

# A STUDY OF EFFECT OF PRESSURE, TEMPERATURE AND STEAM/NATURAL GAS RATIO ON REFORMING PROCESS FOR AMMONIA PRODUCTION

M. S. ALI, S. M. Zahangir, A. Z. M. Badruddoza and M. R. Haque

Department of Chemical Engineering  
Bangladesh University of Engineering and Technology

## Abstract

A solution for calculating equilibrium composition of steam reforming products has been found out at different pressure, temperature and steam/natural gas ratio. A simple program has been developed with the help of the software MATLAB version 5.3.1. This program was used to determine the performance of reforming reaction in process plant, where natural gas and steam were used as feed. This program has also been used to study the effect of changing the operating values of different parameters those govern the reforming process. Process conditions of primary reformer and secondary reformer of different fertilizer factories of Bangladesh have been used for testing the validity of the theoretical analysis of steam reforming.

## Introduction

There are seven urea fertilizer factories in Bangladesh. In primary reforming of ammonia process natural gas reacts with steam at certain temperature and pressure to produce carbon monoxide, carbon-dioxide and hydrogen. In secondary reforming 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 maximum possible conversion of natural gas in steam reforming can be found from the theory of chemical equilibrium<sup>1, 2, 3, 4, 5, 6, 7, 8, 9</sup>. The chemical equilibrium of reforming reaction does not depend on catalyst; it depends on temperature, pressure and composition of the reactants (i.e. steam/natural gas ratio).

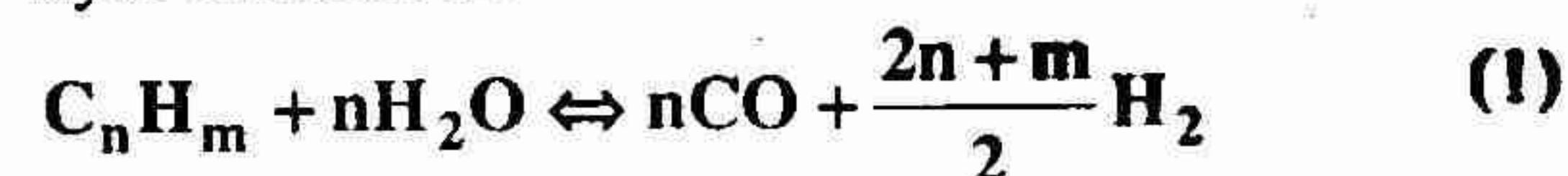
According to Le-Chatelliere principle<sup>10</sup>, the conversion of natural gas increases with the decrease of pressure. Reforming reaction is an endothermic reaction. So a large amount of heat is required to shift the reaction in the forward direction. Again, the conversion of natural gas will be increased with the increase of temperature. On decreasing reforming temperature, the effect is reversed. According to the law of mass action, the rate of chemical reaction is proportional to the active mass of each of the reactants present in the system. Again, sufficient steam is required to prevent coking of the catalyst. As a result, the

different variables and conditions which affect the reactions in the reforming units need to be studied.

This study is aimed to determine the favourable temperature, pressure and steam/NG ratio of reforming reaction. The data were collected from steam reforming units of seven fertilizer factories. The data were compiled and have been compared with the practical values of the operating steam reforming units of the existing fertilizer factories<sup>11,12</sup>

## Chemical Equilibria of Reforming Reactions

The general equilibrium for steam reforming of hydrocarbon is:



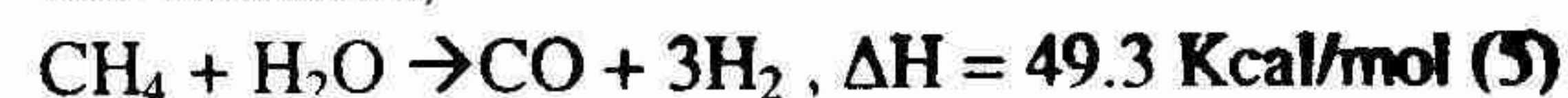
This is an endothermic reaction.

In the reforming process for ammonia production, a small amount of H<sub>2</sub> gas is recycled with feed natural gas to convert all higher hydrocarbon of alkane group to methane at low temperature in presence of nickel catalyst<sup>13, 14</sup>.



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

For methane,



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



A mixture of  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  is consequently obtained, the composition of which is defined by appropriate chemical equilibrium.

### Relation between Equilibrium Constant and Temperature

The standard property changes of a reaction, such as  $\Delta G^\circ$  and  $\Delta H^\circ$ , vary with the equilibrium temperature. The dependence of  $\Delta G^\circ$  on  $T$  is given by <sup>8, 15</sup>,

$$\frac{d \frac{\Delta G^\circ}{RT}}{dT} = -\frac{\Delta H^\circ}{RT^2} \quad (7)$$

But, 
$$\frac{\Delta G^\circ}{RT} = -\ln K \quad (8)$$

Therefore, 
$$\frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (9)$$

If  $\Delta H^\circ$  is negative, the reaction is exothermic. The equilibrium constant  $K$  decreases as the temperature increases. Conversely,  $K$  increases with  $T$  for an endothermic reaction.

If  $\Delta H^\circ$  is assumed independent of  $T$ , integration of equation (9) leads to a simple result from an initial temperature  $T_1$

$$\ln \frac{K}{K_1} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T} - \frac{1}{T_1} \right) \quad (10)$$

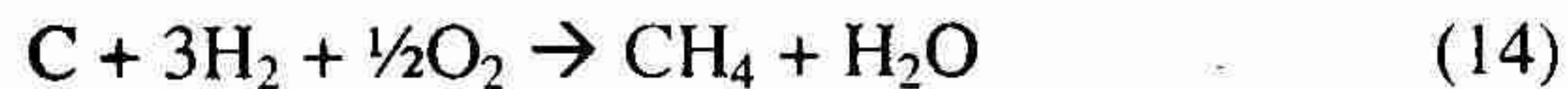
This approximate equation implies that a plot of  $K$  vs. reciprocal of absolute temperature is a straight line. A plot of  $\ln K$  vs.  $1/T$  for reforming reaction and water-gas shift reaction illustrates this linearity and the value of slope varies from -ve to +ve according to the type of reaction. Thus the equation (10) provides a reasonably accurate relation for the interpolation and extrapolation of equilibrium-constant data.

### Equilibrium Constants of Reforming Reaction

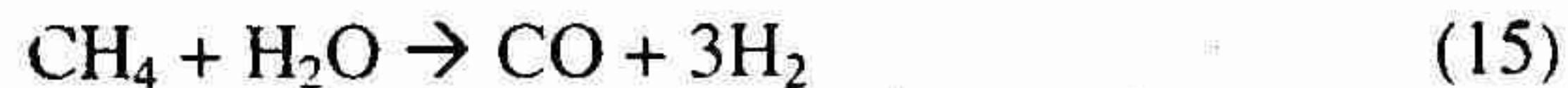
Some common reactions related to reforming reaction are as follows:



By adding equations (12) and (13) we find



Subtracting equation (11) from equation (14) the overall reforming reaction is:



If  $\Delta G_1$ ,  $\Delta G_2$ ,  $\Delta G_3$  are the Gibbs free energy for reactions (11), (12), and (13) respectively and  $\Delta G$  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 (11), (12) and (13) be  $K_1$ ,  $K_2$  and  $K_3$  respectively, and the equilibrium constant for reforming is  $K$ .

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

Therefore, 
$$K = \frac{K_1}{K_2 K_3} \quad (16)$$

From the plot of  $\ln K$  vs.  $1/T$  :  $K_1$ ,  $K_2$  and  $K_3$  the equilibrium constants for three different reactions at different temperatures can be known, and finally from equation (16), the equilibrium constant for the reforming at the respective temperature can be calculated.

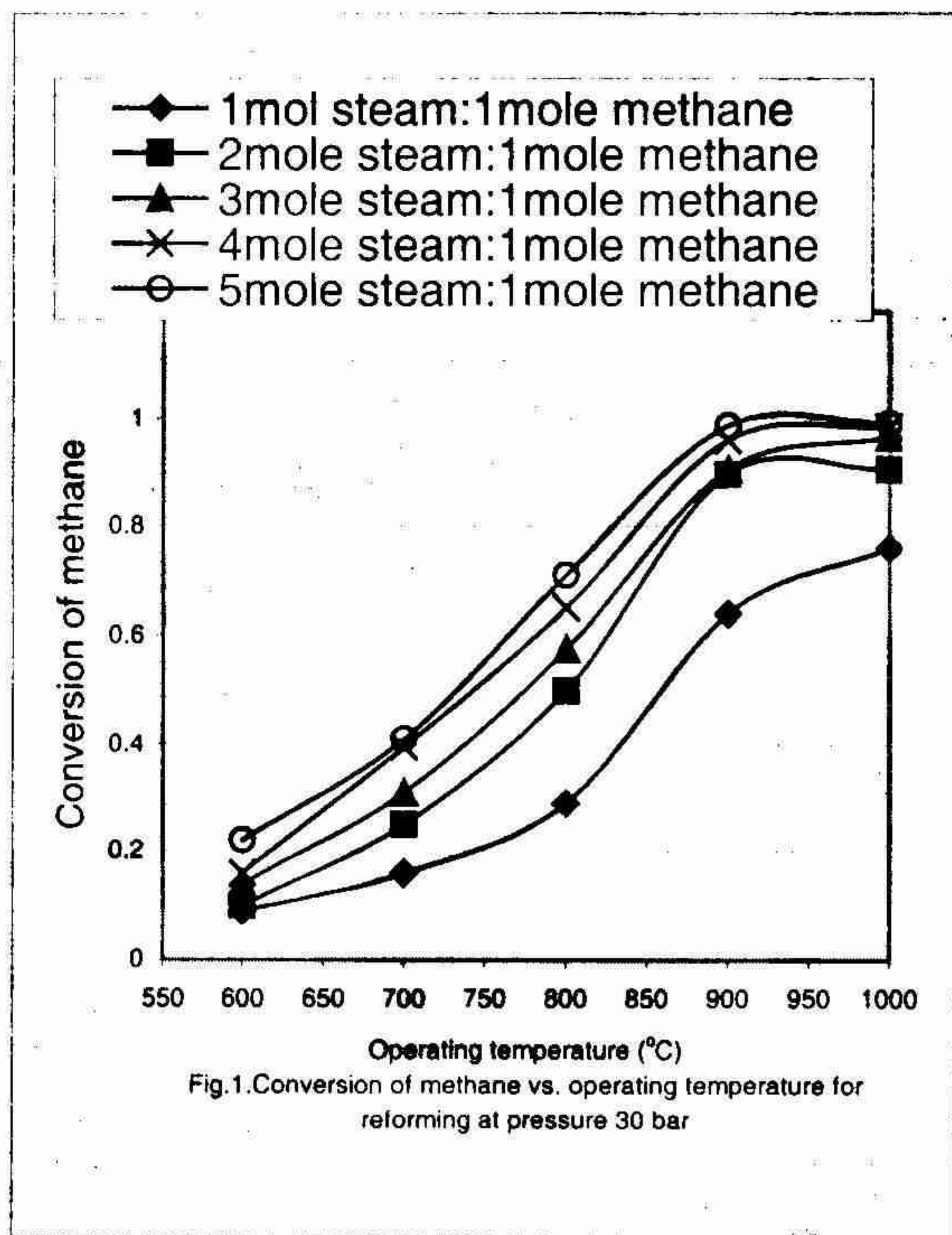
### Results and Discussions

In theoretical calculation, theory of chemical equilibrium has been applied for finding out the maximum conversion of natural gas in steam reforming process. 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.

### Influence of Temperature on Reforming Reaction

Figure 1 shows that at a pressure of 30 bar and steam/methane ratio of 1, methane conversion is 9% at temperature 600°C. Similarly conversion of methane is 16%, 64%, and 76% at temperatures 700°C, 900°C and 1000°C respectively. When steam/methane ratio is 2, methane conversion is 10%,

25%, 89.5%, and 90.5% at temperatures 600°C, 700°C, 900°C and 1000°C respectively.



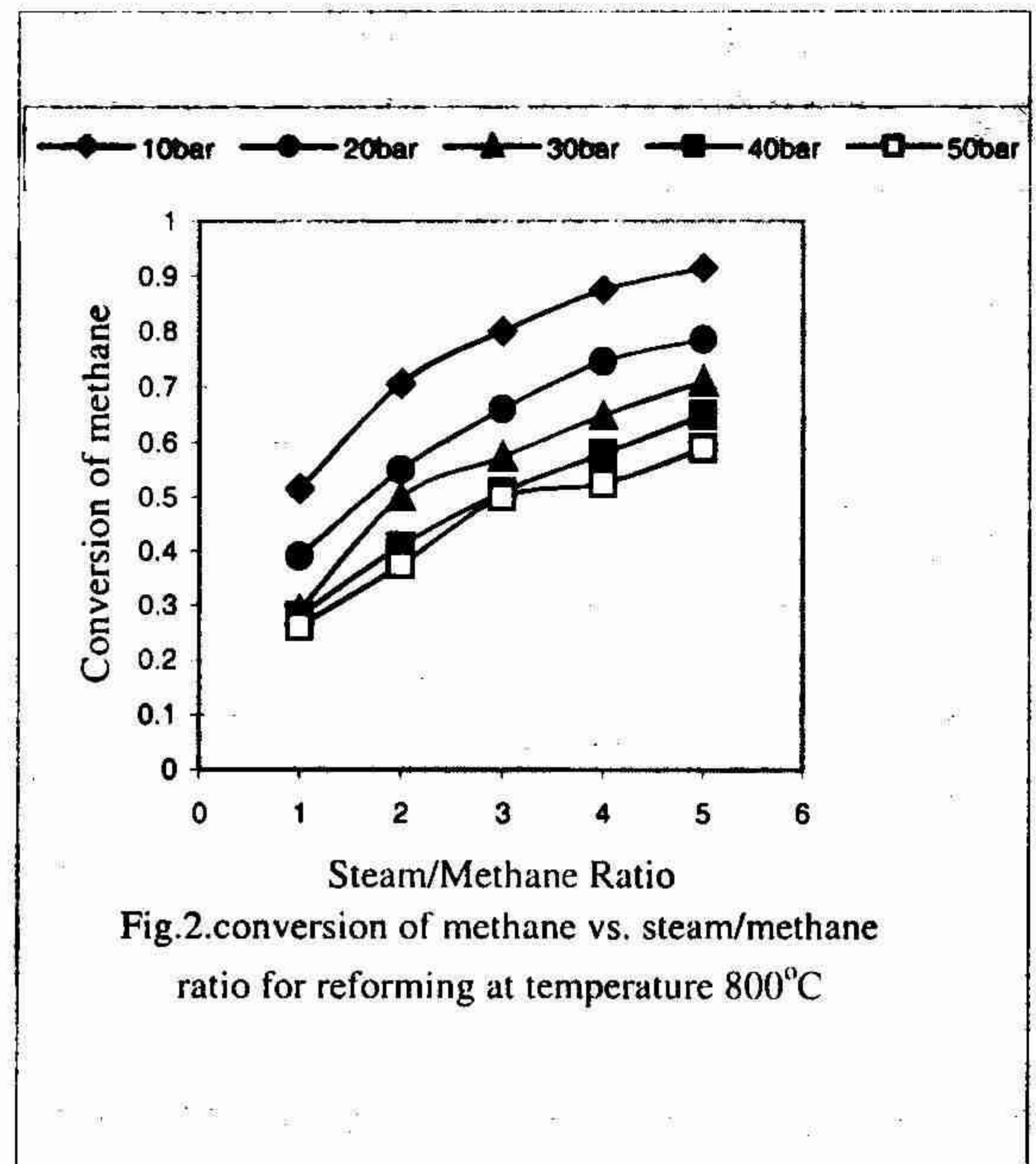
The same effect has been observed at pressure 10 and 20 bar<sup>8</sup>. So at constant pressure and constant steam/methane ratio, the conversion of methane increases with the increase of temperature. On decreasing temperature, the effect is reversed. If low temperature is selected for any reforming system, other variables such as pressure should be decreased or steam/methane ratio should be increased for higher conversion of methane.

### Influence of Steam/Methane Ratio on Reforming Reaction

From Fig. 2 it can be seen that at temperature 800 °C and pressure 10 bar remain constant, methane conversion is 51.5% at steam/methane ratio = 1. Conversion of methane is 70.5%, 80%, 87.5% and 91.5% at steam/methane ratio = 2, 3, 4, and 5 respectively. When pressure is 30 bar, methane conversion is 29% at steam/methane ratio = 1. Conversion of methane is 50%, 57.5%, 65% and 71% at steam/methane ratio 2, 3, 4, and 5 respectively.

The same effect was observed at temperatures of 700 °C and 1000 °C<sup>8</sup>. From these figures it is seen that at constant temperature and constant pressure, methane conversion increases with the increase of steam/methane ratio. In the modern process steam/NG ratio is 1.4 to 3.5<sup>16</sup>. It is

known that sufficient amount of steam is needed in reforming to prevent coking of the catalyst. At the same time, utilities consumption is usually most economical at design steam to natural gas ratio of 1.4 to 3.5. Maximum steam/natural gas ratio, high temperature and low pressures are favourable conditions for maximum conversion of natural gas



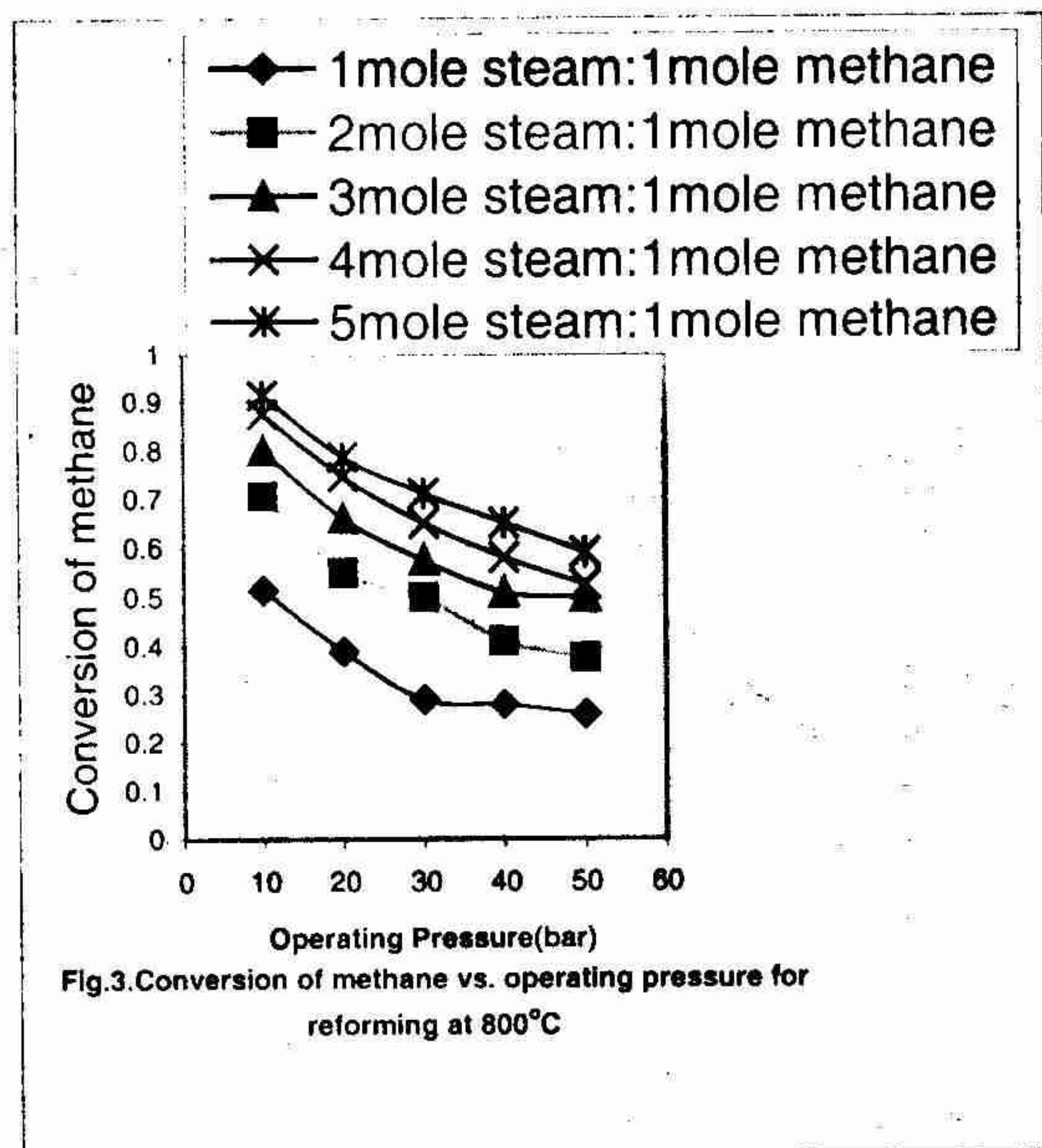
### Influence of Pressure on Reforming Reaction

From Fig. 3 it can be seen that when temperature is 800 °C and steam/methane ratio of 1 remains constant methane conversion is 51.5% at pressure 10 bar. Conversion of methane is 39%, 29%, 28% and 26% at pressures 20 bar, 30 bar, 40 bar, and 50 bar respectively. When steam/methane ratio is 2, methane conversion is 70.5% at pressure 10 bar. Conversion of methane is 55%, 50%, 41% and 37.5% 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 decreases with increasing pressure.

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

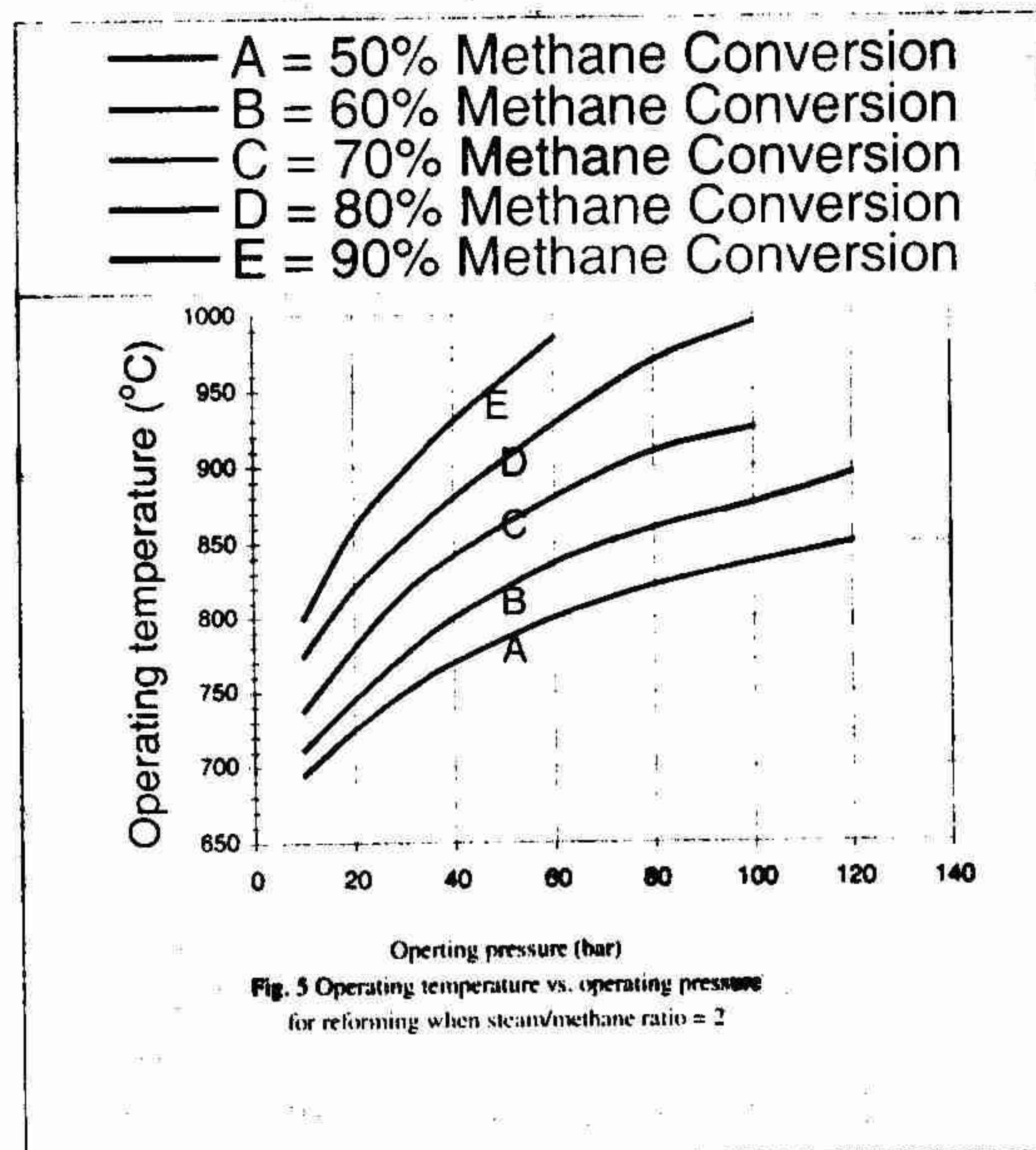
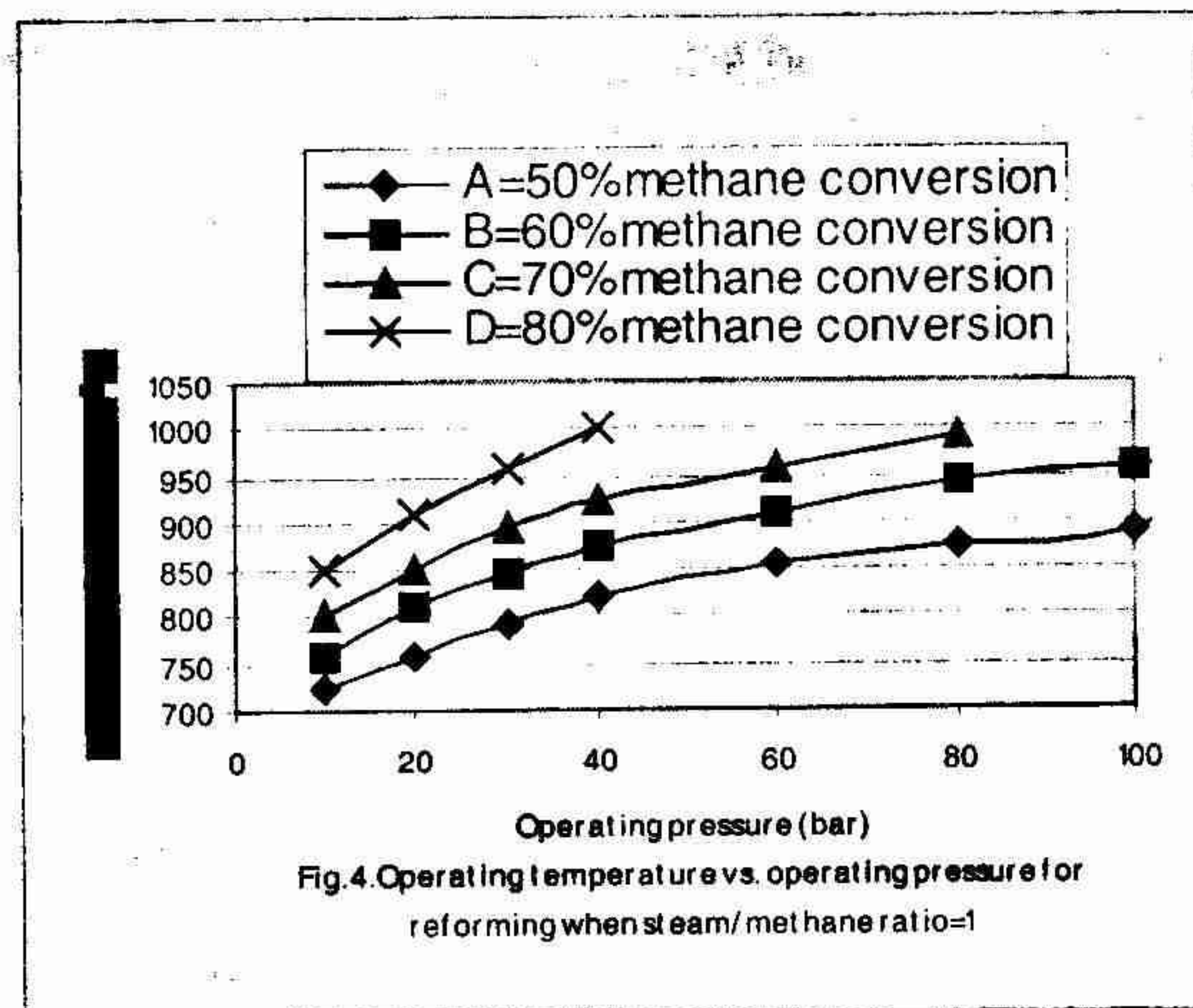
Figure 4 shows the variations of operating temperature with pressure at different methane

conversion at steam/methane ratio of 1. Fig.4 indicates 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 pressure of 10 bar is applied for 50% conversion operating temperature should be 725°C. If 20 bar, 30 bar, 40 bar and 60 bar pressures are applied, temperatures should be 760°C, 793°C, 820°C and 855°C respectively for the 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 60 bar; but operating temperature should be 760°C, 810°C, 845°C, 875°C and 910°C respectively.

From Fig 5. it can be seen that when steam/methane ratio is 2, for a specific conversion(50%) of methane, different pressures such as 10 bar, 20 bar, 30 bar, 40 bar and 60 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 60 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 but operating temperatures must be high for the same conversion of methane. In modern process industries high operating pressure is selected for reforming due to economic reasons<sup>11</sup>.



### Comparison of Plant Data and Calculated Data

By the developed computer program for the theoretical values for reforming units outlet equilibrium compositions of primary reformer and secondary reformer of different fertilizer factories (ZFCL, JFCL, CUFL, UFFL, NGFF, PUFF & KAFCO) have been calculated. A comparison of the theoretical values and actual outlet composition of the mentioned factories have been made. This theory based calculated data has been compared with the actual data for testing the validity of the program developed in this work with the help of the software MATLAB Version 5.3.1.<sup>11</sup> From the calculated data, it can be 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 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. Theoretical calculation of natural gas reforming products was performed on the basis of methane only and the more higher hydrocarbons are ignored. Again, the plot of  $\ln K$  vs.  $1/T$  which has been used for theory based calculation, is the representation of approximate equation. The other reasons for which the calculated values are not equal to the actual values because of the process itself, condition and composition of natural gas, the catalysts used etc.

The catalysts play important role in reforming process. But influence of catalyst on the reforming reaction has not been studied, because it is considered that equilibrium conversion and chemical equilibrium of the reaction depends on the thermodynamic properties only and not on the catalyst behaviour. However, from the actual data analysis of different fertilizer factories, it can be seen that the calculated values are in reasonable agreement with the actual values in reforming units of process plants.

From the data it is revealed 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 ( $756^{\circ}\text{C} - 819^{\circ}\text{C}$ ) 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,  $796^{\circ}\text{C}$  and 3.3 respectively. The same parameters of KAFCO primary reformer are 33 bar,  $756^{\circ}\text{C}$  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 the conversion of natural gas in JFCL primary reformer is higher than that of KAFCO. Primary reformer outlet pressure of NGFF is as low as 6.2 bar. As a result the primary reformer outlet temperature has been selected low such as  $655^{\circ}\text{C}$ . For maximum conversion of natural gas steam/NG ratio has been selected 6.1 for this reforming process.

## Conclusion

In the 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 is selected for its reforming process for higher conversion of natural gas.

## References

1. Abrash, H.I., and Hardcastle, K.I., "Chemistry", Glenco Pub., California, 81, pp. 205-208, 329-345.
2. Andrews, D.H., "Introductory Physical Chemistry", McGraw-Hill, New York, pp. 229-244 (1970).
3. Blue, E.M., "Regenerable Catalyst Highlights, New Reforming Process", Chevron Research Co., San Francisco, Hydrocarbon Processing, 48 (9), pp 141-144, September (1969).
4. Kumar, Sanjoy, "Gas Production Engineering", Vol. 4, Gulf Publishing Company, Book Division, London, pp. 39-382, (1987).
5. Levine, I.N., "Physical Chemistry", Third edition, McGraw-Hill, New York, pp. 297-312, (1988)
6. Mee, A.J., "Physical Chemistry", Sixth edition, The English Language Book Society, London, pp. 341-358, (1962).
7. Pauling, L., "General Chemistry", Third Edition, W.H. Freeman, San Francisco, pp. 381-413, (1970).
8. Smith, J.M. and Van Ness, H.C., "Introduction to Chemical Engineering Thermodynamics", Fourth edition, McGraw-Hill Company, New York, pp. 105-133, 496-548, (1987).
9. Willcox, Dave and Kung, H.H., "Interpretation of Equilibrium Exchange Rate for Nonelementary Reactions", AIChE Journal, 30 (5), pp 725-731 September, (1984).
10. Campbell, J.A., "Chemical Systems: Energetics Dynamics Structure", W.H. Freeman & Co., San Francisco, pp. 228-236, 721-741, (1970).
11. Badruddoza, A.Z.M. and Haque, M.R., "Effect of Pressure, Temperature and Steam/Natural Gas

- Ratio on Reforming Process for Ammonia Production", Undergraduate Thesis, BUET February (2004).
12. Jahangir, S.M., 'A study of the Influence Pressure, Temperature, Steam/Natural Gas ratio On Reforming Process for Ammonia Production", M.Sc. Thesis, BUET, pp.3-10, June (2000).
  13. Bibby, D.M.; Chang, C.D.; Howe, R.F.; and Yurchak, S. ed., "Methane Conversion", Vol. 36, Elsevier, Amsterdam, (1988).
  14. Toon, E.R., Ellis, G.L. and Broodkin, J., "Foundation of Chemistry", Hott, Rineheart and Winston, Inc, New York, pp 416-450 (1968).
  15. Boyington, R., and Masterton, W.L., "Student's guide to Masterton & Slowinski's Chemical Principles", Second edition, W.B. Saunders Co., Philadelphia, pp. 163-202.
  16. Munim, Jusif, "Process and Operations in Ammonia Plant", First Edition, P.T. Paper Sriwidjaya, Palambang, pp. 1-68, (1979).
-