

CHAPTER II

REVIEW OF METHANOL SYNTHESIS

In 1905, the French chemist Paul Sabatier suggested that methanol might be synthesized by hydrogenating carbon monoxide. For the following historical details and further references see Reference (1). M. Patart adapted the Haber process to synthesize methanol from carbon monoxide and hydrogen, and patented the process in 1921 over a temperature range of 300° to 600°C with a pressure of 150 to 200 atm. The Badische Company set up the first commercial synthetic methanol plant at Leunawerke, Germany in 1923 covered by a very broad patent. They began exporting methanol to the U.S. in February 1924 at a cost of only two-thirds the existing wood-derived methanol cost.

In 1926 Commercial Solvents Corporation began producing synthetic methanol in the U.S. using hydrogen and carbon dioxide formed during the fermentation of corn, and DuPont also began production using carbon monoxide and hydrogen which were obtained as by-products of ammonia synthesis (2).

Most methanol commercially manufactured today is made by passing a synthesis gas containing hydrogen and carbon monoxide or carbon dioxide over a catalyst under pressure and at elevated temperatures (See Table 2.1, equation 1,2). Chromium and zinc or copper oxides are used as catalysts with pressures and temperatures ranging from 50 to 350 atm and up to 400°C depending on the catalysts

and synthesis gas mixture. The synthesis gas has usually been formed by gasifying fossil fuels. This must be purged of all sulfur compounds to protect the synthesis catalyst. The synthesis gas is then reacted with steam in the water-gas shift reaction to shift the ratio of gases closer to the stoichiometric ratio of 2:1 or 3:1

Table 2.1 Reactions and Standard Free Energies for Methanol Synthesis

Reaction	$\Delta G_R^{\circ}(T)$, kJ/mol
1. $2 \text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH} (\text{g})$	$-105.0 + 0.238T$
2. $3 \text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_3\text{OH} (\text{g}) + \text{H}_2\text{O}(\text{g})$	$-64.9 + 0.200T$
3. $\text{CH}_4 + \text{SO}_3 \rightarrow \text{CH}_3\text{OH} + \text{SO}_2$	$-38.9 + 0.122T$
4. $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_3\text{OH} (\text{g})$	$-133.5 + 0.561T$
5. $\text{CO} + \text{CH}_3\text{OH} \rightarrow \text{HCOOCH}_3 + 2\text{H}_2 \rightarrow 2 \text{CH}_3\text{OH}$	---
6. " CH_2 " + $\text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} (\text{g})$	$-42.3 + 0.004T$
7. $\text{C} + \text{H}_2\text{O} (\text{g}) \rightarrow \text{CO} + \text{H}_2$	$+133.9 + 0.141T$
8. $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}$	$+110.5 - 0.089T$
9. $\text{CH}_4 + \text{H}_2\text{O} (\text{g}) \rightarrow \text{CO} + 3\text{H}_2$	$+215.9 - 0.234T$
10. $\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	$-28.5 - 0.182T$
11. " CH_2 " + $\text{H}_2\text{O} \rightarrow \text{CO} + 2\text{H}_2$	$+147.3 - 0.234T$
12. Coal + $\text{O}_2, \text{H}_2\text{O} \rightarrow \text{CO}, \text{H}_2$	---
13. Wood + $\text{O}_2, \text{H}_2\text{O} \rightarrow \text{CO}, \text{H}_2$	---
14. $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	$40.2 + 0.037T$

The corresponding reactions and some alternate synthesis reactions that have been proposed are given in Table 2.1(2). A linearized fit of the standard free energies of formation and combustion of important species in the synthesis and gasification reactions are summarized in Table 2.2

Table 2.2 Standard Free Energies of Formation and Combustion of Species Important in Methanol Manufacture (1)

Substance	$\Delta G_f^{\circ}(T)$ (a) kJ mol ⁻¹	$\Delta G_c^{\circ}(T)$ (b) kJ mol ⁻¹
1. CH ₃ OH (g)	-215 + 0.149T	-668 - 0.045T
2. CH ₃ OH(l)	-251 + 0.252T	-633 - 0.149T
3. H ₂ O (g)	-244 + 0.052T	0
4. H ₂ O (l)	-285 + .160T	0
5. H ₂	0	-244 + 0.052T
6. CO ₂	-395 + 0.0T	0
7. CO	-110 + 0.089T	-285 + 0.089T
8. C	0	-395 + 0.0T
9. CH ₄	-820 + .093T	-801 + 0.011T
10. "CH ₂ "(c)	- 13 + 0.093T	-628 + 0.041T
11. "Coal"(d)	- 31	-246
12. "Wood"(e)	- 48	-148

Conversion Factor: 1 cal = 4.1840J

(a) The standard free energy of formation from the elements. Reed (1) fit the available data to a linear equation of the form $\Delta G = \Delta H - T\Delta S$ over the range 300 to 1200K, so that the two constants in each equation are the effective values of ΔH_f° and $-\Delta S_f^{\circ}$ over this range. Estimated accuracy, ± 2 k J.

(b) This is the low free energy of combustion of CO₂ and H₂O (g) (analogous to the low heating value for the fuel, LHV). The high free energy of combustion to CO₂ + H₂O(l) is calculated by adding $-9.7 + 0.026T$ kJ per mol of water in the combustion products.

for more accurate comprehensive data. Further research is concentrating on an understanding of the kinetics and mechanisms, and of including the effects of carbon dioxide in the synthesis gas.

The production rate of methanol attainable in a plant depends on the equilibrium concentration of methanol in the reacting gases, and the rate at which this equilibrium can be approached. These in turn are dependent on the gas composition, the catalyst used and the pressure, temperature and rate (space velocity) at which the gases contact the catalyst. An excellent review of the details is given by Paul (1).

2.1 Thermodynamic Equilibrium of Methanol Synthesis Reaction

The equilibrium between carbon monoxide, hydrogen and methanol is highly dependent on the temperature and on the partial pressures of the gases. For the reaction.



the equilibrium constant is

$$K = \frac{f_{\text{CH}_3\text{OH}}}{(f_{\text{CO}})(f_{\text{H}_2})^2} = e^{-\Delta G/RT}$$

where f_i is the fugacity of the component gases and where

the Gibbs free energy is

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -25,100 + 56.8T \text{ kcal/mole} \end{aligned} \quad (1)$$

Using a cubic heat capacity equation, Woodward (2) gives the general free energy equation shown below

$$\Delta G^{\circ} = -74,622 + 67.28T \ln T - 0.04682T^2 + 4.259 \times 10^{-6}T^3 \\ + 0.339 \times 10^{-9}T^4 - 202 T \text{ J/gmol}$$

For an ideal mixture, the activity coefficients are unity and $f_i = P_i \gamma_i = \gamma_i y_i P$. Thus

$$K = \frac{P_{\text{CH}_3\text{OH}}}{(P_{\text{CO}})(P_{\text{H}_2})^2} \cdot \frac{\gamma_{\text{CH}_3\text{OH}}}{\gamma_{\text{CO}}(\gamma_{\text{H}_2})^2} \\ = \frac{Y_{\text{CH}_3\text{OH}}}{(Y_{\text{CO}})(Y_{\text{H}_2})^2} \cdot \frac{\gamma_{\text{CH}_3\text{OH}}}{\gamma_{\text{CO}}(\gamma_{\text{H}_2})^2} \cdot \frac{1}{P^2}$$

where Y_i = mole fraction of component i at equilibrium, P = total pressure (atm)

P_i = partial pressure of component i , and

γ_i = fugacity coefficient of component i . The term $Y_{\text{CH}_3\text{OH}} / Y_{\text{CO}} Y_{\text{H}_2}^2$ is referred to as K_N , $\gamma_{\text{CH}_3\text{OH}} / \gamma_{\text{CO}} \times \gamma_{\text{H}_2}^2$ as K_Y , so that

$$K = K_N \times K_Y \times P^{-2}$$

The equilibrium constant K is expressed as :

$$\log K = 3971T^{-1} - 7.492 \log T + 1.77 \times 10^{-3}T - 3.11 \times \\ 10^{-8} T^2 + 9.218$$

Values of the fugacity ratio K_Y for methanol were given by Woodward (2).

Figure 2.1 shows a set of isothermal curves of K_Y versus pressure for the reaction $\text{CO} + 2 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$, shown by Woodward(2). With the values of K_Y obtained from this graph, the effect of pressure on the reaction at 300°C was calculated and shown in Table 2.3

Table 2.3 Effect of Pressure on the Reaction $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$
 at 300°C . ($K = 2.32 \times 10^{-4}$)

Pressure, atm	K_Y	K_N	Composition of equilibrium gases			%Conversion to liquid CH_3OH in one pass
			P_{CO}	P_{H_2}	$P_{\text{CH}_3\text{OH}}$	
10	0.96	0.0242	3.32	6.65	0.036	0
25	0.90	0.161	8.15	16.29	0.56	1.7
50	0.80	0.725	15.3	30.6	4.1	8.0
100	0.61	3.80	25.2	50.5	24.3	24.2
200	0.38	24.4	34.2	68.4	97.4	48.7
300	0.27	77.4	37.7	75.4	186.9	62.3

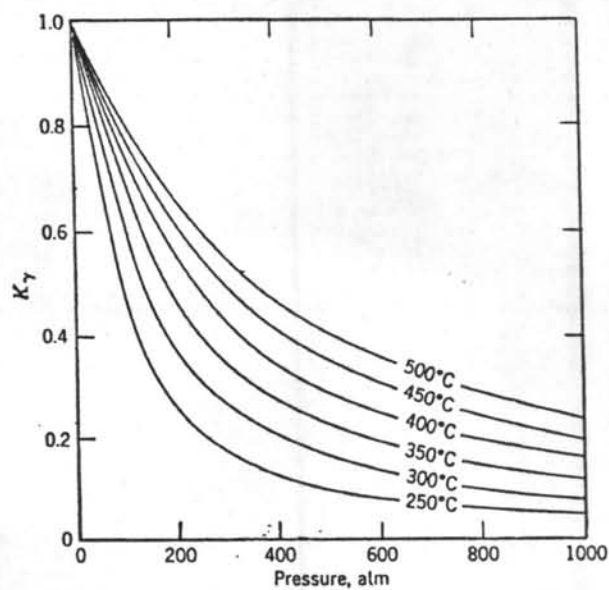


Figure 2.1 Values of K_Y for the Reaction $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$

The mole fraction of methanol can thus be described by :

$$Y_{\text{CH}_3\text{OH}} = \frac{K \cdot (Y_{\text{CO}}) (Y_{\text{H}_2})^2 P^2}{K_Y}$$

Since K_Y increases with temperature but decreases against pressure, while K decreases exponentially with temperature but is independent of pressure, the equilibrium composition of methanol $Y_{\text{CH}_3\text{OH}}$ increases with pressure but decreases rapidly against increasing temperature. This is in accordance with the basic observations obtained by applying Le Chatelier's rule to the reaction, which is highly exothermic and in which three moles of gaseous reactant result in one of gaseous product. Thus high pressure and low temperature would move the reaction toward completion.

Although stoichiometry calls for a hydrogen-carbon monoxide molar ratio of 2:1 in practice this is seldom used. Due to the difficulty in dispersing the heat of reaction, molar ratio as high as 6:1 is sometimes employed in the cycle gas; the excess hydrogen aids in dispersing the heat. This also brings about an increased conversion of carbon monoxide to methanol, although the conversion per pass on the basis of total gas charged will decrease. This is illustrated in Table 2.4

Table 2.4 Methanol Conversion at Equilibrium at Different H_2/CO Ratios at 300 Atm. and 300°C .

H_2/CO ratio	%CO converted to CH_3OH	% CH_3OH in exit gas
2:1	83.2	62.3
6:1	98.0	14.1

2.2 Kinetics of the Methanol Synthesis Reaction

The rate at which conversion to the equilibrium concentration of methanol is approached very much depends on complex function of the catalyst used and the conditions within the reactors. The overall reaction rate is the rate of reaction of the synthesis gas minus the rate of decomposition of the methanol. These in turn are modified by the catalyst and the composition and condition of the species absorbed on it. These are further complicated by non-ideality of the gas mixture inhomogeneity in the physico-chemical characteristics of the catalyst, variation in temperature, and the rate of the gases contacting the catalysts.

Natta et.al. (3) developed a basic formula for the reaction rate for methanol synthesis, which was based on the Langmuir absorption isotherm.

$$r_c = \frac{f_{CO} f_{H_2}^2 - f_{CH_3OH}/K}{(A + B f_{CO} + C f_{H_2} + D f_{CH_3OH})^3}$$

The fugacities $f_i = Y_i \gamma_i P$ and A, B, C and D are functions of reaction temperature and the particular catalyst used, which must be determined experimentally.

The above equation was complemented with isothermal tests on a zinc oxide-chrome oxide catalyst.

In 1958, Uchida and Ogino (4) conducted further experiments on zinc oxide-chrome oxide catalysts over the pressure range of 8.83 to 14.70 MPa (1,280 to 2,133 psi). They used a variation of the rate equation based on the Temkin logarithmic adsorption isotherm. The effect of temperature, pressure and volumetric flow

rate on the methanol yield over an industrial zinc-chromium catalyst as a function of size have been studied (1) by using similar equations. Higher temperatures improved the yield but decreased the purity of the methanol formed, while smaller particle size improved both the yield and the quality. Increased pressure and volumetric flow rate also improved both the yield and quality of the methanol formed. They deduced an activation energy of 36.4 kcal/mol.

Recently attention has been focussed on low temperature copper based catalysts. Computer models have been developed and tested against laboratory and commercial reactors (1).

Next the effects of temperature, contact time, hydrogen to carbon monoxide ratio, and the carbon dioxide concentration on methanol yield are investigated to obtain optimal design parameters.

2.3 Catalyst and Operating Conditions of Methanol Synthesis

Researchers conducted extensive studies on copper based catalysts in the thirties searching for suitable selective catalysts with high reactivity and long life under operating conditions. Catalysts were found, which had high initial activity and suitable selectivity, but most suffered from short active lifetime, and exhibited a strong sensitivity to poisons, especially sulfur. Longer acting catalysts using zinc and chromium oxides were chosen instead, at the expense of lower activity. These catalysts required higher temperatures and consequently higher pressures to obtain sufficiently fast reaction rates. Temperatures were typically between 300° and 400°C with corresponding pressures of 300 to 350 atm. A 72% zinc oxide 28% chromium oxide catalyst, for instance, was reported

to have an optimum activity at 375°C. Small percentages of other metal oxides are often added to promote the activity. Natta et.al., for instance, made extensive studies on the use of copper oxide as a promoter (3).

Imperial Chemicals Incorporated began searching for a more active catalyst that would permit the use of lower pressures. They developed some copper oxide based catalysts suitable for pressures under 100 atm, which they introduced in 1967. These catalysts were sensitive to high temperatures and had to be kept below 300°C. They were also quickly poisoned by sulfur, and so the feedstock had to be stringently desulfurized. Typical conditions were 50 - 100 atm with temperatures ranging between 250°C and 270°C (5).

The low pressure process gave a typical yield of 2.5% methanol in the exit gases as compared with 5.5% in the high pressure process. This entailed much higher recirculation of the unreacted gases, but this was more than compensated for by the large reduction in energy required for compression of the synthesis gases. Combined compression and circulation energy is typically 270 kWh/ton for the low pressure process as compared with 470 kWh/ton for the high pressure process. This 40% reduction in pumping energy represented a major saving in energy and cost, particularly in this era of rapidly increasing energy costs (1).

There have been recent reports that metallic catalysts of Pt, Pd, Ir, and Rh (6) as well as homogeneous catalysts of $\text{Rh}(\text{CO})_5$ and $\text{HCo}(\text{CO})_4$ are also selective methanol catalysts.

Hosaka (7) has reported an alcohol synthesis, in which reaction of CO with H₂ over Rh-Pt cluster compounds at 250-320°C and 20-150 Kg/cm² gave ethanol, methanol, CH₄, C₂H₆, and C₃H₈ with 5-20% efficiency.

Ramaroson, Kieffer and Kiennemann (8) studied reaction of carbon monoxide-hydrogen and of carbon dioxide-hydrogen on copper-zinc catalysts promoted by metal oxides of Groups III and IV. The hydrocondensation of both carbon oxides in the presence of Cu-Zn catalysts produced hydrocarbons and alcohols. The selectivity of such reaction was influenced by the nature of the promoting oxides. SiO₂, for example, gave principally CH₄, and rare earth metal oxides led mainly to the formation of CH₃OH. Chain growth was observed only in CO reactions and was favored at high temperatures. Formate intermediates were identified by trapping with (CH₃)₂SO₄ to produce CH₃OCHO and CH₃OOCH₃. The results were discussed in terms of a possible mechanism of syntheses from CO and from CO₂.

Leonov et.al. (9) reported coproduction of methanol and higher alcohols at high temperatures in the presence of a Zn-Cr catalysts with potassium compounds as promoters. The alcohols were separated, and the unreacted gas was recycled to the reactor after separation of CO₂ by adsorption with a mixture of methanol (68.4-71.22%), C₂-C₆ alcohols (9.77-18.8%), (CH₃)₂O (0.8-3.0%), and H₂O (10.49-19.34%) at 340-370°C in the presence of a V-containing catalyst. The alcohol mixture contained 0.75-2.30 Vol.% CO₂.

Asakawa (10) prepared methanol using a copper-zinc catalyst. The reaction of CO and/or CO₂ with H₂ was catalyzed by Cu, Zn, and at least one of the metals Al, Cr, V, Mg, and Mn. Thus, a CO-CO₂

mixture might be hydrogenated over a Cu-Zn-Al mixture to give methanol.

Passariello (11) studied some catalysts and their use for synthesis of methanol. Catalysts containing oxides of Cu, Al, Zn and Cr were found useful, at 220-270°C under low pressure, for the preparation of methanol from a H₂-CO mixture. A catalyst containing CuO 30%, ZnO 50%, Cr₂O₃ 16% and Al₂O₃ 3% was used at 250°C, 100 bars to prepare methanol from a 65.0:6.8:11.3:16.8 H-CO-CO₂-N mixture, giving 1 kg methanol/1. catalyst/h.