A STUDY OF THE INFLUENCE OF PRESSURE, TEMPERATURE, STEAM/NATURAL GAS RATIO ON REFORMING PROCESS FOR AMMONIA PRODUCTION

BY

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A THESIS
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CERTIFICATION OF THESIS WORK

We, the undersigned, certify that S.M. JAHANGIR, candidate for the degree of Master of Science in Engineering (Chemical) has presented his thesis on the subject "A STUDY OF THE INFLUENCE OF PRESSURE, TEMPERATURE, STEAM/NATURAL GAS RATIO ON REFORMING PROCESS FOR AMMONIA PRODUCTION". The thesis is acceptable in form and content. The student demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on June 21, 2000.

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ABSTRACT

The purpose of the thesis work is to study the influence of pressure temperature, steam/natural gas ratio on reforming process for ammonia production.

The thesis work is divided in two steps. In first step, a solution for calculating equilibrium composition of the products of the steam reforming at particular pressure, temperature and steam/natural gas ratio has been found out from the graphical representation of lnK vs. 1/T involve in the process. A large number of data representing conversion analysis of steam reforming of methane at different pressure, temperature and steam/natural gas ratio have been calculated and graphical representation showing influence of pressure, temperature and steam/natural gas ratio has been plotted. From the calculated values and graphical representation it can be seen that conversion of natural gas increases with the increase of temperature and steam/NG ratio, and decreases with the increase of operating pressure. If operating pressure has to be increased, for maximum conversion of natural gas both temperature and steam/natural gas ratio or any of them should be increased to compensate the decrease of conversion of natural gas at high pressure.

In second step, for testing the validity of the theoretical analysis of steam reforming of natural gas, process conditions of primary reformer and secondary reformer of seven fertilizer factories in Bangladesh have been used to calculate the theoretical outlet compositions of the reformers. The fertilizer factories whose data have been used are Zia Fertilizer Company Ltd. (ZFCL), Jamuna Fertilizer Company Ltd. (JFCL), Polash Urea Fertilizer Factory (PUFF), Natural Gas Fertilizer Factory (NGFF), Urea Fertilizer Factory Ltd. (UFFL), Chittagong Urea Fertilizer Ltd. (CUFL), and Karnaphuli Fertilizer Company Ltd (KAFCO). A comparison has been performed showing the theoretical values and the actual outlet equilibrium compositions of reformers of different processes. A small discrepancy of theoretical values and actual values have been observed and the causes for these discrepancy have also been described.

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CHAPTER - 1

INTRODUCTION

There are seven urea fertilizer factories in Bangladesh. In ammonia process of these factories, the process of steam reforming of natural gas requires natural gas and steam to produce CO, CO_2 and H_2. Design parameters of the reforming processes of these fertilizer factories are different from each other. But operation and control technique and some other features of reforming processes are same. The findings of this thesis work will help to give a clear idea of reforming process to the people involved with urea fertilizer production.

The reforming of natural gas is completed in two steps. The first step is known as primary reforming where natural gas reacts with steam at certain temperature and pressure to produce carbon monoxide, carbon-dioxide and hydrogen. Steam/natural gas can be used at different ratios. The second step is known as secondary reforming. The exit gases from the primary reformer react with air in the secondary reformer top chamber. Air is added in this chamber where hydrogen reacts with oxygen to produce steam. Unreacted methane again reacts with steam at the bottom chamber of the secondary reformer to complete reforming of natural gas.

The amount of steam and air needed can be determined from stoichiometry. In practice, amount of steam used in reforming is more than the stoichiometric amount. Excess amount of steam is used in order to get more conversion of natural gas and to prevent carbon formation on the catalyst surface. The reactions which are thermodynamically favourable may occur at inconveniently slow rates. But the reaction will reach the equilibrium state. The equilibrium conversion of reaction does not depend on catalyst; it depends on the thermodynamics properties.

The maximum possible conversion of natural gas in steam reforming can be known by using theory of chemical equilibrium [1, 2, 6, 11, 12, 13, 15, 21, 26]. The chemical equilibrium of reforming reaction depends on temperature, pressure and composition of the reactants (i.e. steam/natural gas ratio). The influence of pressure, temperature and steam/natural gas ratio on reforming process for ammonia production has been studied in this research work.

The objectives of the thesis work are:

(i) To study the influence of temperatures on reforming reaction of ammonia process.

(ii) To study the influence of steam/natural gas ratio on reforming reaction.

(iii) To study the influence of pressure on reforming reaction.

(iv) If high operating pressure is selected for reforming process, how other variables have to be adjusted.

CHAPTER – 2

LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter conversion of higher hydrocarbon to methane, usage ratio of reforming from stoichiometry, operating variables of reforming, development of equation of the chemical equilibrium constant of reforming reaction, reforming problems and favourable conditions of reforming, selection technique of operating variable of reforming, influence of secondary reformer top chamber combustion on reforming reaction and basic control of ammonia plant have been described.

2.1.1 Conversion of Higher Hydrocarbon to Methane

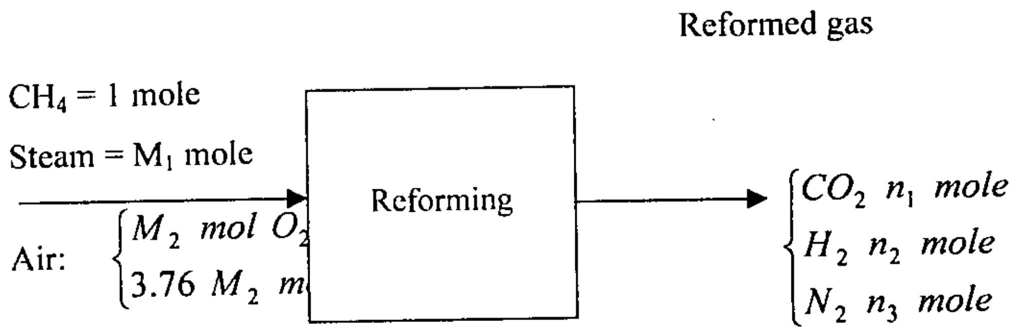
In the reforming process for ammonia production, a small amount H_2 gas is recycled with feed natural gas. So, all higher hydrocarbon of alkane group will be converted to methane at low temperature in presence of nickel catalyst [4, 5, 23].

$$C_2H_6 + H_2 = 2CH_4$$
$$C_3H_8 + 2H_2 = 3CH_4$$
$$C_4H_{10} + 3H_2 = 4CH_4$$

So, theoretical calculation of natural gas reforming products can be performed on the basis of methane.

2.1.2 Calculation of Usage Ratios from Stoichiometry of Reforming Reaction

In the process of reforming, natural gas, steam and air are converted to CO_2, H_2 and N_2.



Assumptions:

1. Methane is completely converted
2. Air composed of 21% mole O_2 and 79% mole Nitrogen
3. The reactions are happening according to the following equations

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Now, from stoichiometry,

$$\left(\frac{H_2O}{CH_4}\right)_{stoic} = 2.0$$

$$\left(\frac{O_2}{H_2}\right)_{Stoic} = 2.0$$

$$\left(\frac{N_2}{O_2}\right)_{Stoic\ in\ the\ air} = 3.79$$

For ammonia production: ($N_2 + 3H_2 = 2NH_3$)

$$\left(\frac{H_2}{N_2}\right)_{Stoic} = 3.0$$

Let, the limiting reactant = CH_4

Basis: 1 mole CH_4

So, Steam (H_2O) requirement = 2 mole according to the reaction

H_2 production = 4 mole according to the reaction

As, methane is completely converted (assumed).

So, CO_2 produced, n_1 = 1 mole

Let, the extent of reaction = ε

O_2 at the inlet of reforming process = ε mole

N_2 at the inlet of reforming process = $3.76\ \varepsilon$ mole

H_2O (steam) at the inlet of reforming process = $(2 - 2\varepsilon)$ mole

H_2 at the outlet of reforming process = $(4 - 2\varepsilon)$ mole

Now, $$\left(\frac{H_2}{N_2}\right)_{Stoic} = 3.0 \text{ (for Ammonia Production)}$$

Or, $$\frac{4-2\varepsilon}{3.76\varepsilon} = 3.0$$

Or, $4 - 2\varepsilon = 11.28\varepsilon$

Or, $13.28\varepsilon = 4.0$

$$\varepsilon = \frac{4.0}{13.28}$$

$$= 0.30$$

So, O_2 at the inlet of reforming, $M_2 = \varepsilon = 0.30$ mole

N_2 at the inlet of reforming, $n_3 = 3.76\ M_2 = 1.13$ mole

Steam at the inlet of reforming, $M_1 = 2 - 2\varepsilon$ mole

$= 2 - 2 \times 0.3$

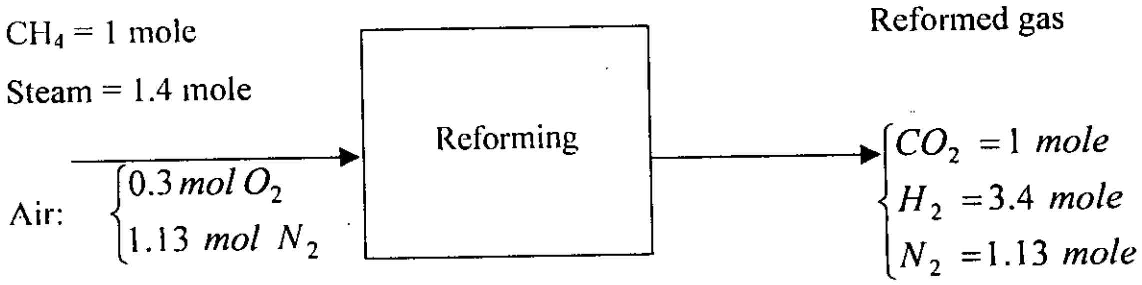
$= 1.4$ mole

H_2 at the outlet of reforming, $n_2 = 4 - 2\varepsilon$

$= 4 - 2 \times 0.3$

$= 3.4$ mole

Now,



2.1.3 Reforming Operating Variables

The operating variables for reforming are pressure, temperature, and steam/natural gas ratio. Natural gas and steam are supplied in the primary reformer inlet. Air is supplied for the requirement of N_2 during secondary reforming.

(i) Pressure:

From the reforming reactions, it can be seen that the total moles of products is higher than the moles of reactants, and the reaction is also reversible. So, according to Le-Chatteliere principle [8] the conversion of natural gas will increase with the decrease of pressure. Ever since an increase in the primary reforming pressure has made possible reductions in the cost and energy consumption of ammonia plants, the extent of that increase, that is, the optimum pressure, has come under considerable study. Because this pressures, when coupled with contemporary energy management systems, have afforded a reduction in both plan investment and fuel (or feed) costs. The key to the success of these systems is the pronounced increase in equilibrium constant brought about by increasing reforming temperatures to the limits of contemporary tube alloys. The consequent equilibrium constants permit reaction rates high enough for satisfactory reforming in a single pass through the catalyst-filled tubes.

The kinetics of high pressure steam – methane reforming have been studied by Atrochenko and Zviaginzev [22] at pressures up to 41 atm, temperatures of 873 – 1073 K, steam-to-methane ratios of 0.5 – 4.0, and space velocities of 3,000 – 50,000 hr^{-1}, in a laboratory reactor with a diameter of 25 mm. The diameter of the catalyst pellets was 3 – 4 mm, the free space was 70%, and the catalyst volume was 10 cm^3. The space velocity corresponding to this contact time indicates the effects of increase in pressure.

The contact time τ (in sec), was determined by:

$$\tau = \frac{3600}{1000} \times \frac{mV_pP273}{TQ_{CP}^0}$$

where

m = the free space between the catalyst particles, fraction;

V_p = the useful volume of the reaction zone, cm^3;

P = the reaction pressure, atm;

T = the reaction temperature, K and

Q_{cp}^0 = the arithmetic average of the volumes of the incoming and outgoing steam – gas mixtures at standard conditions.

The authors reported that at pressures of 6, 11, 26 and 41 atm, the corresponding space velocity was about 3000, 8000, 12,000, and 19,000 hr^{-1}. Under these conditions of study, equilibrium can be achieved in about 0.20 – 0.25 sec.

(ii) Temperature:

Reforming reaction is an endothermic reaction. So a large amount of heat is required to shift the reaction in the forward direction. Again, the conversion of natural gas will be increased with the increase of temperature. On decreasing reforming temperature, the effect is reversed.

(iii) Steam/Natural Gas Ratio:

According to the low of mass action, the rate of chemical reaction is population to the active mass of each of the reactants present in the system. In the reforming process, maximum amount of steam is introduced for maximum conversion of natural gas. Again, sufficient steam is required to prevent coking the catalyst. At the same time, utility consumption will increase. So, in the modern process steam/NG ratio is kept 1.4 to 3.5 [14].

In primary reforming natural gas and steam passes through the nickel catalyst where natural gas is partially reformed. The partially reformed gas from the primary reformer enters the secondary reformer inlet chamber. Air is supplied in this chamber for combustion, where chromium oxide catalyst is used. From the stoichiometric calculation it is seen that Air/NG ratio is to be 1.43 for the requirement of $H_2/N_2 = 3$ for ammonia production. From the combustion zone of the secondary reformer the flow passes through a bed of nickel catalyst to complete the reforming reaction. Maximum efficiency of the overall reforming operation requires that as much reforming as possible be done in this partial – combustion step. Utilization of combustion energy reduces the fuel gas requirement in the primary reforming furnace. However, the amount of air charged to the secondary reformer is set by the nitrogen requirements, so the degree of overall reforming will be regulated by variation of primary reformer temperatures. Increasing the air flow will raise the temperature and a decrease firing rate in the primary reformer furnace should be used to compensate as conditions dictate. When conditions are at an optimum and a change in feed gas flow is necessary, a proportional change in the same direction of the air rate will be required to maintain the H_2/N_2 balance.

2.1.4 Problem of Reforming

Again possible carbon formation reaction during reforming process is as follows [3, 14]:

$$2CO \rightarrow C + CO_2$$

The carbon formation reaction is definitely unwanted since it forms carbon, increases the pressure drop through the reformer, and coats the surface of the catalyst, thereby rendering it inactive. The equilibrium constant for the carbon formation reaction is

$$K_p = \frac{P_{CO_2}}{P^2_{CO}} = \frac{Px_{CO_2}}{P.P.x^2_{CO}} = \frac{x_{CO_2}}{P.x^2_{CO}}$$

The requirement for carbon reaction quite clear, namely, carbon will deposit on the catalyst of the composition of the gases is such that

$$\frac{x_{CO_2}}{x^2_{CO}} \leq PK_p$$

Thus carbon deposition can be prevented in the following ways.

i) Reducing pressure

ii) Increasing temperature to reduce the values of K_p

iii) Increasing the ratios of steam to hydrocarbon to shift more carbon monoxide over to carbon dioxide.

2.1.5 Favourable Conditions of Reforming Process

Maximum steam/Natural gas ratio, high temperature and low pressures are favourable conditions for maximum conversion of natural gas and it will also prevent carbon deposition on the catalyst surface.

2.2 CHEMICAL EQUILIBRIA OF REFORMING REACTIONS

The general equilibrium for steam reforming of hydrocarbon [25] is

$$C_nH_m + nH_2O \leftrightarrow nCO + \frac{2n+m}{2}H_2 \text{ (Endothermic)}$$

For methane,

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 49.3 \text{ Kcal/mol}$$

At the same time, water-gas shift equilibrium is established

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -9.84 \text{ Kcal/mol}$$

A mixture of H_2, CO, CO_2 and CH_4 is consequently obtained, the composition of which is defined by appropriate chemical equilibrium.

Thermodynamic and Kinetic considerations suggest that the conversion of methane to carbon monoxide requires low pressure and high temperature [9, 10]. Pressure have no effect on the shift conversion of CO to CO_2, but this shift conversion is favourable at low temperatures. Both these reactions require presence of catalyst.

Favourable conditions of reforming reaction and shift conversion reaction can be found from the analysis of the relation among equilibrium constants, extent of reaction, pressure and temperatures.

2.2.1 Relation between Equilibrium Constant and Temperature

The standard property changes of a reaction, such as ΔG^0 and ΔH^0, vary with the equilibrium temperature. The dependence of ΔG^0 on T is given by [7, 21]:

$$\frac{d\left(\frac{\Delta G}{RT}\right)}{dT} = \frac{-\Delta H^{o}}{RT}$$

But, $\frac{\Delta G^{o}}{RT} = -\ln K$

Therefore, $$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^{2}} \qquad (1)$$

Equation (1) gives the effect of temperature on equilibrium constant, hence the equilibrium yield.

If ΔH_o is negative, the reaction is exothermic, the equilibrium constant decreases as the temperature increases.

Conversely, K increases with T for an endothermic reaction. If ΔH^{o}, the standard enthalpy change (Heat) of reaction is assumed independent of T, integration of equation (1) leads to a simple result

$$\ln\frac{K}{K_1} = -\frac{\Delta H^{o}}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right) \qquad (2)$$

This approximate equation implies that a plot of K vs. reciprocal of absolute temperature is a straight line. A plot of lnK vs. 1/T for a number of common reactions, shown in Fig. 2.1 illustrates this linearity. Another plot for reforming reaction has been shown in Fig. 2.2. Thus the equation (2) provides a reasonably accurate relation for the interpolation and extrapolation of equilibrium – constant data.

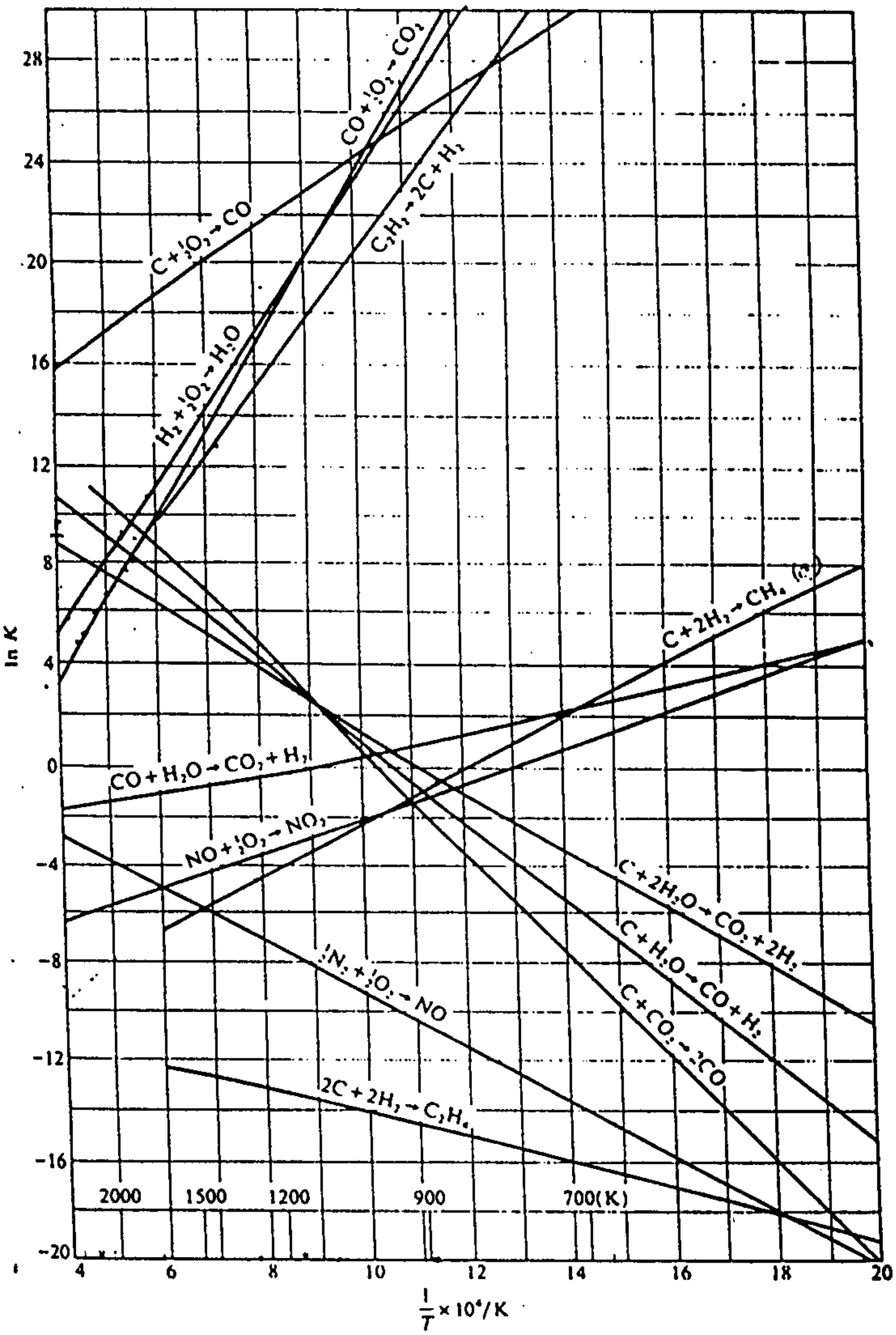


Figure 2·1 Equilibrium constants as a function of temperature for some common reactions.

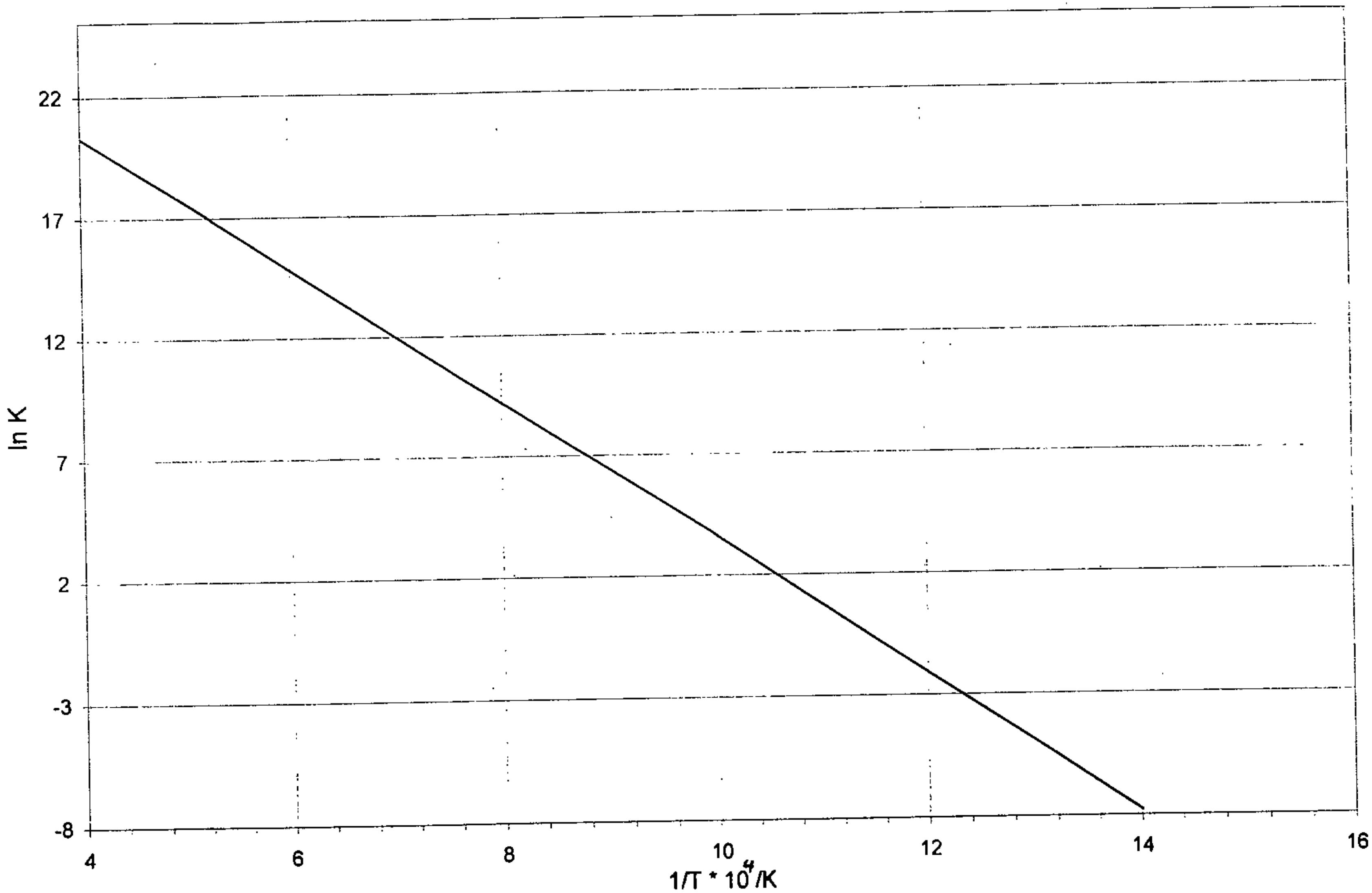


Fig. 2.2 Equilibrium constant as a function of temperature for the reforming reaction

$CH_4 + H_2O = CO + 3H_2$

2.2.2 Equilibrium Constants of Reforming Reaction

Some common reactions related to reforming reaction are as follows:

$$C + \frac{1}{2}O_2 \rightarrow CO \tag{1}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{2}$$

$$C + 2H_2 \rightarrow CH_4 \tag{3}$$

By adding equations (2) and (3) we find

$$C + 3H_2 + \frac{1}{2}O_2 \rightarrow CH_4 + H_2O \tag{4}$$

Subtracting equation (4) from equation (1), we find

$$- 3H_2 \rightarrow CO - CH_4 - H_2O$$

Therefore, $CH_4 + H_2O \rightarrow CO + 3H_2$ (5)

If ΔG_1, ΔG_2, ΔG_3 are the Gibbs free energy for reactions (1), (2), and (3) and ΔG is the Gibbs free energy for reforming reaction,

$$\Delta G = \Delta G_1 - \Delta G_2 - \Delta G_3$$

Let, the equilibrium constants of equation (1), (2) and (3) be K_1, K_2 and K_3 respectively, and the equilibrium constant reforming is K.

$$- \ln K = - \ln K_1 + \ln K_2 + \ln K_3$$

or, $\ln K = \ln K_1 - \ln K_2 - \ln K_3$

or, $\ln K = \ln \frac{K_1}{K_2 K_3}$

Therefore, $K = \frac{K_1}{K_2 K_3}$ (6)

From the graph of lnK vs. 1/T : K_1, K_2 and K_3 of three different reactions at different temperatures can be known and finally from equation (6), the equilibrium constant for the reforming at the respective temperature can be calculated.

Now, assume ε is the extent of reaction for the equation $CH_4 + H_2O \rightarrow CO + 3H_2$

(i) If 1 mole H_2O (steam) and 1 mole CH_4 are available for reforming; then,

$$n_{CH_4} = 1-\varepsilon, \qquad n_{H_2O} = 1-\varepsilon,\ n_{CO} = \varepsilon,\ n_{H_2} = 3\varepsilon$$

$$n = n_o + \nu\varepsilon = 2 + 2\varepsilon$$

$$K_{reform} = \frac{y_{CO}\, y_{H_2}^3\, p^2}{y_{CH_4} \cdot y_{H_2O}}$$

$$= \frac{\dfrac{\varepsilon}{2+2\varepsilon} \cdot \left(\dfrac{3\varepsilon}{2+2\varepsilon}\right)^3}{\left(\dfrac{1-\varepsilon}{2+2\varepsilon}\right)\left(\dfrac{1-\varepsilon}{2+2\varepsilon}\right)} p^2$$

$$= \frac{27\varepsilon^4\, p^2}{(2+2\varepsilon)^2\,(1-\varepsilon)^2}$$

(ii) If 2 mole H_2O (steam) and 1 mole CH_4 are available.

$$K_{reform} = \frac{27\varepsilon^4}{(3+2\varepsilon)^2\,(1-\varepsilon)(2-\varepsilon)} p^2$$

(iii) If 3 mole H_2O (steam) and 1 mole CH_4 are available, then

$$K_{reform} = \frac{27\varepsilon^4}{(4+2\varepsilon)^4\,(1-\varepsilon)(3-\varepsilon)} p^2$$

(iv) If 4 mole H_2O (steam) and 1 mole CH_4 are available, then

$$K_{reform} = \frac{27\varepsilon^4 . p^2}{(5+2\varepsilon)^4 (1-\varepsilon)(4-\varepsilon)}$$

(v) If 5 mole H_2O (steam) and 1 mole CH_4 are available, then

$$K_{reform} = \frac{27\varepsilon^4 . p^2}{(6 + 2\varepsilon)^4 (1-\varepsilon)(5-\varepsilon)}$$

(vi) If 6 mole H_2O (steam) and 1 mole CH_4 are available, then

$$K_{reform} = \frac{27\varepsilon^4 . p^2}{(7 + 2\varepsilon)^4 (1-\varepsilon)(5-\varepsilon)}$$

2.2.3 Equilibrium Constant of Water Gas-Shift Reaction

Let, ε is the extent of reaction for the equation $CO + H_2O \Leftrightarrow CO_2 + H_2$

(i) If 1 mole H_2O (steam) and 1 mole CO are available for shift reaction, then–

$$n_{CO} = 1-\varepsilon, \qquad n_{H_2O} = 1-\varepsilon$$

$$n_{CO_2} = \varepsilon, \qquad n_{H_2} = \varepsilon$$

$$n = n_o + \nu\varepsilon = 2 + 0 = 2$$

Mole fraction in equilibrium are –

$$y_{CO} = \frac{1-\varepsilon_C}{2}, \qquad y_{H_2O} = \frac{1-\varepsilon_C}{2}$$

$$y_{CO_2} = \frac{\varepsilon_C}{2}, \qquad y_{H_2} = \frac{\varepsilon_C}{2} /$$

$$K_{shift} = \frac{y_{H_2} \cdot y_{CO_2}}{y_{CO} \cdot y_{H_2O}} = \frac{\frac{\varepsilon_C}{2} \cdot \frac{\varepsilon_C}{2}}{\frac{(1-\varepsilon_C)}{2} \cdot \frac{(1-\varepsilon_C)}{2}}$$

$$= \frac{\varepsilon_C^2}{(1-\varepsilon_C)^2}$$

(ii) If 2 mole H_2O (steam) and 1 mole CO are available, then

$$K_{shift} = \frac{\varepsilon_C^2}{(1-\varepsilon_C)(2-\varepsilon_C)}$$

(iii) If 2 mole H_2O (steam) and 1 mole CO are available, then

$$K_{shift} = \frac{\varepsilon_C^2}{(1-\varepsilon_C)(3-\varepsilon_C)}$$

(iv) If 4 mole H_2O (steam) and 1 mole CO are available, then

$$K_{shift} = \frac{\varepsilon_C^2}{(1-\varepsilon_C)(4-\varepsilon_C)}$$

(v) If 5 mole H_2O (steam) and 1 mole CO are available, then

$$K_{shift} = \frac{\varepsilon_C^2}{(1-\varepsilon_C)(5-\varepsilon_C)}$$

(vi) If 6 mole H_2O (steam) and 1 mole CO are available, then

$$K_{shift} = \frac{\varepsilon_C^2}{(1-\varepsilon_C)(6-\varepsilon_C)}$$

2.2.4 Influence of Secondary Reformer (Top Chamber) Combustion on its Reforming Process

Let, initial moles at 800°C, methane = 1 mole, air = 1.43 mole, steam = 4 moles and pressure 30 bar. So the composition of primary reformer outlet will be as follows:

Component	moles
CH_4	0.35
H_2	1.95
CO	0.33
CO_2	0.32
H_2O	3.35
N_2	1.13
O_2	0.30

[From theory based calculated values of table 4.4 and from stoichiometric calculation of section 2.1.2]

Now, assume the following two combustion reactions occur at the top chamber of the secondary reformer. K_1 and K_2 are equilibrium constants of these reactions respectively.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad (I)$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad (II)$$

Stoichiometric numbers $v_{i,j}$ can be arranged as follows:

J	CH_4	H_2	CO	CO_2	H_2O	N_2	O_2	v_i
1	0	-1	0	0	1	0	-½	-½
2	0	0	-1	-1	0	0	-½	-½

$$y_{H_2} = \frac{1.95 - \varepsilon_1}{7.87 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}$$

$$y_{CO} = \frac{0.33 - \varepsilon_2}{7.87 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}$$

$$y_{CO_2} = \frac{0.32 + \varepsilon_2}{7.87 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}$$

$$y_{H_2O} = \frac{3.35 + \varepsilon_2}{7.87 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}$$

$$y_{O_2} = \frac{0.3 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}{7.87 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}$$

$$y_{N_2} = \frac{1.13}{7.87 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}$$

$$y_{CH_4} = \frac{0.35}{7.87 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2}$$

$$K_1 = \frac{(3.35 + \varepsilon_1)(7.87 - \frac{1}{2}\varepsilon_1 \frac{1}{2}\varepsilon_2)^{\frac{1}{2}}}{(1.95 - \varepsilon_1)(0.3 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2)}$$

$$K_2 = \frac{(0.32 + \varepsilon_2)(7.87 - \frac{1}{2}\varepsilon_1 \frac{1}{2}\varepsilon_2)^{\frac{1}{2}}}{(0.33 - \varepsilon_1)(0.3 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2)}$$

Data for chemical equilibrium constant

Temperature (°C)	Chemical equilibrium constant	
	K_1	K_2
600	8.77×10^{11}	7.2×10^{10}
700	0.26×10^{11}	3.23×10^{10}
800	0.13×10^{11}	0.37×10^{10}
1000	0.14×10^{10}	0.79×10^{9}

The values of K is so large that the quantity $(0.3 - \frac{1}{2}\varepsilon_1 - \frac{1}{2}\varepsilon_2)$ which appears in the denominator of the expression for each K to be nearly zero.

This means that mole fraction of oxygen in the equilibrium mixture is very small. For practical purposes, no oxygen will remain unreacted after combustion in the secondary reformer top chamber.

Now, the equation which have been supposed to occur at the top of the secondary reformer are

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

The above equations can be included in the formation reaction of reforming product CO and CO_2. This has been discussed in the section 2.2.2.

2.3 SELECTION OF THE OPTIMUM OPERATING VARIABLES OF STEAM REFORMING

Selection of a best operating variable depends on the economic balance of ammonia yield, production capacity, utility consumption, catalyst life etc. [16, 17, 18, 19, 20, 23]. But in this research work, optimum operating variables are discussed by the analysis of reaction characteristics.

2.3.1 Operating Pressure Selection

The reforming reaction is less favourable at high pressures. In synthesis of ammonia, synthesis-gas (mixture of hydrogen and nitrogen) are compressed at high pressures. Since the volume of the feed gas is much smaller than the volume of the reformed gases, it is easier and cheaper to compress the gases before reforming. If pressures of the synthesis gas production units (primary and secondary reformer) are increased, the energy for synthesis gas compressor will be required in a lower amount.

2.3.2 Adjusting Steam/Natural Gas Ratio and Temperatures

Natural gas is considerably more valuable than steam. So, it is usual practice to feed less expensive steam in excess than the valuable natural gas to increase its conversion. Selection of high reforming pressure decrease the conversion of natural gas. Again, if there is a slip of natural gas through outlet of secondary reformer, it acts as an inert in the synthesis loop and decrease the ammonia yield. So, steam/Natural gas ratio and temperatures are to be adjusted in such a way so that maximum conversion of natural gas is possible [14, 17].

2.4 BASIC CONTROL OF AMMONIA PROCESS

The whole ammonia plant has three basic controls [23]:

1. Feed gas determines the production rate and is set by steam/feed gas ratio.
2. Air rate determines the hydrogen/nitrogen ratio and is set by air /feed gas ratio
3. Suction pressure of the synthesis gas compressor sets the operating pressure of the circuit from primary reformer to synthesis gas Compressor.

To protect the primary reformer and other elements from carbon deposition and to increase or decrease production rate, process steam is adjusted accordingly and the ratio controller will automatically adjust the feed gas rate. The design setpoints of the ratio controller of steam to feed gas ratio is based on a feed gas composition with a molecular weight. If the composition changes, the operators should adjust the setpoints accordingly. The process air rate is set by the air to feed gas ratio controller.

The pressure in the circuit from the primary reformer to the synthesis gas compressor suction is set by the suction pressure of the synthesis gas compressor and the pressure drop in the equipment within the circuit. The synthesis gas compressor suction pressure is maintained on pressure control which adjusts the speed of the machine to compress all of the gas coming to the machine into the synthesis loop. The operating pressure of the synthesis loop is set by the amount of synthesis gas going to the synthesis gas compressor and other operating parameters in the synthesis loop.

CHAPTER – 3

PROCESS DESCRIPTION

3.1 INTRODUCTION

There was no experimental setup in the laboratory to investigate the individual influence of pressure, temperature and steam/methane ratio on reforming reaction. Operating data of reforming units of seven fertilizer factories existing in different parts of Bangladesh and their laboratory analysis data have been collected. Based on these data primary reformer outlet and secondary reformer outlet equilibrium compositions have been calculated. Individual influence of pressure, temperature and steam/methane ratio on reforming reaction has been analyzed by theory based calculation.

A simplified flow diagram of reforming process, schematic diagrams of primary reformer and secondary reformer, and a description of primary reformer and secondary reformer have been included in this chapter.

3.2 DESCRIPTION OF REFORMING PROCESS

A simplified flow diagram of reforming process is shown in Fig. 3.1. Description of this flow diagram is given below:

The sequence of the process for the production of reforming can be simplified as: Cleaning of raw material, Desulphurization and Reforming.

Primary raw material for ammonia is natural gas. Other than natural gas the raw materials for the ammonia production are water for steam production, and atmospheric air is as the source of nitrogen. Ammonia is produced from hydrogen and

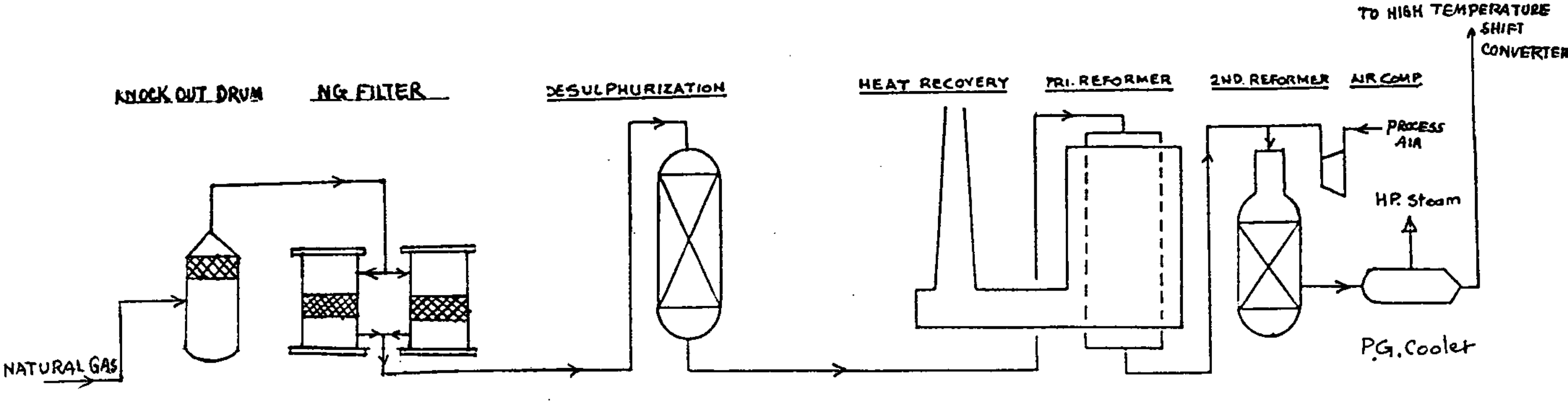


Fig 3·1 : A SIMPLIFIED FLOW DIAGRAM OF REFORMING PROCESS .

nitrogen. Nitrogen can be easily obtained from air, but hydrogen can not. The reforming process used in most of the ammonia plant is the steam reforming process.

Natural gas contains a little amount of oil particles, dust particles and moisture etc. For the purification of this gas, the gas passes through knock out drum, cyclone separator, dust separator, filter etc. This gas is first preheated (90-100°C) in the preheater and then heated in the coil of flue gas duct convection section (390-400°C). Natural gas contains compounds, which can poison catalyst, must be treated properly. Hydrogen sulfide is easily removed by Zinc Oxide in presence of cobalt molybdenum catalyst.

$$ZnO + H_2S = ZnS + H_2O$$

In the reforming process for ammonia production, a small amount H_2 gas is recycled with feed natural gas. So, all higher hydrocarbon of alkane group will be converted to methane at low temperature in presence of nickel catalyst [4,23].

$$C_2H_6 + H_2 = 2CH_4$$
$$C_3H_8 + 2H_2 = 3CH_4$$
$$C_4H_{10} + 3H_2 = 4CH_4$$

The treated natural gas is then mixed with steam and reformed at 700 ~ 800 °C over a nickel based catalyst in primary reformer. The following reactions occur.

$$CH_4 + H_2O = CO + 3H_2$$

$$CO + H_2O = CO_2 + H_2$$

The reforming reactions are highly endothermic where heat is supplied by combustion of a mixture of purge gas, cracked gas and undesulphurised natural gas. The products of primary reformer, H_2. CO and CO_2 together with some amount of unconverted methane and steam, enter into the secondary reformer. Air is added to provide nitrogen and oxygen. The reactions occurring over nickel oxide catalyst are

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

$$2CO + O_2 = 2CO_2$$

$$2H_2 + O_2 = 2H_2O$$

The reformed gases leaving the secondary reformer at 900 ~ 1000 ^{0}C. are cooled by generating high-pressure steam and partly preheating boiler feed water before entering to high temperature shift converter.

3.3 DESCRIPTION OF PRIMARY REFORMER

The primary reformer is shown in Fig. 3.2. The primary reformer is designed as a box type furnace with usually some vertical rows of 40-50 tubes each. To ensure uniform heating of reformer tubes, forced-draught burners are arranged in the ceiling of furnace. The burners can also be arranged at two sidewalls.

Flue-gas ducts are arranged between the tube rows on the reformer bottom. The flue-gases are withdrawn through slots in the sidewalls of the ducts. These gases are fed to the waste heat recovery system. To compensate for varying pressure drops of flue gas streams across the height and length of the reformer box, the number of slots per unit of length over the length of the flue-gas ducts is not uniform.

The feed (natural gas plus process steam) is fed in to the reformer tubes through an inlet manifold system arranged above the reformer ceiling. The feed flows through the catalyst beds from top to bottom. The process gas flows from the reformer tubes into the refractory-lined header system, the tubes being directly mounted on and welded on the headers.

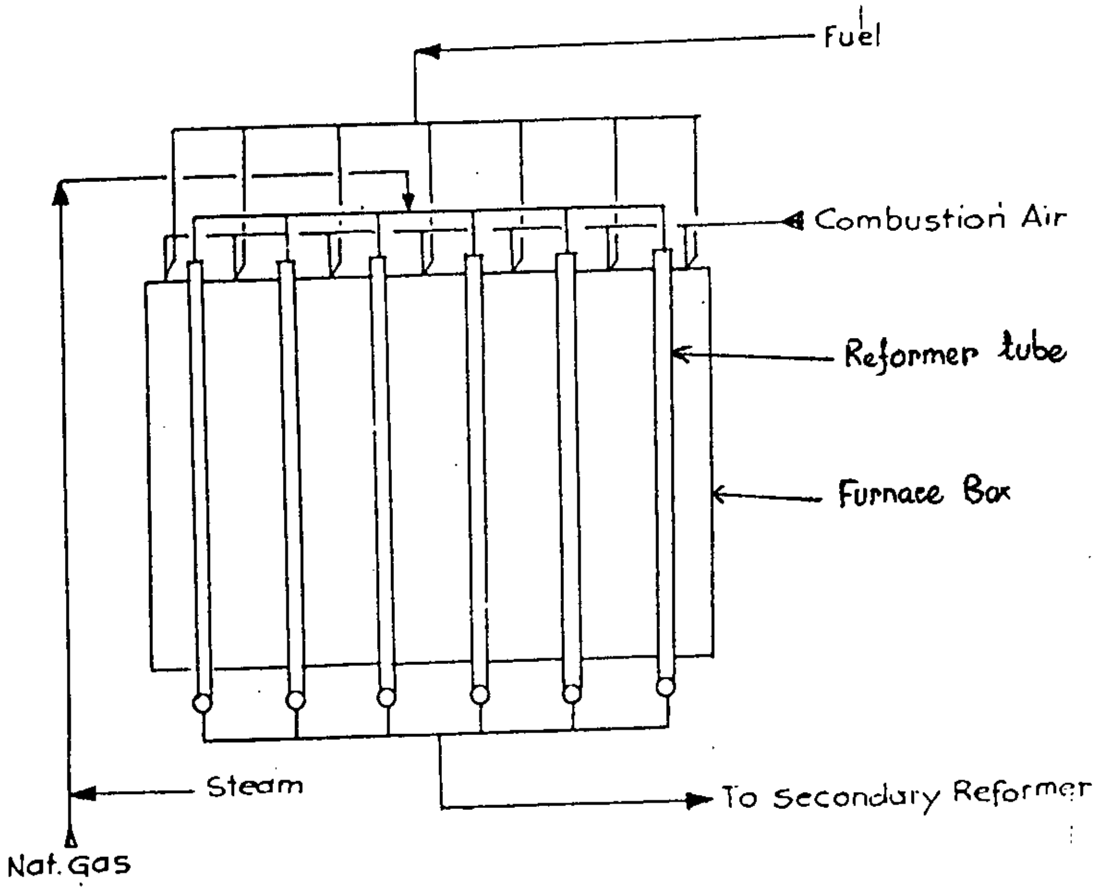


Fig. 3.2 A SCHEMATIC DIAGRAM OF PRIMARY REFORMER

Typical dimensions of the box type chamber are [25]:

Height : 10 m
Width : 15 m
Length : 19 m

3.3.1 Burner System

The burners are arranged in rows, running parallel to the reformer tube rows. They are of forced draught type and designed for burning natural gas, tail gas or a mixture of tail gas and natural gas in the same burner. The burners are designed for 110% capacity i.e. reformer capacity is not reduced even if several burners fail temporarily. The burners can be operated within a range of 1:4. This means that reformer load may be reduced to about 30% without having to shutdown any burners.

Atmospheric air is used as combustion air and is supplied to the burners by combustion air fan via a preheater and a pipeline in which the flow metering and regulating devices are arranged.

3.3.2 Reformer Tubes

The reformer tubes are made of alloys containing about 25% Cr, 20% Ni, 0.35% C and 1.5% Nb and balance Fe.

Typical criteria can be summarized as follows [25]:
Design pressure: 35 bar
Design temperature: 900 °C
Inside diameter: 100 mm
Wall thickness: 15 mm

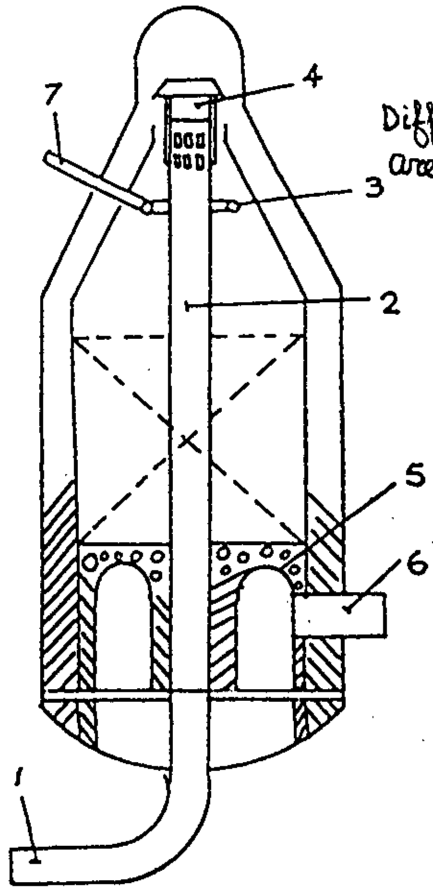
Heated length: 10 m

Total length: 12 m

3.4 DESCRIPTION OF SECONDARY REFORMER

Schematic diagram of the secondary reformer is given in Fig. 3.3. The process gas from primary reformer enters the vessel through a central tube which flows upward and is discharged via slots. Then it passes through the open end of the tube into the upper cylindrical section of the secondary reformer. Devices for diverting the gas stream are installed at the open end of the central tube. The gas is mixed with air and burnt. The flame develops in the conical section. The heated gas passes through the catalyst bed and another layer of inert material. It is then discharged via slots into the annular arch at the bottom of the vessel, where the gas flows via nozzle to the waste heat boiler.

The secondary reformer has a multi-layered bricklining wall. Because of the reducing nature of the gas atmosphere, all bricks combing into contact with the process gas are made of refractory material with a high allumina content (99% Al_2O_3). The SiO_2 content is less than 0.60%, the Fe_2O_3 content being smaller than 0.2%. The remaining layers serve as thermal insulation and take up any thermal expansion. While the temperature in the combustion chamber is 1300°C, the shell temperature is only 100°C. The entire secondary reformer is provided with a water jacket, in order to ensure adequate cooling in case of flaws in the bricklining, thus obviating the need to shut down the unit. The level in the water jacket is controlled automatically and displayed in the control room.



Different parts of the secondary reformer are :-

1. Inlet nozzle.
2. Central tube.
3. Burner
4. Gas Inlet to Combustion Chamber.
5. Annular Arch Chamber.
6. Outlet Nozzle.
7. Air Inlet

Fig.3.3. A SCHEMATIC DIAGRAM OF SECONDARY REFORMER

3.5 OPERATING DATA OF REFORMING UNIT OF DIFFERENT FERTILIZER FACTORIES OF BANGLADESH

The operating data which have been collected from different fertilizer factories of Bangladesh are:

- Process parameters of primary reformer such as steam/natural gas ratio, pressure, temperature and natural gas composition of primary reformer inlet and outlet, comparison of primary reformer inlet natural gas composition, comparison of primary reformer outlet reformed gas composition.

- Secondary reformer inlet airflow i.e. Air/natural gas ratio,
- Secondary reformer outlet pressure, temperature and composition and comparison of secondary reformer outlet composition.

The above mentioned data have been included in the appendix – B.

CHAPTER – 4

RESULTS AND DISCUSSIONS

4.1 INTRODUCTION

The thesis work was carried out to investigate the influence of pressure, temperature, and steam/natural gas ratio on reforming process. In the calculation of usage ratios from stoichiometry of reforming process, it is found that for complete conversion of each mole of methane 1.4 mole steam should be used. If theory of chemical equilibria is applied for finding out the usage ratio of steam/methane, it is found that at constant pressure and temperature, conversion of methane increases with the increase of steam/methane ratio. If high temperature and low operating pressure is applied, higher conversion can be achieved with low steam/methane ratio. All these data related to the influence of pressure, temperature, and steam/natural gas ratio on reforming process have been arranged in the tabular form in Appendix – A.

From collected data of different fertilizer factories in Bangladesh, it is seen that operating data of reforming process are different from each other. So individual influence of pressure, temperature and steam/ methane ratio can not be observed. But the validity of the theory-based calculation can be justified by the collected operating data. These data also show that low pressure has been used for maximum conversion of natural gas in older reforming process. But in modern reforming process, high pressure has been used for reforming of natural gas.

4.2 ANALYSIS OF THEORY BASED CALCULATED DATA

In theoretical calculation, theory of chemical equilibrium has been applied for finding out the maximum conversion of natural gas in steam reforming process. In the calculation of equilibrium conversion, the influence of catalyst on the reforming reaction has not been considered, because the equilibrium conversion of the reaction depends on the thermodynamic properties and not on the catalyst behaviour.

From Table 4.1 it can be observed that at a constant steam/methane ratio (1), methane conversion increases with the increase of temperature. At the same steam/methane ratio and at constant pressure (10 bar), methane conversion is higher at 700°C than that of the conversion at 600°C. This conversion increases gradually at 800°C, 900°C and 1000°C. If pressure is increased such as 30 bar, 40 bar or 50 bar, methane conversion at each constant pressure increases with the increase of temperature. But at each operating temperature conversion of methane gradually decreases at 20 bar, 30 bar, 40 bar or 50 bar pressure than the conversion of methane at 10 bar pressure.

From Table 4.2 it can be seen that at constant pressure (10 bar) and constant steam/methane ratio (2), conversion of methane increases from 0.22 to 0.99 with the increase of temperature from 600°C to 1000°C. At the same steam/methane ratio, and temperature at 600°C, conversion of methane decreases from 0.22 to 0.06 with the increase of pressure from 10 bar to 50 bar. At each temperatures of 700°C, 800°C, 900°C and 1000°C, conversion of methane decreases with the increase of pressure from 10 bar to 50 bar. But as the steam/methane ratio has been increased, methane conversion is higher than the methane conversion at steam/methane ratio = 1.

From Table 4.3 it can be seen that if steam/methane ratio = 3, methane conversion increases from 0.275 to 0.992 when temperature increases from 600°C to 1000°C and methane conversion decreases from 0.275 to 0.11 when pressure increases for 10 bar to 50 bar i.e., methane conversion increases with the increase of temperature while it decrease with pressure. But as the steam/methane ratio has been increased, methane conversion is higher than that of steam/methane ratio = 2 or 1.

From Table 4.4 and 4.5 it can be seen that if steam/methane ratio is 4 and 5 respectively, methane conversion decrease with the increase of pressure. Although methane conversion to carbon monoxide decreases with the increase of pressure, it is possible to attain greater conversion of methane at higher pressure, if steam/methane ratio or temperature is increased.

Table – 4.1 Fractional conversion of methane during steam reforming at different pressures and temperatures, when steam/methane ratio = 1

($CH_4 + H_2O = CO + 3H_2$, when steam = 1 mole)

Fractional conversion at different temperatures of the reforming unit					
Pressure (Bar)	600°C	700°C	800°C	900°C	1000°C
10	0.15	0.31	0.515	0.84	0.89
20	0.10	0.22	0.39	0.74	0.82
30	0.09	0.16	0.29	0.64	0.76
40	0.075	0.15	0.28	0.62	0.70
50	0.06	0.12	0.26	0.53	0.67

Table – 4.2 Fractional conversion of methane during steam reforming at different pressures and temperatures, when steam/methane ratio = 2

($CH_4 + H_2O = CO + 3H_2$ when steam = 2 mole)

Fractional conversion at different temperatures of the reforming unit					
Pressure (Bar)	600°C	700°C	800°C	900°C	1000°C
10	0.22	0.41	0.705	0.975	0.99
20	0.155	0.30	0.55	0.92	0.965
30	0.10	0.25	0.50	0.895	0.905
40	0.085	0.215	0.41	0.81	0.895
50	0.07	0.195	0.375	0.75	0.855

Table – 4.3 Fractional conversion of methane during steam reforming at different pressures and temperatures, when steam/methane ratio = 3

($CH_4 + H_2O = CO + 3H_2$ when steam = 3 mole)

Fractional conversion at different temperature of the reforming unit					
Pressure (Bar)	600°C	700°C	800°C	900°C	1000°C
10	0.275	0.505	0.80	0.99	0.992
20	0.205	0.375	0.66	0.94	0.985
30	0.140	0.31	0.575	0.905	0.965
40	0.120	0.29	0.51	0.90	0.935
50	0.110	0.245	0.50	0.86	0.930

Table – 4.4 Fractional conversion of methane during steam reforming at different pressures and temperatures, when steam/methane ratio = 4

($CH_4 + H_2O = CO + 3H_2$ when steam = 4 mole)

Fractional conversion at different temperature of the reforming unit					
Pressure (Bar)	600°C	700°C	800°C	900°C	1000°C
10	0.325	0.59	0.875	0.992	0.993
20	0.23	0.49	0.745	0.985	0.991
30	0.16	0.395	0.65	0.96	0.985
40	0.15	0.32	0.58	0.945	0.965
50	0.14	0.28	0.525	0.920	0.945

Table – 4.5 Fractional conversion of methane during steam reforming at different pressures and temperatures, when steam/methane ratio = 5

($CH_4 + H_2O = CO + 3H_2$ when steam = 5 mole)

Fractional conversion at different temperature of the reforming unit					
Pressure (Bar)	600°C	700°C	800°C	900°C	1000°C
10	0.365	0.65	0.915	0.997	0.999
20	0.270	0.50	0.785	0.991	0.996
30	0.220	0.41	0.71	0.978	0.991
40	0.180	0.36	0.65	0.960	0.985
50	0.170	0.33	0.59	0.945	0.976

During reforming process a water-gas shift reaction occurs, which is exothermic in nature. From Table 4.6 it can be seen that if steam/CO ratio = 1, CO conversion gradually decrease at temperatures 200°C, 400°C, 600°C, 700°C, 800°C, 900°C and 1000°C; but if steam/CO ratio is increased CO conversion at higher temperature can be increased.

Although CO conversion to CO_2 decreases with the increase of temperature, it is possible to attain greater conversion of CO to CO_2 at higher temperature, if steam/CO ratio is increased.

Table – 4.6 Fractional conversion of CO to CO_2 at different temperatures during shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$)

	Fractional conversion of CO to CO_2 at different temperatures						
Moles of steam	200°C	300°C	400°C	700°C	800°C	900°C	1000°C
1	0.92	0.879	0.78	0.56	0.50	0.47	0.444
2	0.99	0.98	0.93	0.73	0.65	0.629	0.598
3	0.996	0.99	0.96	0.81	0.72	0.714	0.641
4	0.997	0.993	0.974	0.85	0.82	0.766	0.679
5	0.998	0.995	0.98	0.88	0.87	0.868	0.775
6	0.999	0.996	0.992	0.92	0.89	0.85	0.83

4.3 GRAPHICAL ANALYSIS OF STEAM REFORMING OPERATING VARIABLES

By the graphical analysis of the theoretical values, the influence of pressure, temperature and steam/methane ratio on the reforming process of methane can be explained easily.

4.3.1 Influence of Temperature on Reforming Reaction

From Fig. 4.1 it is seen that when pressure = 10 bar and steam/methane ratio = 1 remain constant, methane conversion is 12% at temperature 600°C. Conversion of methane is 35%, 75%, and 88% at temperatures 700°C, 900°C and 1000°C respectively. When steam/methane ratio is 2, methane conversion is 21% at temperature 600°C. Conversion of methane is 45%, 87%, and 97% at temperatures 700°C, 900°C and 1000°C respectively.

From Fig. 4.2 it is seen that when pressure (20 bar) and steam/methane ratio = 1 remain constant, methane conversion is 10% at temperature 600°C. Conversion of methane is 21%, 72%, and 82% at temperatures 700°C, 900°C and 1000°C respectively. When steam/methane ratio is 2, methane conversion is 14% at temperature 600°C. Conversion of methane is 30%, 80%, and 91% at temperatures 700°C, 900°C and 1000°C respectively.

So at constant pressure and constant steam/methane ratio, conversion of methane increase with the increase of temperature. On decreasing temperature, the effect is reversed. If low temperature is selected for any reforming system, other variables such as pressure should be decreased or steam/methane ratio should be increased for higher conversion of methane.

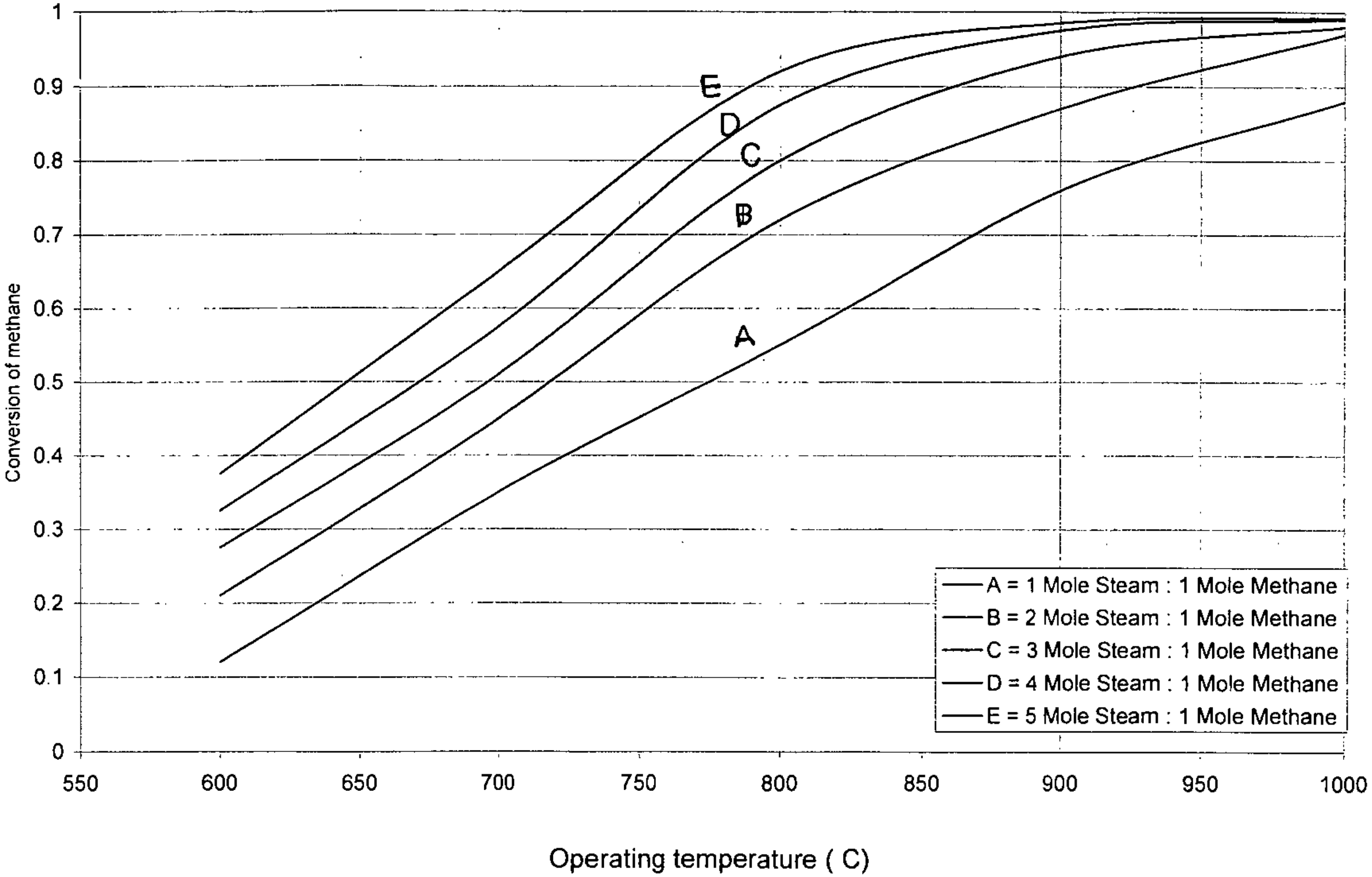


Fig. 4.1 Conversion of methane vs. operating temperature for reforming at pressure 10 bar

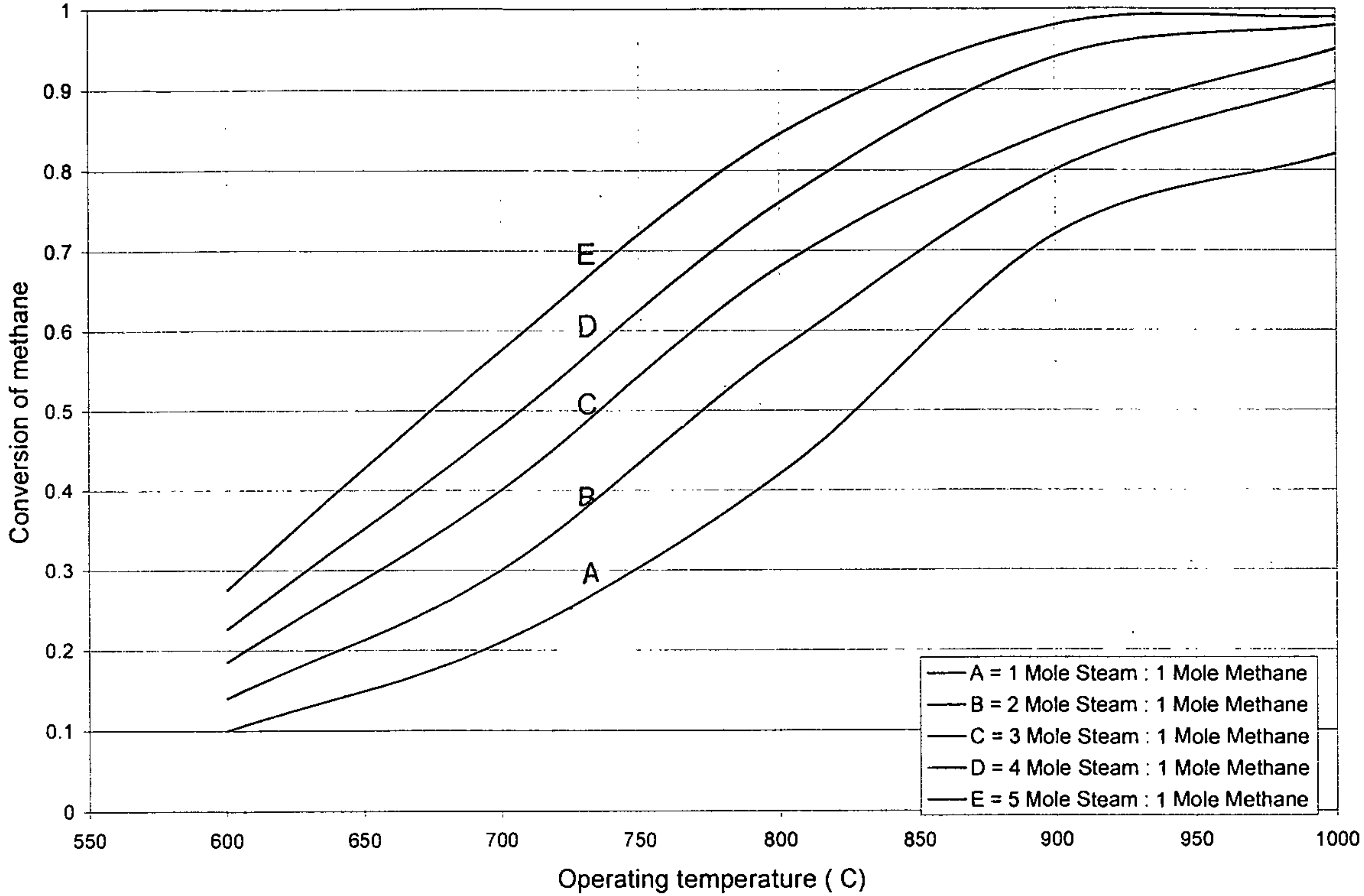


Fig. 4.2 Conversion of methane vs. operating temperature (C) for reforming at pressure 20 bar

4.3.2 Influence of Steam/Methane Ratio on Reforming Reaction

From Fig. 4.3 it is seen that when temperature (1000 °C) and pressure (10 bar) remain constant, methane conversion is 88% at steam/methane ratio = 1. Conversion of methane is 98%, 99%, 99.2% and 99.5% at steam/methane ratio = 2, 3, 4, and 5 respectively. When pressure is 30 bar, methane conversion is 76% at steam/methane ratio = 1. Conversion of methane is 91%, 96.5%, 98% and 98.5% at steam/methane ratio 2, 3, 4, and 5 respectively.

From Fig. 4.4 it is seen that when temperature (700 °C) and pressure (10 bar) remain constant, methane conversion is 31.5% at steam/methane ratio = 1. Conversion of methane is 42%, 51%, 58% and 65% at steam/methane ratio 2, 3, 4, and 5 respectively. When pressure is 30 bar, methane conversion is 15.5% at steam/methane ratio = 1. Conversion of methane is 25%, 32%, 39% and 44% at steam/methane ratio 2, 3, 4, and 5 respectively.

So, at constant temperature and constant pressure, methane conversion increase with the increase of steam/methane ratio. It is known that sufficient amount of steam is needed in reforming to prevent coking of the catalyst. At the same time, utilities consumption will increase. For other than minor deviations, the operation is usually most economical at closely approaching design steam to natural gas ratio 1.4 to 3.5.

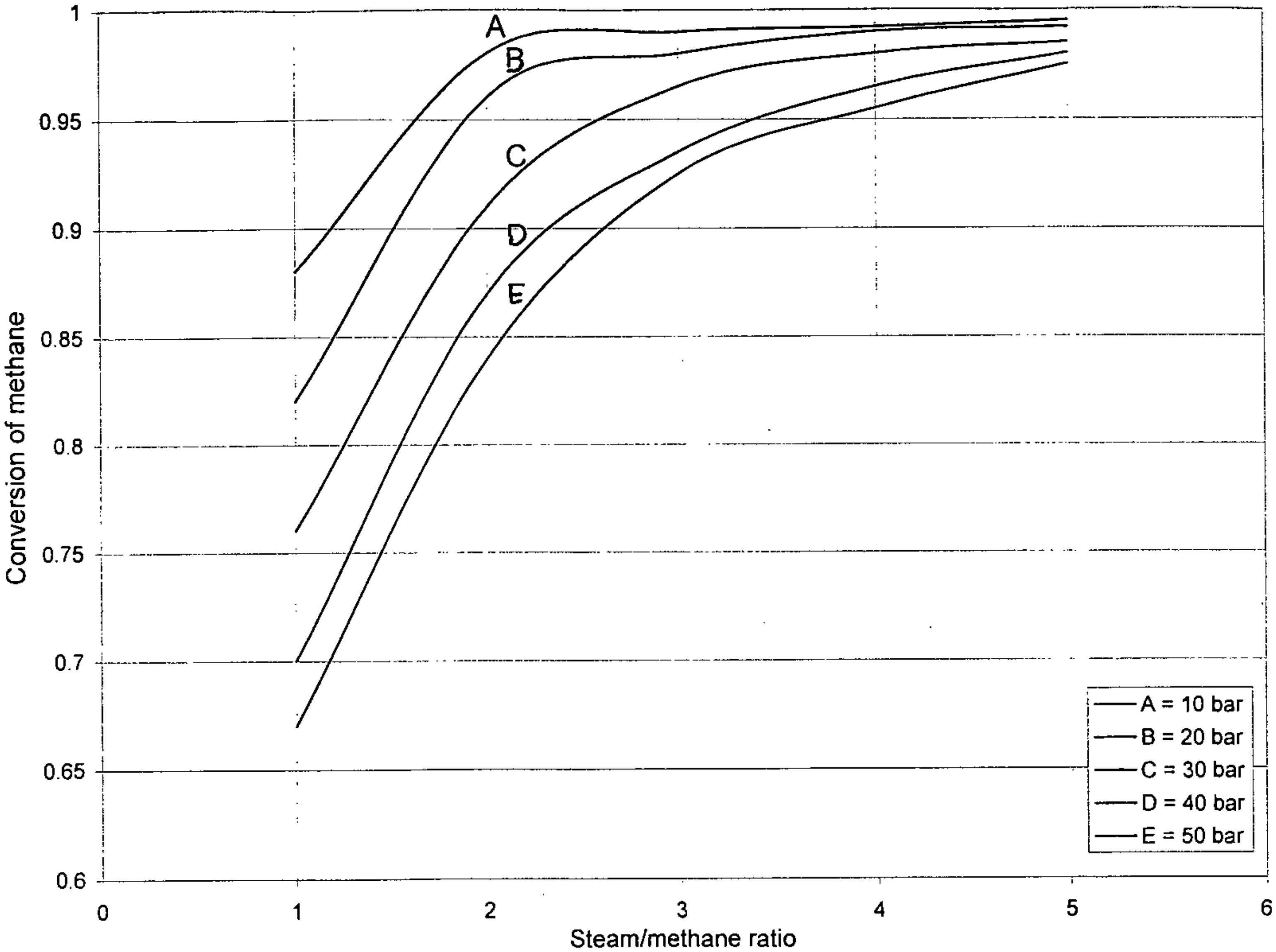


Fig. 4.3 Conversion of methane vs. steam/methane ratio for reforming at temperature 1000 C

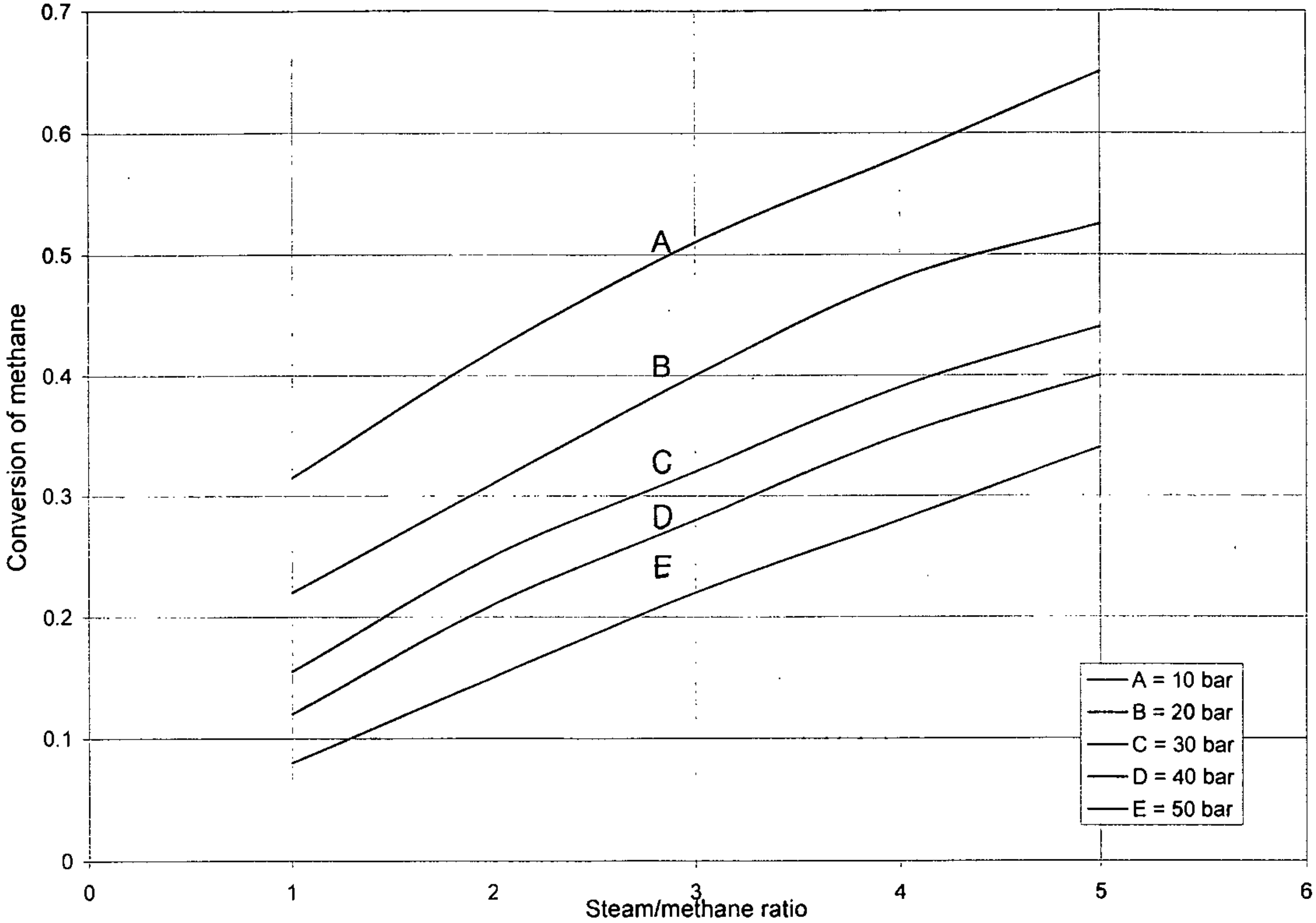


Fig. 4.4 Conversion of methane vs. steam/methane ratio for reforming at 700 C

4.3.3 Influence of Pressure on Reforming Reaction

From Fig. 4.5 it is seen that when temperature (1000 ^{o}C) and steam/methane ratio = 1 remain constant methane conversion is 89% at pressure 10 bar. Conversion of methane is 85.5%, 82%, 77% and 72% at pressures 20 bar, 30 bar, 40 bar, and 50 bar respectively. When steam/methane ratio is 2, methane conversion is 97% at pressure 10 bar. Conversion of methane is 95.5%, 93%, 90% and 86% at pressures 20 bar, 30 bar, 40 bar, and 50 bar respectively.

From Fig. 4.6 it is seen that when temperature (900 ^{o}C) and steam/methane ratio = 1 remain constant, methane conversion is 86% at constant pressure 10 bar. Conversion of methane is 77%, 69.5%, 62% and 55% at pressures 20 bar, 30 bar, 40 bar, and 50 bar respectively. When steam/methane ratio is 2, methane conversion is 94% at pressure 10 bar. Conversion of methane is 89%, 84%, 80% and 76% at pressures 20 bar, 30 bar, 40 bar, and 50 bar respectively.

So, at constant temperature and constant steam/methane ratio, methane conversion decreases with the increase of pressure. The increasing pressure has an effect similar to decreasing temperature. i.e. conversion of methane will decrease with increasing pressure.

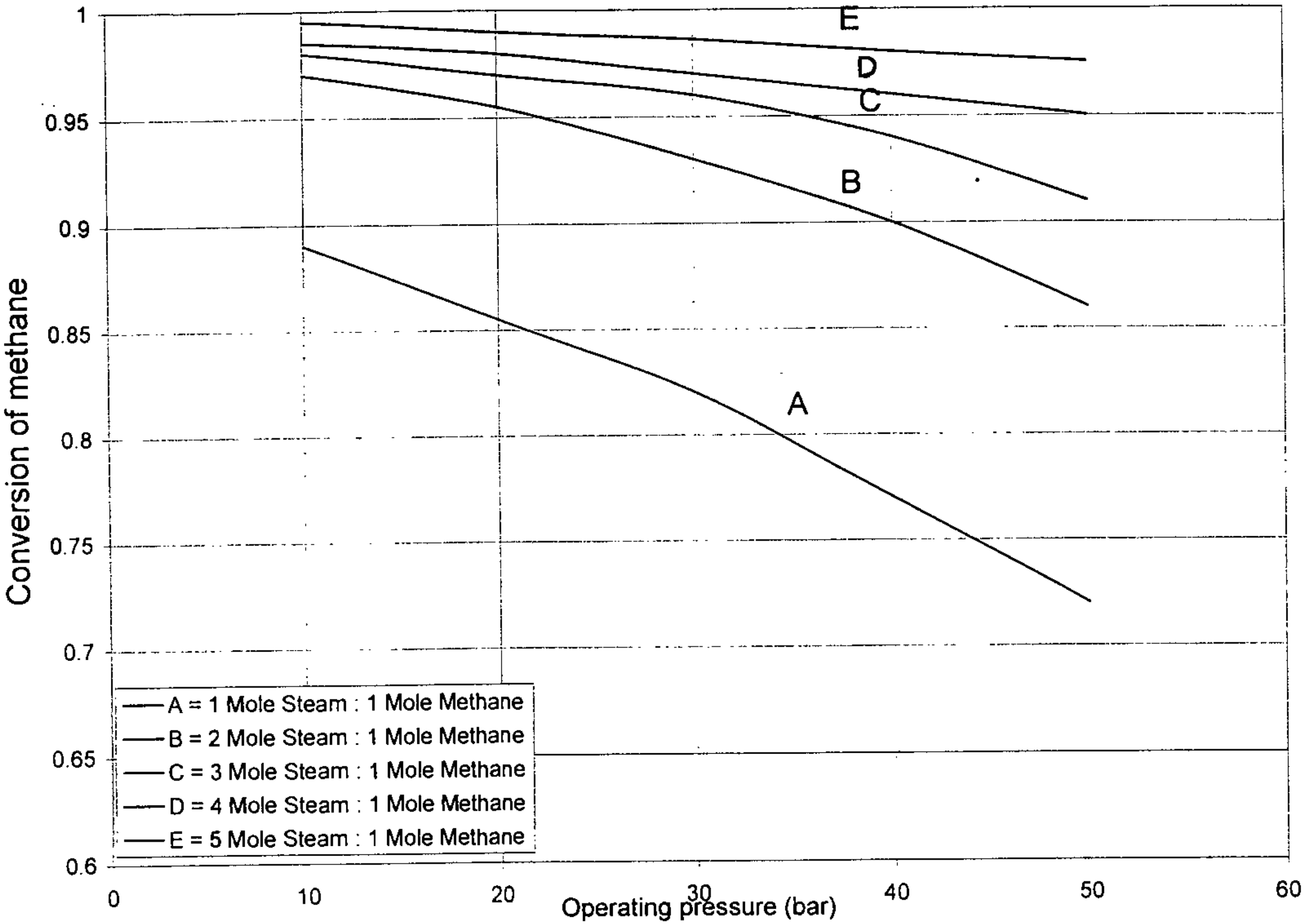


Fig. 4.5 Conversion of methane vs. operating pressure for reforming at 1000 C

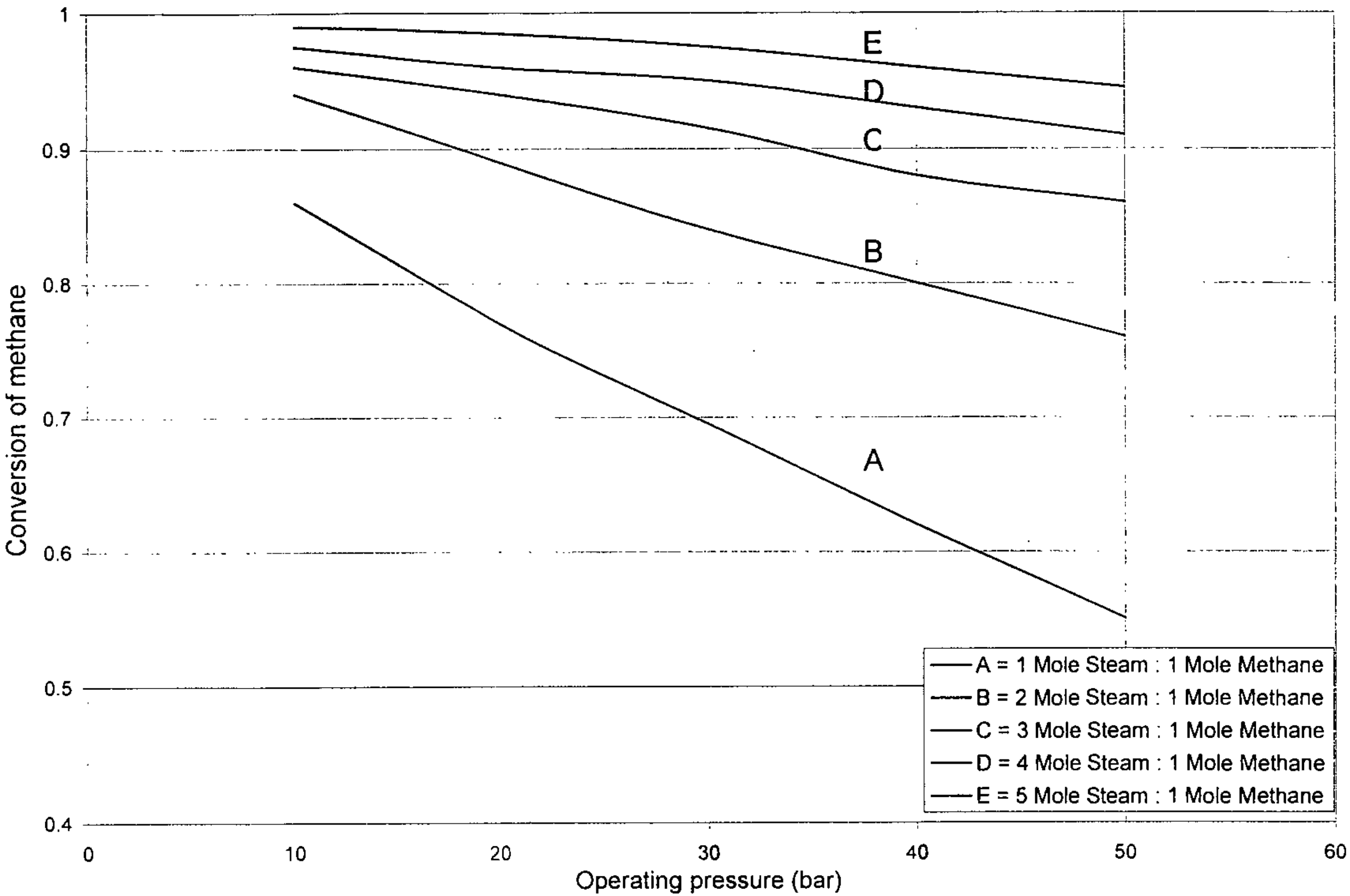


Fig. 4.6 Conversion of methane vs. operating pressure (bar) at 900 C

4.3.4 Adjustment of Temperature, Pressure and Steam/Methane Ratio for Getting Different Conversion of Methane

From Fig. 4.7 it is seen that when steam/methane ratio remains constant, for a specific conversion of methane (50%) different operating pressures such as 10 bar, 20 bar, 30 bar, 40 bar etc. can be applied. When 10 bar pressure is applied for 50% conversion operating temperature should be 725°C. If 20 bar, 30 bar, 40 bar and 50 bar pressures are applied, temperatures should be 760°C, 793°C, 820°C and 855°C respectively for same conversion of methane in steam reforming. For 60% conversion of methane operating pressure can be selected as 10 bar, 20 bar, 30 bar, 40 bar and 50 bar; but operating temperature should be 760°C, 810°C, 845°C, 875°C and 910°C respectively.

From Fig 4.8 it is seen that when steam/methane ratio is 2, for a specific conversion of methane, different pressures such as 10 bar, 20 bar, 30 bar, 40 bar and 50 bar can be selected for reforming reaction; but temperature should be 695°C, 725°C, 750°C, 770°C and 800°C respectively. For 60% conversion of methane operating pressure can be selected as 10 bar, 20 bar, 30 bar, 40 bar and 50 bar; but operating temperature should be 712°C, 745°C, 772°C, 800°C and 837°C respectively.

So, at a specific steam/methane ratio high operating pressures can be selected for the process but operating temperatures must be high for the same conversion of methane. In modern process high operating pressure is selected for reforming due to economic reasons.

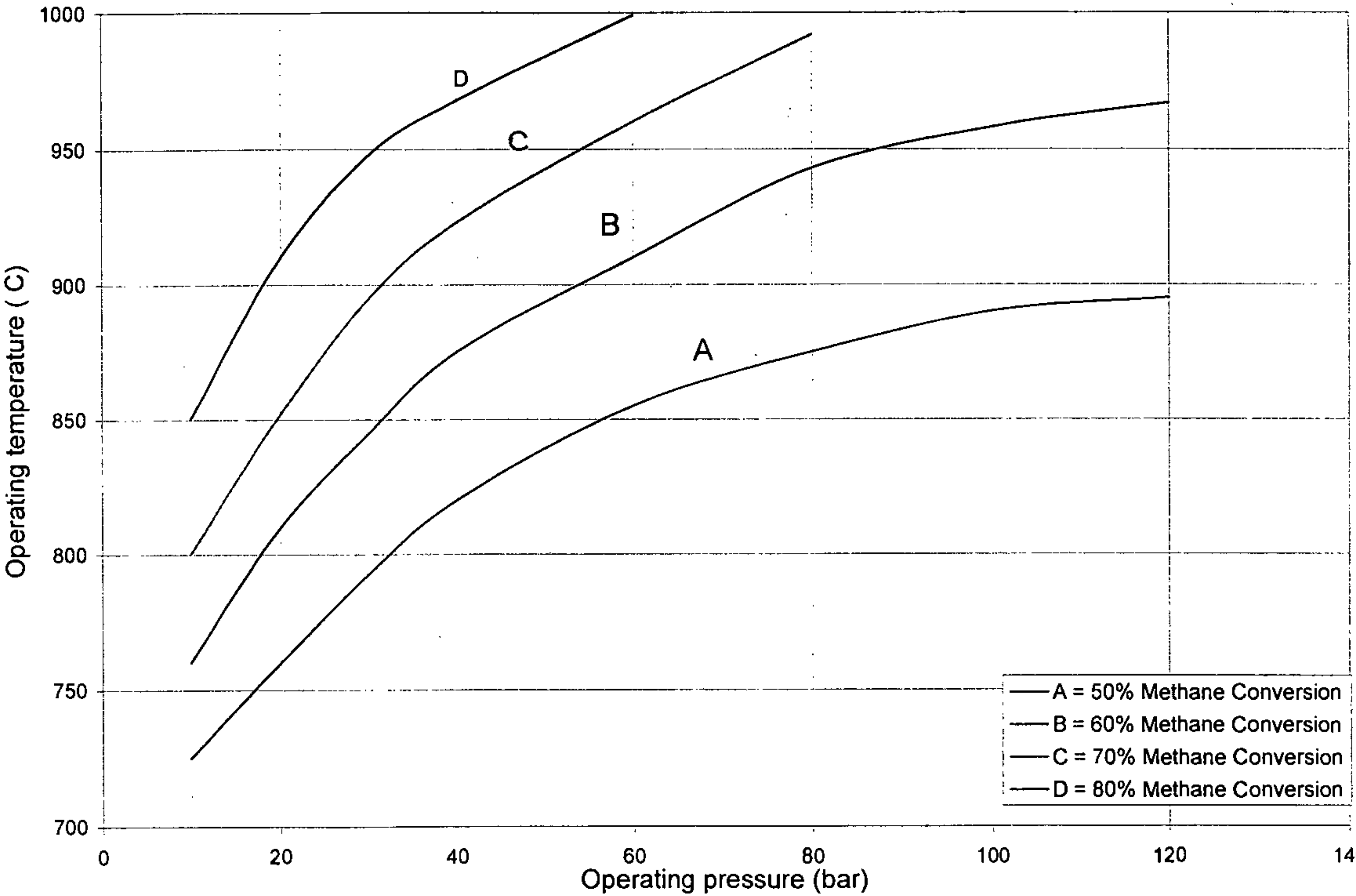


Fig. 4.7 Operating temperature vs. operating pressure for reforming when steam/methane ratio = 1

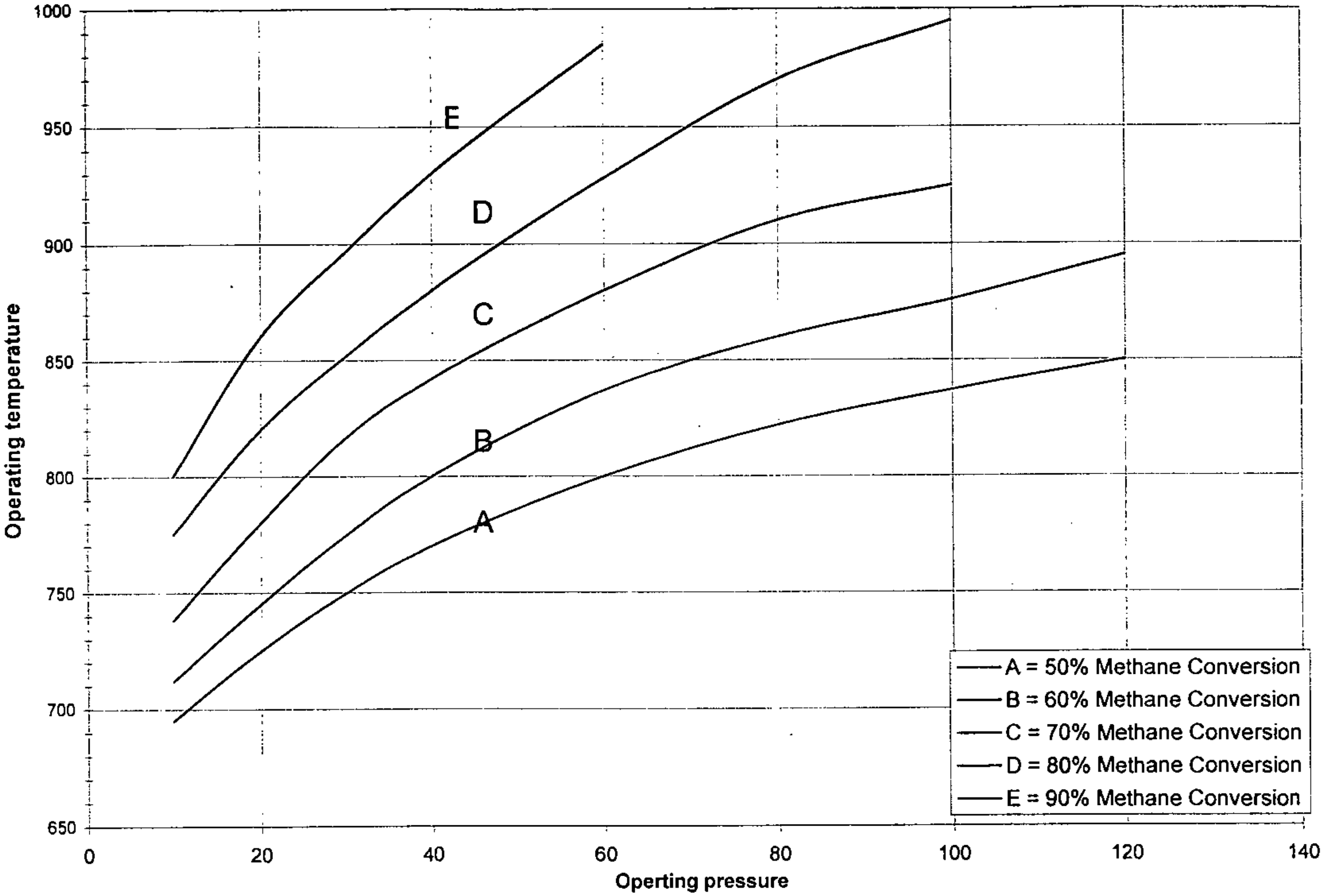


Fig. 4.8 Operating temperature vs. operating pressure for reforming when steam/methane ratio = 2

4.4 COMPARISON OF PLANT DATA AND THEORY BASED CALCULATED DATA

As there was no experimental arrangement in the laboratory to investigate individual influence of pressure, temperature and steam/methane ratio on reforming reaction, operating data of reforming units of different fertilizer factories have been collected. By the developed equation of the chemical equilibria for reforming reaction, outlet equilibrium compositions of primary reformer and secondary reformer of Zia Fertilizer Company Ltd., Urea Fertilizer Factory Ltd., Polash Urea Fertilizer Factory, Natural Gas Fertilizer, Chittagong Urea Fertilizer Ltd. and Karnaphuli Fertilizer Co. Ltd. have been calculated. A comparison of the theoretical values and actual outlet composition of the mentioned factories have been made. These theory based calculated data have been compared with the actual data for testing the validity of the equation of chemical equilibria for reforming reaction. Comparison of the reformers actual outlet compositions with the theory based calculated compositions are presented in Tables 4.7, 4.8, 4.9, 4.10, 4.11, 4.12 and 4.13. From the theory based calculated data, it is seen that the outlet compositions of the primary reformer and secondary reformer are similar with the actual data. A small discrepancy has been observed in the theory based calculation of the reformer outlet composition and actual composition, because in theoretical calculations, all gases have been considered as ideal, but practically it is not correct. Again, the graph lnK vs. 1/T which has been used for theory based calculation, is the representation of approximate equation.

$$\ln \frac{K}{K_1} = - \frac{\Delta H^o}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

However, the main objectives of this thesis work are to study the influence of pressure, temperature and steam/natural gas ratio on the reforming process for

Table 4.7: Operating data of reforming units of ZFCL and comparison of the actual outlet composition with the theory based calculated composition

Parameter	Primary Reformer Inlet	Primary Reformer outlet		Secondary Reformer	
Air/NG				1.43 (Inlet)	
Pressure (bar)	35.4	31.85		31.0 (Outlet)	
Temperature (°C)	455	788		982	
Steam/ NG	3.8	-		-	
Composition		Actual	Theoretical	Actual	Theoretical
CH_4 (%)	98.24	9.59	10.42	0.3	0.24
C_2H_6 (%)	1.44				
C_3H_8 (%)	0.01				
C_4H_{10} (%)					
CO (%)		9.0	9.2	12.08	11.49
CO_2 (%)	0.01	10.68	10.5	8.04	8.67
H_2 (%)	-	70.16	69.42	56.89	57.1
N_2 (%)	0.30	0.56	0.45	22.42	23.15
Ar (%)	0.01	0.01	0.009	0.27	0.02

Table 4.8: Operating data of reforming units of JFCL and comparison of the actual outlet composition with the theory based calculated composition

Parameter	Primary Reformer Inlet	Primary Reformer outlet		Secondary Reformer	
Air/NG				1.43 (Inlet)	
Pressure (bar)	34.7	31.30		31.0 (Outlet)	
Temperature (°C)	520	696		997	
Steam/ NG	3.30	-		-	
Composition		Actual	Theoretical	Actual	Theoretical
CH_4 (%)	92.26	11.46	11.55	0.25	0.24
C_2H_6 (%)	1.71				
C_3H_8 (%)	0.48				
C_4H_{10} (%)	0.19				
CO (%)		9.13	9.55	12.95	13.48
CO_2 (%)	0.29	10.36	9.77	7.36	6.89
H_2 (%)	3.53	68.56	68.60	55.58	55.95
N_2 (%)	1.53	0.48	0.48	23.58	23.43
Ar (%)	0.01	0.01	0.03	0.28	0.20

Table 4.9: Operating data of reforming units of CUFL and comparison of the actual outlet composition with the theory based calculated composition

Parameter	Primary Reformer Inlet	Primary Reformer outlet		Secondary Reformer	
Air/NG				1.43 (Inlet)	
Pressure (bar)	36.76	32.80		31.9 (Outlet)	
Temperature (°C)	520	819		1001	
Steam/ NG	3.00	-		-	
Composition		Actual	Theoretical	Actual	Theoretical
CH_4 (%)	90.64	10.52	12.44	0.25	0.28
C_2H_6 (%)	3.26				
C_3H_8 (%)	0.77				
C_4H_{10} (%)	0.57				
CO (%)		9.40	9.39	12.83	13.34
CO_2 (%)	0.48	10.63	9.82	7.75	6.74
H_2 (%)	2.88	69.04	67.75	56.39	56.00
N_2 (%)	1.88	0.40	0.58	22.50	23.60
Ar (%)	0.01	0.01	0.01	0.28	0.04

Table 4.10: Operating data of reforming units of PUFF and comparison of the actual outlet composition with the theory based calculated composition

Parameter	Primary Reformer Inlet	Primary Reformer outlet		Secondary Reformer	
Air/NG				1.43 (Inlet)	
Pressure (bar)	23.00	20.00		19.50 (Outlet)	
Temperature (°C)	450	780		980	
Steam/ NG	3.50	-		-	
Composition		Actual	Theoretical	Actual	Theoretical
CH_4 (%)	99.50	9.95	9.39	0.30	0.20
C_2H_6 (%)					
C_3H_8 (%)					
C_4H_{10} (%)					
CO (%)		8.25	9.24	11.40	12.5
CO_2 (%)	0.21	11.75	10.79	9.08	7.70
H_2 (%)		70.00	70.57	57.00	56.4
N_2 (%)	0.28	0.01	0.01	22.22	23.05

Table 4.11: Operating data of reforming units of UFFL and comparison of the actual outlet composition with the theory based calculated composition

Parameter	Primary Reformer Inlet	Primary Reformer outlet		Secondary Reformer	
Air/NG				1.43 (Inlet)	
Pressure (bar)	33.00	29.50		28.50 (Outlet)	
Temperature (°C)	400	788		997	
Steam/ NG	3.8	-		-	
Composition		Actual	Theoretical	Actual	Theoretical
CH_4 (%)	97.11	11.21	9.25	0.22	0.14
C_2H_6 (%)	1.77				
C_3H_8 (%)	0.38				
C_4H_{10} (%)	0.25				
CO (%)		8.71	9.63	12.59	11.84
CO_2 (%)	0.21	11.02	10.89	7.80	8.64
H_2 (%)		68.98	70.13	55.39	56.45
N_2 (%)	0.28	0.08	0.07	23.69	22.9
Ar (%)	0.30	0.10	0.07	0.30	0.10

Table 4.12: Operating data of reforming units of NGFF and comparison of the actual outlet composition with the theory based calculated composition

Parameter	Primary Reformer Inlet	Primary Reformer outlet		Secondary Reformer	
Air/NG				1.43 (Inlet)	
Pressure (bar)	8.3	6.3		6.2 (Outlet)	
Temperature (^{o}C)	380	655		730	
Steam/ NG	6.1	-		-	
Composition		Actual	Theoretical	Actual	Theoretical
CH_4 (%)	95.00	7.50	6.66	0.70	0.80
C_2H_6 (%)	3.1				
C_3H_8 (%)	0.70				
C_4H_{10} (%)	0.20				
CO (%)	-	5.00	5.23	7.00	5.52
CO_2 (%)	0.60	14.00	14.50	12.00	13.36
H_2 (%)	-	73.30	73.45	59.70	58.00
N_2 (%)	0.40	0.20	0.11	20.60	22.32

Table 4.13: Operating data of reforming units of KAFCO and comparison of the actual outlet composition with the theory based calculated composition

Parameter	Primary Reformer Inlet	Primary Reformer outlet		Secondary Reformer	
Air/NG				1.43 (Inlet)	
Pressure (bar)	37.5	33		32 (Outlet)	
Temperature (°C)	520	780		950	
Steam/ NG	2.86	-		-	
Composition		Actual	Theoretical	Actual	Theoretical
CH_4 (%)	90.00	14.7	14.88	0.75	0.572
C_2H_6 (%)	3.44	-			
C_3H_8 (%)	0.73				
C_4H_{10} (%)	0.10				
CO (%)	-	7.0	9.13	11.60	12.88
CO_2 (%)	0.37	10.5	9.69	7.50	7.37
H_2 (%)	3.63	67.0	65.7	56.00	55.36
N_2 (%)	1.73	0.5	0.58	23.50	23.79
Ar (%)	0.068	0.03	0.02	0.30	0.028

ammonia production. From the actual data analysis of different fertilizer factories, it can be seen that the expected theoretical values of the reformer outlet equilibrium compositions have the similarity with the actual values of the same.

From Table 4.14 it is seen that design pressures of ZFCL, JFCL, CUFL, UFFL and KAFCO primary reformers' outlet are 31.85 bar, 31.3 bar, 32.8 bar, 29.5 bar and 33 bar respectively. These pressures are high for reforming process. So, high operating temperatures (756°C – 819°C) have been selected for these reformers to compensate the decrease in conversion of natural gas due to high operating pressures.

Pressure, temperature and steam/NG ratio of JFCL primary reformer outlet are 31.3 bar, 796°C and 3.3 respectively. These parameters of KAFCO primary reformer are 33 bar, 756°C and 2.86 respectively. So, the operating parameters of JFCL primary reformer are favourable for natural gas conversion than those of KAFCO. In composition analysis of these two plants, it is seen that conversion of natural gas in JFCL primary reformer is higher than that of KAFCO. But the amount of fuel to increase the reforming temperature and process steam for KAFCO reformers are lower than those of JFCL.

Primary reformer outlet pressure of NGFF is 6.2 bar, which is low. So, the primary reformer outlet temperature (655°C) has been selected as low. For maximum conversion of natural gas steam/ NG has been selected (6.1) for this reforming process.

Table 4.14 Process parameters and NG conversion of primary reformer and secondary reformer of seven different fertilizer industries of Bangladesh

Process parameter		ZFCL	JFCL	CUFL	PUFF	UFFL	NGFF	KAFCO
1^0 RF outlet pressure (bar)		31.85	31.3	32.8	20.0	29.5	6.3	33
2^0 RF outlet pressure (bar)		31.0	31.0	31.9	19.5	28.5	6.2	32
1^0 RF inlet temp. (^{0}C)		455	520	520	450	400	380	520
1^0 RF outlet temp. (^{0}C)		788	796	819	780	790	655	756
2^0 RF outlet temp. (^{0}C)		992	997	1001	980	997	730	928
2^0 RF inlet air/NG (mole Basis)		1.43	1.43	1.43	1.43	1.43	1.43	1.43
Steam/NG ratio (wt. Basis)		3.8	3.3	3.0	3.5	3.8	6.1	2.86
1^0 RF NG conversion	Theoretical	0.654	0.625	0.630	0.700	0.683	0.747	0.560
	Actual	0.640	0.623	0.655	0.670	0.640	0.720	0.540
2^0 RF NG conversion	Theoretical	0.993	0.989	0.990	0.980	0.993	0.977	0.980
	Actual	0.985	0.983	0.985	0.977	0.990	0.963	0.973

CHAPTER – 5

CONCLUSIONS

From the calculated data and graphical analysis following decisions can be made.

During steam reforming of natural gas, conversion of natural gas increases with the increase of temperature, decrease of pressure and increase of steam/natural gas ratio.

Design pressures of ZFCL, JFCL, CUFL, UFFL and KAFCO reformers are high. So, high operating temperatures have been selected for these reformers to compensate the decrease in conversion of natural gas due to high operating pressures.

Pressure, temperature and steam/NG ratio of JFCL reformers are favourable for natural gas conversion than those of KAFCO. So, conversion of natural gas in JFCL reformers is higher than that of KAFCO.

Pressure in the reforming process of NGFF is low. So, lower operating temperature could be selected for its reforming process for higher conversion of natural gas.

CHAPTER - 6

SUGGESTION FOR FURTHER WORK

1. To observe the individual influence of temperature, pressure steam/Natural gas ratio on reforming independently, experimental arrangement can be set up in the laboratory.
2. To find optimum usage ratio of steam/Natural gas and other operating variables economic analysis of the ammonia process can be performed.
3. To optimize the use of fuel, a study can be performed for maximum co-generation of steam at the outlet of the secondary reformer.
4. A study can be performed for maximum recovery heat on basis of the setting up of gas burner for primary reformer catalyst tube heating.
5. A study can be performed for maximum heat recovery on the basis of the arrangement of different preheater in the reformer flue gas duct.

NOMENCLATURE

CUFL	Chittagong Urea Factory Limited
ΔG	Free energy change
ΔG^{0}	Standard free energy change
ΔH	Enthalpy change
ΔH^{0}	Standard enthalpy change
JFCL	Jamuna Fertilizer Company Limited
KAFCO	Karnaphuli Fertilizer Company Limited
K	Chemical equilibrium constant
n_i	No. of each mole reactant
n	No. of total moles
NG	Natural gas
NGFF	Natural Gas Fertilizer Factory Limited
P	Pressure, bar
PUFF	Polash Urea Fertilizer Factory Limited
T	Absolute temperature, °K
UFFL	Urea Fertilizer Factory Limited
y_i	Fraction of moles of the species
ZFCL	Zia Fertilizer Company Limited
ε	Extent of reaction
ν	Stoichiometric co-efficient.

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APPENDIX – A

THEORY BASED CALCULATED DATA OF REFORMING UNITS

Table – A.1: Reforming pressure at specific fractional conversion of methane (varying with different moles of steam)

($CH_4 + H_2O = CO + 3H_2$; Temp. = 600°C, K = 0.368, P = ?)

Fractional conversion methane	Pressure required at the primary reforming vessel with different moles of steam				
	1 mol H_{20} (Bar)	2 mol H_2O (Bar)	3 mol H_2O (Bar)	4 mol H_2O (Bar)	5 mol H_2O (Bar)
	2.36	5.09	8.2	11.7	15.52
0.4	1.225	2.71	4.37	6.22	8.24
0.5	0.7	2.28	3.13	3.7	4.9
0.6	0.415	1.38	1.65	2.34	3.1
0.7	0.243	0.43	1.14	1.51	2.0
0.8	0.13	0.41	0.68	0.96	1.2
0.9	0.055	0.13	0.38	0.545	0.72
0.99	0.0047	0.06	0.1	0.14	0.19

Table – A.2: Reforming pressure at specific fractional conversion of methane (varying with different moles of steam)

($CH_4 + H_2O = CO + 3H_2$; Temp. = 700°C, K = 5.75, P = ?)

Fractional conversion methane	Pressure required at the primary reforming vessel with different moles of steam				
	1 mol H_{2O} (Bar)	2 mol H_2O (Bar)	3 mol H_2O (Bar)	4 mol H_2O (Bar)	5 mol H_2O (Bar)
	9.33	20.13	32.44	46.21	61.38
0.4	4.84	10.73	17.29	24.59	32.58
0.5	2.76	9.04	12.39	14.65	19.38
0.6	1.64	4.02	6.53	9.27	12.24
0.7	0.96	2.58	4.22	6.00	7.91
0.8	0.86	1.63	2.68	3.8	4.76
0.9	0.56	0.72	1.51	1.77	2.84
0.99	0.018	0.23	0.4	0.58	0.75

Table – A.3: Reforming pressure at specific fractional conversion of methane (varying with different moles of steam)

($CH_4 + H_2O = CO + 3H_2$; Temp. = 800°C, K = 181, P = ?)

Fractional conversion methane	Pressure required at the primary reforming vessel with different moles of steam				
	1 mol H_2O (Bar)	2 mol H_2O (Bar)	3 mol H_2O (Bar)	4 mol H_2O (Bar)	5 mol H_2O (Bar)
0.3	95.57	112.97	181.99	259.29	344.39
0.4	27.17	60.24	97.01	137.94	182.49
0.5	15.51	50.73	69.51	82.20	108.74
0.6	9.2	22.59	36.65	52.00	59.93
0.7	5.38	14.49	23.68	33.63	44.39
0.8	2.91	9.2	15.04	21.36	26.70
0.9	1.21	2.12	8.48	12.1	15.94
0.99	0.105	1.31	2.24	3.17	4.21

Table – A.4: Reforming pressure at specific fractional conversion of methane (varying with different moles of steam)

($CH_4 + H_2O = CO + 3H_2$; Temp. = 900°C, K = 3827, P = ?)

Fractional conversion methane	Pressure required at the primary reforming vessel with different moles of steam				
	1 mol H_{2O} (Bar)	2 mol H_2O (Bar)	3 mol H_2O (Bar)	4 mol H_2O (Bar)	5 mol H_2O (Bar)
0.3	240.71	519.46	836.00	1199.00	1592.00
0.4	125.00	277.00	446.00	638.00	845.00
0.5	71.34	233.00	319.00	380.00	503.00
0.6	42.32	103.00	168.00	240.00	317.00
0.7	24.75	66.00	109.00	155.00	205.00
0.8	13.41	42.00	69.00	98.00	123.00
0.9	5.58	23.00	39.00	56.00	74.00
0.99	0.48	6.06	10.29	14.64	19.50

Table – A.5: Reforming pressure at specific fractional conversion of methane (varying with different moles of steam)

($CH_4 + H_2O = CO + 3H_2$; Temp. = 1000°C, K = 10405, P = ?)

Fractional conversion methane	Pressure required at the primary reforming vessel with different moles of steam				
H_2O	1 mol H_{2O} (Bar)	2 mol H_2O (Bar)	3 mol H_2O (Bar)	4 mol H_2O (Bar)	5 mol H_2O (Bar)
0.3	396.00	856.54	1379.9	1965.80	2611.00
0.4	206.00	461.00	735.60	1045.80	1386.00
0.5	117.00	384.60	527.08	623.30	825.00
0.6	69.00	171.3	277.00	394.27	521.00
0.7	40.00	109.86	179.50	255.01	337.00
0.8	22.00	69.18	114.04	162.00	205.00
0.9	9.21	22.12	64.35	92.00	121.00
0.99	0.79	9.99	16.97	24.14	31.93

Table – A.6: Conversion of methane during steam reforming at different temperature and at constant pressure (10 bar)

	Conversion of methane at pressure 10 bar				
Temperature	1 Mole Steam : 1 Mole Methane	2 Mole Steam : 1 Mole Methane	3 Mole Steam : 1 Mole Methane	4 Mole Steam : 1 Mole Methane	5 Mole Steam : 1 Mole Methane
600	0.12	0.21	0.275	0.325	0.375
700	0.35	0.45	0.51	0.575	0.65
800	0.55	0.72	0.8	0.875	0.92
900	0.76	0.87	0.94	0.975	0.985
1000	0.88	0.97	0.98	0.99	0.992

Table – A.7: Conversion of methane during steam reforming at different temperature and at constant pressure (20 bar)

	Conversion of methane at pressure 20 bar				
Temperature	1 Mole Steam : 1 Mole Methane	2 Mole Steam : 1 Mole Methane	3 Mole Steam : 1 Mole Methane	4 Mole Steam : 1 Mole Methane	5 Mole Steam: 1 Mole Methane
600	0.1	0.14	0.185	0.226	0.275
700	0.21	0.3	0.4	0.48	0.575
800	0.42	0.575	0.68	0.76	0.845
900	0.72	0.8	0.85	0.94	0.98
1000	0.82	0.91	0.95	0.98	0.99

Table – A.8: Conversion of methane during steam reforming at different temperature and at constant pressure (30 bar)

	Conversion of methane at pressure 30 bar				
Temperature	1 Mole Steam : 1 Mole Methane	2 Mole Steam : 1 Mole Methane	3 Mole Steam : 1 Mole Methane	4 Mole Steam : 1 Mole Methane	5 Mole Steam : 1 Mole Methane
600	0.055	0.1	0.12	0.15	0.22
700	0.17	0.25	0.32	0.38	0.46
800	0.36	0.5	0.575	0.65	0.72
900	0.65	0.775	0.875	0.925	0.975
1000	0.76	0.92	0.96	0.98	0.99

Table – A.9: Conversion of methane during steam reforming at different temperature and at constant pressure (40 bar)

	Conversion of methane at pressure 40 bar				
Temperature	1 Mole Steam : 1 Mole Methane	2 Mole Steam : 1 Mole Methane	3 Mole Steam : 1 Mole Methane	4 Mole Steam : 1 Mole Methane	5 Mole Steam : 1 Mole Methane
600	0.06	0.12	0.14	0.16	0.18
700	0.15	0.22	0.28	0.32	0.36
800	0.275	0.42	0.52	0.575	0.65
900	0.575	0.77	0.88	0.93	0.96
1000	0.75	0.875	0.95	0.98	0.98

Table – A.10: Conversion of methane during steam reforming at different temperature and at constant pressure (50 bar)

	Conversion of methane at pressure 50 bar				
Temperature	1 Mole Steam : 1 Mole Methane	2 Mole Steam : 1 Mole Methane	3 Mole Steam : 1 Mole Methane	4 Mole Steam : 1 Mole Methane	5 Mole Steam : 1 Mole Methane
600	0.045	0.08	0.12	0.14	0.175
700	0.12	0.18	0.24	0.28	0.34
800	0.25	0.375	0.5	0.64	0.72
900	0.45	0.68	0.82	0.92	0.95
1000	0.67	0.86	0.93	0.975	0.98

Table – A.11: Conversion of methane during steam reforming at different steam/methane ratio at constant temperature (1000 °C)

	Conversion of methane at temperature 1000 °C				
Steam/ Methane ratio	50 bar	40 bar	30 bar	20 bar	10 bar
1	0.67	0.7	0.76	0.82	0.88
2	0.84	0.87	0.91	0.96	0.98
3	0.925	0.935	0.965	0.98	0.99
4	0.955	0.965	0.98	0.99	0.992
5	0.975	0.98	0.985	0.992	0.995

Table – A.12 Conversion of methane during steam reforming at different steam/methane ratio at constant temperature (900 °C)

	Conversion of methane at temperature 900 °C				
Steam/ Methane ratio	50 bar	40 bar	30 bar	20 bar	10 bar
1	0.53	0.6	0.645	0.74	0.84
2	0.725	0.775	0.825	0.92	0.975
3	0.86	0.89	0.91	0.95	0.982
4	0.92	0.94	0.95	0.975	0.986
5	0.96	0.965	0.975	0.98	0.99

Table – A.13: Conversion of methane during steam reforming at different steam/methane ratio at constant temperature (800 °C)

	Conversion of methane at temperature 800 °C				
Steam/ Methane ratio	50 bar	40 bar	30 bar	20 bar	10 bar
1	0.226	0.275	0.325	0.39	0.512
2	0.35	0.41	0.45	0.55	0.7
3	0.44	0.51	0.575	0.66	0.8
4	0.525	0.59	0.65	0.75	0.875
5	0.59	0.65	0.71	0.78	0.92

Table – A.14: Conversion of methane during steam reforming at different steam/methane ratio at constant temperature (700 °C)

	Conversion of methane at temperature 700 °C				
Steam/ Methane ratio	50 bar	40 bar	30 bar	20 bar	10 bar
1	0.08	0.12	0.155	0.22	0.315
2	0.15	0.21	0.25	0.31	0.42
3	0.22	0.28	0.32	0.4	0.51
4	0.28	0.35	0.39	0.48	0.58
5	0.34	0.4	0.44	0.525	0.65

Table – A.15: Conversion of methane during steam reforming at different steam/methane ratio at constant temperature (600 °C)

	Conversion of methane at 600 °C		
Steam/ Methane ratio	30 bar	20 bar	10 bar
1	0.05	0.1	0.14
2	0.09	0.15	0.21
3	0.14	0.2	0.275
4	0.19	0.25	0.325
5	0.25	0.31	0.375

Table – A.16: Conversion of methane during steam reforming at different pressure at constant temperature (1000 °C)

	Conversion of methane at temperature 1000 °C				
Pressure	1 Mole Steam: 1 Mole Methane	2 Mole Steam: 1 Mole Methane	3 Mole Steam: 1 Mole Methane	4 Mole Steam: 1 Mole Methane	5 Mole Steam: 1 Mole Methane
10	0.89	0.97	0.98	0.985	0.995
20	0.855	0.955	0.97	0.98	0.99
30	0.82	0.93	0.96	0.97	0.986
40	0.77	0.9	0.94	0.96	0.98
50	0.72	0.86	0.91	0.95	0.975

Table – A.17: Conversion of methane during steam reforming at different pressure at constant temperature (900 °C)

	Conversion of methane at temperature 900 °C				
Pressure	1 Mole Steam: 1 Mole Methane	2 Mole Steam: 1 Mole Methane	3 Mole Steam: 1 Mole Methane	4 Mole Steam: 1 Mole Methane	5 Mole Steam: 1 Mole Methane
10	0.86	0.94	0.96	0.975	0.99
20	0.77	0.89	0.94	0.96	0.985
30	0.695	0.84	0.915	0.95	0.975
40	0.62	0.8	0.88	0.93	0.96
50	0.55	0.76	0.86	0.91	0.945

Table – A.18: Conversion of methane during steam reforming at different pressure at constant temperature (800 °C)

	Conversion of methane at temperature 800 °C				
Pressure	1 Mole Steam: 1 Mole Methane	2 Mole Steam: 1 Mole Methane	3 Mole Steam: 1 Mole Methane	4 Mole Steam: 1 Mole Methane	5 Mole Steam: 1 Mole Methane
10	0.55	0.69	0.77	0.85	0.89
20	0.46	0.6	0.675	0.745	0.78
30	0.35	0.5	0.57	0.63	0.67
S40	0.25	0.41	0.47	0.53	0.58
50	0.18	0.31	0.38	0.45	0.51

Table – A.19: Conversion of methane during steam reforming at different pressure at constant temperature (700 °C)

	Conversion of methane at temperature 700 °C				
Pressure	1 Mole Steam: 1 Mole Methane	2 Mole Steam: 1 Mole Methane	3 Mole Steam: 1 Mole Methane	4 Mole Steam: 1 Mole Methane	5 Mole Steam: 1 Mole Methane
10	0.51	0.67	0.74	0.85	0.97
20	0.42	0.58	0.66	0.76	0.86
30	0.34	0.5	0.57	0.67	0.76
40	0.265	0.42	0.49	0.58	0.67
50	0.18	0.32	0.4	0.48	0.58

Table – A.20: Requirement of pressure and temperature during steam reforming of methane at constant steam/methane ratio (1)

	Requirement of temperature at steam/methane = 1			
Pressure	50% Methane Conversion	60% Methane Conversion	70% Methane Conversion	80% Methane Conversion
10	725	760	800	850
20	760	810	852	910
30	793	845	895	948
40	820	875	923	968
60	855	910	960	999
80	875	943	992	
100	890	958		
120	895	967		

Table – A.21: Requirement of pressure and temperature during steam reforming of methane at constant steam/methane ratio (2)

	Requirement of temperature at steam/methane = 2				
Pressure	50% Methane Conversion	60% Methane Conversion	70% Methane Conversion	80% Methane Conversion	90% Methane Conversion
10	695	712	738	775	800
20	725	745	780	820	860
30	750	772	820	852	897
40	770	800	842	880	930
60	800	837	880	925	985
80	822	860	910	970	
100	837	875	925	995	
120	850	895			

Table – A.22: Requirement of pressure and temperature during steam reforming of methane at constant steam/methane ratio (3)

	Requirement of temperature at steam/methane = 3					
Pressure	40% Methane Conversion	50% Methane Conversion	60% Methane Conversion	70% Methane Conversion	80% Methane Conversion	90% Methane Conversion
10	660	687	715	737	767	805
20	695	720	745	775	810	855
30	727	748	780	810	840	890
40	748	770	800	835	866	925
60	776	797	832	865	910	960
80	795	820	860	895	940	
100	810	830	870	910	948	

Table – A.23: Requirement of pressure and temperature during steam reforming of methane at constant steam/methane ratio (4)

	Requirement of temperature at steam/methane = 4					
Pressure	40% Methane Conversion	50% Methane Conversion	60% Methane Conversion	70% Methane Conversion	80% Methane Conversion	90% Methane Conversion
10	625	664	698	718	740	775
20	675	702	735	755	790	825
30	710	740	765	785	820	855
40	737	760	782	812	848	890
60	773	787	812	840	880	923
80	790	805	835	870	908	960
100	798	820	850	890	922	980

Table – A.24: Requirement of pressure and temperature during steam reforming of methane at constant steam/methane ratio (5)

	Requirement of temperature at steam/methane = 5					
Pressure	40% Methane Conversion	50% Methane Conversion	60% Methane Conversion	70% Methane Conversion	80% Methane Conversion	90% Methane Conversion
10	610	645	675	710	730	772
20	653	700	732	753	775	812
30	690	730	765	787	810	837
40	712	750	790	812	825	860
60	740	775	815	837	855	900
80	760	790	825	860	880	930
100	770	800	832	870	895	965

APPENDIX – B

PLANT DATA OF DIFFERENT REFORMING UNITS

Table B.1: Process parameters of primary reformer and secondary reformer of seven different fertilizer industries of Bangladesh

Process parameter	ZFCL	JFCL	CUFL	PUFF	UFFL	NGFF	KAFCO
1^0 RF inlet pressure (bar)	35.4	34.7	36.76	23.0	33.0	8.3	37.5
1^0 RF outlet pressure (bar)	31.85	31.3	32.8	20.0	29.5	6.3	33
2^0 RF outlet pressure (bar)	31.0	31.0	31.9	19.5	28.5	6.2	32
1^0 RF inlet temp. (^{0}C)	455	520	520	450	400	380	520
1^0 RF outlet temp. (^{0}C)	788	796	819	780	790	655	756
2^0 RF outlet temp. (^{0}C)	992	997	1001	980	997	730	928
2^0 RF inlet air/NG (mole Basis)	1.43	1.43	1.43	1.43	1.43	1.43	1.43
Steam/NG ratio (wt. Basis)	3.8	3.3	3.0	3.5	3.8	6.1	2.86

Table B.2 Composition of primary reformer inlet of different plant

Composition	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	C_4H_{10} (%)	CO (%)	CO_2 (%)	H_2 (%)	N_2 (%)	Ar (%)
ZFCL 1° RF inlet	98.24	1.44	0.01	-	-	0.01	-	0.3	0.01
JFCL 1° RF inlet	92.26	1.71	0.48	0.19	-	0.29	3.53	1.53	0.01
CUFL 1° RF inlet	90.64	3.26	0.77	0.57	-	0.48	2.88	1.88	0.01
PUFF 1° RF inlet	99.5	-	-	-	-	0.21	-	-	0.28
UFFL 1° RF inlet	97.11	1.77	0.38	0.25	-	0.21	-	0.28	0.3
NGFF 1° RF inlet	95.0	3.1	0.7	0.2	-	0.6	-	0.4	-
KAFCO 1° R-F inlet	90.0	3.44	0.73	0.10	-	0.37	3.63	1.73	-

Table B.3: Composition of primary reformer outlet of different plant

Composition	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	C_4H_{10} (%)	CO (%)	CO_2 (%)	H_2 (%)	N_2 (%)	Ar (%)
ZFCL 1^o RF outlet	9.59	-	-	-	9.0	10.68	70.16	0.56	0.01
JFCL 1^o RF outlet	11.46	-	-	-	9.13	10.36	68.56	0.48	0.01
CUFL 1^o RF outlet	10.52	-	-	-	9.4	10.63	69.04	0.40	0.01
PUFF 1^o RF outlet	9.95	-	-	-	8.25	11.75	70.0	-	0.01
UFFL 1^o RF outlet	11.2	-	-	-	8.71	11.03	68.98	0.08	0.01
NGFF 1^o RF outlet	7.5	-	-	-	5.0	14.0	73.3	0.20	-
KAFCO 1^o RF outlet	14.7	-	-	-	7.0	10.5	67.0	0.03	0.5

Table B.4: Composition of secondary reformer outlet of different plant

Composition	CH_4 (%)	C_2H_6 (%)	C_3H_8 (%)	C_4H_{10} (%)	CO (%)	CO_2 (%)	H_2 (%)	N_2 (%)	Ar (%)
ZFCL 2° RF outlet	0.3	-	-	-	12.08	8.04	56.89	22.42	0.27
JFCL 2° RF outlet	0.25	-	-	-	12.95	7.36	55.58	23.58	0.28
CUFL 2° RF outlet	0.25	-	-	-	12.83	7.75	56.39	22.5	0.28
PUFF 2° RF outlet	0.3	-	-	-	11.4	9.08	57.0	21.93	0.28
UFFL 2° RF outlet	0.24	-	-	-	12.59	7.8	55.39	23.69	0.3
NGFF 2° RF outlet	0.7	-	-	-	7.0	12.0	59.7	20.6	-
KAFCO 2° RF outlet	0.75	-	-	-	11.6	7.5	56.0	23.5	-

APPENDIX - C

SAMPLE CALCULATION

Sample Calculation for Reforming Units of ZFCL

Primary reformer inlet composition:

CH_4 = 98.24%

C_2H_6 = 1.44

C_3H_8 = 0.01

CO_2 = 0.01

N_2 = 0.3

Ar = 0.01

After conversion of higher hydrocarbon into methane, amount of component becomes:

$CH_4 = (98.24\% + 1.44\% \times 2 + 0.01\% \times 3) = 101.15\%$

$CO_2 = \quad = 0.01\%$

$N_2 = \quad = 0.3\%$

$Ar = \quad = 0.01\%$

Let , CH_4 = 1 mole,

∴ CO_2 = 0.0001 mole,

N_2 = 0.003 mole, and

Ar = 0.0001 mole

Primary reformer inlet $\frac{Steam}{NG}\ ratio = 3.8$ (wt. basis)

$$\therefore \quad \frac{Steam}{NG} = 3.8\frac{gm}{gm}\left|\frac{16\ gm}{1\ mole}\right|\frac{1\ mole}{18\,gm} = 3.37\frac{mole}{mole}$$

Primary reformer outlet operating conditions

Pressure = 31.85 bar

Temperature = 788°C = 1061°K

Now, $\frac{1}{T}K^{-1} \times 10^4 = 9.42$

$\therefore$ K = 164.32 (from Fig. 2.2)

Now, The reforming reaction is, $CH_4 + H_2O = CO + 3H_2$

At the equilibrium point,

$n_{CH_4} = 1-\varepsilon,$ $n_{H_2O}, = 3.37 - \varepsilon,$ $n_{H_2} = 3\varepsilon,$

$n_{CO} = \varepsilon,$ $n_{CO_2} = 0.0001 + \varepsilon,$ Diluent = 0.0031

$$\therefore \ K_{reform} = \frac{\left(\frac{\varepsilon}{4.3732 + 2\varepsilon}\right)\left(\frac{3\varepsilon}{4.3732 + 2 + \varepsilon}\right)^3}{\left(\frac{1-\varepsilon}{4.3732 + 2\varepsilon}\right)\left(\frac{3.37 - \varepsilon}{4.3732 + 2\varepsilon}\right)} p^2$$

$$\text{or,} \quad \frac{K_{reform}}{p^2} = \frac{\left(\frac{\varepsilon}{4.3739 + 2\varepsilon}\right)\left(\frac{3\varepsilon}{4.3732 + 2\varepsilon}\right)^3}{\left(\frac{1 - \varepsilon}{4.3732 + 2\varepsilon}\right)\left(\frac{3.37 - \varepsilon}{4.3732 + 2\varepsilon}\right)}$$

$$\text{or, } \frac{164.32}{(31.85)^2} = \frac{27\varepsilon^4}{(3.3732+2\varepsilon)^2(1-\varepsilon)(3.37-\varepsilon)}$$

$$\text{or, } 0162 = \frac{27\varepsilon^4}{(4.3732+2\varepsilon)^2(1-\varepsilon)(3.37-\varepsilon)}$$

$\therefore$ $\varepsilon = 0.654$

The shift reaction in the primary reformer is, $CO + H_2O = CO_2 + H_2$

At the equilibrium point of the shift reaction,

$n_{CO} = 0.654-\varepsilon$, $n_{H_2O} = 2.716-\varepsilon$, $n_{CO_2} = 0.0001 + \varepsilon$

$n_{H_2} = 1.962+\varepsilon$, $n_{CH_4} = 0.346-\varepsilon$, Diluent = 0.0031

$$K_{shift} = \frac{y_{H_2}\cdot y_{CO_2}}{y_{CO}\cdot y_{H_2O}} = \frac{\left(\frac{1.962+\varepsilon}{5.6812}\right)\times\left(\frac{0.0001+\varepsilon}{5.6812}\right)}{\left(\frac{0.654-\varepsilon}{5.6812}\right)\times\left(\frac{2.716-\varepsilon}{5.6812}\right)}$$

$$= \frac{(1.962+\varepsilon)(0.0001+\varepsilon)}{(0.654-\varepsilon)(2.716-\varepsilon)}$$

Temperature, T°K = 788°C = 1061°K, $1/T \times 10^4/K = 9.42$

$\therefore$ $K_{shift} = 1.117$ (from Fig. 2.1)

Now,

$$1.117 = \frac{(1.962+\varepsilon)(0.0001+\varepsilon)}{(0.654-\varepsilon)(2.716-\varepsilon)}$$

$\therefore \varepsilon = 0.349$

$n_{CO} = 0.305$ $n_{H_2O} = 2.367$ $n_{CO_2} = 0.3491$

$n_{H_2} = 2.311$ $n_{CH_4} = 0.346$ $n_{N_2} = 0.0031$

$n_{Ar} = 0.0001$

Primary reformer outlet composition on dry basis:

$y_{CO} = 9.2$ $y_{CO_2} = 10.5$ $y_{H_2} = 69.73$

$y_{CH_4} = 10.42$ $y_{N_2} = 0.09$ $y_{Ar} = 0.001$

Material Balance At the Secondary Reformer top chamber

Supplied oxygen = 0.3 mole

$\therefore$ Produced steam (H_2O) = 0.6

H_2 lost = (2.311 – 0.6) mole = 1.711 mole

Total mole of H_2O (steam) = (2.367 + 0.6) mole = 2.967 moles

N_2 = 1.13 moles

At the equilibrium point of the secondary reformer bottom chamber,

$n_{CH_4} = .346 - \varepsilon,$ $n_{H_2O}, = 2.967 - \varepsilon,$ $n_{H_2} = 1.711 + 3\varepsilon,$

$n_{CO} = 0.305 + \varepsilon,$ Diluent = 0.3521

Secondary reformer outlet operating conditions:

Pressure = 31.0 bar

Temperature, T°K = (989 + 273)°K = 1262°K

∴ 1/T°K × 10^4 = 7.92

$K_{reform.}$ = 10938 (from Fig. 2.2)

$$K_{reform} = \frac{\left(\frac{0.305+\varepsilon}{7.11+2\varepsilon}\right)\left(\frac{3\varepsilon+1.711}{7.11+2\varepsilon}\right)^3}{\left(\frac{0.346-\varepsilon}{7.11+2\varepsilon}\right)\left(\frac{2.967-\varepsilon}{7.11+2\varepsilon}\right)} p^2$$

$$\text{or, } \frac{10938}{(31)^2} = \frac{(0.305+\varepsilon)(3\varepsilon+1.711)^3}{(3.3732+2\varepsilon)^2(1-\varepsilon)(3.37-\varepsilon)}$$

$$\text{or, } 11.38 = \frac{(0.305+\varepsilon)(3\varepsilon+1.711)^3}{(7.11+2\varepsilon)^2(0.346-\varepsilon)(2.967-\varepsilon)}$$

$\varepsilon = 0.339$

$n_{CO} = 0.644$ $n_{H_2} = 2.728$, $n_{CH_4} = 0.007$

$n_{H_2O} = 2.628$ $n_{CO_2} = 0.3491$,

The shift reaction in the secondary reformer is, $CO + H_2O = CO_2 + H_2$

At the equilibrium point of the shift reaction,

$n_{CO} = 0.644-\varepsilon$, $n_{H_2O} = 2.628-\varepsilon$, $n_{CO_2} = 0.3491+\varepsilon$

$n_{H_2} = 2.728+\varepsilon$

$$\text{Now,}\quad K_{shift} = \frac{(0.3491+\varepsilon)(2.728+\varepsilon)}{(0.644-\varepsilon)(2.628-\varepsilon)}$$

Temperature, T°K = (989 + 273)°K = 1262°K

1/T°K × 10^4 = 7.92

∴ K_{shift} = 0.818 (from Fig. 2.1)

Now,

$$0.818 = \frac{(0.3491+\varepsilon)(2.728+\varepsilon)}{(0.644-\varepsilon)(2.628-\varepsilon)}$$

$$= 0.818$$

$$\therefore\ \varepsilon = 0.075$$

n_{CO} = 0.5685, $n_{H_2O} = 2.5585$ $n_{CO_2} = 0.4246$

$n_{H_2} = 1.1331$ $n_{CH_4} = 0.007$ $n_{N_2} = 1.1331$

$n_{Ar} = 0.0001$

Secondary reformer outlet composition on dry basis:

y_{CO} = 11.49% $y_{CO_2} = 8.67\%$ $y_{H_2} = 57.1\%$

$y_{CH_4} = 0.24\%$ $y_{N_2} = 23.15\%$ $y_{Ar} = 0.02\%$