

CHAPTER IV

SIMULATION RESULTS AND DISCUSSION

4.1 Effect of Reaction Conditions and Methanol Presence in the Feed Gas on the Rate of Methanol Synthesis

Before carrying out design and optimization of the adiabatic four-stage plug-flow packed-bed reactor, it is interesting to find out how reaction conditions, especially temperature, and how small presence of methanol in the feed gas affect the kinetic rate of methanol synthesis.

As we already know, industrial methanol synthesis reactors have to be operated at relatively high pressure in order to improve the yield of methanol. With an active catalyst, such as that used in the ICI low-pressure methanol process, the operating pressure typically ranges from 50 to 100 atm, with around 80 atm reportedly being an optimum. On the other hand, a conventional (high-pressure) methanol process is usually operated at pressures ranging from 200 to 350 atm.

Since the semi-empirical kinetic rate expression used here was developed by Natta et.al. for a high-temperature (high-pressure) catalyst, and the parameters A,B,C,D in the expression were obtained at high pressures, it has been decided to use a pressure of 200 atm in the whole simulation work.

Regarding the effect of reaction temperature, it is well-known that, from the viewpoint of thermodynamic (chemical) equilibrium, the yield of methanol is favored by a low reaction temperature. From the kinetic viewpoint, however, all present catalysts are not active enough around room temperature. Thus, a compromised operating temperature exists. For example, a low-pressure catalyst typically requires a temperature range of 250-320°C; whereas a high pressure catalyst calls for a higher range (around 350-400°C). Because of the difference in operating temperatures, a low-pressure catalyst is sometimes called "low-temperature" type; and the high-pressure, "high-temperature" type.

At present, all modern methanol plants employ low-pressure processes because a tremendous savings in compression energy can be realized in comparison to high-pressure processes. Nevertheless, for the case in which synthetic gasoline is of prime interest and there is no special justification to have separate syngas-to-methanol and methanol-to-gasoline processes, it is more advantageous to synthesize gasoline directly from syngas in one combined step by physical mixing of a high-temperature methanol synthesis catalyst and a zeolitic gasoline synthetic catalyst. The main reason is that the optimal temperature range of ZSM-5 catalyst happens to coincide nicely with that of a high-temperature methanol catalyst. Furthermore, the yield of gasoline is likewise enhanced at high pressures.

Now that the operating pressure in this simulation work has been chosen as 200 atm, the next logical task is to find out how the reaction temperature affects the pure kinetic rate of methanol production. In addition, since the CO conversion per pass of all industrial methanol processes are around 5-15%, it is imperative that

unreacted syngas be recirculated for further conversion. Therefore, it is conceivable that the recycled gas will contain a slight amount of methanol, which also affects the kinetic rate of methanol synthesis.

Figure 4.1 shows the effect (base on equation (3.1)) of reaction temperature and methanol concentration (mole percent) on the true rate. Obviously, a methanol concentration of up to 3 mole% can reduce the rate by more than half (Note from Figures 4.11-4.14 that the outlet concentration of methanol from each reactor stage is kept under 3 mole% in the simulated industrial reactor). A high concentration of methanol not only suppresses the synthesis rate but also favors other side reactions, such as the dehydration of methanol to dimethyl ether (DME). This is one reason why most industrial methanol reactors are operated at relatively low CO conversion per pass (5-15%) and high hourly gaseous space velocity ($10,000\sim 20,000 \text{ hr}^{-1}$).

From Figure 4.1, we see that the operating ranges of temperatures should be around $340\sim 350^\circ\text{C}$ at the inlet of each stage (when the methanol concentration is relatively low) and around $380\sim 390^\circ\text{C}$ at the outlet. Dashed lines are used in Figure 4.1 for temperatures over 390°C because Natta's parameters are given only within the range of $320\sim 390^\circ\text{C}$, presumably because a higher temperature can cause the catalyst to rapidly lose activity, and even shorten its life. Thus, we conclude that our reactor should be designed and operated such that the inlet temperatures are not lower than 340°C and the outlet values, not higher than 390°C .

4.2 Scope of the Present Simulation Study

The present simulation study may be divided into three phases, as follows :

Phase I : Investigating the Effects of Temperature, Pressure and Space Velocity on the Kinetic Rate of Methanol Production

Phase II : Design of an Adiabatic Plug-Flow Four-Stage Reactor

Phase III: Selection of Optimum Bypassing and Quenching to Maximize Methanol Production Rate

In Phase I, we want to study the relative effects of temperature, pressure, $GHSV^*$ on the kinetic rate of methanol production by relying on Natta's semi-empirical model. This phase may be subdivided into two cases, as follows :

1. Study the effects of pressure and temperature on the kinetic rate (equation(3.1)) by choosing a number of pressures (25-259 atm) and varying the temperature (195-395°C) at each pressure.

2. Study the effects of $GHSV^*$ (i.e. the gaseous volume at 70°F, 14.7 psi of the limiting reactant feed (CO) per hour per unit volume of effective catalyst bed) and average temperature on the overall rate of methanol production at a constant pressure and the effects of pressure and average temperature on the overall rate of methanol production at a constant $GHSV^*$. In this case, the average temperature is varied from 220-380°C. Furthermore, an one-stage plug-flow packed-bed reactor, whose cross-sectional area is 3.14 m^2 and the effective length is 1.2 m is operated adiabatically without quenching or cooling.

Specifically, in the latter case, the effect of $GHSV^*$ on methanol production rate within the temperature range (220-380°C) is studied by choosing a number of $GHSV^*$'s ($670-4000 \text{ hr}^{-1}$). This is done by varying the amount of feed gas while the pressure is kept at 40 atm.

Similarly, the effect of pressure on overall methanol production rate within the temperature range (220-380°C) is studied by choose a number of pressures in range of 20-200 atm while keeping the GHSV* at 6500 hr⁻¹.

In the case, the feed gas contains only H₂ and CO at the ratio of 2:1, and the average gas temperature is taken as 0.5(inlet gas temperature + outlet gas temperature).

In Phases II and III, the total molar flow rate of the feed gas, its composition, and temperatures before and after preheating are assumed given. In Phase II, we want to design a reactor that can synthesize up to 850 metric tons of methanol per day (about 1107 kmol/hr) at a reasonable efficiency and without violating a maximum temperature of 390°C in each reactor stage. It is assumed that 66 mole% of the total feed is fed directly into the first reactor stage, the remaining 34 mole% being bypassed for quenching. Of the total bypassed gas, 30, 32 and 38 mole%, respectively, are used to quench the effluent gas coming out of the first, second and third stage. The question of interest is what should be the common diameter (cross-sectional area) and common height of each reactor stage, that meet the above objective without violating the upper limit on temperature.

In Phase III, we wish to know whether it would be possible to improve the performance of the reactor designed in phase II by varying the percentage β_1 at which the total feed gas is sent into the first reactor stage and the percentages, $\beta_2, \beta_3, \beta_4$, at which the bypassed gas is splitted for quenching the effluent gas of the first, second and third stage, respectively. Again, one important condition

is that at no time should the reaction temperature in any stage exceed 390°C .

4.3 Simulation Results and Discussion

Phase I: The Effects of Temperature, Pressure and Space Velocity on Methanol Production Rate

Figures 4.2, 4.3 show the effects of pressure ranging from 25 to 100 atm, and from 100 to 295 atm, respectively, on the kinetic rate of methanol synthesis within the temperature range of $195-395^{\circ}\text{C}$. We see that the kinetic rate increases with increasing pressure in all cases, except for the pressure range of 200-250 atm, in which the effect of pressure is unstable. This instability has also been reported by Natta. Interestingly, at the lower temperature end, the kinetic rate is found to decrease against increasing pressure.

Figures 4.4 illustrates the effects of GHSV^* ($670-4000\text{ hr}^{-1}$) and average temperature ($220-380^{\circ}\text{C}$) on methanol production rate at 40 atm. Similarly, Figures 4.5 and 4.6 reveal the effects of pressure in the ranges of 20-80 atm and 140-200 atm, respectively, and average temperature on methanol production rate at a GHSV^* around 6500 hr^{-1} .

From Figure 4.4, we see that at GHSV^* around 670 hr^{-1} , the overall methanol production rate increases with temperature in the range of $220-300^{\circ}\text{C}$, the peak of production rate being around 300°C . The production rate then decreases against temperature above 300°C . At the GHSV^* increases, the peak of production rate clearly shifts to a higher temperature. Thus at GHSV^* 's around 1000 hr^{-1} ,

2000 hr⁻¹, and 4000 hr⁻¹, the peaks appear at 310°C, 320°C, and 330°C, respectively. We also see that generally a higher GHSV* will yield a higher overall methanol production rate, except for the low temperature end, since the gas feed rate becomes higher.

From Figures 4.5 and 4.6 we see that the overall methanol production increases remarkably with pressure, again except for the low temperature end.

From this study we may conclude that a satisfactorily overall rate of methanol production can be obtained by employing an a equally high pressure and high GHSV*. The optimum temperature will depend on both the selected pressure and GHSV*, shifting to a higher value as either of them increases. Of course, there exists an upper constrain on the GHSV*. If it is too high, then the costs of separation and purification of crude methanol will very expensive.

Phase II: Reactor Design

The common data for both phases are listed below :

Total molar flow rate of feed	=	48,560 kmol/hr
Molar flow rate of CO	=	6,000 kmol/hr
Molar flow rate of H ₂	=	40,000 kmol/hr
Molar flow rate of CH ₃ OH	=	160 kmol/hr
Molar flow rate of H ₂ O	=	400 kmol/hr
Molar flow rate of inert gas	=	2,000 kmol/hr
Temperature of inlet gas to the first bed	=	340°C
Pressure of inlet gas to the first bed	=	200 atm

Temperature of bypassed gas	=	200 °C
Catalyst : ZnO-Cr ₂ O ₃	($\frac{3}{8}$ " x $\frac{3}{8}$ " cylindrical pellets)	
Bulk density of catalyst	=	1600 kg/m ³
Bed voidage	=	0.32

Table 4.1 summarizes the results of simulation based upon various combination of reactor length and cross-sectional area. Also shown are the temperature of effluent gas from each reactor stage, TS_i .

Obviously, Runs no.1 and 2 fail to meet the production target of 1107 (kmol/hr) of methanol because the reactor volumes are simply too small. Though the reactor volumes of Runs no. 3,4 and 5 are essentially the same, the rates of methanol production appear to increase slightly as the cross-sectional area increases. This might seem puzzling at first, but it is simply due to the fact that the pressure drop across the catalyst bed becomes slightly less when the cross section is larger. This in turn increases the rate expression (equations(3.1)) slightly.

Clearly when a larger reactor is used, as in Runs no. 6 and 7, the rate of methanol production also rises. When we look at the specific rate of methanol production, i.e. the production rate per unit volume of reactor, however, we clearly see that the specific rates are highest for Run no.5 and second highest for Run no.4,6. But Run no.5,6 is not acceptable because its outlet gas temperature exceeds 390°C. This leads us to conclude that the "best" design is given by Run no.4, in which the cross-section area is 3.14 m² and the total effective length is 4.8 m. In this case the gaseous hourly space velocity is 9734 hr⁻¹, a number closely comparable to industrial practice.

Phase III : Selection of "optimum" Bypassing and Quenching

Now that we have obtained a "best" reactor design (Run no.4 of Table 4.1) in phase II, the next question is "Would it be possible to enhance the methanol production capacity by varying the relative amount of feed gas sent directly into the first stage (i.e. value of β_1) and the relative amounts of quench gas (i.e. values of β_2 and β_3 with $\beta_4 = 1 - \beta_2 - \beta_3$)". In this work, we decide to search for the best combination of β_1 , β_2 and β_3 by method of trial and error.

Table 4.2 summarizes the simulation results obtained by using various combinations of β_1 , β_2 and β_3 . We see that, when β_1 is larger (i.e. the relative amount of feed gas sent directly into the first stage is large), the first-stage outlet temperature will automatically become low because of cooling effect. On the other hand, the relative amounts of quench gas will be smaller (even though β_2 and β_3 are kept constant), thus raising the outlet temperatures of subsequent stages as well as their cooling effect.

From Figures 4.1 we see that even a small presence of methanol in the gas can significantly suppress the kinetic rate of methanol production. Thus if β_1 is the same, maximization of methanol production may be achieved by keeping $\beta_2 < \beta_3 < \beta_4$, provided the outlet temperatures of stages three and four are close to but do not exceed the upper limit of 390°C .

In summary, for a given total reactor volume with all four stages being equal in size, total methanol production capacity is maximized under the following conditions.

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1. Keep β_1 as large as possible, so that a high production rate of methanol may be realized while maintaining a reasonably high outlet temperature from the first stage.
2. In addition, it is advantageous to keep $\beta_2 < \beta_3 < \beta_4$, so that proper dilution and proper quenching be achieved at all subsequent stages.

3. Ideally the outlet temperatures should be :

$$TS_1 \leq TS_2 \leq TS_3 \leq TS_4 \leq 390^\circ\text{C}$$

whereas , the inlet temperatures should be :

$$TI_4 \geq TI_3 \geq TI_2 \geq TI_1 \geq 340^\circ\text{C}$$

so that reasonably high production rates occur in later stages.

Going over Table 4.2, we see that Run no.6 yields the highest production capacity without violating the temperature upper limit. The merit of keeping β_1 as high as possible is evident when we compare Run no.6 with Run no.11, in which the values of all β_i 's except β_1 are the same. The advantage of keeping $\beta_2 < \beta_3 < \beta_4$ is evident when we compare Runs no.10 with no.11, or Runs no.7 with no.8..

Actually, even Run no.6 might be improved further by slightly increasing β_3 and decreasing β_4 accordingly, in such a way that TS_4 is closer to 390°C and $TS_3 \leq TS_4$. However, this is not carried out because the expected improvement is quite small. In any case, we might say that Run no.6 (with $\beta_1 = 0.66, \beta_2 = 0.30, \beta_3 = 0.32$ and $\beta_4 = 0.38$) represents a relatively optimal set of operating conditions for methanol production.

Figures 4.7 to 4.10 show the temperature profiles and CO conversion profiles inside the four stages, respectively, for Run no.6 of Table 4.2. The concentration profiles of CO, H₂ and CH₃OH in the four stages are shown in Figures 4.11, 4.12, 4.13 and 4.14 respectively, while Figures 4.15 summarizes the flowsheet balances for Run no.6.

In summary, the relevant data for Run no.6 are as follows;

Reactor corss-sectional area	= 3.14 m ²
Total effective length of reactor	= 4 x 1.2 m
Total molar flow rate of CO	= 6,000 kmol/hr
Total molar flow rate of H ₂	= 40,000 kmol/hr
Total molar flow rate of CH ₃ OH	= 160 kmol/hr
Total molar flow rate of H ₂ O	= 400 kmol/hr
Total molar flow rate of N ₂	= 2,000 kmol/hr
Inlet temperature of first bed	= 340°C
Inlet pressure of first bed	= 200 atm
Bypassed gas temperature	= 200°C
Ratio of gas flow rate into the first bed reactor to total feed rate	= 0.66
Ratio of quench gas stream no.1 to total bypassed gas	= 0.30
Ratio of quench gas stream no.2 to total bypassed gas	= 0.32
Ratio of quehcn gas stream no.3 to total bypassed gas	= 0.38

The total methanol production capacity is 1160 kmol/hr or 891 metric tons/day.

In this work, the design and optimum operation of the methanol reactor have been dealt with separately. The best result will, however, be obtained only when these two questions are considered simultaneously from the design stage, i.e. not after design, work has been completed. The scope of the recommendation is, however, too complicated to be treated here.

Table 4.1 Simulation Results of Methanol Synthesis for the Case of $\beta_1 = 0.66$, $\beta_2 = 0.30$, $\beta_3 = 0.32$, $\beta_4 = 0.38$

RUN NO.	Cross Section Area, m ²	Effective Length of Reactor, m	Effective Volume of Reactor, m ³	TS ₁ [*] °C	TS ₂ [*] °C	TS ₃ [*] °C	TS ₄ [*] °C	CH ₃ OH Production Rate, kmol/hr	Specific Rate CH ₃ OH Production, kmol/hr.m ³
1	3.14	4 x 1.0	12.56	369	371	370	362	858	68.31
2	2.90	4 x 1.2	13.92	373	379	381	377	1031	74.07
3	2.90	4 x 1.3	15.08	376	386	390	387	1152	76.39
4	3.14	4 x 1.2	15.07	376	386	390	388	1160	76.97
5	3.77	4 x 1.0	15.08	376	386	391	389	1172	77.72
6	3.14	4 x 1.3	16.33	380	393	398	396	1257	76.97
7	3.77	4 x 1.2	18.10	386	402	408	404	1361	75.19

*TS_i is the temperature of effluent gas from stage i.

Table 4.2 Simulation Results for Methanol Synthesis
 (Cross-Sectional Area = 3.14 m², Effective Length of Reactor = 4 x 1.2 m)

RUN NO.	BED 1				BED 2				BED 3				BED 4				Total CH ₃ OH Production Rate, kmol/hr
	β_1	TI ₁ *	TS ₁	R ₁ **	β_2	TI ₂ *	TS ₂	R ₂ **	β_3	TI ₃ *	TS ₃	R ₃ **	β_4	TI ₄ *	TS ₄	R ₄ **	
1	0.79	340	369	279	0.33	355	386	325	0.35	372	399	309	0.32	386	407	255	1168
2	0.72	340	373	286	0.35	352	383	307	0.35	363	390	298	0.30	374	396	270	1162
3	0.71	340	373	287	0.30	354	387	317	0.35	366	393	300	0.35	374	396	270	1174
4	0.70	340	374	288	0.39	349	378	289	0.39	356	380	278	0.22	368	391	272	1128
5	0.70	340	374	288	0.38	349	379	293	0.38	357	382	283	0.24	369	391	272	1136
6	0.66	340	376	293	0.30	353	386	309	0.32	363	390	292	0.38	366	388	265	1160
7	0.65	340	377	294	0.32	351	384	300	0.35	358	384	281	0.33	363	384	262	1138
8	0.65	340	377	294	0.29	353	387	309	0.35	361	388	288	0.36	364	386	263	1155
9	0.65	340	377	294	0.30	352	385	307	0.33	361	388	288	0.37	363	385	263	1153
10	0.62	340	380	298	0.34	348	380	284	0.34	353	378	264	0.32	356	376	244	1091
11	0.62	340	380	298	0.30	352	385	301	0.32	359	386	282	0.38	359	380	252	1132
12	0.62	340	380	298	0.32	350	382	294	0.32	357	383	276	0.36	358	378	249	1116
13	0.61	340	380	299	0.42	342	368	241	0.32	344	364	219	0.26	347	365	213	972
14	0.61	340	380	299	0.31	350	384	295	0.33	356	382	272	0.36	356	376	244	1111
15	0.61	340	380	299	0.30	351	385	298	0.32	358	385	278	0.38	357	377	246	1122
16	0.60	340	381	301	0.32	349	382	288	0.35	352	377	259	0.33	353	373	233	1080
17	0.50	340	391	313	0.30	347	382	271	0.35	343	363	202	0.35	334	345	134	920

*TI₁ is the temperature of inlet gas to stage 1, °C

**R₁ is the methanol production rate of stage 1, kmol/hr

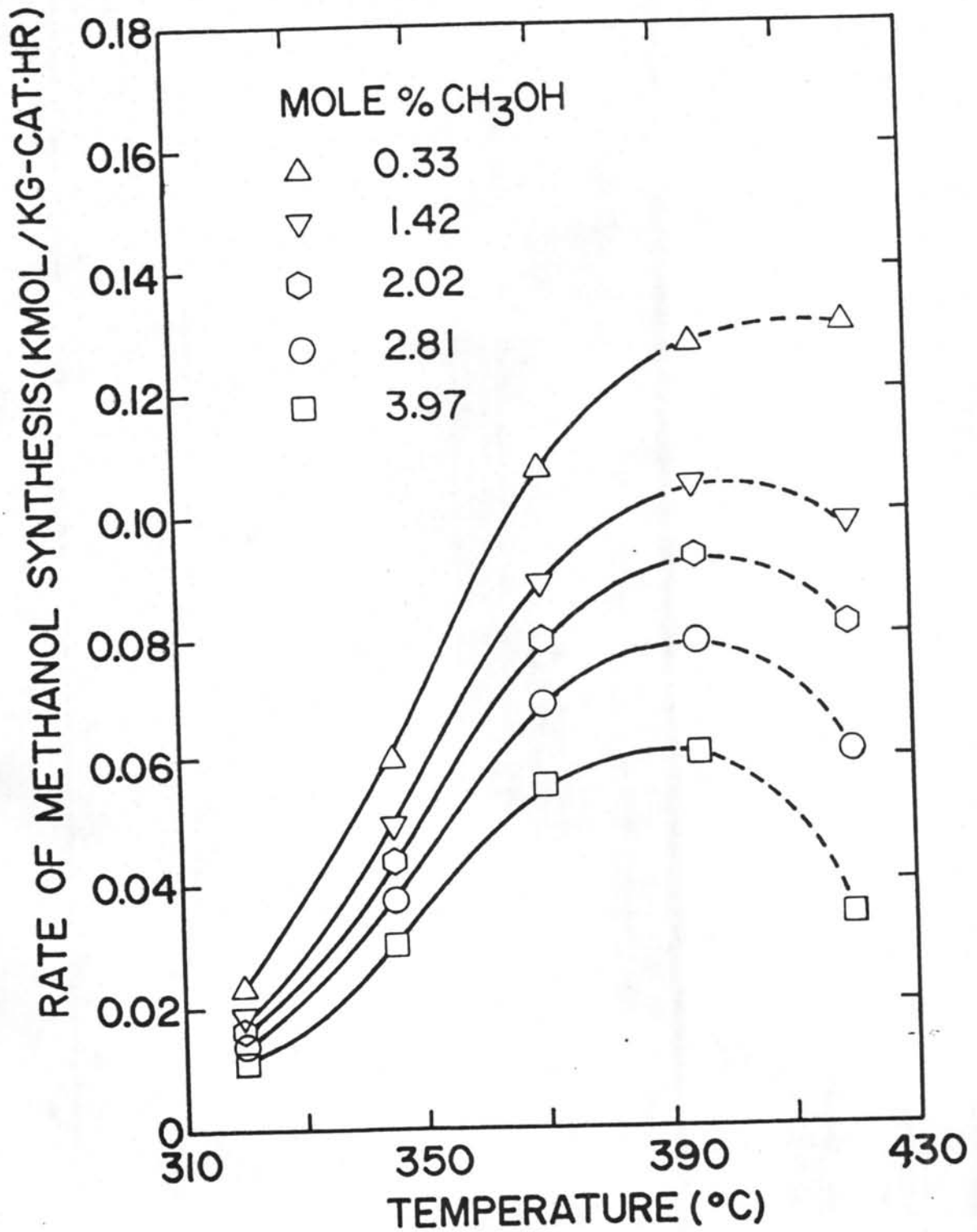


Figure 4.1 Effects of Temperature and Methanol Composition in Feed on Kinetic Rate

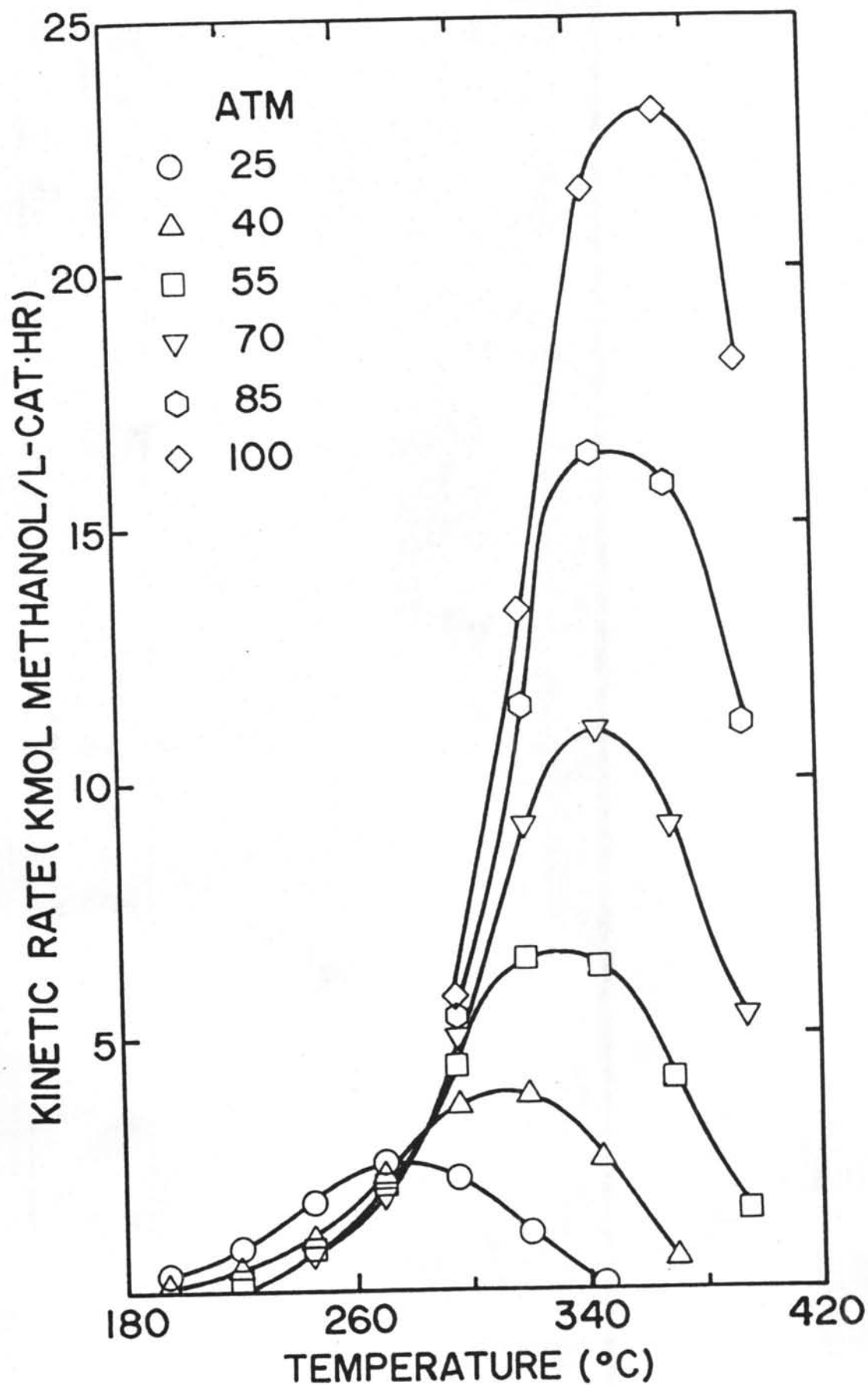


Figure 4.2 Effects of Pressure and Temperature on Kinetic Rate

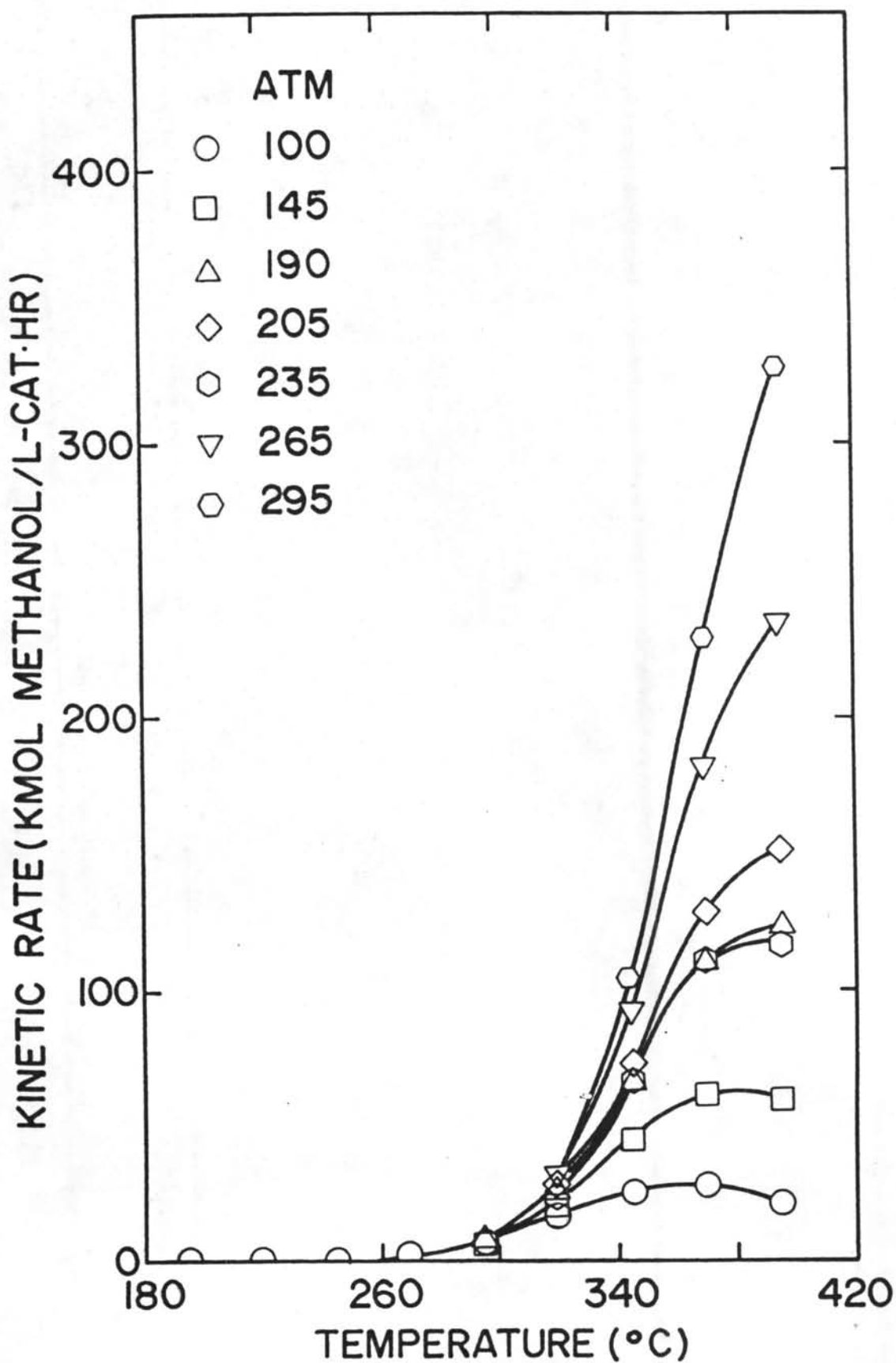


Figure 4.3 Effects of Pressure and Temperature on Kinetic Rate

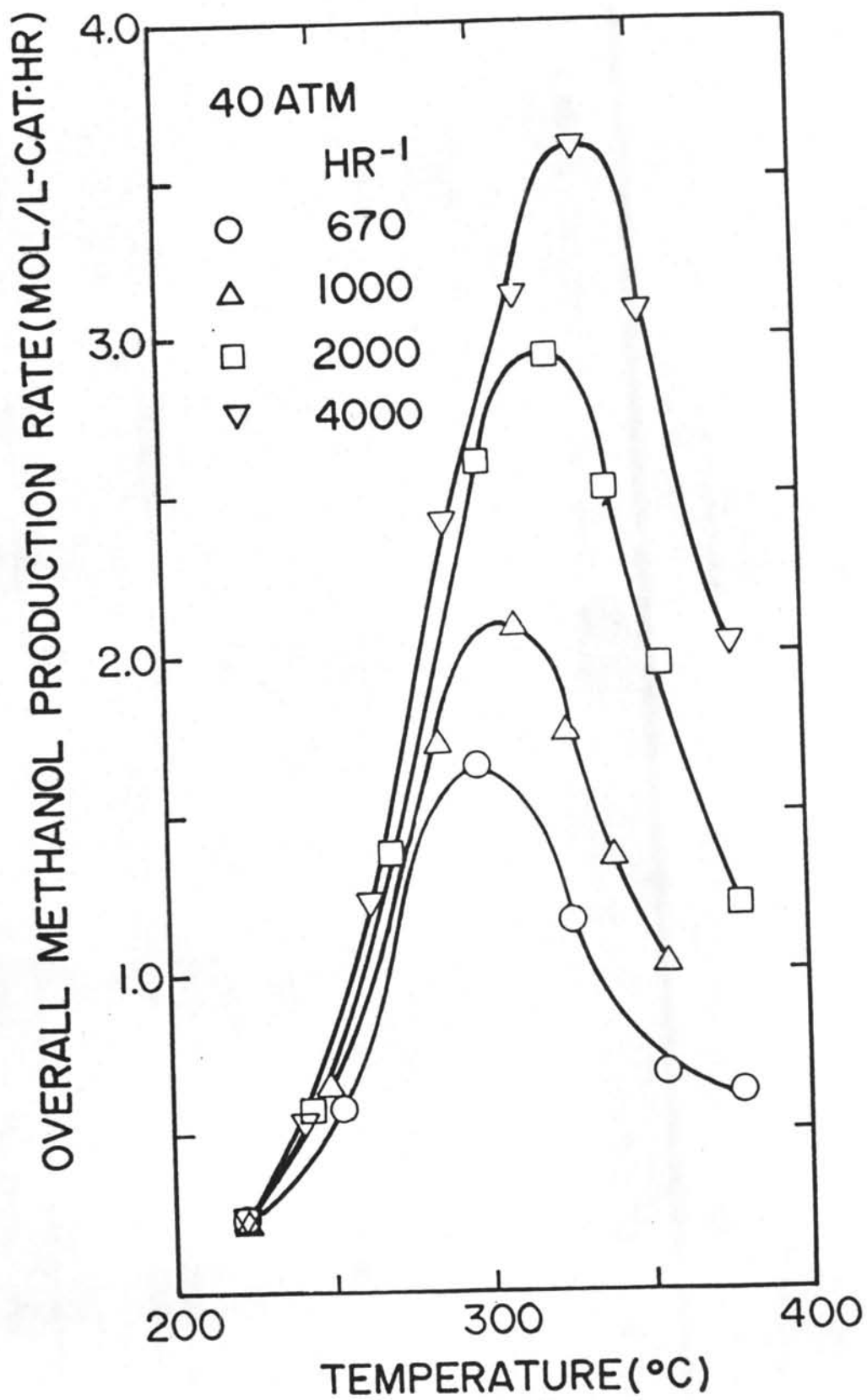


Figure 4.4 Effects of GHSV* and Temperature on Overall Methanol Production Rate

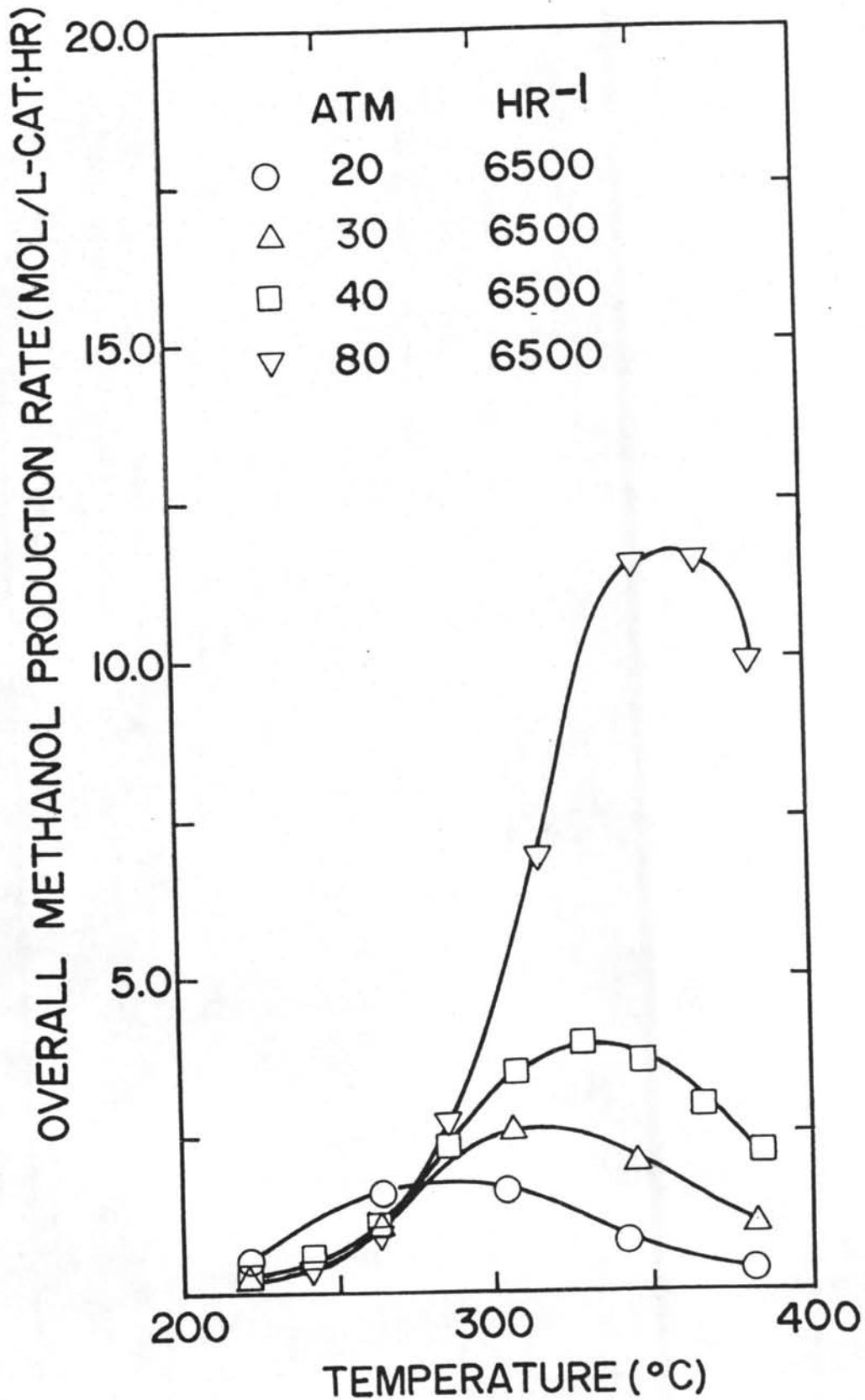


Figure 4.5 Effects of Pressure and Temperature on Overall Methanol Production Rate

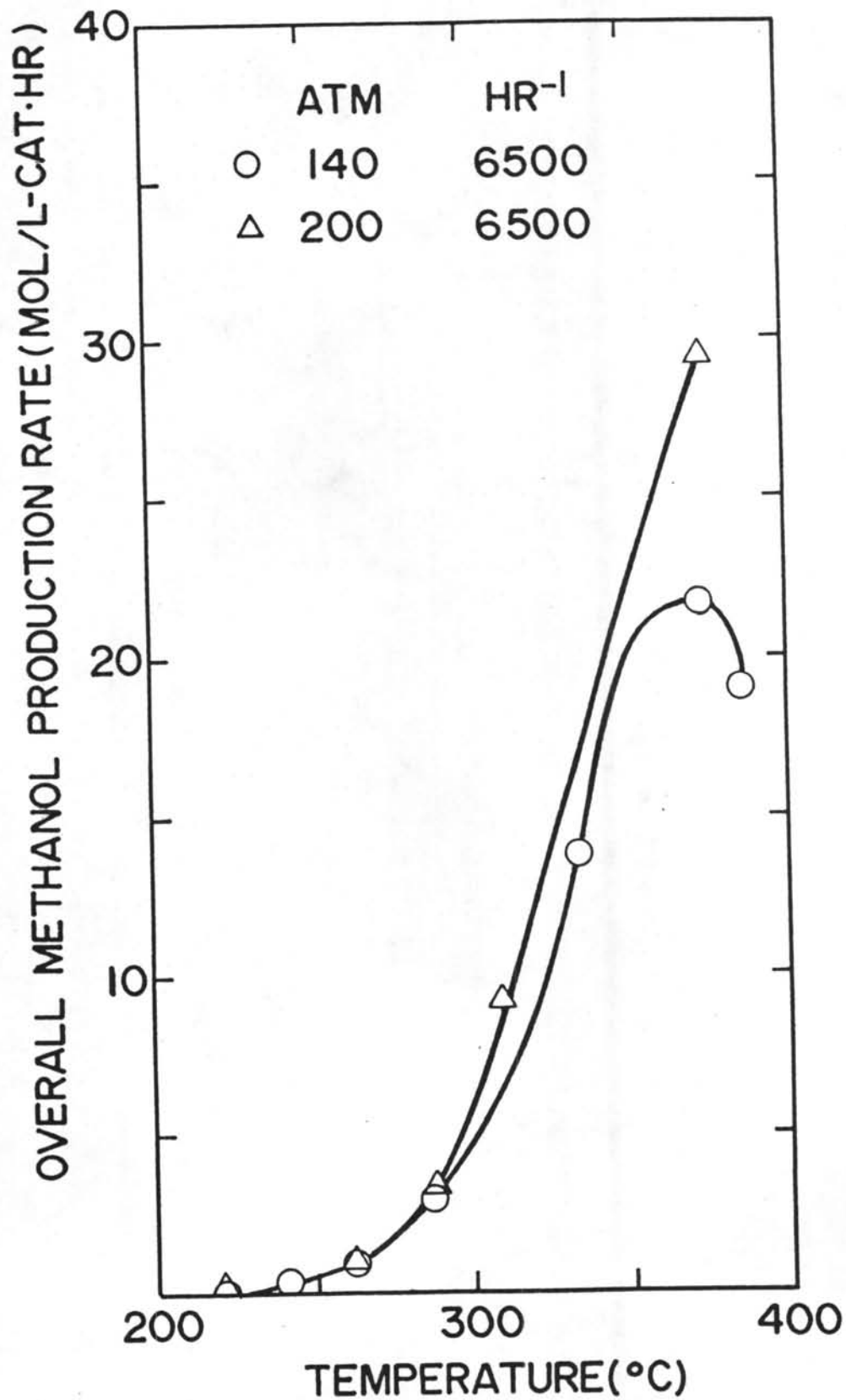


Figure 4.6 Effects of Pressure and Temperature on Overall Methanol Production Rate

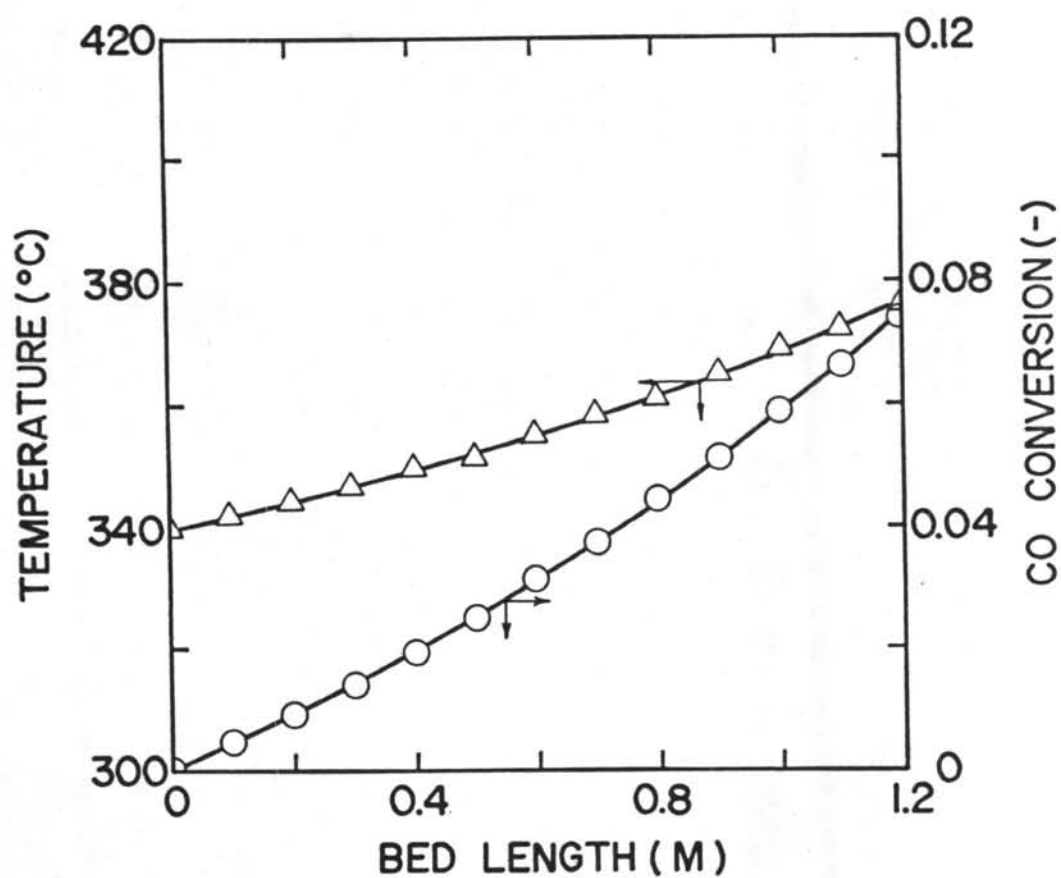


Figure 4.7 Temperature Profiles and CO Conversion Profiles in the First Stage of Reactor (Run no.6 Table 4.2)

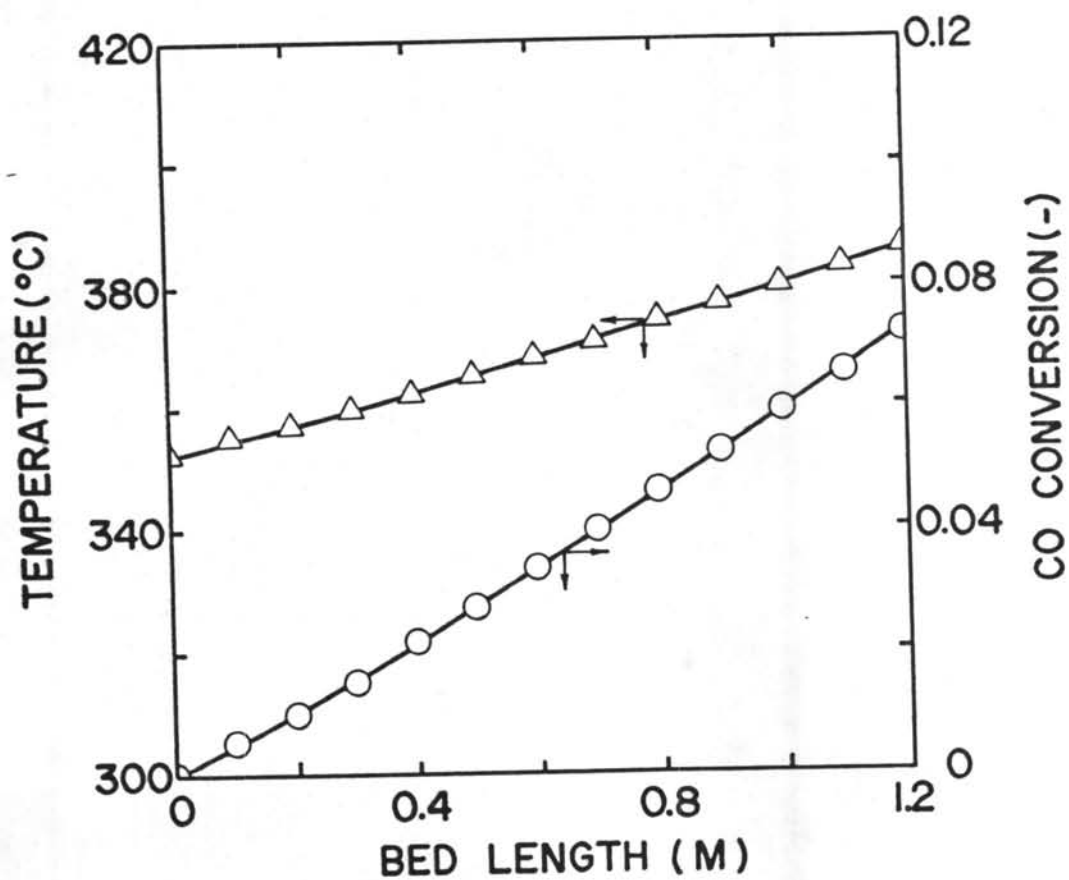


Figure 4.8 Temperature Profiles and CO Conversion Profiles in the Second Stage of Reactor (Run no.6 Table 4.2)

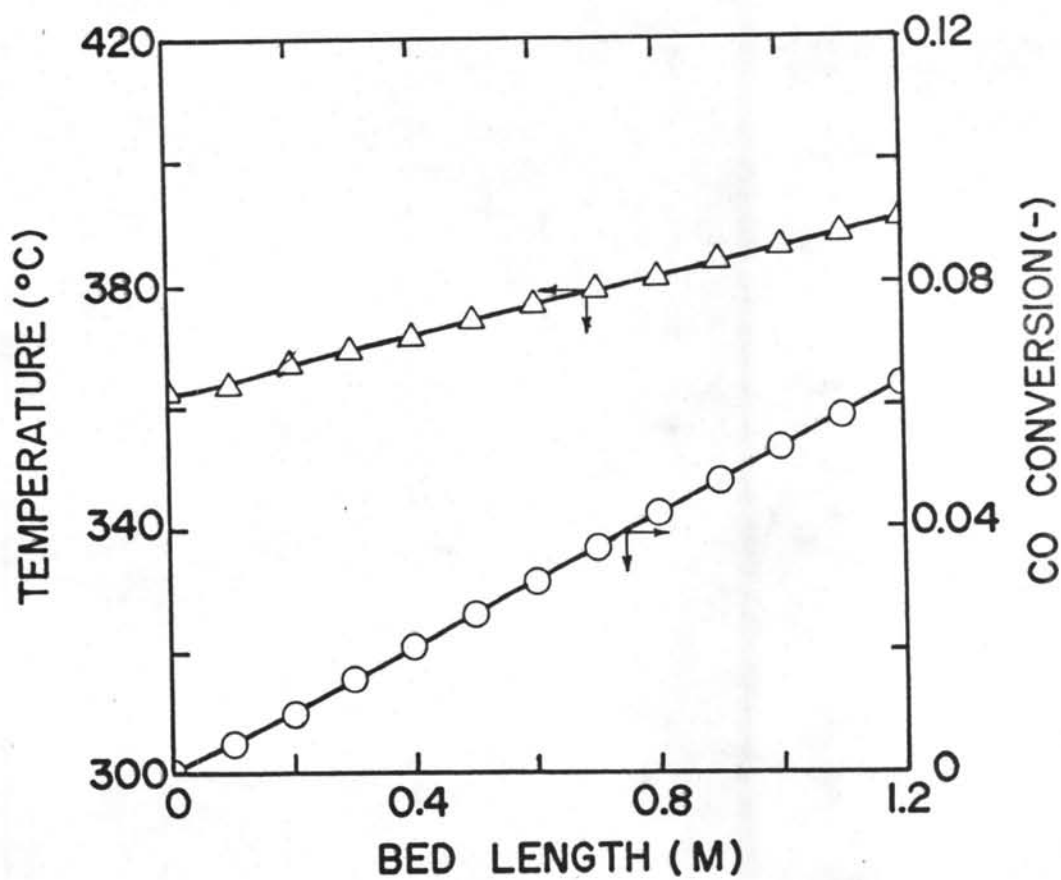


Figure 4.9. Temperature Profiles and CO Conversion Profiles in the Third Stage of Reactor (Run no.6 Table 4.2)

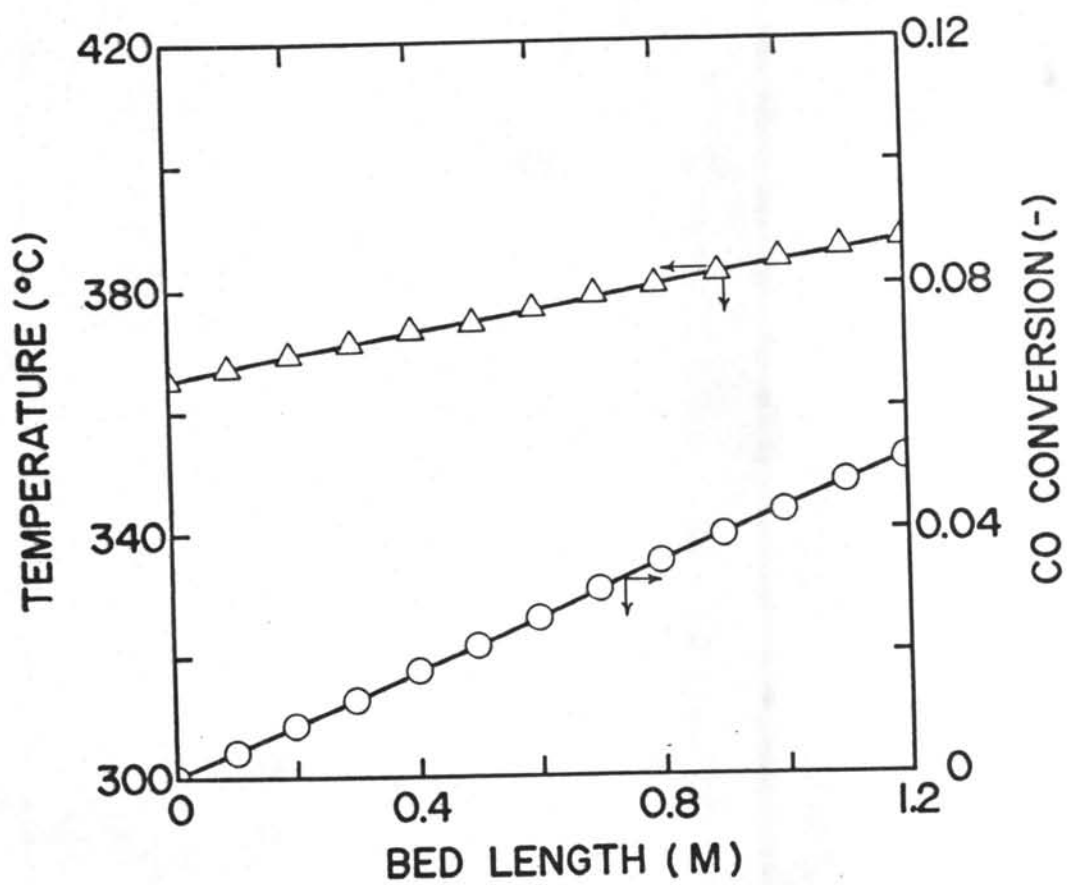


Figure 4.10 Temperature Profiles and CO Conversion Profiles
in the Fourth Stage of Reactor
(Run no.6 Table 4.2)

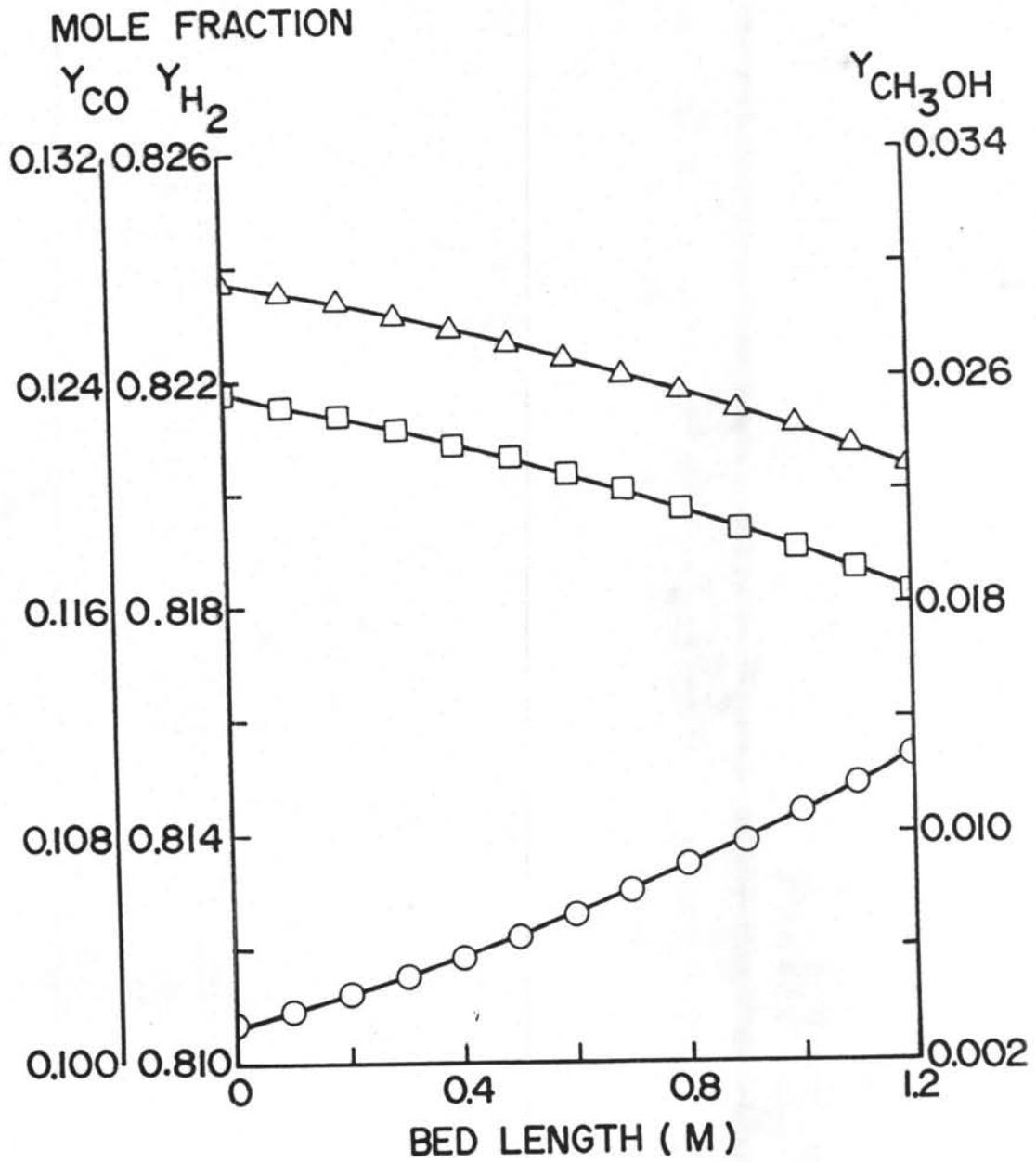


Figure 4.11 Concentration Profiles in First Stage of Reactor

(○ CH_3OH △ H_2 □ CO)

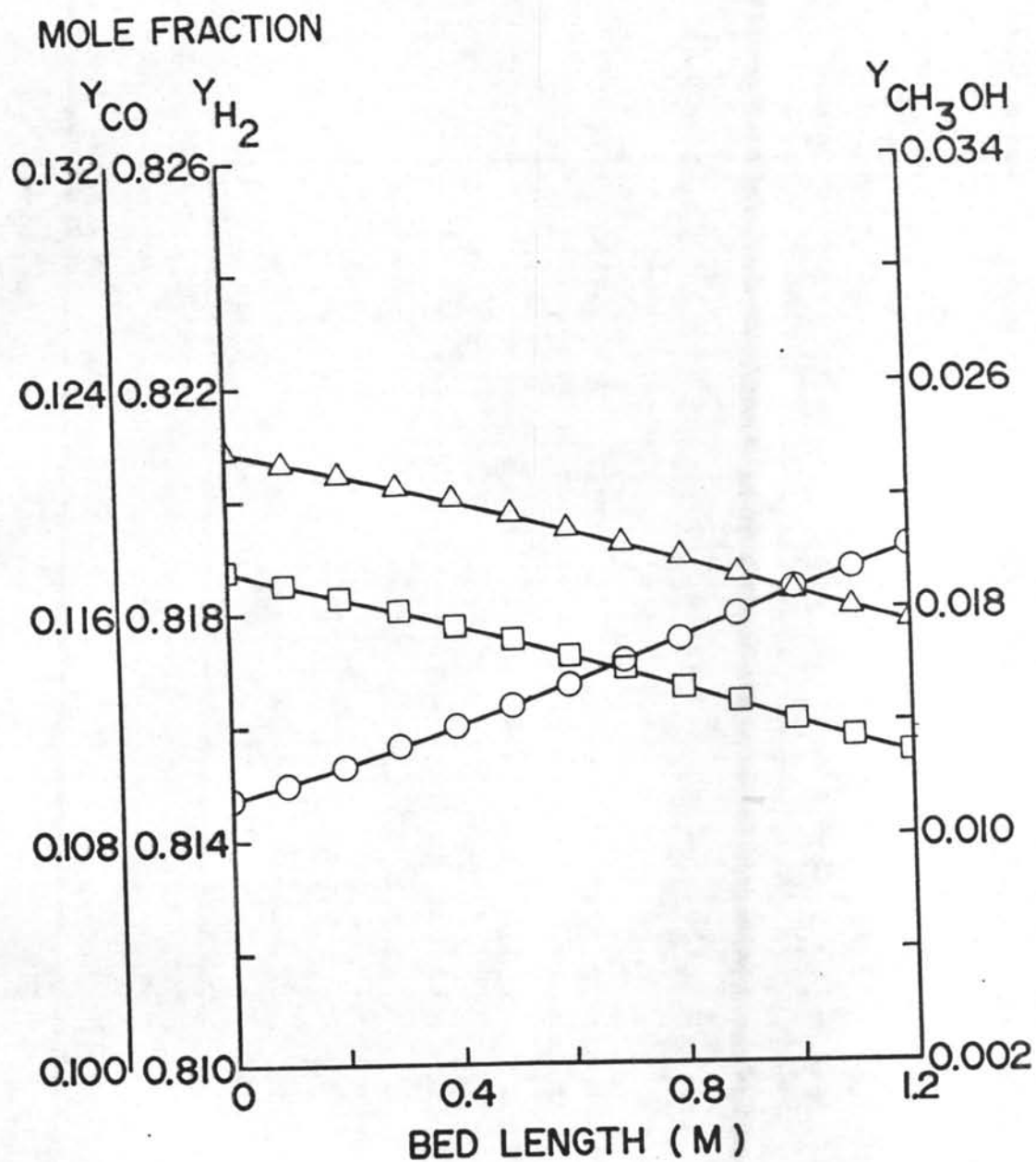


Figure 4.12 Concentration Profiles in Second Stage of Reactor

(○ CH_3OH △ H_2 □ CO)

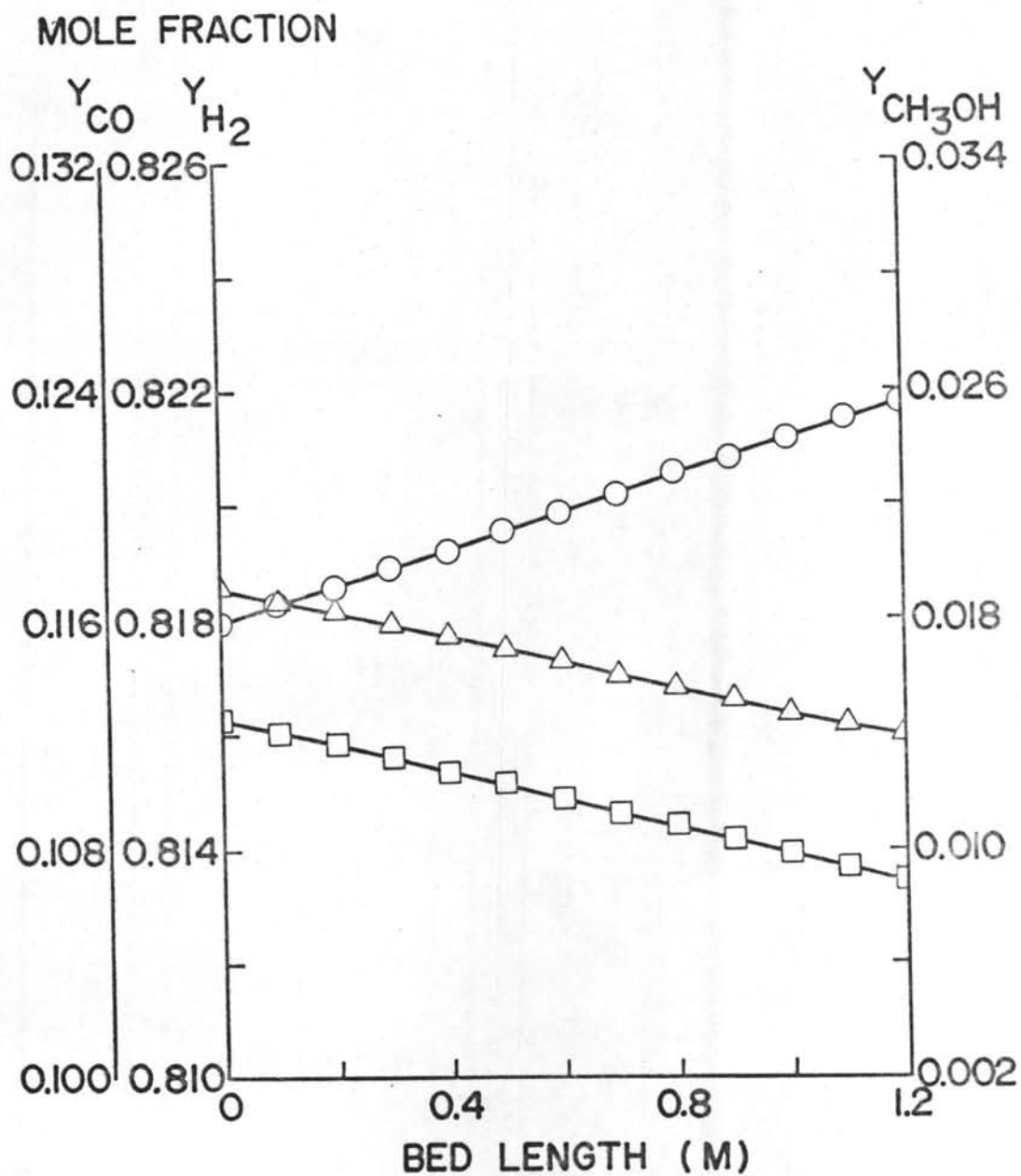


Figure 4.13 Concentration Profiles in Third Stage of Reactor

(○ CH₃OH △ H₂ □ CO)

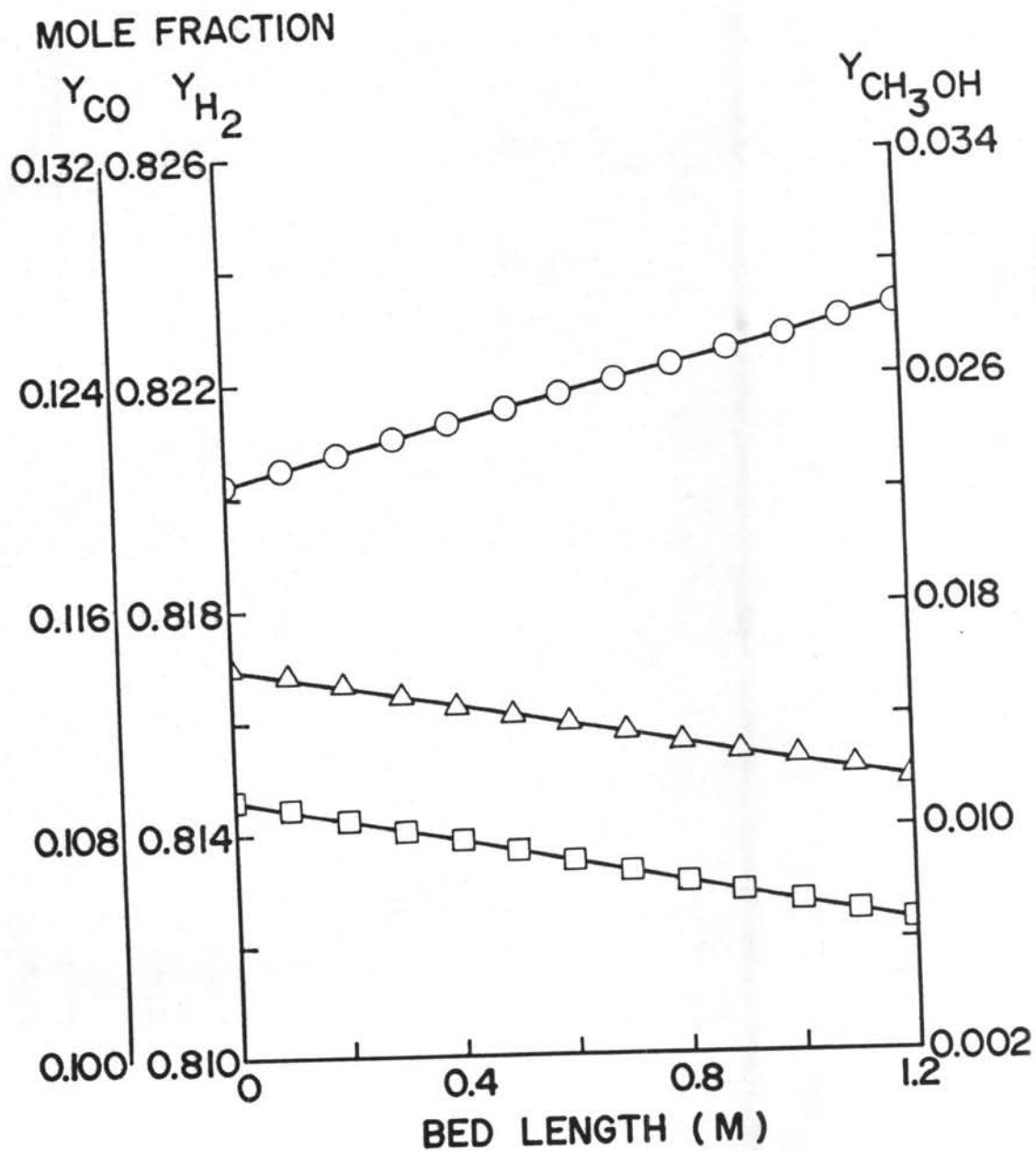


Figure 4.14 Concentration Profiles in Fourth Stage of Reactor

(○ CH_3OH △ H_2 □ CO)

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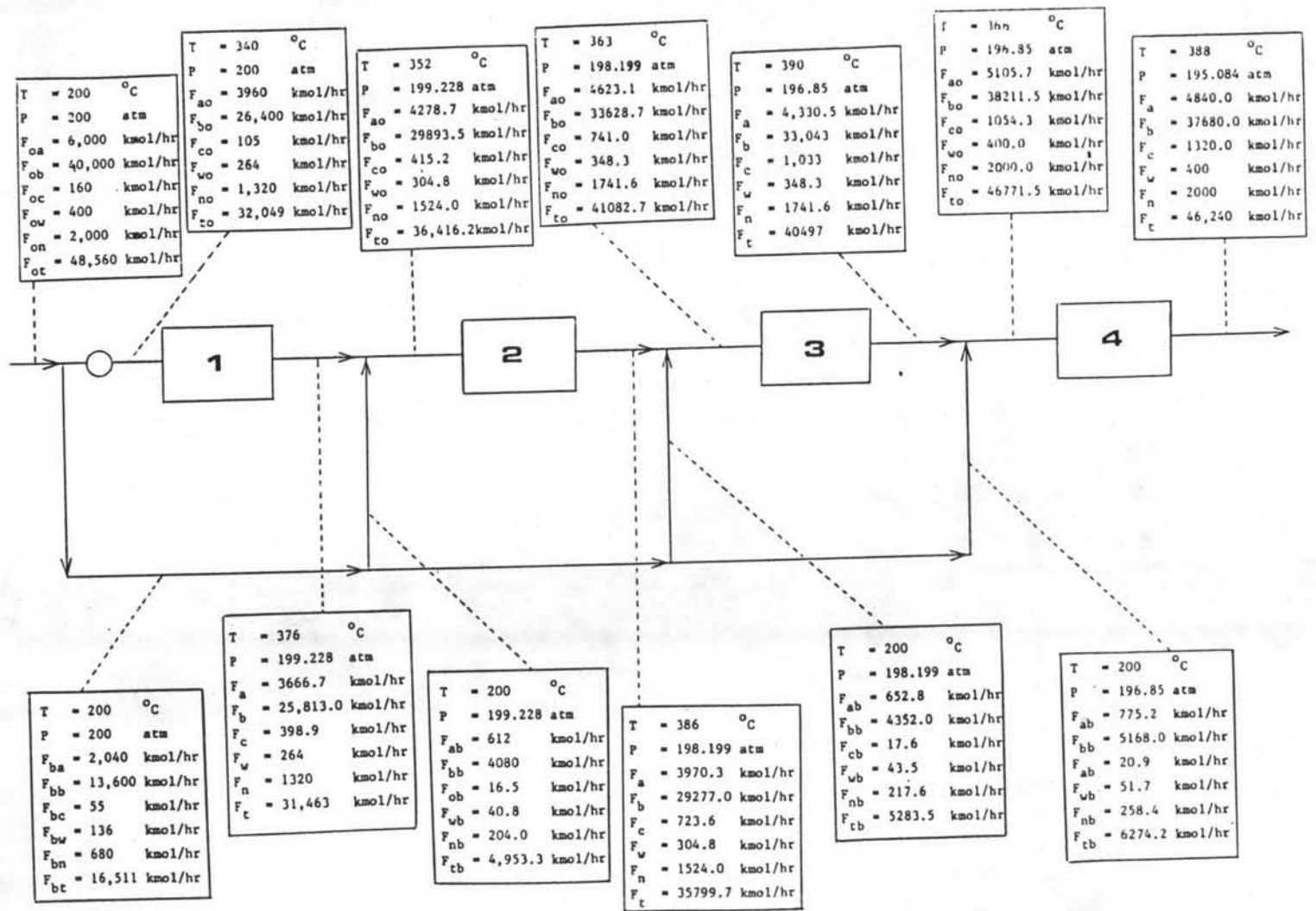


Figure 4.15 Flowsheet Balances for Methanol Reactor (Run no.6, Table 4.2)