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Thermodynamic Equilibrium Analysis of Natural Gas Steam Reforming In Basra Fertilizer Plant

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Abstract: Equilibrium analysis of natural gas steam reforming is carried out in the present paper. A simulation program based Evaluation of Equilibrium Constant (EEC) method is developed to calculate the equilibrium composition of the five steam reforming species (CH_4 , H_2O , H_2 , CO , and CO_2). Industrial information taken from primary reforming plant of existing ammonia unit in the State Company of Fertilizers South Region in Basra/ Iraq is employed as input data of simulator.

The performance of the primary reformer is evaluated relative to results of equilibrium analysis. The influence of operating temperature reforming temperature (400–1000 °C), pressure (10-40) bar and steam-to-carbon ratio ($\text{S/C} = 2\text{--}5$) on the yield hydrogen and CO is studied.

It was established that complete conversion of methane is recorded at 1000 °C. It was also found that it is necessary to work at temperature (700-900) °C to obtain a significant increasing in the hydrogen yield with reducing the operating pressure and/or increasing steam to carbon mole ratio.

Keywords: Steam reforming, thermodynamic equilibrium, Fertilizer plant.

INTRODUCTION

Steam reforming process acts an important role to produce hydrogen from natural gas. Natural gas, which is mainly consisting of CH_4 , reacts with steam to produce synthesis gas (H_2 and CO) (1).

Steam reforming process is preferred in ammonia plants because it produces more ratio of H_2/CO than other process (H_2/CO is 3) (2). In Basra Fertilizer plant, steam reforming of natural gas is carried out in a catalytic tubes is centered into a furnace to supply heat. The catalytic tubes and furnace called primary reforming unit.

The maximum possible conversion of natural gas in steam reforming can be found from theory of chemical equilibrium. The chemical equilibrium of reforming reaction does not depend on catalyst; it depends on temperature, pressure and composition of the reactants (steam /natural gas mole ratio) (1).

A thermodynamic equilibrium analysis including five chemical species (CH_4 , H_2O , H_2 , CO , CO_2) is performed to determine the adequate range for temperature, pressure and steam-methane ratio and to calculate the equilibrium concentration of products. The equilibrium analysis is based on the method of Evaluation of Equilibrium Constant (EEC) which is based on stoichiometric reaction equations³. Thermodynamic equilibrium sets a theoretical limit on the extent to which reactants can be converted into products and this limit cannot be changed by catalyst. The choice of catalyst that could achieve this limit. **Table-1** show the feed composition of natural gas operating conditions of primary reformer in ammonia unite of Basra Fertilizer plant which are used as input data to simulation computer program:

Table-1: Operating condition of primary reformer plant

Parameter	Value and unit
T_{in}	550 °C
P_{in}	34.4 bar
S/C	4.8
F_{in}	1394.2 kmol/hr
Natural gas composition% (Dry basis)	
CH_4	88.11
H_2	3.44
CO_2	6.5
CO	0
(Ar+N ₂)	1.95

EXPERIMENTAL PROCEDURE

Chemical reaction of steam reforming: Two independent reactions are carried out through steam reforming process. The first reaction is methane steam reforming (MSR), which is endothermic reaction, and the second is water gas shift reaction (WGS), which is exothermic reaction (3).



The reactions MSR and WGS are both equilibrium reactions and a global reaction can be expressed with a forward and a backward reaction rate. The rate at which the reactions occur depends on the distance to the equilibrium position (thermodynamics) and the speed at which the reactions occur (kinetics). The thermodynamic part of the chemistry is the ratio of the forward to the backward reaction speed. This ratio, which is temperature dependent, can be calculated by the distance to the equilibrium at which both reactions are equal in speed. The equilibrium constant for partial pressures (K) is used to this end (3).

Chemical Equilibrium Analysis: Conversion at equilibrium is calculated from the coupled set of equations for equilibrium constant for the two reactions (4).

$$K_{SR}^{eq} = \frac{f_{CO} \cdot f_{H_2}^3}{f_{CH_4} \cdot f_{H_2O}} \quad (3)$$

$$K_{WGS}^{eq} = \frac{f_{CO_2} \cdot f_{H_2}}{f_{CO} \cdot f_{H_2O}} \quad (4)$$

Where:

$$f_i = \text{fugacity coeff.}_i \cdot P_i \quad (5)$$

For pressures sufficiently low or temperature sufficiently high, the equilibrium mixture behaves essentially as an ideal gas. In this case the fugacity coeff. $_i=1$. (5)

$$f_i = p_i \quad (6)$$

since:

$$K_{SR}^{eq} = \frac{P_{CO} \cdot P_{H_2}^3}{P_{CH_4} \cdot P_{H_2O}} \quad (7)$$

$$K_{WGS}^{eq} = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} \quad (8)$$

The standard Gibbs free energy changes (ΔG_{T_0}) at system temperature T used in analysis of the reactions is calculated by the following equation:

$$\frac{\Delta G_T^0}{RT} = \frac{\Delta G_0^0 - \Delta H_0^0}{RT_0} + \frac{\Delta H_0^0}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^0}{R} dT - \int_{T_0}^T \frac{\Delta C_p^0}{RT} dT \quad (9)$$

Meanwhile, the equilibrium constant (K) of the reactions can be predicted by the following

Equation (5):

$$K = \exp\left(\frac{-\Delta G^0}{RT}\right) \quad (10)$$

Material balance: The gas mixture at equilibrium contains five component: CH_4 , H_2O , H_2 , CO_2 and CO in addition to inert material (N_2+Ar). Two extents of reactions or conversion variables can be calculated from the following two equations:

$$X_{CH_4} = \frac{F_{CH_4in} - F_{CH_4out}}{F_{CH_4in}} \quad (11)$$

$$X_{CO_2} = \frac{F_{CO_2out} - F_{CO_2in}}{F_{CH_4in}} \quad (12)$$

The molar flow rate for each component is obtained from material balance on reactor:

$$F_{CH_4out} = F_{CH_4in} (1 - X_{CH_4}) \quad (13a)$$

$$F_{H_2Oout} = F_{H_2Oin} - F_{CH_4in} (X_{CH_4} + X_{CO_2}) \quad (13b)$$

$$F_{H_2out} = F_{H_2in} + F_{CH_4in} (3X_{CH_4} + X_{CO_2}) \quad (13c)$$

$$F_{COout} = F_{COin} + F_{CH_4in} (X_{CH_4} - X_{CO_2}) \quad (13d)$$

$$F_{CO_2out} = F_{CO_2in} + F_{CH_4in} X_{CO_2} \quad (13e)$$

$$F_{inert,out} = F_{inert,in} \quad (13f)$$

$$F_{total,out} = F_{total,in} + 2F_{CH_4in} X_{CH_4} \quad (13g)$$

The partial pressures of species are then given by:

$$P_{CH_4} = P_t \cdot \frac{F_{CH_4in} (1 - X_{CH_4})}{F_{total,in} + 2F_{CH_4in} X_{CH_4}} \quad (14a)$$

$$P_{H_2O} = P_t \cdot \frac{F_{H_2Oin} - F_{CH_4in} (X_{CH_4} + X_{CO_2})}{F_{total,in} + 2F_{CH_4in} X_{CH_4}} \quad (14b)$$

$$P_{H_2} = P_t \cdot \frac{F_{H_2in} + F_{CH_4in} (3X_{CH_4} + X_{CO_2})}{F_{total,in} + 2F_{CH_4in} X_{CH_4}} \quad (14c)$$

$$P_{CO} = P_t \cdot \frac{F_{COin} + F_{CH_4in} (X_{CH_4} - X_{CO_2})}{F_{total,in} + 2F_{CH_4in} X_{CH_4}} \quad (14d)$$

$$P_{CO_2} = P_t \cdot \frac{F_{CO_2in} + F_{CH_4in} X_{CO_2}}{F_{total,in} + 2F_{CH_4in} X_{CH_4}} \quad (14e)$$

By substituting the partial pressures of five components in the two equations of (7) and (8) results:

$$K_{SR}^{eq} = \left(\frac{P_t}{F_{tot}} \right)^2 \frac{[F_{COin} + F_{CH_4in} (X_{CH_4} - X_{CO_2})][F_{H_2in} + F_{CH_4in} (3X_{CH_4} + X_{CO_2})]^3}{F_{CH_4in} (1 - X_{CH_4}) [F_{H_2Oin} - F_{CH_4in} (X_{CH_4} + X_{CO_2})]} \quad (15)$$

$$K_{WGS}^{eq} = \frac{[F_{CO_2in} + F_{CH_4in} X_{CO_2}][F_{H_2in} + F_{CH_4in} (3X_{CH_4} + X_{CO_2})]^3}{[F_{COin} + F_{CH_4in} (X_{CH_4} - X_{CO_2})][F_{H_2Oin} - F_{CH_4in} (X_{CH_4} + X_{CO_2})]} \quad (16)$$

The two non-linear equations system is solved instantaneously by Newton method to find the unknown values of two conversions.

The yield of H₂ and CO are defined by:

$$Yield_{H_2} = \frac{F_{H_2out} - F_{H_2in}}{F_{CH_4in}} \quad (17)$$

$$Yield_{CO} = \frac{F_{COout}}{F_{CH_4in}} \quad (18)$$

RESULTS AND DISCUSSION

Thermodynamic equilibrium study is achieved on steam methane reforming process which is used to produce ammonia in Basra Fertilizer plant. A simulation program based on EEC method is developed to calculate the species equilibrium composition of steam reforming process. In this paper, the effect of three important operating conditions in reforming process (Temperature, pressure and steam to carbon ratio) on conversion and yield of H_2 and CO is studied from thermodynamic equilibrium point of view. Information of input natural gas composition, operating temperature and pressure are used as input parameter to the simulation program.

Methane and CO_2 conversion:

Temperature: The equilibrium values of the conversions and composition variable at pressure (34.4 bar) are shown in figures (1) and (2). This gives an idea of the values for them that can be expected in the reactor, especially at high temperature.

Figure-1 shows the two reaction (SR and WGS) progress when the temperature increases. In case of SR reaction (CH_4 conversion), a monotonic behavior is shown. According to Le-Chatelliere principle, the endothermic reaction requires more heat to shift the reaction to forward. An opposite behavior for WGS reaction which is an exothermic reaction, (CO_2 conversion) reverses its trend above $800^\circ C$. This phenomena due to change the sign of its free energy from negative to positive. This makes the WGS reaction nonspontaneous above $800^\circ C$.

The maximum difference between two conversion values at $1000^\circ C$. The same trend is also shown in figure-2 where the composition of CO_2 reach to its maximum value at $800^\circ C$. Since the overall process is endothermic, so conversion increases with temperature. Figure-2 shows that, at high reforming temperature, less water is remained and more hydrogen is yield. It can be seen that a complete conversion of methane can be obtained when the temperature reaches $1000^\circ C$. Although, Very little conversion can be achieved below $500^\circ C$. The maximum change in methane, water and hydrogen focuses between $500^\circ C$ and $800^\circ C$ before the WGS reaction reverse its trend.

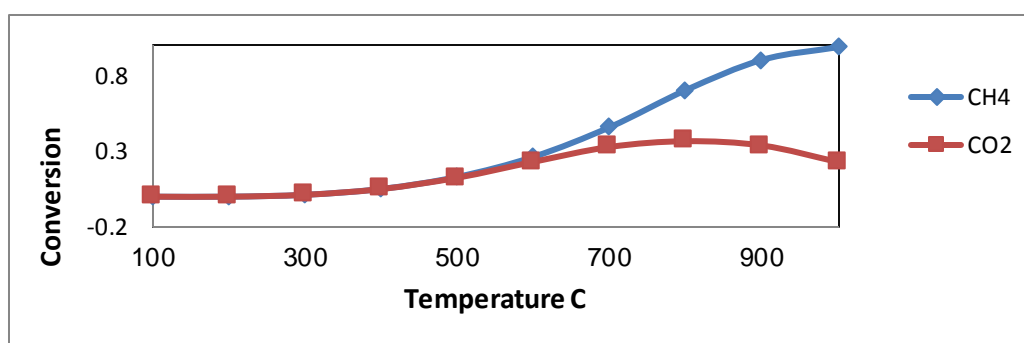


Figure-1: Variation of conversion of MSR and WGS with temperature.

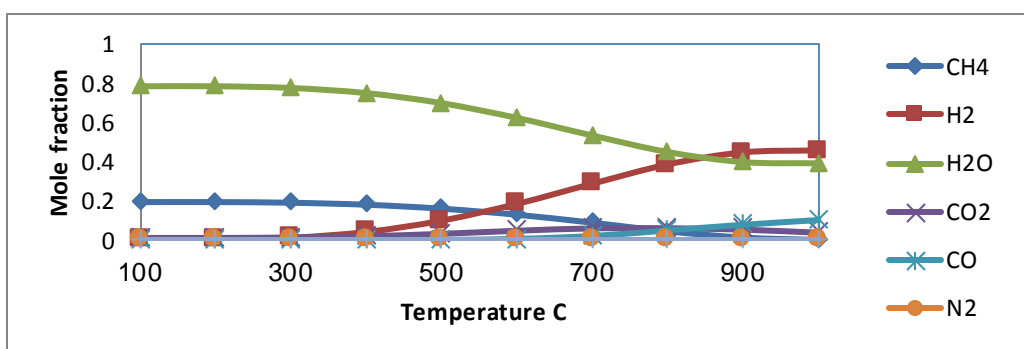


Figure-2: Variation of reactant and product mole fractions with temperature.

Pressure: Figure-3 shows that, at 800 °C, increasing pressure reduces the methane conversion. In steam reforming reaction the number of reactant is higher than number of mole of product. As Le-Chatelier's principle states, increasing the pressure favors the side of the equilibrium with the least number of gaseous molecules.

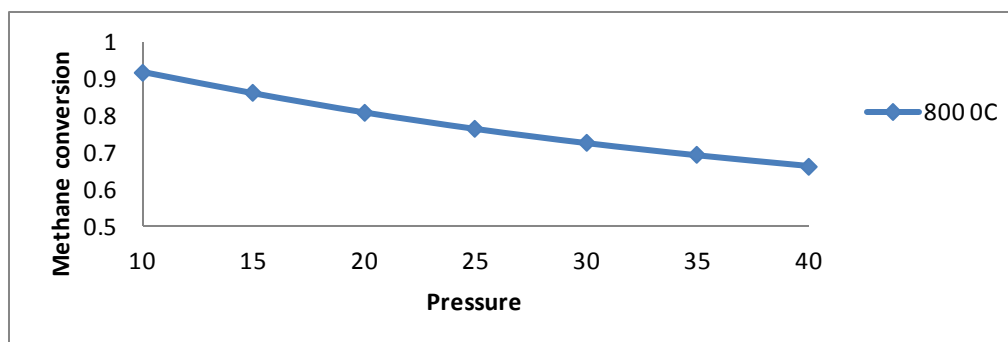


Figure-3: Effect of pressure on methane conversion at 800 °C.

Figure-4 illustrates that the highest conversion of methane can be produced at higher temperature and lower pressure i.e at 1000 °C and 10 bar. It can be seen from figure-4 the rising pressure from 10 bar to 40 bar has no significant effect on methane conversion at very high and very low temperature. That points to that the effect of temperature on conversion is higher than effect of pressure. The maximum reduction in conversion at 700 °C and 800 °C, where methane conversion values are lowered by 0.27 and 0.25 respectively.

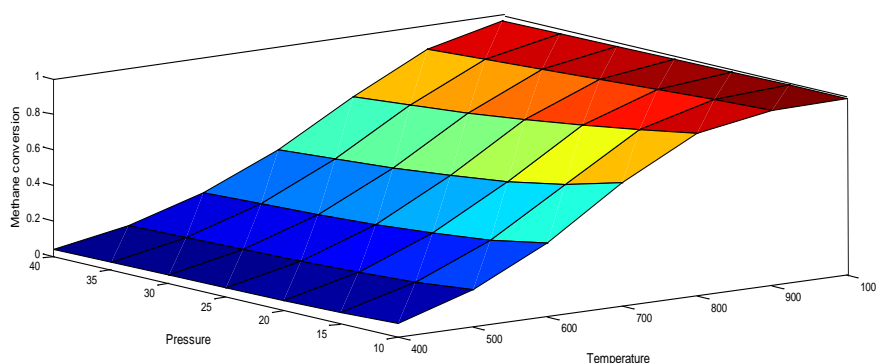


Figure-4: Effect of pressure and temperature on methane conversion

Figure-5 shows the effect of both temperature and pressure rising on CO₂ conversion (WGS reaction). It can be seen that at high temperature, the CO₂ conversion does not influence by pressure rising, since the value of conversion remains constant at 0.221 at 1000 °C. However, the range of temperature that pressure has effect on conversion is from 500 °C to 900 °C. As a result to pressure reducing from 40 to 10 bar, the peak of curve move from 800 °C to 700 °C.

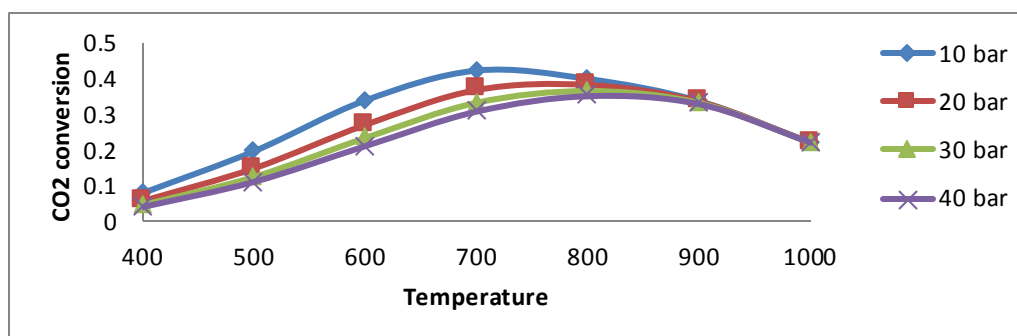


Figure-5: Effect of pressure and temperature on CO₂ conversion

Steam to carbon ratio (SCR): According to the law of mass action; the rate of chemical reaction is proportional to the active mass of each reactant present in the system. As a result, increasing mole flowrate of steam causes increasing of methane conversion.

The SCR is an important parameter affecting hydrocarbon steam reforming (SR). Relatively high SCR are not only required to achieve high hydrogen yields, but they also are essential to prevent the formation of solid carbon, especially with feeds containing large-chain (higher) hydrocarbons. In conventional steam reformer of methane, should be higher than 1.7 (6).

As shown in **figure-6** at constant pressure, the increasing the mole ratio of steam to carbon rises the methane consumption.

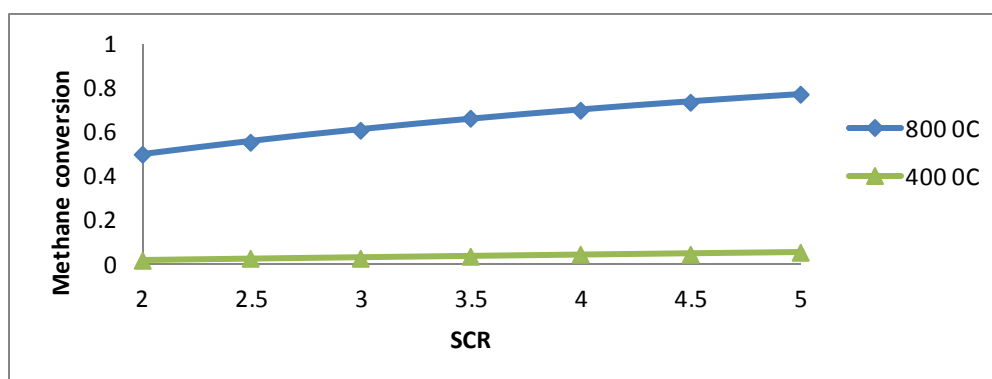


Figure-6: Effect SCR on methane conversion at 34.4 bar

Figure-7 represents the variation on SCR and temperature on methane conversion. It can be seen that at high mole ratio of steam to carbon, the rising temperature from 900 °C to 1000°C has no predominant effect on methane conversion.

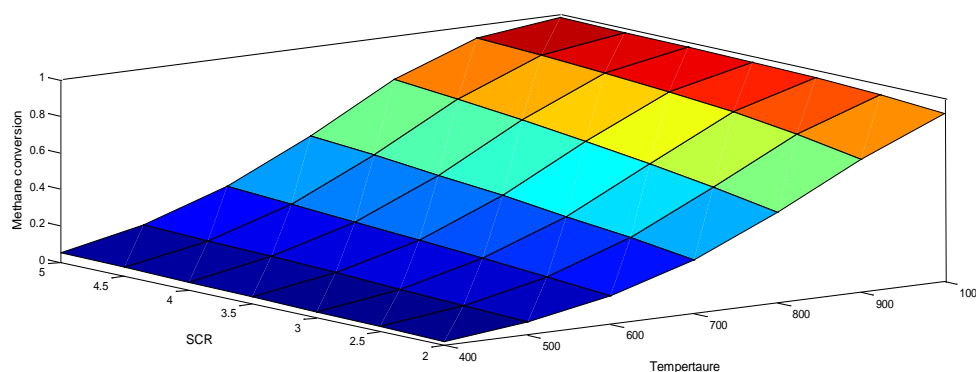


Figure-7: Effect of Temperature and SCR on methane conversion at 34.4 bar

Figure -8 shows the effect of pressure and SCR increasing on methane conversion. The minimum and maximum values of conversion at 800 °C are 40 bar and SCR= 2 and 10 bar and SCR=5 respectively. Also it is shown that maximum change in methane conversion when the operating pressure rises from 10 to 40 bar is 0.29 at SCR=3.

From **figure-9** it can be noted that higher flow rate of steam favors higher production of CO₂. It can be observed that increasing the SCR does not change the position of maximum conversion i.e 800 °C remains the peak point.

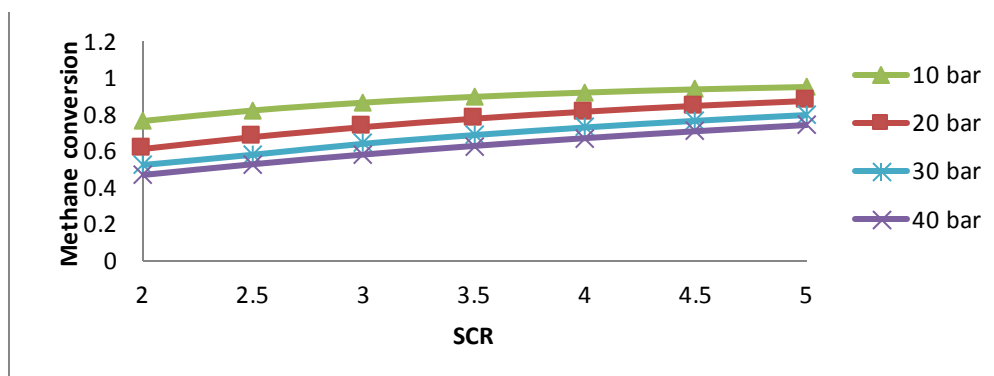


Figure-8: Effect of Pressure and SCR on methane conversion at 800 °C

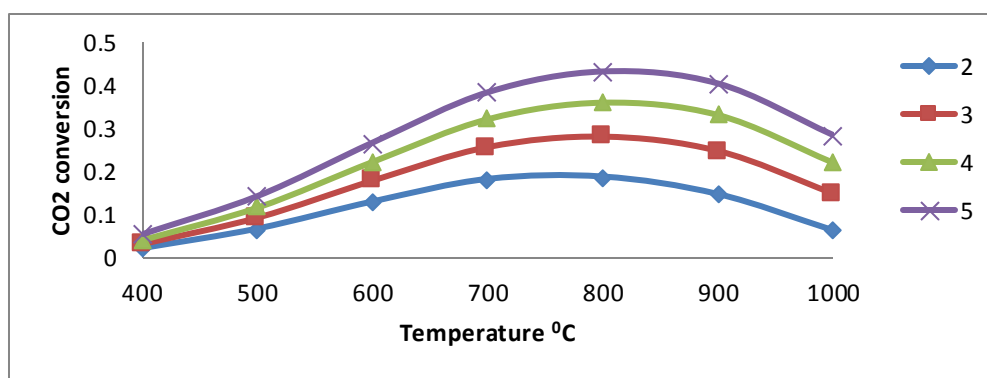


Figure-9: Effect of temperature and SCR on methane conversion at 34.4 bar

Hydrogen and CO yield: From the eqs. (1) and (2), it is shown that hydrogen is produced from two reactions SR and WGS reactions. Since value of hydrogen yield depends on the conversion values of two reactions.

Figure-10 illustrates that maximum yield of hydrogen is produced at 10 bar and 900 °C. as the methane conversion behavior with temperature and pressure, the maximum effect of pressure increasing on hydrogen yield focuses at 700 and 800 °C.

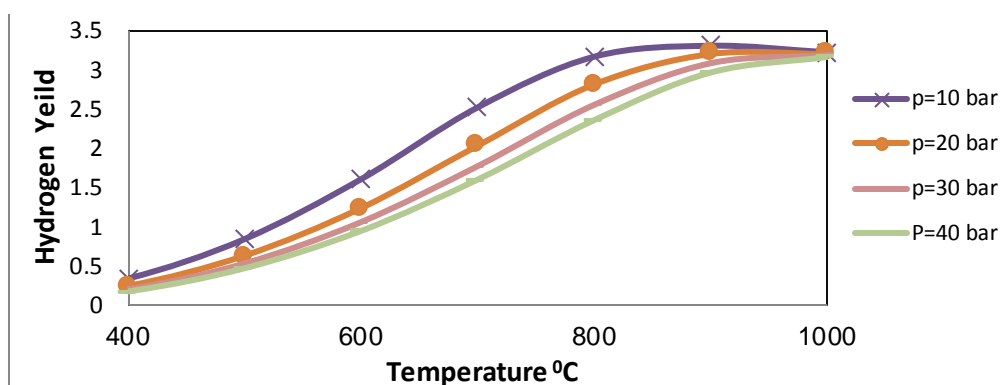


Figure-10 Effect of temperature and pressure on hydrogen yield.

Since CO is produced from the reaction (1) and consumed in reaction (2) where the rate two reactions have opposite trend with temperature, figure (11) shows the effect of temperature rise on CO yield. It can be noticed that maximum yield of CO is at 1000 °C. Also it can be illustrated from this figure that Pressure effect has no valuable effect at mainum and maximum .However the maxium effect of pressure on CO yield focuses in 800 °C.

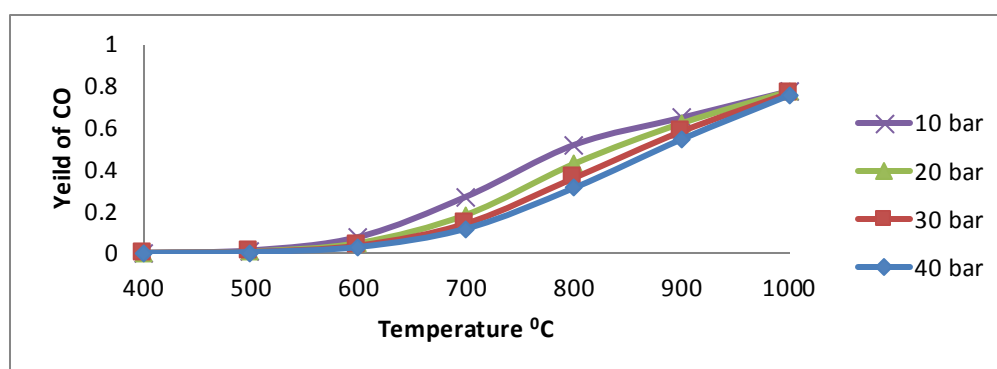


Figure-11: Effect of temperature and pressure on CO yield.

In figure-12 it can be observed that the maximum value of hydrogen yield at 1000 °C when SCR=5. It is expected that hydrogen yield increases with the increasing of steam-to-carbon ratio because the equilibrium reactions. It is not interesting to increase SCR values higher than 5 because it does not result in any significant gain in hydrogen yield and besides processing of feeds with high SCR requires larger reactor sizes and more heat to evaporate the feed.

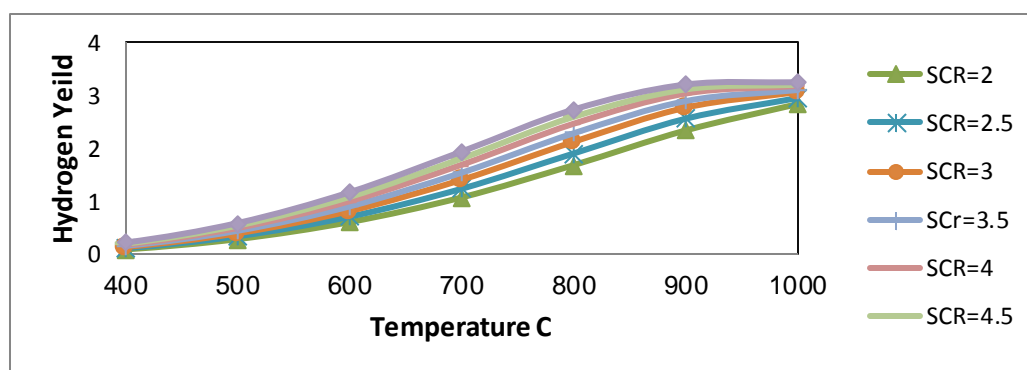


Figure-12: Effect of temperature and SCR on hydrogen yield at 34.4 bar

At the same time, hydrogen equilibrium concentration also increases with the increase from 600 °C to 800 °C. This is mainly because steam reforming occurs simultaneously with the WGS reaction. However, change of H₂ yield is not prominent above 900 K because of the inhibition of the exothermic WGS reaction. Also at high mole flow rate of steam, rising the temperature from 900 to 1000 °C has no effect on hydrogen yield.

Figure-13 shows that the maximum increase in Hydrogen yield when mole ratio of steam to carbon rises from 2 to 5 is at 800 °C at pressures 20, 34 and 40 bar.

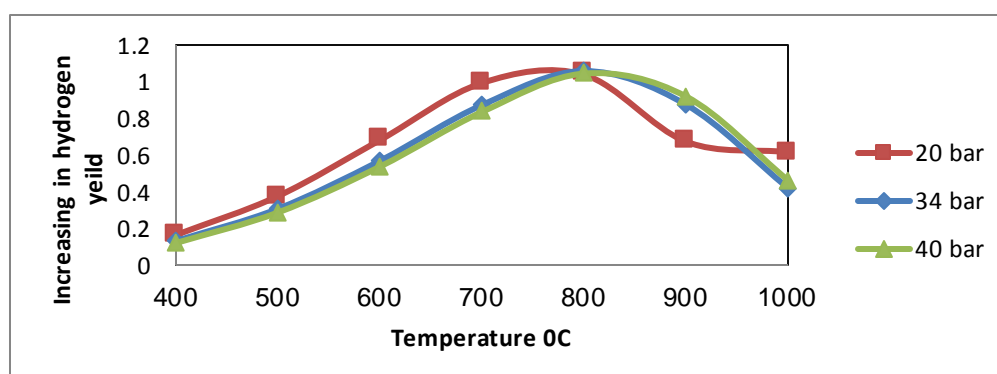


Figure-13: Effect of temperature, pressure and SCR on hydrogen yield

The influence of variation of temperature and SCR on CO yield is shown in figure-14. It is observed that, there is no significant change in the yield of CO below 900 °C relative to SCR rising. This is attributed to high rate of WGS reaction in which CO is consumed to CO₂. Moreover the addition of a large excess of steam in reactor feed gas at 1000 °C enables high-equilibrium conversions of carbon monoxide.

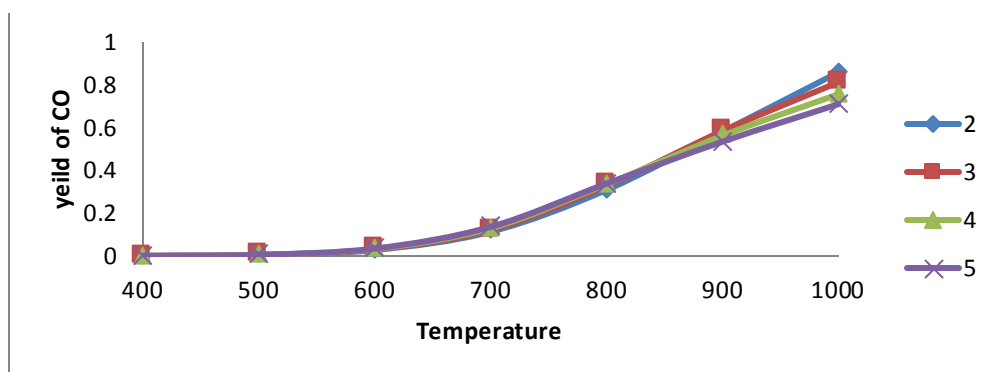


Figure-14: Effect of temperature and SCR on CO yield at 34.4 bar

CONCLUSIONS

In this study, the experimental work in reforming plant of existing ammonia unit in the State Company of Fertilizers South Region in Basra/ Iraq is performed. Authors have studied the effect of three important operating conditions that, temperature, pressure and steam to carbon ratio in reforming process on conversion to find out yield of H₂ and CO from thermodynamic equilibrium point of view.

They have observed that a complete conversion of methane can be obtained when the temperature reaches at higher temperature at lower pressure i.e 1000 °C and 10 bar. At temperature range (500-1000) °C, the conversion of methane can be raised when the pressure is reduced and/or excess of steam is added to feed gas mixture.

It is observed that at 1000 °C, the pressure change has no significant effect on methane conversion and this effect has disappeared for H₂ and CO yield this mean temperature has more effect than pressure on steam reforming progress. Oppositely, at the same temperature, the values of H₂ and CO yield can be changed when the values of SCR has changed.

Finally, it can be seen that. to shift the equilibrium of WGS reaction to form the more H₂, it necessary to use excess water, low reaction temperature.

Nomenclature:

T : Temperature (K)

P : Pressure (bar)

cp : Heat capacity (kJ/kmol.K)

f : Fugacity (bar)

F: Molar flowrate (kmol/hr)

G : Free energy (kJ/kmol)

H : Heat of reaction (kJ/mol)

K^{eq} : Equilibrium constant

R : Universal gas constant (kJ/kmol.K)

X : Conversion

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