

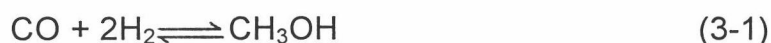
CHAPTER III



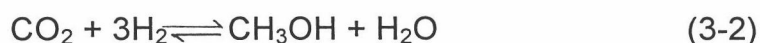
THEORY

3.1 Preparation of synthesis gas [25]

The methanol synthesis, at basic level, has practically always been expressed via the hydrogenation of carbon monoxide, i.e.



Some investigators are of the opinion that CO hydrogenation is the principal chemical reaction. Others believe that the methanol synthesis over Cu-based catalyst proceeds exclusively via hydrogenation of carbon dioxide, i.e.



Hence, according to the proportion of CO and CO₂, the gaseous mixture required for conversion must have a hydrogen to carbon molar ratio between 2 and 3. Such a gas can be obtained, as mentioned above, by partial oxidation, gasification, or steam reforming.

3.1.1 Schemes involving partial oxidation with oxygen [26]

To convert methane, it is theoretically possible to adjust the oxygen content to obtain an effluent in which the H_2/CO ratio is close to 2. In practice, it is necessary to consider the losses resulting from the formation of methane during the synthesis of methanol, and aim for an H_2/CO ratio of around 2.25, which is ideal for this conversion.

This value can be obtained by diverting part of the gas stream to a steam converter that removes excess CO and supplies an equivalent amount of hydrogen (shift conversion). Using a standard absorption process, it is then necessary to remove the CO_2 up to the maximum concentration acceptable by the catalyst employed to conduct the methanol synthesis.

The basic scheme is hence very similar to those to produce hydrogen and ammonia. The same applies to the conversion of heavy products, for which partial oxidation and gasification are generally more suitable. The presence of sulfur compounds in the raw materials used requires the consideration of two main variants, depending on the possibilities of the catalyst for CO shift conversion (diagram a and b in Fig. 3.1).

- (a) Scheme a : this catalyst cannot tolerate sulfur derivatives. The feed stock must therefore first be desulfurized to a residual sulfur content of 0.05 to 0.1 ppm. The gas then partly passes through the CO conversion unit, and is then remixed with the untreated fraction and partly decarbonated.
- (b) Scheme b : the catalyst is resistant to sulfur compounds. Partial CO conversion is followed by simultaneous desulfurization and decarbonation.

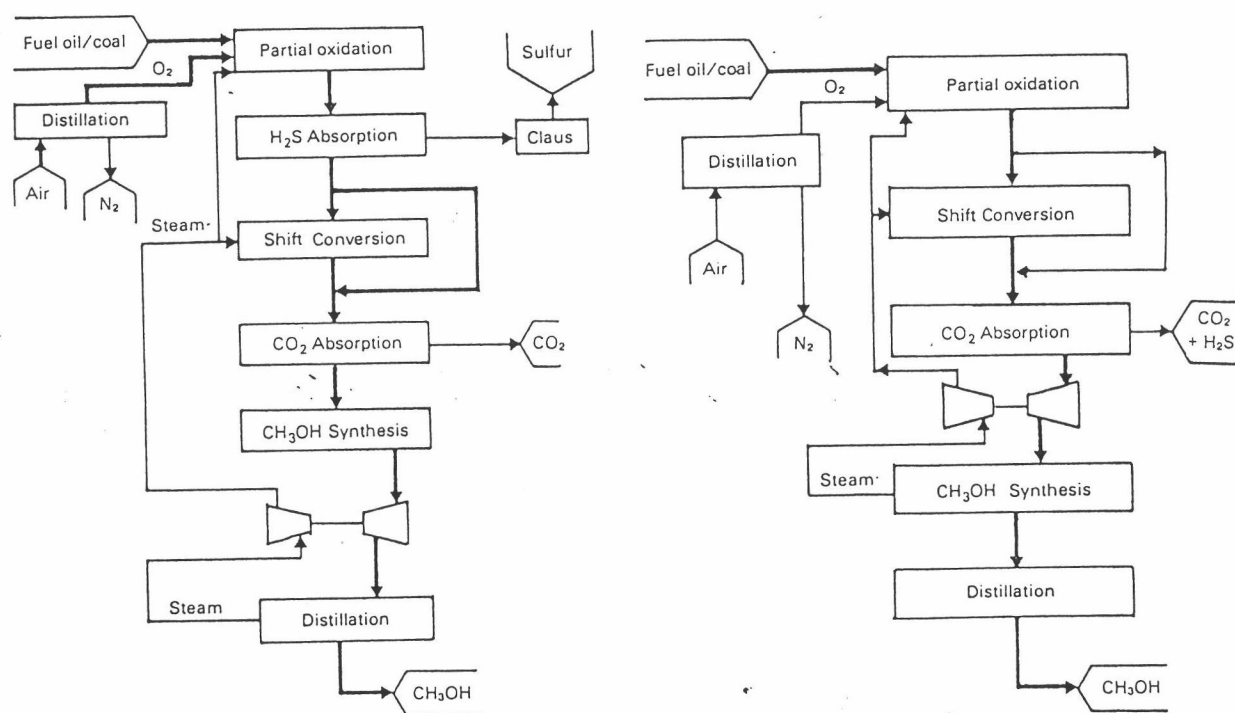


Fig. 3.1 Base schemes for methanol manufacture using partial oxidation.

In both scheme, the installation of a sulfur barrier(such as zinc oxide) is recommended to protect the synthesis catalyst, which does not tolerate sulfur compounds.

With the processes currently used to obtain methanol, which operate at low pressure(6 to $9 \cdot 10^6$ Pa absolute), it is possible to eliminate the auxiliary compressor, which was formerly indispensable to introduce the synthesis gas in the requisite operating conditions.

Among the other technological variants are two effluent cooling possibilities at the exit of partial oxidation or gasification, namely the generation of high-pressure steam or direct water quench. The latter is uninteresting for the production of methanol, since intensive conversion is not the ultimate objective.

Since desulfurization must be total whereas decarbonation is only partial, it is interesting to employ a solvent capable of removing not only H_2S but also COS , performing this selectively in relation to CO_2 . The ideal processes in these conditions are those employing physical solvents (Selexol, Rectisol, etc.).

3.1.2 Scheme based on hydrocarbon steam reforming [26]

These are considerably simplified in comparison with those for the production of high-purity hydrogen or synthesis gas for ammonia. This is because CO conversion, CO_2 removal and methanation are eliminated. However, an auxiliary compressor is necessary in this case.

As shown in Fig. 3.2, the unit is reduced to two major sections :

- (a) Feedstock pretreatment designed to remove all trace of sulfur compounds or other impurities detrimental to the synthesis catalyst, such as chlorine.
- (b) The steam reforming furnace with its auxiliary flue-gas heat recovery facilities.

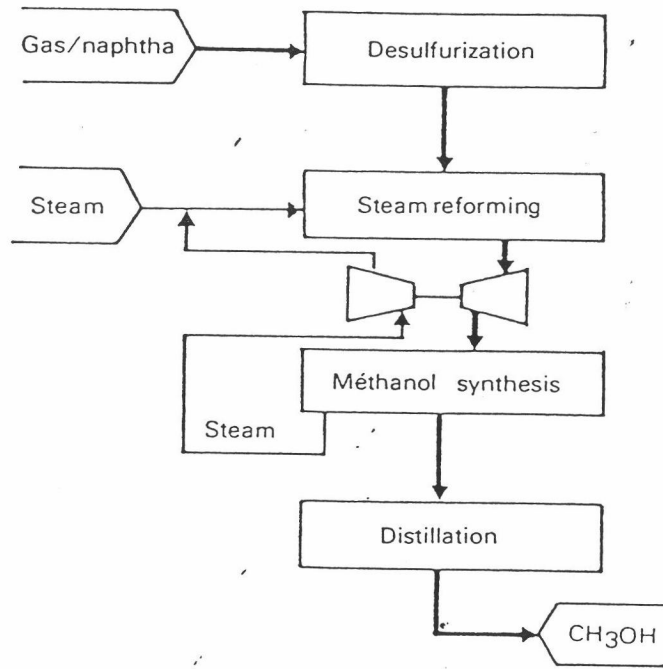


Fig. 3.2 Base scheme for methanol manufacture using steam reforming

This simplification is associated with the actual reforming operation which, as shown by table 3.1, leads, for methane, to a hydrogen/carbon ratio normally lying between 3 and 4, depending on the CO and CO₂ content of the effluent, whereas the desired value should lie between 2 and 3

Table 3.1 H₂O/CH₄ ratio variation in steam reforming

| T(°C) | 650 | 700 | 800 | 850 | 990 |
|---|------|------|------|------|-------|
| 1. H ₂ O/CH ₄ = 1 H ₂ /CO | 4.66 | 4.00 | 3.07 | 3.00 | 3.00 |
| 2. H ₂ O/CH ₄ = 1.5 H ₂ /CO | 5.75 | 4.63 | 3.96 | 3.70 | 3.70 |
| 3. H ₂ O/CH ₄ = 2 H ₂ /CO | 6.90 | 5.00 | 4.70 | 4.54 | 4.48 |
| 4. H ₂ O/CH ₄ = 3.5 H ₂ /CO | - | - | - | - | 10.25 |

The gas obtained from methane is hence either too rich in hydrogen, or too poor in carbon. This can be remedied as follows :

- (a) By purging, which results in a loss of energy connected in particular with the separation and compression of excess hydrogen.
- (b) Or by the addition of CO₂, taken for example from the CO₂ removal unit associated with ammonia production, or recovered from the flue gases of the reforming furnace. This addition can be made upstream or downstream of the steam reforming unit. The former alternative is more interesting in principle, because part of the CO₂ is then converted to CO,

and , in case of a temporary shortage of make-up carbon dioxide, the composition of the reformed gas varies only slightly.

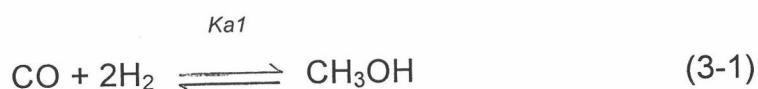
Unconverted methane present in the reforming effluent behaves in the successive operations like an inert diluent. To prevent its built-up in the recycle, which constitutes the methanol “synthesis loop” , a purge is necessary.

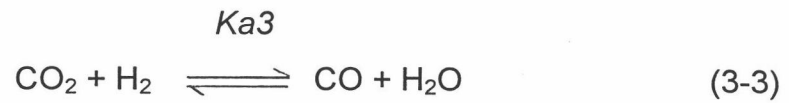
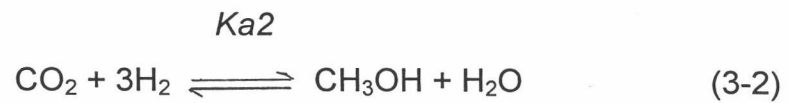
The carbon deficit observed in methane steam reforming does not occur if naphtha feedstock is converted. In autothermal processes using fuel oil as a feedstock, sufficient quantities of excess carbon dioxide are available within the installation itself. This gas is recycled from a scrubbing unit.

3.2 Thermodynamic aspects of methanol synthesis [25]

The reactions between CO and H₂, as well as between CO₂ and H₂ are both reversible and exothermic. They are also thermodynamically unfavorable, showing positive Gibbs free-energy changes due to reaction at temperatures higher than 150° C for CO hydrogenation and 180° C for CO₂ hydrogenation, respectively. The fact that both reactions are exothermic and in addition, proceed under volume contraction shows that the highest conversions - and thus the highest methanol yield- are obtained at low temperatures and high pressures.

Three reactions can be considered to occur in methanol synthesis





The equilibrium constants of the reactions (3-1)-(3-3) are defined as follows

$$K_{a1} = \frac{a_{\text{CH}_3\text{OH}}}{a_{\text{CO}} a_{\text{H}_2}^2} \quad (3-4)$$

$$K_{a2} = \frac{a_{\text{CH}_3\text{OH}} a_{\text{H}_2\text{O}}}{a_{\text{CO}_2} a_{\text{H}_2}^3} \quad (3-5)$$

$$K_{a3} = \frac{a_{\text{CO}} a_{\text{H}_2\text{O}}}{a_{\text{CO}_2} a_{\text{H}_2}} \quad (3-6)$$

where

$$a_j = \varphi_j p_j \quad (3-7)$$

$$K_{a1} = K_{\varphi 1} K_{p1} \quad (3-8)$$

$$K_{a2} = K_{\varphi 2} K_{p2} \quad (3-9)$$

$$K_{a3} = K_{\varphi 3} K_{p3} \quad (3-10)$$

Where

$$K_{\varphi 1} = \frac{\varphi_{\text{CH}_3\text{OH}}}{\varphi_{\text{CO}} \varphi_{\text{H}_2}^2}; \quad K_{p1} = \frac{p_{\text{CH}_3\text{OH}}}{p_{\text{CO}} p_{\text{H}_2}^2} \quad (3-11)$$

$$K_{\varphi 2} = \frac{\varphi_{\text{CH}_3\text{OH}} \varphi_{\text{H}_2\text{O}}}{\varphi_{\text{CO}_2} \varphi_{\text{H}_2}^3}; \quad K_{p2} = \frac{p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}^3} \quad (3-12)$$

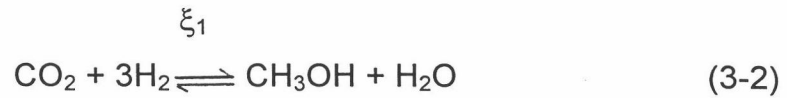
$$K_{\phi 3} = \frac{\phi_{\text{CO}} \phi_{\text{H}_2\text{O}}}{\phi_{\text{CO}_2} \phi_{\text{H}_2}} \quad K_{p3} = \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{CO}_2} p_{\text{H}_2}} \quad (3-13)$$

The value of K_{a1} , K_{a2} , K_{a3} can be calculated from the well-known relationship :

$$-\Delta G_i^0 = RT \ln K_{a_i} \quad ; \quad i = 1,2,3 \quad (3-14)$$

The chemical equilibria of the methanol synthesis (only from carbon monoxide) and the reverse water gas shift reaction were determined experimentally in a fixed-bed reactor by Graaf et al.(1986). It was found that the chemical equilibria could be described very well by thermodynamical data based on ideal gas behaviour in combination with a correction for the non-ideality of the gas mixture as predicted by the Soave-Redlich-Kwong equation of state. This correction for non-ideality resulted in significantly better agreement with experimental data than a correction based on the original Redlich-Kwong equation of state, the Peng-Robinson equation of state, the virial equation truncated after the second virial coefficient, Lewis and Randall's rule, or not correcting at all for non ideality. A striking result was that the ideal gas law gave better results than the Redlich-Kwong equation, the virial equation truncated after the second virial coefficient and the Lewis and Randall's rule. According to Chang et al.(1986), either the Soave-Redlich-Kwong equation or the Peng-Robinson equation of state can be used profitably. Chang et al. noted that the calculations require the use of fugacity coefficients that depend on composition to estimate the nonidealities of the coexisting species in a reaction mixture.

Comprehensive studies on thermodynamics of methanol synthesis were carried out by Skrzypek et al.(1990). The two-reaction system



was analysed.

Defining two equilibrium conversion for reactions (3-2) and (3-3), respectively :

$$\xi_1^{\text{eq}} = \frac{\Delta N_{\text{CH}_3\text{OH}}}{N_T^0} = \frac{N_{\text{CH}_3\text{OH}}^{\text{eq}} - N_{\text{CH}_3\text{OH}}^0}{N_T^0} \quad (3-15)$$

Where all computations were performed for $N_{\text{CH}_3\text{OH}}^{\text{eq}} = 0$, and

$$\xi_2^{\text{eq}} = \frac{\Delta N_{\text{CO}}}{N_T^0} = \frac{N_{\text{CO}}^{\text{eq}} - N_{\text{CO}}^0}{N_T^0} \quad (3-16)$$

The following expression for the mole-fraction of each component can then be easily obtained :

$$\chi_{\text{CO}_2}^{\text{eq}} = \frac{\chi_{\text{CO}_2}^0 - \xi_1^{\text{eq}} - \xi_2^{\text{eq}}}{1 - 2\xi_1^{\text{eq}}} \quad (3-17)$$

$$\chi_{\text{H}_2}^{\text{eq}} = \frac{\chi_{\text{H}_2}^0 - 3\xi_1^{\text{eq}} - \xi_2^{\text{eq}}}{1 - 2\xi_1^{\text{eq}}} \quad (3-18)$$

$$\chi_{\text{H}_2\text{O}}^{\text{eq}} = \frac{\xi_1^{\text{eq}} + \xi_2^{\text{eq}}}{1 - 2\xi_1^{\text{eq}}} \quad (3-19)$$

$$\chi^{\text{eq}}_{\text{CH}_3\text{OH}} = \frac{\xi^{\text{eq}}_1}{1-2\xi^{\text{eq}}_1} \quad (3-20)$$

It should be noted that the conversion degree defined above refer to an initial total N^0_T moles in the mixture, but not to selected components as is usually done. This approach was imposed by the fact that reaction (3-3) changes its direction for mixtures containing initially even a small quantity of CO. Under such conditions, CO_2 becomes a reactant of reaction (3-2) and a product in reaction (3-3). Hence, the defining of the conversion degree with respect to CO_2 would be inconvenient.

The equilibrium conversions ξ^{eq}_1 and ξ^{eq}_2 were found by solving numerically a non-linear system of two algebraic equations as follows :

$$(K_x)_2 = \left[\frac{\chi_{\text{CH}_3\text{OH}} \chi_{\text{H}_2\text{O}}}{\chi_{\text{CO}_2} \chi^3_{\text{H}_2}} \right]_{\text{eq}} = \frac{\xi^{\text{eq}}_1 (\xi^{\text{eq}}_1 + \xi^{\text{eq}}_2) (1-2\xi^{\text{eq}}_1)^2}{(\chi^0_{\text{CO}_2} - \xi^{\text{eq}}_1 - \xi^{\text{eq}}_2) (\xi^0_{\text{H}_2} - 3\xi^{\text{eq}}_1 - \xi^{\text{eq}}_2)^3} \quad (3-21)$$

$$(K_x)_3 = \left[\frac{\chi_{\text{CO}} \chi_{\text{H}_2\text{O}}}{\chi_{\text{CO}_2} \chi_{\text{H}_2}} \right]_{\text{eq}} = \frac{(\chi^0_{\text{CO}} + \xi^{\text{eq}}_2) (\xi^{\text{eq}}_1 + \xi^{\text{eq}}_2)}{(\chi^0_{\text{CO}_2} - \xi^{\text{eq}}_1 - \xi^{\text{eq}}_2) (\chi^0_{\text{H}_2} - 3\xi^{\text{eq}}_1 - \xi^{\text{eq}}_2)} \quad (3-22)$$

Where

$$(K_x)_2 = K_{P2} P_T^2 \quad (3-23)$$

$$(K_x)_3 = K_{P3} \quad (3-24)$$

The detailed results for the computations were used to plot the exemplary curves illustrated below, where particular compounds are numbered as follows :

$$\text{CO} = 1, \text{CO}_2 = 2, \text{H}_2 = 3, \text{CH}_3\text{OH} = 4, \text{and H}_2\text{O} = 5$$

Figures (3-3)-(3-9) present isobars in the co-ordinate system ξ^{eq}_1 vs T , ξ^{eq}_2 vs T and χ^{eq}_i vs T for the initial gaseous mixture without CO.

From the presented diagrams it is shown that both temperature and pressure have a considerable effect on the equilibrium conversion degree of direct methanol synthesis and the reverse water-gas shift, and also on the equilibrium mole fractions of the components.

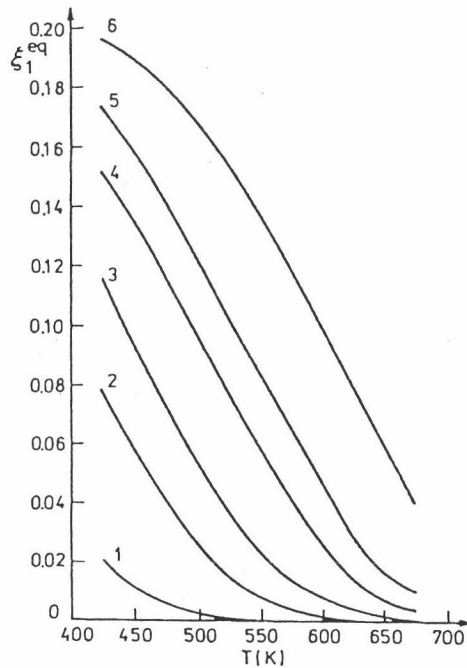


Fig. 3.3 Dependence of equilibrium conversion degree ξ^{eq}_1 to methanol on temperature ($\chi^{0}_{CO} = 0$, $\chi^{0}_{CO_2} = 0.20$, $\chi^{0}_{H_2} = 0.70$)
 (1) 1.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa, (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

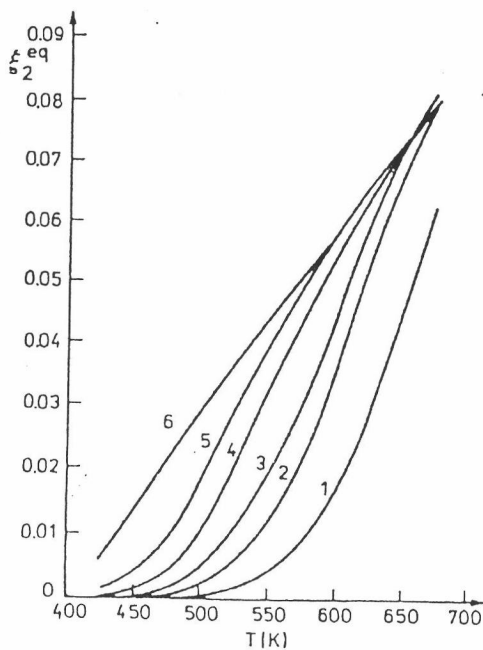


Fig. 3.4 Dependence of equilibrium conversion degree ξ^{eq}_2 of reverse water-gas shift reaction on temperature ($\chi^{0}_{CO} = 0$, $\chi^{0}_{CO_2} = 0.20$, $\chi^{0}_{H_2} = 0.70$)
 (1) 30 MPa, (2) 15 MPa,
 (3) 10 MPa, (4) 5 MPa,
 (5) 2.5 MPa, (6) 0.5 MPa

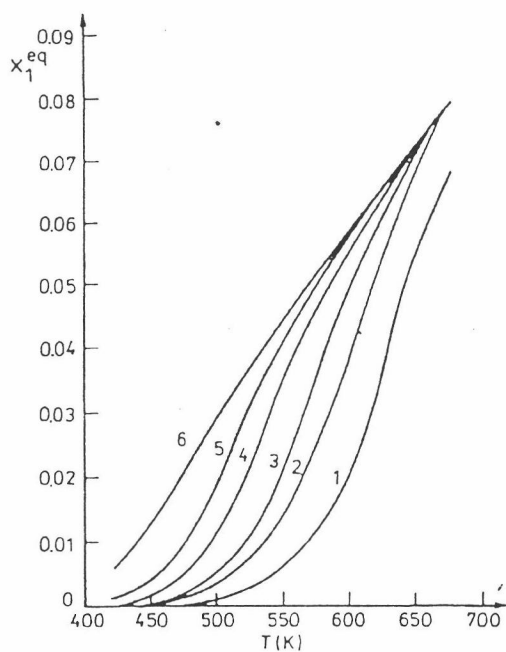


Fig. 3.5 Dependence of equilibrium mole fraction of CO on temperature
 $(\chi_{CO}^0 = 0, \chi_{CO_2}^0 = 0.20, \chi_{H_2}^0 = 0.70)$
 (1) 30 MPa, (2) 15 MPa,
 (3) 10 MPa (4) 5 MPa,
 (5) 2.5 MPa, (6) 0.5 MPa

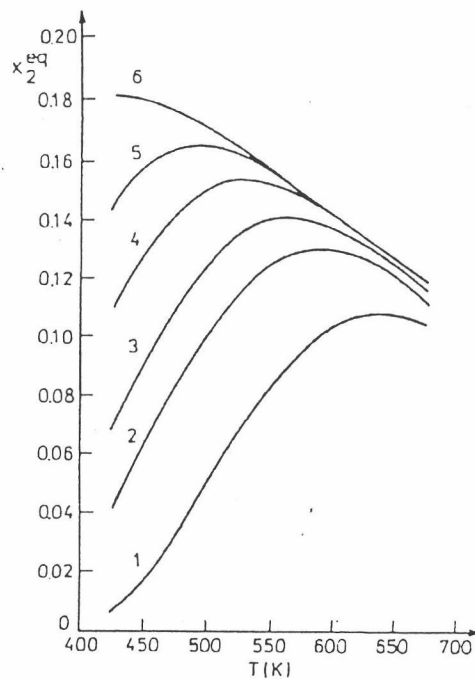


Fig. 3.6 Dependence of equilibrium mole fraction of CO₂ on temperature
 $(\chi_{CO}^0 = 0, \chi_{CO_2}^0 = 0.20, \chi_{H_2}^0 = 0.70)$
 (1) 30 MPa, (2) 15 MPa,
 (3) 10 MPa (4) 5 MPa,
 (5) 2.5 MPa, (6) 0.5 MPa

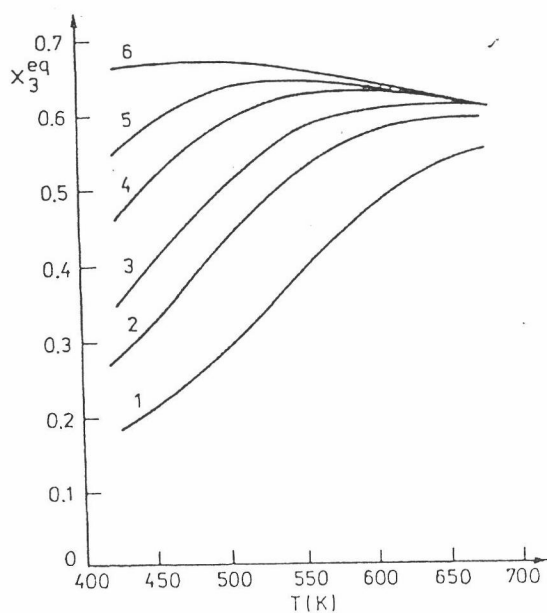


Fig. 3.7 Dependence of equilibrium mole fraction of H₂ on temperature
 $(\chi_{CO}^0 = 0, \chi_{CO_2}^0 = 0.20, \chi_{H_2}^0 = 0.70)$
 (1) 30 MPa, (2) 15 MPa,
 (3) 10 MPa (4) 5 MPa,
 (5) 2.5 MPa, (6) 0.5 MPa

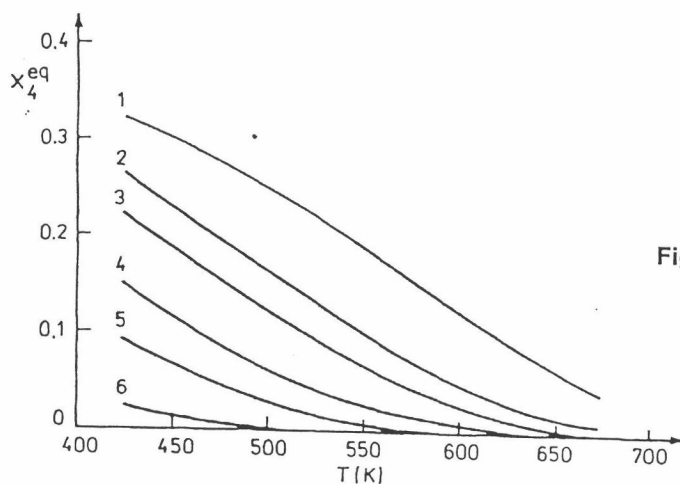


Fig. 3.8 Dependence of equilibrium mole fraction of MEOH on temperature ($\chi_{\text{CO}}^0 = 0$, $\chi_{\text{CO}_2}^0 = 0.20$, $\chi_{\text{H}_2}^0 = 0.70$)
 (1) 30 MPa, (2) 15 MPa,
 (3) 10 MPa (4) 5 MPa,
 (5) 2.5 MPa, (6) 0.5 MPa

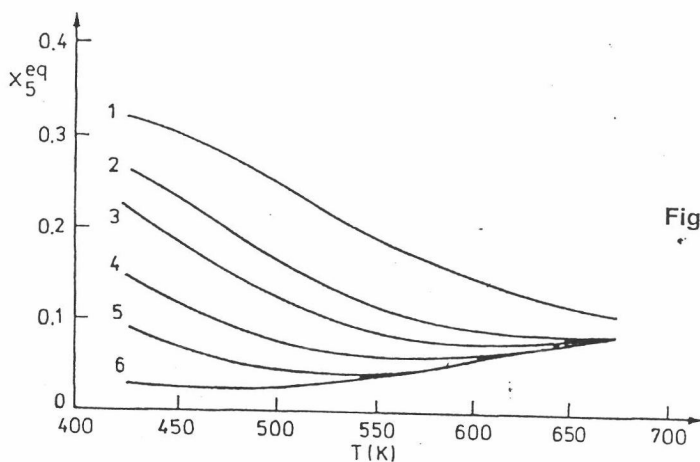


Fig. 3.9 Dependence of equilibrium mole fraction of H₂O on temperature ($\chi_{\text{CO}}^0 = 0$, $\chi_{\text{CO}_2}^0 = 0.20$, $\chi_{\text{H}_2}^0 = 0.70$)
 (1) 30 MPa, (2) 15 MPa,
 (3) 10 MPa (4) 5 MPa,
 (5) 2.5 MPa, (6) 0.5 MPa

The equilibrium conversion degree ξ_1^{eq} of the main reaction increases distinctly with increasing pressure and decreases strongly as the temperature is increased. Within a temperature range of 453 K (180°C) to 543 K (270°C) i.e. industrial methanol synthesis conditions over copper-containing catalysts, the decrease in ξ_1^{eq} is almost linear with a steep slope to the curve at pressures of 2.5-15 MPa. On the contrary, the equilibrium conversion degree ξ_2^{eq} of the side reaction increases strongly with increased temperature and decreases as the pressure increases.

The curves of the equilibrium mole fractions χ^{eq}_4 and χ^{eq}_1 for methanol and CO, respectively, are analogous to those of the respective equilibrium conversions, ξ^{eq}_1 and ξ^{eq}_2 . The isobars for the equilibrium mole fractions for CO₂ and water are interesting. In many cases, the equilibrium mole fraction of CO₂ increases initially with temperature, passes through a maximum, and then decreases. In contrast, the equilibrium mole fraction of water decreases initially, passes through a minimum, and then increases with increased temperature.

For comparison, Figs (3-10)-(3-16) present isobars for the analogous co-ordinate system, but for an initial gaseous mixture with a large amount of CO. It is seen that if CO is present in the synthesis gas, the equilibrium conversion degree ξ^{eq}_2 practically becomes negative, i.e. the water-gas shift reaction takes place:



When the reactants contain no CO and consist only of CO₂ and H₂ (and possibly inert components) ξ^{eq}_2 is always positive. Base on the detailed results of the computations, the effects of the initial concentrations of CO₂, CO and H₂ on the equilibrium conversions ξ^{eq}_1 and ξ^{eq}_2 were then analyzed.

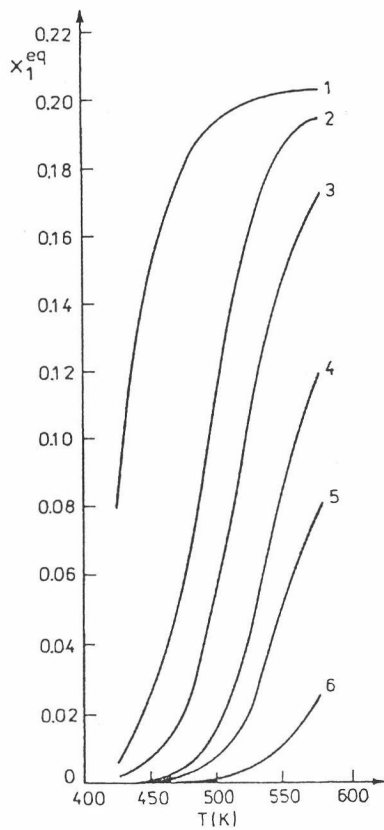
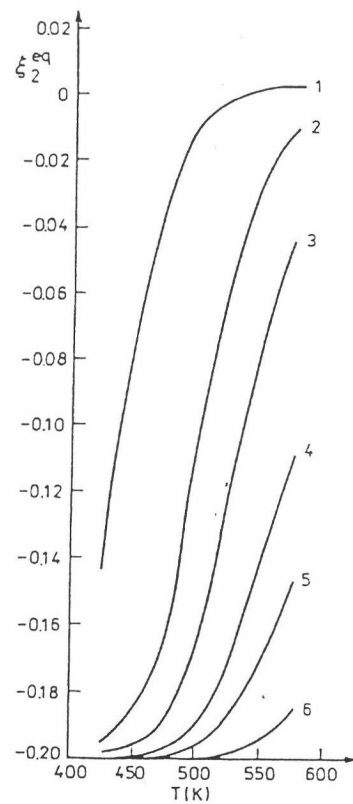
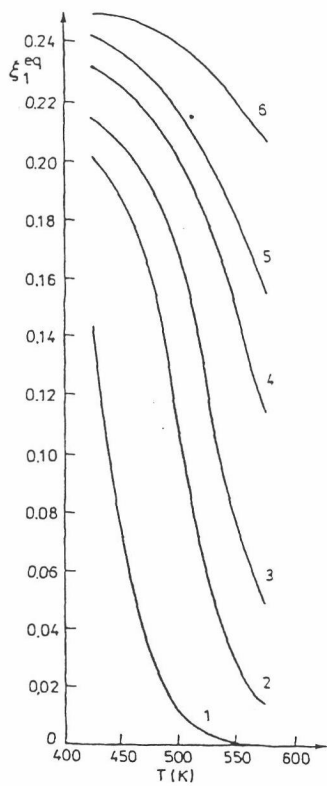


Fig. 3.10 Dependence of equilibrium conversion degree ξ_1^{eq} to methanol on temperature ($\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$)
 (1) 0.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

Fig. 3.11 Dependence of equilibrium conversion degree ξ_2^{eq} of conversion water-gas shift reaction on temperature ($\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$)
 (1) 0.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

Fig. 3.12 Dependence of equilibrium mole fraction of CO on temperature ($\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$)
 (1) 0.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

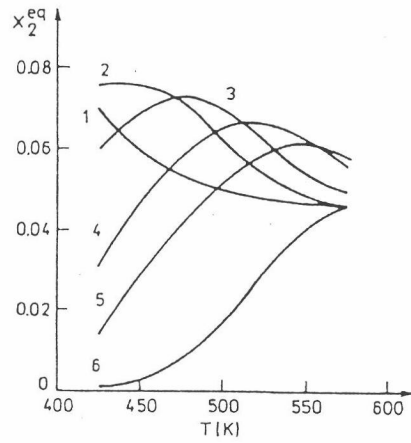


Fig. 3.13 Dependence of equilibrium mole fraction of CO₂ on temperature
 ($\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$)
 (1) 0.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

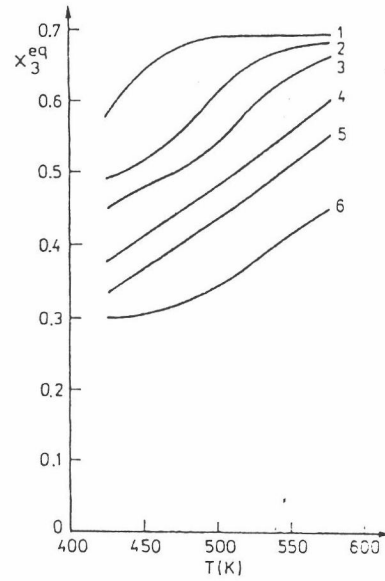


Fig. 3.14 Dependence of equilibrium mole fraction of H₂ on temperature
 ($\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$)
 (1) 0.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

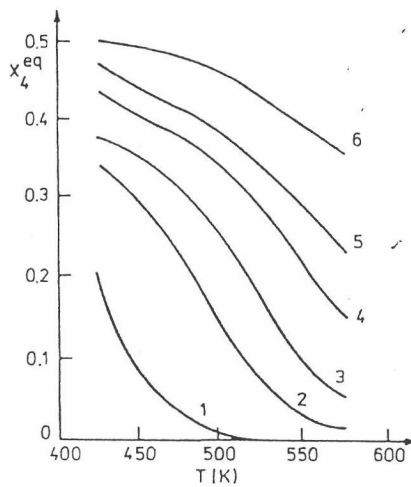


Fig. 3.15 Dependence of equilibrium mole fraction of MeOH on temperature
 ($\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$)
 (1) 0.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

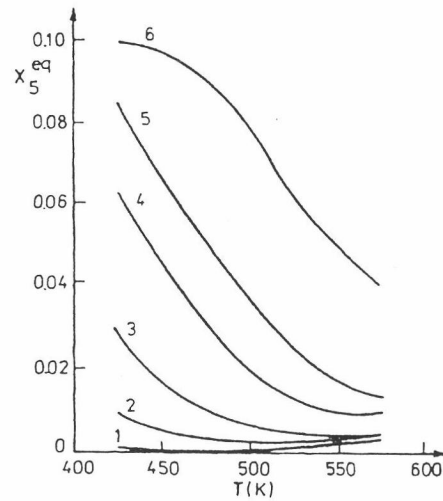


Fig. 3.16 Dependence of equilibrium mole fraction of H₂O on temperature
 ($\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$)
 (1) 0.5 MPa, (2) 2.5 MPa,
 (3) 5.0 MPa (4) 10 MPa,
 (5) 15 MPa, (6) 30 MPa

The effect of the initial CO_2 concentrations was examined both in the absence of CO and also when it was present in the synthesis gas. The respective isotherms and isobars in the co-ordinate system of ξ_1^{eq} or ξ_2^{eq} vs χ_{CO}^0 are presented in figs. (3-17) and (3-18). From these diagrams it can be seen that the effect of the initial CO_2 concentration is considerable, when the synthesis gas contains no CO. A significant increase in ξ_1^{eq} and ξ_2^{eq} is observed with increasing initial mole fraction of CO_2 . When the synthesis gas contains CO, the corresponding curves are much more flattened. It indicates a relatively low effect of initial CO_2 concentration in the synthesis gas containing CO.

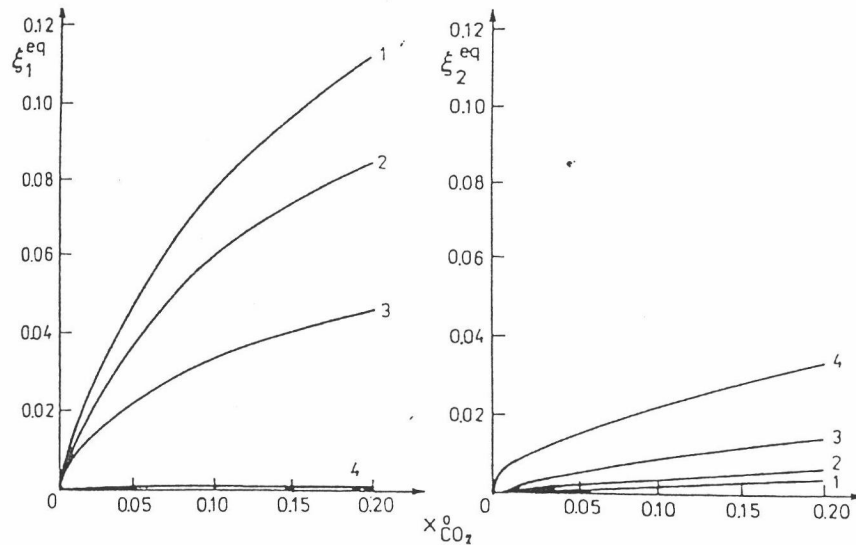


Fig. 3.17 Effect of initial mole fraction of CO_2 on equilibrium conversion degree ξ_1^{eq} and ξ_2^{eq}
 ($\chi_{\text{CO}}^0 = 0$, $\chi_{\text{H}_2}^0 = 0.70$, $T = 513 \text{ K}$)
 (1) 15 MPa, (2) 10 MPa,
 (3) 5.0 MPa (4) 0.5 MPa

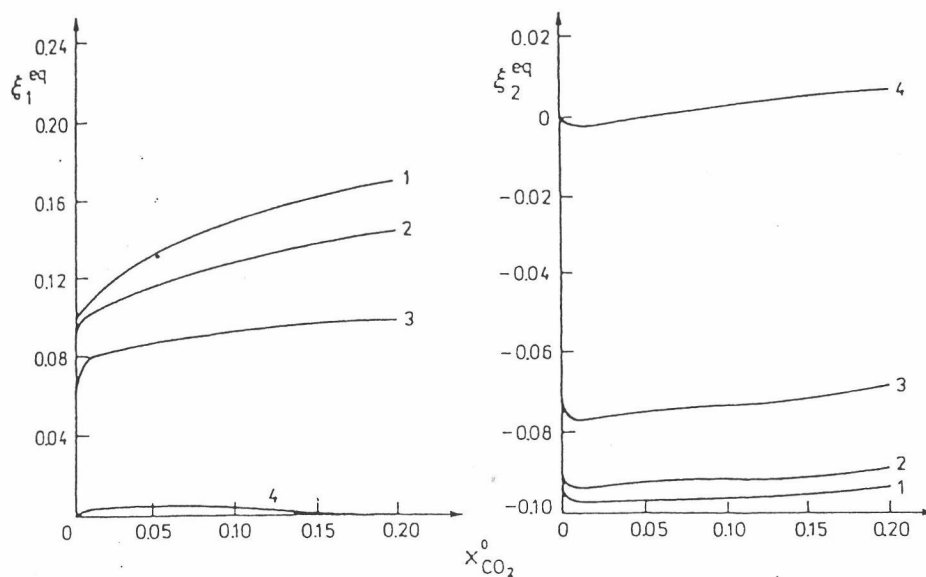


Fig. 3.18 Effect of initial mole fraction of CO_2 on equilibrium conversion degree ξ_1^{eq} and ξ_2^{eq}
 $(\chi_{\text{CO}}^0 = 0.10, \chi_{\text{H}_2}^0 = 0.70, T = 513 \text{ K})$
 (1) 15 MPa, (2) 10 MPa,
 (3) 5.0 MPa (4) 0.5 MPa

The effect of the initial CO concentration on the equilibrium conversion degree is shown in fig.(3-19). The presence of CO in the synthesis gas is highly advantageous in direct methanol synthesis from CO_2 . A large increase in the equilibrium conversion ξ_1^{eq} to methanol is seen in fig.(3-19)., while the increased initial concentration of CO decreases ξ_2^{eq} and reaction (3-3) then proceeds in the reverse direction. Owing to this change in the direction of the course of reaction (3-3), the advantageous considerable increase in the equilibrium conversion degree ξ_1^{eq} for the main reaction is observed. It is interesting that the function of ξ_1^{eq} and ξ_2^{eq} vs the initial mole fraction of CO are represented as straight lines.

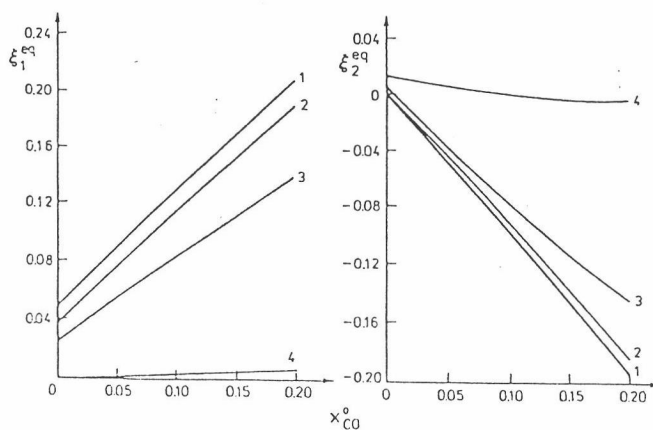


Fig. 3.19 Effect of initial mole fraction of CO on equilibrium conversion degree ξ_1^{eq} and ξ_2^{eq}
 $(\chi_{\text{CO}_2}^0 = 0.05, \chi_{\text{H}_2}^0 = 0.70, T = 513 \text{ K})$
 (1) 15 MPa, (2) 10 MPa,
 (3) 5.0 MPa (4) 0.5 MPa

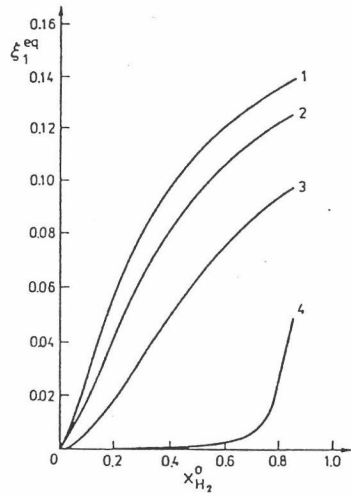


Fig. 3.20 Effect of initial mole fraction of H_2 on equilibrium conversion degree ξ_1^{eq} , ($\chi_{CO}^0 = 0.10$, $\chi_{CO_2}^0 = 0.05$, $T = 513$ K)
(1) 15 MPa, (2) 10 MPa,
(3) 5.0 MPa (4) 0.5 MPa

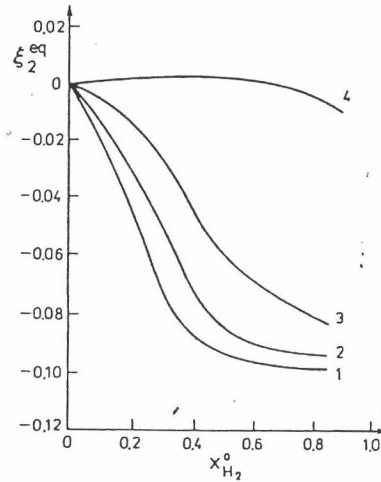


Fig. 3.21 Effect of initial mole fraction of H_2 on equilibrium conversion degree ξ_2^{eq} , ($\chi_{CO}^0 = 0.10$, $\chi_{CO_2}^0 = 0.05$, $T = 513$ K)
(1) 15 MPa, (2) 10 MPa,
(3) 5.0 MPa (4) 0.5 MPa

The effect of the initial hydrogen concentration is presented in fig.(3-20) and (3-21). This effect is highly significant. The higher the initial hydrogen concentration ; the greater the increase in ξ_1^{eq} and decrease in ξ_2^{eq} .

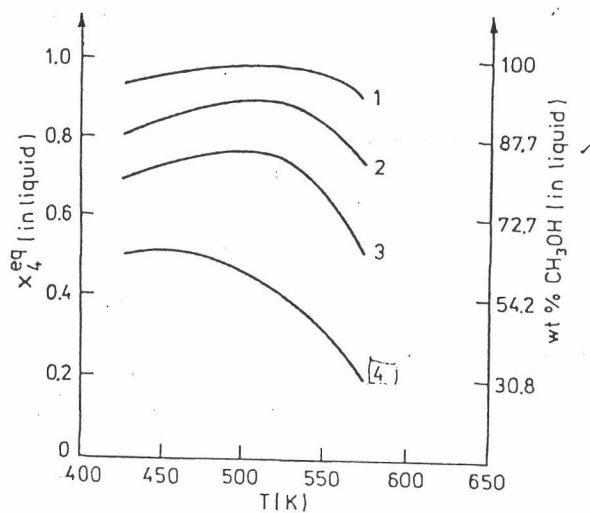


Fig. 3.22 Dependence of concentration of MeOH in liquid products at equilibrium on initial composition of synthesis gas and temperature ($P = 5$ MPa):
(1) $\chi_{CO}^0 = 0.20$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$
(2) $\chi_{CO}^0 = 0.05$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$
(3) $\chi_{CO}^0 = 0.10$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$
(4) $\chi_{CO}^0 = 0$, $\chi_{CO_2}^0 = 0.05$, $\chi_{H_2}^0 = 0.70$

Finally, the dependence of the methanol concentration in the liquid products (methanol + water) on the initial composition of the synthesis gas and temperature is shown in fig.(3-22). If there is no CO in the synthesis gas, the mole fraction of methanol in the liquid products does not exceed 0.5. A considerable increase in the methanol concentration is observed as the initial CO concentration is increased. The curves presented in fig.(3-22) show characteristic maxima against temperature.

3.3 Review of the catalytic systems [25]

3.3.1 Industrial catalysts

First commercialization was in Germany in about 1923 by BASF, using a ZnO-Cr₂O₃ catalyst. Simultaneously, the research was conducted to find other catalysts for methanol synthesis. The most important results obtained in the pre-war period may be summarized as follows :

- copper and its oxides are essential components of the active catalysts
- the activity of composite catalysts is always higher than that of simple ingredients. This synergetic effect has been, until now, the basic principle of operation of the composite oxide catalysts for the synthesis of methanol,
- the catalysts based on a CuO/ZnO system are characterized by a particularly high activity,
- the addition of oxides of high thermal stability, such as Cr₂O₃, Al₂O₃, BeO, increases the resistance of the copper-zinc catalyst to excessively high temperatures during the reaction.

For a long time, the copper-zinc catalyst could not find any practical application, as it was easily poisoned by the impurities present in synthesis gas (S, Cl, metal, and especially, Fe oxides), and also, had a low thermal stability. An industrial application of this catalyst became possible only after the methods of purification of the syngas had been improved and the refractory additives introduced into the catalyst.

The ternary Cu/ZnO/Al₂O₃ catalyst was patented in 1947 by Blasiak and then successfully used in the 50s and 60s in Chemical Works in Oswiecim in the high-pressure methanol synthesis. At the same time Kotowski and Blasiak found that the addition of small amounts of CO₂ into the synthesis gas increased the catalyst activity, whereas at higher concentrations CO₂ had an inhibitory effect. The maximum of activity corresponds to a concentration of about 5% of CO₂. On the other hand, chromite catalysts behave completely differently : CO₂ acts as an inhibitor over the whole range of concentrations. The promoting action of CO₂ is, alongside the synergetic effect, another characteristic property of the copper-zinc catalyst.

A breakthrough in the synthesis of methanol occurred in the 60's and 70's, mainly due to the research conducted by the Imperial Chemical Industries (ICI). A low-pressure process was introduced making use of a catalyst similar to that patented by Blasiak, i.e. Cu/ZnO/M₂O₃ (M= Al, Cr). The majority of the global production of methanol (about 75%) is now based on this technology. The catalyst is obtained by co-precipitation from the solution containing salts of Cu, Zn and Al (Cr), by adding the solution of sodium carbonate.

Modern catalysts for the synthesis of methanol operate at 503-553 K and 5-10 MPa using the H₂/CO/CO₂ syngas , with GHSV of up to 12.000 h⁻¹ and the yield in a range from 0.5 to 1.2 kg. of MeOH / 11 of catalyst /hour. The selectivity relative to methanol excess 99%. The by-products include hydrocarbons, higher alcohols, esters, ethers, and ketones.

3.3.2 Recent catalyst developments

1) Raney Cu/Zn/Al catalysts

The studies on these catalysts have been carried out since the early 80's by Wainwright, Young and co-workers. The composition and properties of catalysts depends on the leaching conditions such as the temperature, time, and concentration of NaOH solution.

2) Catalysts from intermetallic compounds

These are completely new catalytic systems in which intermetallic copper compounds (and, especially, its combinations with rare earth metals) are employed as original substances. Baglin (1981) reported that the catalysts originating from the the compounds of copper and thorium are very active in the synthesis of methanol. These catalysts are, however, less selective compared with those obtained by co-precipitation, especially at higher temperatures.

Intermetallic compounds may be activated by oxidation and subsequent reduction; most often, however, the activation is brought about by heating in the atmosphere of CO and H₂ which, at the same time, constitute the reacting gas. Under these conditions the rare earth metals from a mixture of oxides and hydrides, while copper remains in the strongly dispersed metallic form in close contact with the oxide phase. The reaction occurring during the activation are strongly exothermic making it difficult to control the process temperature which has a crucial effect on the catalytic properties of the final product. The presence of even traces of carbon dioxide leads to the instantaneous and virtually irreversible poisoning of the intermetallic catalysts whereas, as is well known, small amounts of CO₂ increase the activity of the Cu/ZnO/Al₂O₃ catalysts. It seems that, at

present, the most important obstacle to introducing intermetallic catalysts into industrial practice is the cost of purifying the syngas from the trace amounts of CO₂ to prevent catalyst poisoning.

3) Palladium catalysts

Early studies on the use of palladium in synthesis gas conversion have shown that palladium is a poor methanation catalyst. The catalytic properties of this system depend drastically on the type of silica support used, and also, on the presence of impurities. Palladium deposited on supports having pronounced acidic properties (zeolite, alumina) is a methanation catalyst, whereas on weakly acidic (SiO₂) or weakly basic (oxides of rare earth metals) supports methanol is selectively produced. In the case of oxides of intermediate acidity (TiO₂, ZrO₂) the contributions of the two reactions (methanol synthesis and methanation) become comparable with each other. Among the oxides of rare earth metals the most suitable support of palladium catalysts for methanol synthesis is lanthanum oxide.

3.4 Cu/ZnO/Al₂O₃ catalysts

3.4.1 Preparation of catalyst

Preparation of an active catalyst is carried out in three stages :

- Production of a one- or multiples precursor which contains all the components of the catalyst (Cu, Zn, Al) in suitable proportions, in a strongly dispersed form and uniformly distributed over the whole volume. The precursor may be obtained by co-precipitation, kneading, impregnation or leaching of alloys,

- Calcination of the precursor in the air, leading to the decomposition of the primary phase comprised in the precursor (basic carbonates or nitrates, hydroxides, oxalates, citrates etc.) to the appropriate oxides (CuO, ZnO, Al₂O₃),

- Reduction of the calcined precursor, most often in the mixture H₂/N₂, during which copper oxide is reduced to metallic copper, while zinc oxide and Al₂O₃ do not undergo reduction.

1) Co-precipitated precursor phases

The original substances in the preparation of binary (Cu, Zn) or ternary (Cu, Zn, Al) precursors are the nitrates of copper, zinc and aluminium; the precipitating agent is Na₂CO₃ or a mixture of NaHCO₃ and NaOH. The precipitation of the precursor is carried out at an elevated temperature (60-90°C)

There exist three possible variants of precipitation :

(i) simple- the solution of the precipitating agent is added into the solution of metal nitrates. During the precipitation the solution changes from acidic to neutral or weakly basic,

(ii) inverse- the solution of metal nitrates is added into the solution of Na₂CO₃ (NaHCO₃ + NaOH). The solution changes from basic to neutral or weakly acidic or, alternatively, to weakly basic depending on the proportion and concentrations of the solutions used,

(iii) mixed- the solutions of metal nitrates and Na₂CO₃ are added simultaneously into a vessel containing an excess of demineralized water.

By controlling the rate at which the reactants are introduced into the system, pH may be kept constant during the precipitation.

2) Calcined precursor (oxidized state)

The investigation of the calcined precursors using the methods of XRD, ESR, optical spectroscopy and electron microscopy lead to the following conclusions :

- binary precursors calcined at temperatures of 573-578 K consist of the mixture of CuO and ZnO with the crystallite size of 5-20 nm. and 10-25 nm., respectively.

- in ternary precursors after calcination amorphous phases containing Al or Al, Zn predominate; the crystallite size of CuO and ZnO is smaller than that in the system Cu/Zn without Al . The formation of the CuAl_2O_4 spinel was also observed.

- it was found that 2-4% of Cu^{2+} may be dissolved in the ZnO lattice. Also, the formation of the solution of Zn in CuO was observed, together with the creation of the clusters of $(\text{CuO})_n$ on the surface of ZnO.

- both ZnO and CuO may change their morphology (epitaxial growth) depending on the proportion of the individual components and the temperature of calcination

The studies on the structure of the surface of the ZnO/CuO system, it found that over the entire range of concentrations only a single type of the surface Zn is observed, identical with zinc in ZnO. On the other hand, several Cu species are found to exist on the surface. Amorphous CuO is present over the whole range of concentrations; this phase become

dominant at 30-80 weight per cent of CuO. Above the upper limit of this interval the content of amorphous CuO decreases, with crystalline CuO appearing in its place. For catalysts containing less than 30% of CuO a solid solution of Cu^{2+} in ZnO is found alongside amorphous cupric oxide. Its content in the system increases as the concentration of CuO diminishes.

3) Reduction of the precursor

Industrial catalysts are initially reduced with the following mixture of H_2 and N_2 (1-5% of H_2), at temperatures of up to 513 K. Since, during its operation, the catalyst remains in contact with the mixture of hydrogen and CO, the reduction under this conditions has also to be considered. Based on the generally available thermodynamic data, ΔG_{298}^0 may be readily calculated for the reaction of hydrogen and CO with the oxides contained in the catalyst. ΔG_{298}^0 is negative for CuO and Cu_2O , and positive for ZnO and Al_2O_3 . This means that, in contact with hydrogen or carbon monoxide, copper oxides will undergo reduction to metallic copper, while ZnO and Al_2O_3 will not be reduced.

In situ XRD investigations have shown that the reduction of CuO in H_2 is a consecutive reaction, with Cu_2O as an intermediate product. A periodic examination of the reaction products carried out in other studies also demonstrates that Cu_2O is an intermediate product of the reduction by mixture of $\text{H}_2 + \text{N}_2$ and by CO.

3.4.2 Activity of CuO/ZnO/ Al_2O_3 catalysts

The activity of catalysts for methanol synthesis depends on the preparation procedures used during the three stages described in the proceeding sections. By changing the temperature, pH, proportions, the phase composition of the precursor can be modified, thus determining the

distribution and degree of dispersion of the components as well as their mutual interactions in the final product. The phase composition of the precursor may influence the number and quality of the active centers which form on the catalyst surface during calcination and reduction of the precursor. Equally important is the selection of a suitable carrier and promoters, which can both create specific active centers and stabilize them.

3.5 Adsorption of reactants in methanol synthesis

The adsorptive studies are useful in formulating equations which describe the kinetics of catalyst reactions and in defining the rate-limiting step. This, in turn, provides the basis for the kinetic models and for an engineering optimization of the synthesis parameters on an industrial scale. The studies were conducted using a number of experimental techniques, such as infrared spectroscopy (IR), low energy electron diffraction (LEED), high resolution energy electron loss spectroscopy (HREELS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), measurements of surface potential (SP), to determine the structure of adsorptive centers and surface species, static adsorptive techniques which allow the determination of the type of the adsorption isotherm of the isosteric heat of adsorption, dynamic methods mainly thermodesorption spectroscopy (TDS) or thermodesorption (TPD) providing information about the activation energy of desorption and the relative bond energy of surface species.