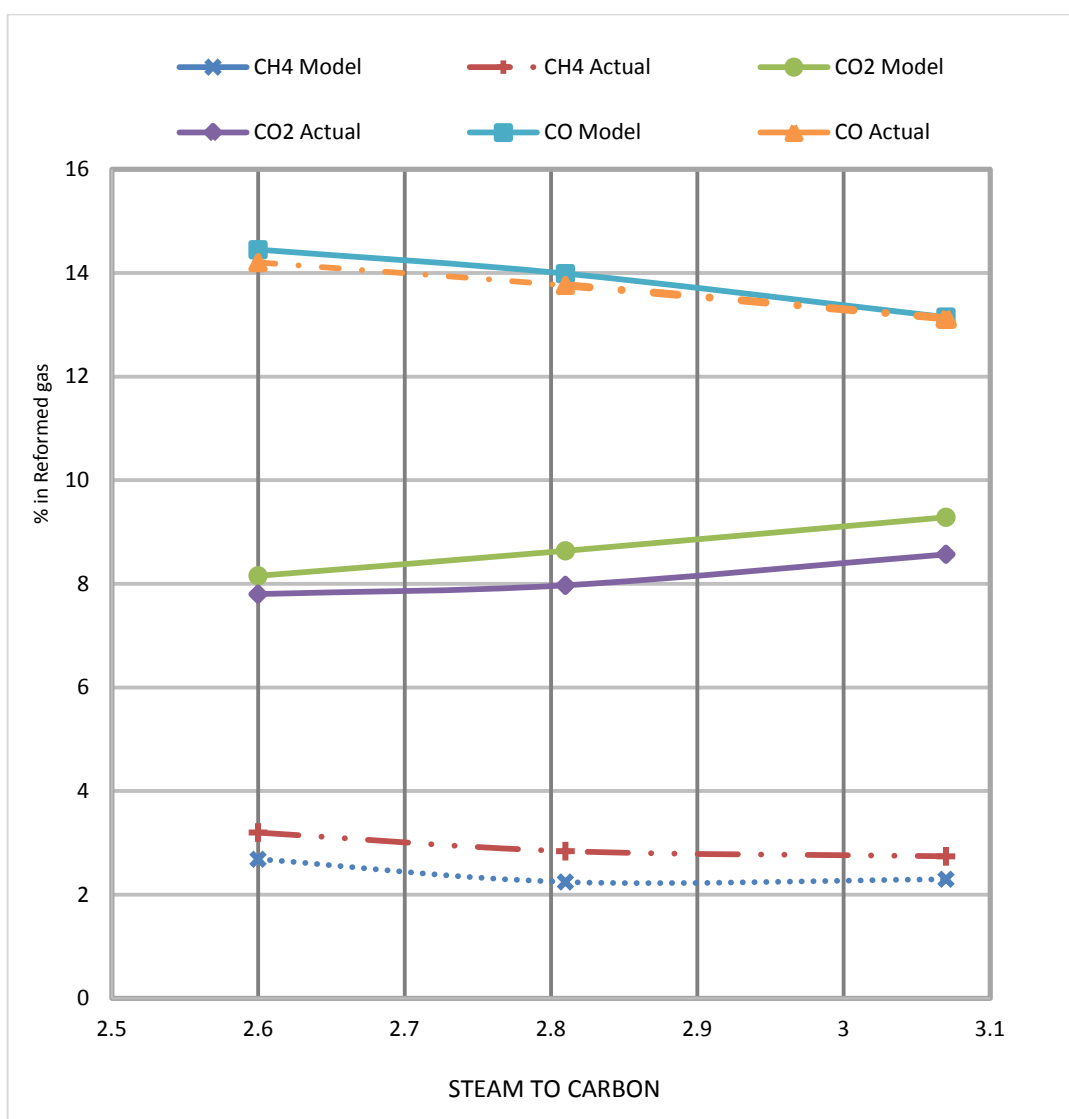
## 3. RESULTS AND DISCUSSION

For better understanding of steam reformer performance, two graphs are drawn. The first (figure 2) shows the percentage of CH<sub>4</sub>, CO<sub>2</sub> and CO in reformed gas as calculated by the model and the corresponding actual data from the plant versus steam to carbon ratio, keeping both working pressure and temperature constant. The second graph (figure 3) is for H<sub>2</sub> percentage in reformed gas, keeping same working parameters as mentioned before.

It is observed that H<sub>2</sub> and CO<sub>2</sub> percentage in reformed gas increases with increasing steam to carbon ratio while CH<sub>4</sub> and CO decrease with increase of steam to carbon ratio.

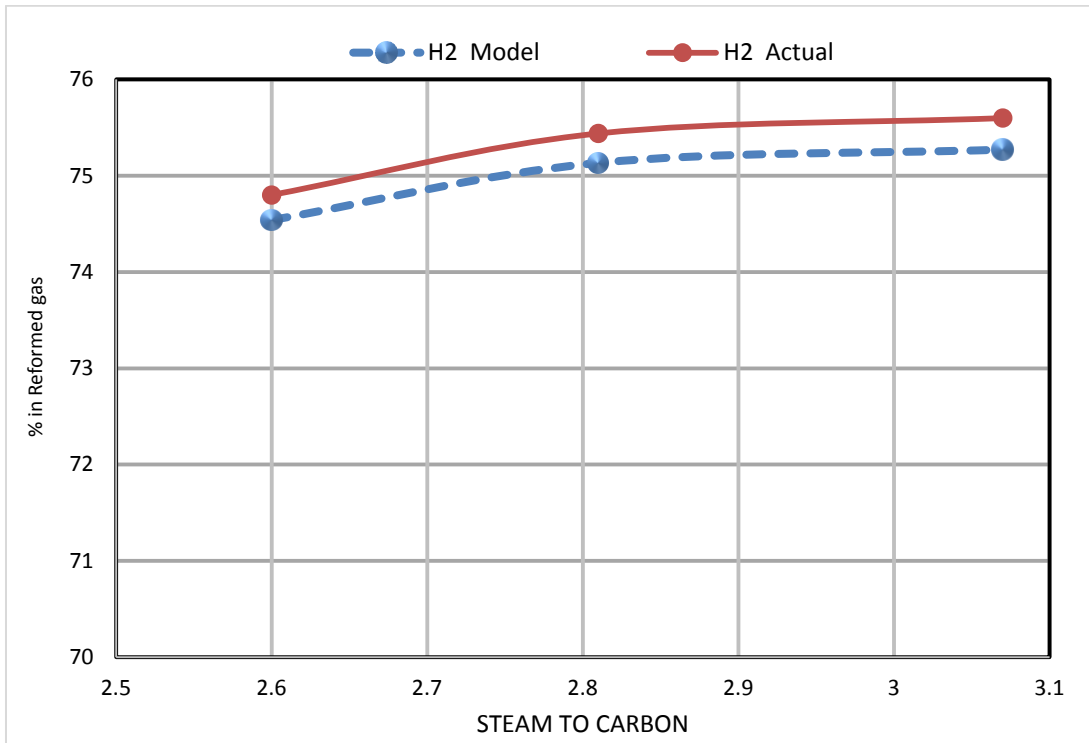
The first graph (figure 4) shows the variation of the percentages of CH<sub>4</sub>, CO<sub>2</sub> and CO in reformed gas as calculated by using the model and the actual plant data with temperature, keeping both, working pressure and steam to carbon ratio constant. While figure 5 depicts the variation of calculated and actual H<sub>2</sub> concentration in reformed gas with temperature, keeping the other two variables constant (figure 4).

Also H<sub>2</sub> and CO percentages in reformed gas increase with increasing temperature whereas CH<sub>4</sub> and CO<sub>2</sub> decrease.

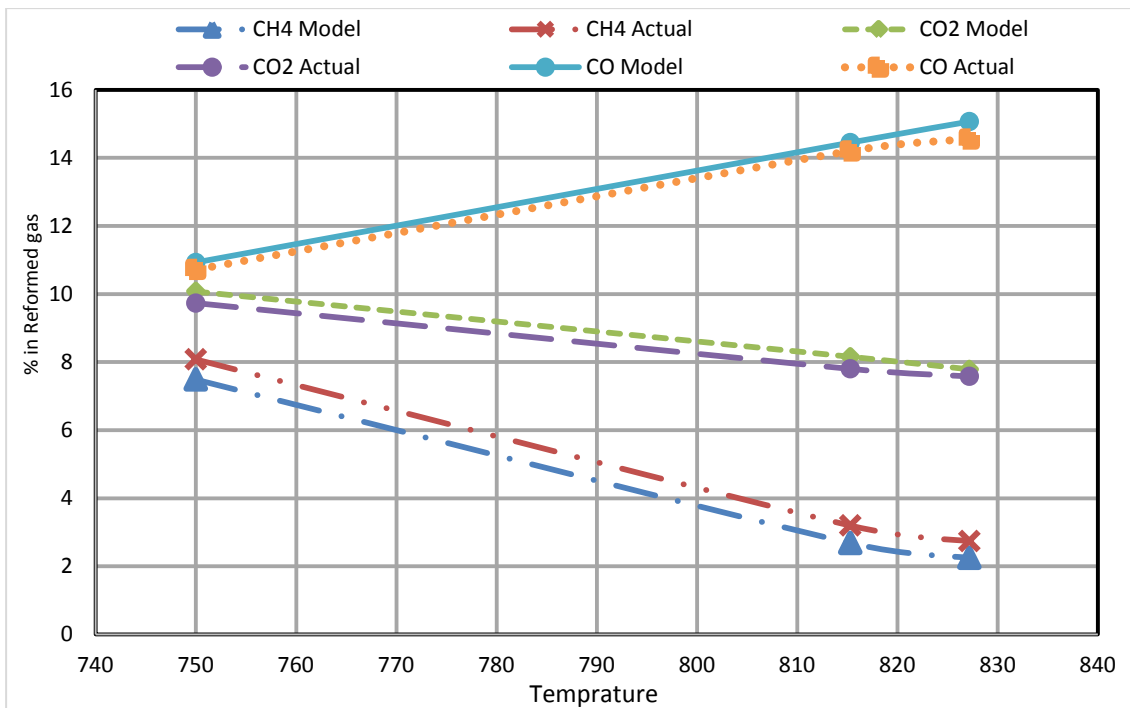


**Fig. 2: Effect of STEAM TO CARBON ratio on CH<sub>4</sub>, CO<sub>2</sub> and CO percentages in reformed gas at a constant temperature of 815°C and pressure of 8.15 kg/cm<sup>2</sup>.**

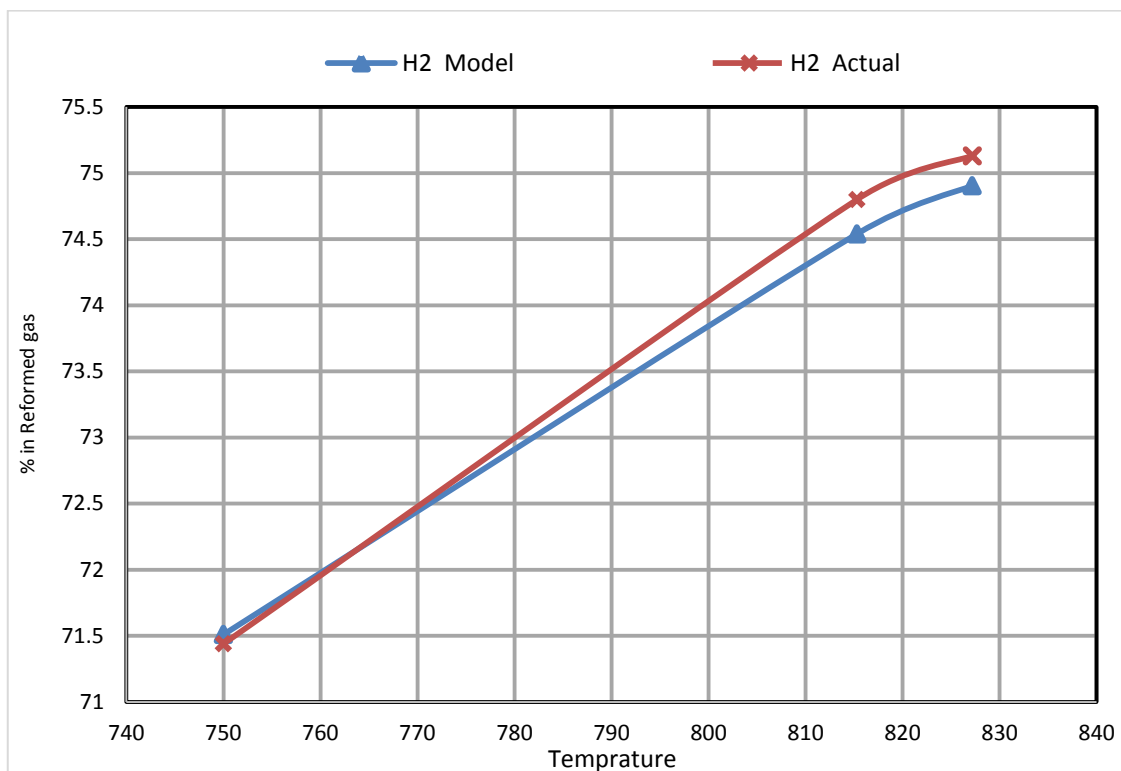




**Fig. 3: Effect of STEAM TO CARBON ratio on H<sub>2</sub> percentage in reformed gas at a constant temperature of 815°C and pressure of 8.15 kg/cm<sup>2</sup>.**



**Fig. 4: Effect of temperature on CH<sub>4</sub>, CO<sub>2</sub> and CO concentration in reformed gas at constant steam to carbon ratio of 2.6 and pressure of 8.15 Kg/cm<sup>2</sup>.**



**Fig. 5: Effect of temperature on H<sub>2</sub> concentration in reformed gas at constant steam to carbon ratio of 2.6 and pressure of 8.15 Kg/cm<sup>2</sup>.**

Reforming of hydrocarbon produces a syngas with H<sub>2</sub>/CO ratio ranging between 2.2 and 4.8 depending on the feed composition. Steam reforming is often conducted with natural gas, which is available worldwide, and at relative low price in large quantities. Steam Methane Reforming (SMR) proceeds in two steps, the reforming reaction in which methane reacts with steam producing H<sub>2</sub> and CO is strongly endothermic (206 kJ/mol), and the water gas shift reaction leads to the conversion of CO to H<sub>2</sub>, which is slightly exothermic(- 41 kJ/mol)[10].

The present study shows that:

- 1 - Methane slip is proportional to  $K_w$  that is inversely proportional to temperature.
- 2 - Methane slip is proportional to  $P_t$ .
- 3 - Methane slip is inversely proportional to steam to carbon ratio [11].
- 4 - The steam methane reforming reaction is strongly endothermic and is therefore favored by increasing temperature. Typical reformer outlet temperatures are in the range of 810–900°C. As the temperature increases, the hydrogen yield increases, which is reflected in a decrease of methane concentration in the reformer effluent, known as methane slip. The higher the H<sub>2</sub> yield, the lesser the amount of feedstock that will be consumed [11].

- 5 - CO concentration is not dependent on reformer working pressure.
- 6 - Higher steam to carbon ratio gives lower CO content.
- 7 - Higher steam to carbon ratio gives higher CO<sub>2</sub> content.
- 8 - High exit temperature gives more CO and less CO<sub>2</sub> because of the exothermic nature of the water-gas shift reaction [11].

The theoretical calculations are in accord with the respective practical data collected at different operation parameters of EZZ direct reduction plant at Suez Elsokhna.

The study is particularly useful for countries where natural gas prices dominate operating cost. The most important parameters to influence natural gas consumption are:

- Methane slip.
- Steam-to-carbon ratio.
- Natural gas composition [12].

#### 4. CONCLUSIONS

The theoretical calculations are in accord with the respective practical data collected at different operation parameters of EZZ direct reduction plant at Suez Elsokhna that mean that this study is helpful in Identification and optimization of process parameters and the optimization of process/design parameters for the minimization of natural gas consumption and tuning of the whole operation.

#### Nomenclature

$K_w$ : Equilibrium constant for steam-methane reaction

$K_z$ : Equilibrium constant for water gas shift reaction P: Reformer pressure

$P_{CO}$ ,  $P_{H_2}$ ,  $P_{N_2}$ ,  $P_{H_2O}$  Partial pressures of CO, H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>O,

C: (All carbon becomes CO),

A: (all hydrogen becomes H<sub>2</sub> except the Hydrogen combined as H<sub>2</sub>O),

B: (H<sub>2</sub>O is equal to all the oxygen not combined as CO).

I: Inert gas.

$D = A + C + I$ ,

$C_1 C_2 \dots$ ;  $C_n$ : Mole fractions of CH<sub>4</sub>... C<sub>n</sub> H<sub>2n+2</sub> in the natural gas fed.

$x_{CO_2}$ ,  $x_{CO}$ ,  $x_{H_2}$ ,  $x_{N_2}$ ,  $x_{H_2O}$  [=] mole fractions of CO<sub>2</sub> CO, H<sub>2</sub> N<sub>2</sub> and H<sub>2</sub>O respectively in the natural gas fed,

r: Steam/carbon molar ratio fed to the reformer: STEAM TO CARBON,

W: is moles of CH<sub>4</sub> produced by reaction,

Z: is moles of CO<sub>2</sub> produced by reaction,

F: total flow

$p_{N_2}$ ,  $p_{CO} \dots p_i$  = Partial pressure of the "i" component,

$P_t$  = Total pressure or reformer working pressure.

$P_i = x_i \cdot P_T$  = component (H<sub>2</sub>, CO, etc.)

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