3.4 Concurrent Synthesis

3.4.1 Operating Conditions

Although there are two steps operating in series, the summation of the two reactions gives the same overall reaction as the current industrial one step synthesis. Hence, the thermodynamics of the concurrent methanol synthesis in one reactor is the same as that of the direct methanol synthesis. Using a methanol rich medium, if the equilibrium partial pressure of methanol equals the vapor pressure of methanol, the concurrent two step reaction will not occur. This gives the maximum temperature which can be used at constant total pressure. Using this as a criterion, an equilibrium relation between temperature and total pressure for the concurrent two step methanol synthesis was calculated for a H_2/CO ratio of 2 and is shown in Figure I.7. The vapor pressure of methanol equals the equilibrium partial pressure of methanol at the conditions represented by the line. The shaded area above the equilibrium line represents possible reaction conditions (temperature and pressure) at which methanol can be produced using the concurrent synthesis. The area below the line represents the conditions under which the concurrent methanol synthesis is thermodynamically impossible. Figure I.7 therefore provides a simple but useful method for determination of the reaction conditions for the methanol concurrent synthesis using methanol as the carrier alcohol. Other H_2 to CO ratios were also used in the calculation and their results showed little difference from assuming an H_2 to CO ratio of two.

Based on the individual studies presented earlier, the carbonylation of MeF is fast while the hydrogenolysis of MeF proceeds relatively slowly. This results in a low finite MeF concentration since the carbonylation step is in equilibrium and the hydrogenolysis step is the rate determining step. Setting Equation I.9 to zero and substituting it into the hydrogenolysis rate equation, we get,

$$r_{MeOH} = \frac{6.31*10^{-4}\exp(-4568/T)C_{Cat,2}C_{MeOH}P_{CO}P_{H2}}{1 + 0.096P_{CO}} \qquad (I.11)$$

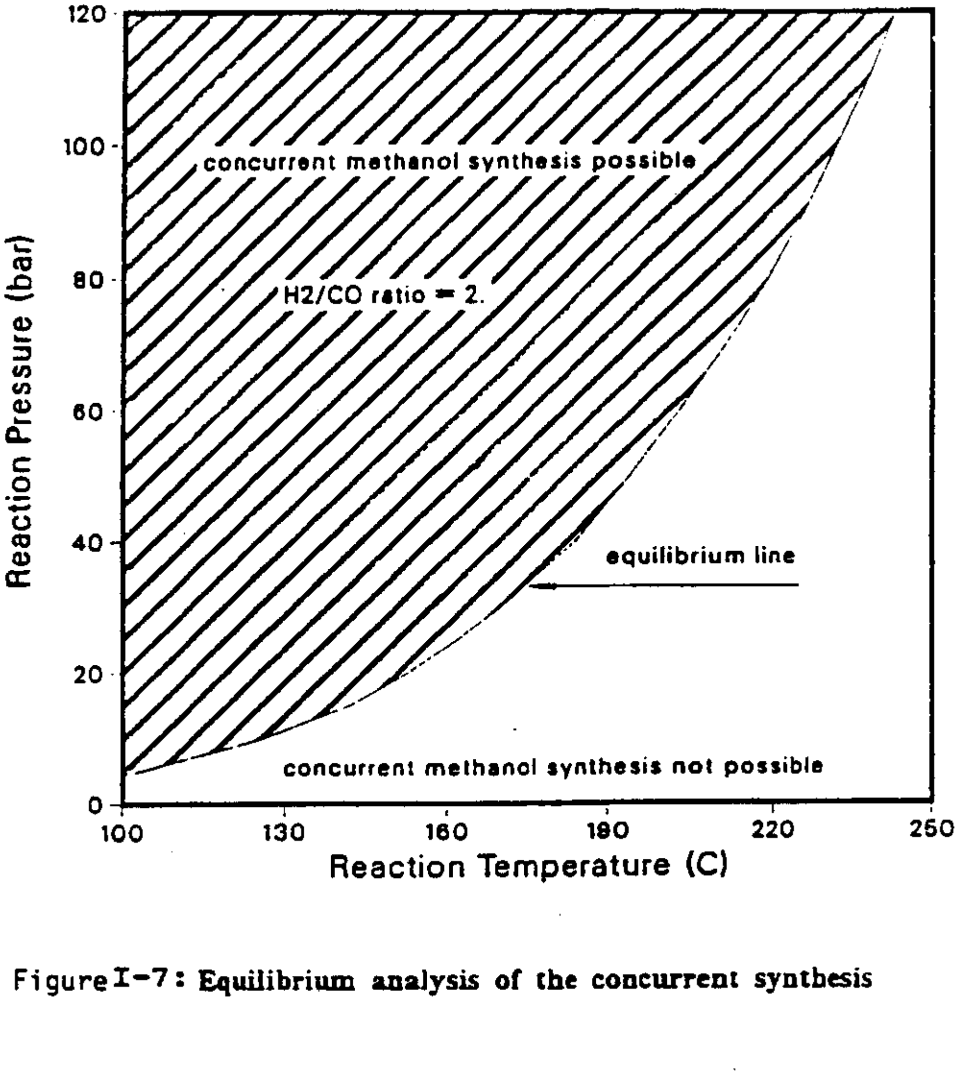

Figure I-7: **Equilibrium analysis of the concurrent synthesis**

Since the MeF concentration in the concurrent synthesis is small, the term C_{MeF} in the denominator of Equation I.10 was neglected in Equation I.11. The experimental operating conditions were then determined from Equation I.11. First the optimum H_2/CO ratio was found by taking the derivative of Equation I.11 with respect to P_{H2}/P_{CO} and setting the result to zero. At 50 to 100 bar (which is the pressure range used for direct methanol synthesis technology), the optimum H_2/CO ratio is in the range of 2.4-3.3. It is obvious that the operating temperature should be in the range of 140 to 180°C if the total pressure is in the range of 30 to 60 bar. These are the conditions used in this part of the work.

Nine runs were made in the 1000 cc autoclave. Results of these runs are summarized in Table I-4. Reaction rates for CO and H_2 were computed by making mass balances over the reactor system. The inlet and outlet gas compositions were determined from GC analysis and flow rates were measured by mass flow meters and a wet test meter.

For all runs the reaction rates of CO and H_2 were found to decrease with time after an initial transient period. Liquid composition analysis for all runs showed that MeF concentrations in the reactor were over 95% of the calculated equilibrium concentrations. This confirms the assumption that carbonylation is in equilibrium. Small amounts of by-products were observed. They were identified by gas chromatogrphy-mass spectroscopy as CO_2, dimethyl ether, and H_2O. Due to the high selectivity of the hydrogenolysis reaction towards methanol, the consumption of H_2 was assumed to be due only to the production of methanol and the methanol production rates were calculated as 50% of the H_2 consumption rates.

3.4.2 Effect of Temperature

The temperature affects the rates of the reactions, the vapor pressure of the solution and the solubilities of the CO and H_2 in the liquid. Figure I.8 shows the results of two runs (runs 4 and 5) made at 140, 160°C and two runs (runs 6 and 7) made at 180°C. Other operating parameters are kept constant. The ratio of H_2/CO consumption was 2±0.1 after the initial transient period.

The rate of reaction was found to decrease with time, the rate decreasing more rapidly at lower temperatures. The reaction rate

TableI-4: Summary of the concurrent runs using a gas-phase reduction for Cu/Cr/Mn catalyst

Run #	T C	P atm	CH_3OK mol/L	Copper Chromite g/L	Feed gas rate cc/min	Feed ratio H_2/CO	Feed CO_2 Vol%	Length of run hours	R_{MeOH} at 40 hrs (m mol/min)
2	121	64	0.14	30	330	1.6–4.	0	65	-
3	140	62	0.43	40	330	2.4–4.1	0	122	-
4	140	62	0.43	40	330	3.	0	258	1.63
5	160	62	0.43	40	300	3.	0	213	1.73
6	180	62	0.43	40	300	3.	0	199	1.1
7	180	62	0.43	40	300	3.	0	121	1.1
8–1	140	62	0.43	40	200	6.	0	172	0.77
8–2*	140	38–62	0.43	40	200	6.	0	53	-
9	160	43	0.43	40	300	3.	0%–6%	75	-

* Run 8–2 is a continuation of Run 8–1.

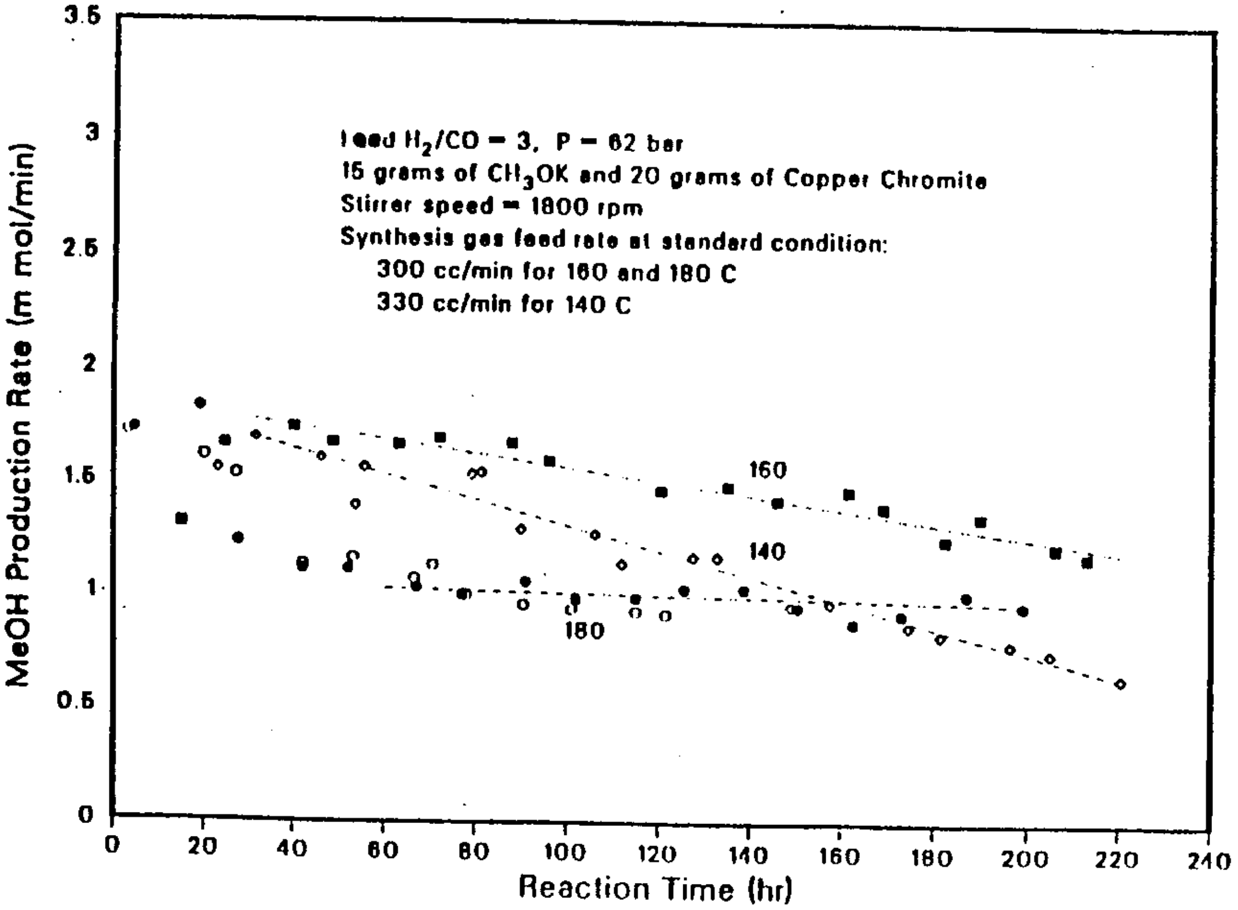

Figure I-8: Effect of temperature on concurrent synthesis is higher at 160°C than at 140°C as predicted by Equation I.11. But the rates at 180°C are significantly lower than predicted. It can be seen that the rate of hydrogenolysis increased to a maximum and then slowly decreased for runs made at 140 and 160°C. However, for the two runs made at 180°C there is a very sharp decrease in rate between 20 and 40 hours, followed by a slow decrease. It was observed that there was as much as 1.5% methane present in the reactor effluent during the first 15 hours for the runs made at 180°C. No methane was found for the runs at 140 and 160°C, and none was found for the runs at 180°C after the first 15 hours. It seems probable that the formation of methane is connected with a change in the catalyst activity.

The byproduct concentrations in the effluent remained constant after the inital transient period for all runs. However, the amount of byproducts CO_2, H_2 and DME increased with increasing temperatures. As listed in Table I.5 there seems to be a strong correlation between the CO partial pressure and the decrease in reaction rate. At lower temperatures, the partial pressure of CO is high and the rate of decrease in reaction rate is high. This is consistent with the partially reversible inhibition effect of CO on the hydrogenolysis rate.

3.4.3 Effect of H_2/CO Ratios

The effect of H_2/CO ratio on the methanol production rate was studied by comparing two runs made at different H_2/CO ratios. No H_2/CO ratio changes were made during each run. Results for methanol production rates at feed H_2/CO ratios of three and six are shown in Figure I.9. The methanol production rate at feed H_2/CO ratio of three is much higher than at the ratio of six in 180 hours operation. But the methanol production rate decreases more rapidly at a feed ratio of three than at a feed ratio of six. This is consistent with the observation that progressive deactivation may result from the interaction of CO with the hydrogenolysis catalyst.

The important parameter influencing the rate is the H_2/CO ratio in the reactor. This ratio depends not only on the feed H_2/CO ratio but also on the reaction rate except when the feed H_2/CO ratio is stoichiometric. Two runs were made in which the H_2/CO ratio was changed in a random fashion to confound the effect of the ratio with the catalyst aging process. A higher MeOH production

TableI-5:Effect of temperature on partial pressure of H_2 and CO in the reactor and on change of reaction rate at constant total pressure*

T C	P_{CO} bar	P_{H2} bar	Change in rate mol/g·min^2
140	11.6	39.4	-4.7×10^{-9}
160	9.4	34.6	-2.5×10^{-9}
180	7.6	27.4	-0.3×10^{-9}

* For runs 4, 5 and 6

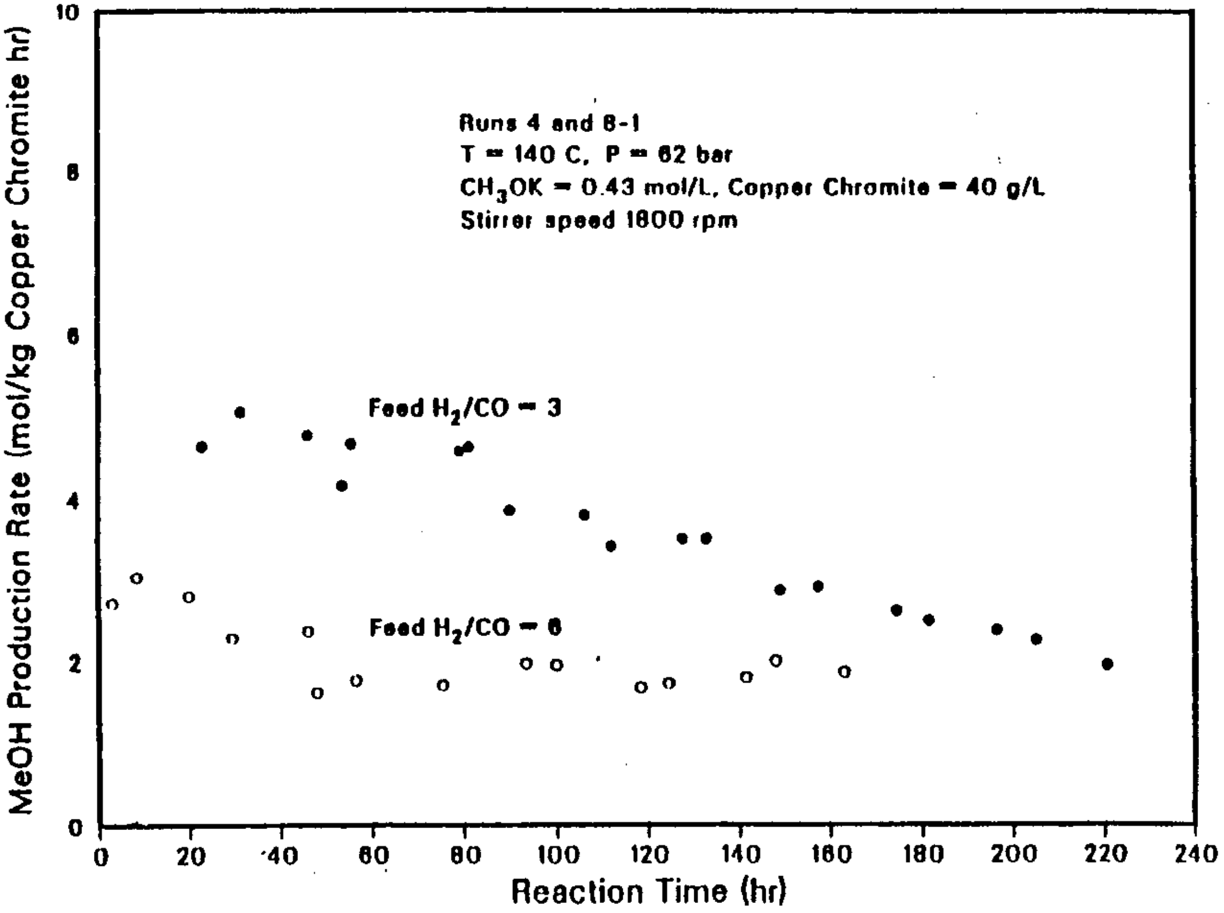

Figure I-9: Concurrent synthesis rates at different feed H_2/CO ratios rate was obtained at a lower H_2/CO ratio. This is consistent with Figure I.9. Additional measurements at lower H_2/CO ratios are needed.

3.4.4 Effect of Total Pressure

The effect of total pressure on methanol production was studied at 140°C, a feed H_2/CO ratio of six and a space velocity of 260 hr^{-1}. It was observed that the catalyst activity did not change with time at this condition. A linear increase of MeOH production rate with increase of total pressure was found. This is illustrated in Figure I.10. The rates predicted from Equation I.11 are also shown and are linear with pressure. The slopes of the two lines are different and we attribute this to the fact that at the lower pressures, the CO partial pressure in the gas is reduced and so deactivation is reduced.

3.4.5 Effect of CO_2

It is well known that CO_2 plays an important role in current industrial gas phase MeOH synthesis; for example, about six volume% of CO_2 added to the synthesis gas is desirable. Since we found that CO_2 is a byproduct of the carbonylation reaction a determination of the effect of CO_2 on the concurrent MeOH synthesis is important. When the reactions were studied separately CO_2 has an effect on both reactions.

CO_2 was deliberately added during run 9 to evaluate its effect. After 26 hrs of operation, CO_2 was added to the reactor as 6% of the total feed. A significant reduction in the reaction rate was immediately observed. Cutting off the CO_2 resulted in a rise in the synthesis gas consumption. Reintroduction of 2% (of the total feed) CO_2 lead to a drop in the synthesis gas consumption rate. The synthesis gas conversion rate is plotted against time in Figure I.11. As expected CO_2 has a negative effect on the concurrent reaction. Liquid analysis showed that the low reaction rate is mainly the effect of decreased hydrogenolysis. The effect of CO_2 on the concurrent synthesis is reversible unlike the effect on the separate hydrogenolysis reaction where the effect is only slightly reversible.

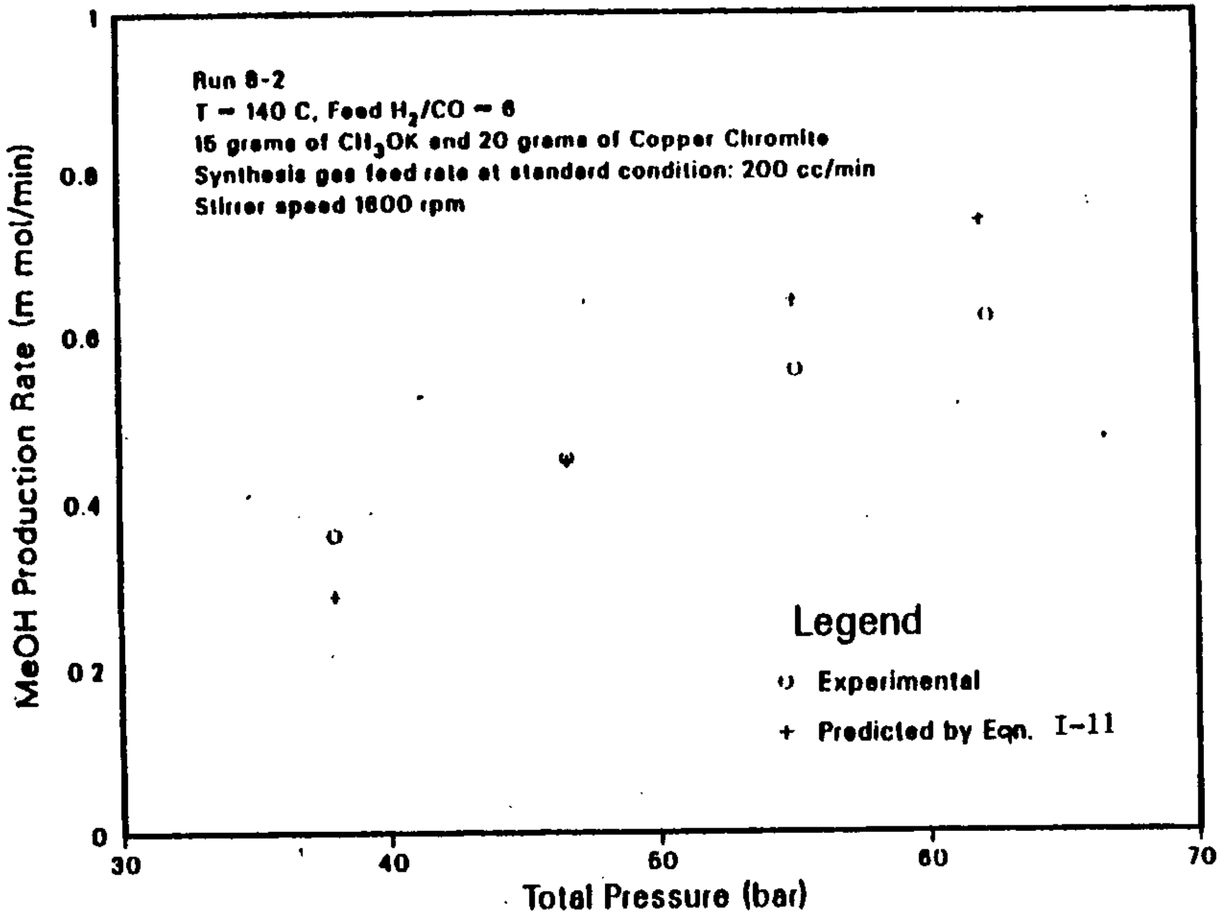

Figure I-10: Effect of total pressure on the concurrent synthesis

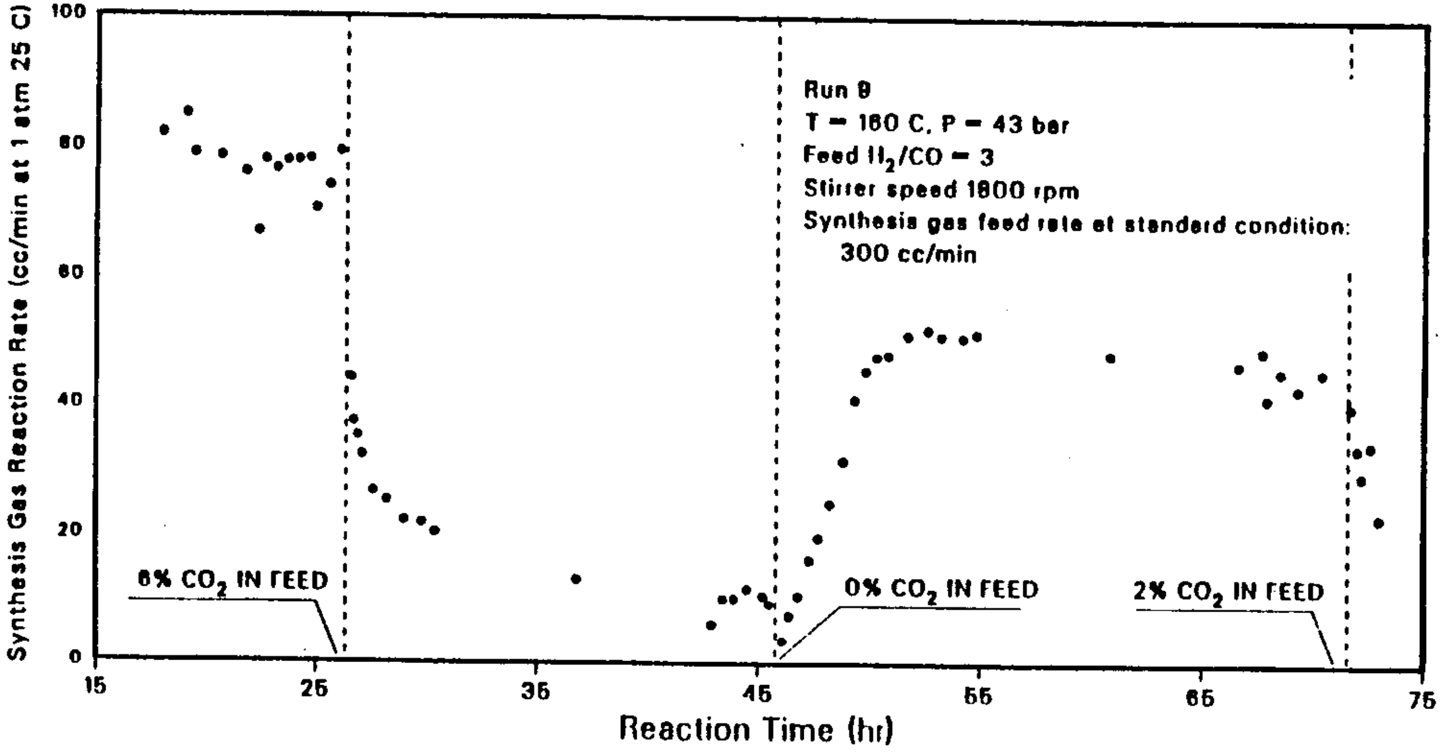

Figure I-11: Effect of CO_2 on the synthesis gas conversion

3.4.6 Effect of Reduction Method on Concurrent Synthesis

These experiments were carried out in a 300 cc reactor. Three runs were made to determine whether an in-situ method of catalyst reduction could be used for the concurrent synthesis. In the first, addition of H_2 and CO began immediately with no separate reduction period. Both catalysts were present. In the second, H_2 was passed through the reactor for 15 hours at 170°C. No KMeO was present. After reduction, the reactor was cooled and KMeO added. In the third, KMeO was present at the beginning of the reduction period. The rates of methanol formation as a function of time are shown in Figure I.12. The in-situ methods, with or without the presence of CH_3OK, give higher hydrogenolysis activity than obtained with no reduction. The decreases in the MeOH production rate with time for the three runs are similar.

The rate of methanol production for in-situ reduction is equal to or higher than the rate obtained using gas phase reduction when rates are expressed per gram of heterogeneous catalyst.

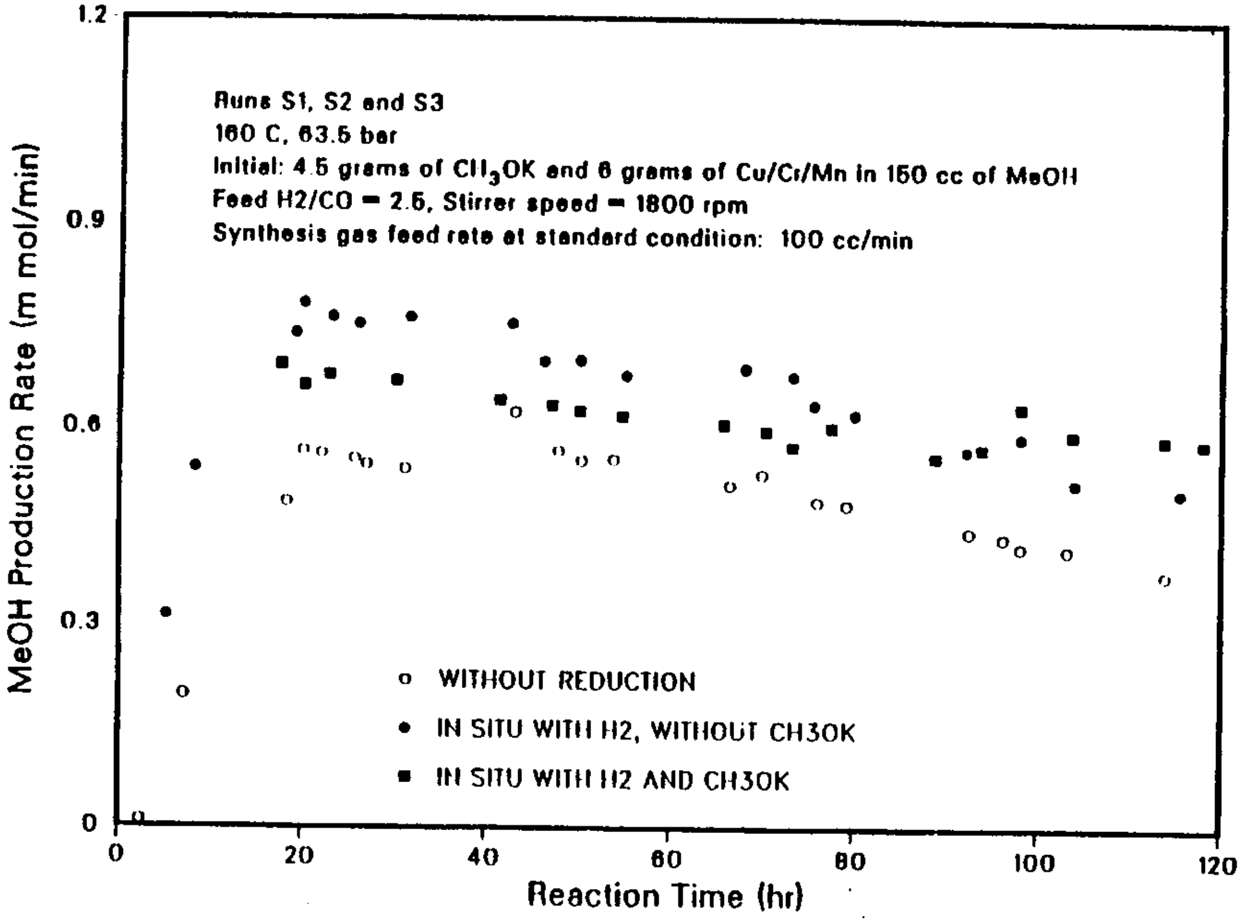

Figure I-12: Effect of hydrogenolysis catalyst reduction method on MeOH production rate

3.5 Concluding Remarks--Methanol Synthesis

The concurrent synthesis of MeOH via MeF can be carried out successfully in a single reactor. This method is superior to the two-step synthesis (Type II) and has advantages over the direct (Type III) synthesis including the commercial process. The concurrent synthesis can be operated at 140 to 160°C (about 100°C lower than the commercial synthesis) and gives high reaction rates without using synthesis gas recycle.

The individual reactions were studied singly and then concurrently. It was found that the behavior of the concurrent synthesis reaction is different from that predicted from studies of the individual reactions. Synergistic effects were observed, including higher MeOH production rates and decreased poisoning by CO, H_2O and CO_2. Interactions between the homogeneous carbonylation catalyst and the heterogeneous catalyst are indicated.

In the concurrent synthesis, the carbonylation reaction is close to equilibrium after an initial transient period. The hydrogenolysis reaction is not in equilibrium. In-situ hydrogenolysis catalyst activation gives as good or better reaction rates than gas phase pre-reduction. The effects of H_2/CO ratio, pressure, catalyst ratio, and temperature were investigated.

3.6 Modelling of Fischer-Tropsch Synthesis in a Slurry Rreactor

A mathematical analysis of a non-isothermal slurry reactor used for Fischer-Tropsch synthesis was carried out. The occurrence of multiple steady states for this reaction had been demonstrated previously in our laboratories (Bhattacharjee et al., 1986). The model includes mass transfer resistance in the slurry phase and the effect of water content on the transport parameters. The effect of temperature on the physical, transport and kinetic parameters for the system were obtained from the published literature.

The model demonstrates that multiple steady states can occur at typical operating conditions. It is also shown that both the presence of water in the Fischer-Tropsch liquid and solids in suspension have important influences on the area of multiplicity in pressure-liquid residence time plots. Details of the model development and results are given in the appendix.

The importance of availability of accurate correlations for mass transport properties when modelling slurry phase Fischer-Tropsch processes is demonstrated. Factors such as poor heat removal, high catalyst activity, high water production, high heat transfer, and large catalyst concentration may result in possible multiple steady states. Commercial slurry reactors should be carefully designed to avoid this possibility.

3.7 Notation

C_{CO} = Concentration of CO in liquid, (mol/l).

C_{MeOH}= Concentration of MeOH in liquid (mol/l).

C_{MeOH}= Concentration of MeF in liquid (mol/l).

$C_{Cat,1}$= Concentration of homogeneous catalyst, (mol/l).

$C_{Cat,2}$= Concentration of heterogeneous catalyst, (g/l).

E = Activation energy for forward reaction in Equation I.5, (kJ/mol).

E'= Activation energy for reverse reaction in Equation I.5, (kJ/mol).

E"= Activation energy for forward reaction in Equation I.6, (kJ/mol).

k = Frequency factor for forward reaction in Equation I.5, ($l^2/mol^2 min$).

k'= Frequency factor for reverse reaction in Equation I.5, ($l^2/mol^2 min$).

k"= Frequency factor for forward reaction in Equation I.6, ($l^2/mol^2 min$).

P = Pressure, (bar).

P_{CO}= Partial pressure of CO, (bar).

r_1, r_H, r_{MeOH} = Rate of carbonylation, hydrogenolysis, and methanol formation in Equations I.5 to I.6 (mol/l min).

T = Temperature, K.

3.8 References

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