

CHAPTER VI

EXPERIMENTAL RESULTS OF METHANOL SYNTHESIS AND DISCUSSION

6.1 Experimental Procedure

A schematic diagram of the fabricated reactor set is shown in Figure 5.3. The maximum design pressure and temperature are 50 atg and 450°C, respectively. The experiment procedure is as follows.

1. Before each experiment, nitrogen gas in the reactor system is replaced by synthesis gas at 5 atg for about 30 minutes. The outlet gas is then analyzed by a Shimadzu GC-8A(TCD) gas chromatograph to ensure that no nitrogen gas remains in the system.
2. The pressure of synthesis gas (at PI-3) is set at the desired value by manipulating the pressure control valve.
3. Needle valve NV-2 is gradually opened until the desired flow rate of synthesis gas is obtained. The flow rate is measured with wet gas meter.
4. The heating furnace is switched on. The system temperature is raised steadily by adjusting two slidacs until the desired temperature is obtained. Temperature measurement is made by inserting two sets of sheathed chromel-alumel (CA) thermocouples into the thermowell of the reactor tube.
5. After the reaction has reached a steady temperature of interest, a 0.5-ml sample is taken at point SP-1 with a pre-heated

insulated syring. The sample is then injected into the Porapak T column of the gas chromatograph to analyze for the concentrations of CH_3OH , CO_2 and hydrocarbons in the product gas.

6. Another 0.5-ml sample is taken at point SP-2 and injected into the MS-5A column of the gas chromatograph to analyze for the concentrations of CO , H_2 , and CH_4 in the product gas.

7. If desired, repeat the experiment at a new temperature by returning to step 4. Otherwise, go to step 8.

8. The experiment is terminated by switching off furnace first. Synthesis gas flow is kept on, sometimes at a reduced rate and pressure, until the temperature of the catalyst drops below 50°C . Next residual synthesis gas in the system is purged with nitrogen gas at 5-10 atg for about 30 minutes.

6.2 Industrial Catalyst and Experimental Conditions Used

In the present experimental work, we are interested in the effects of temperature, pressure and space velocity on methanol synthesis in the presence of an industrial binary catalyst. The catalyst, which is obtained from Catalysts Chemicals, Inc., Far East, has the following characteristics.

Chemical & Physical Properties

Composition	: Zinc and chromium oxides, pre-reduced Zn/Cr = 1.8-2.2
Physical Size & Form	: $\frac{3}{8} \times \frac{3}{8}$ " Cylindrical pellets
Bulk Density	: 1600 ± 150 (kg/m^3)
Side Crush Strength	: > 20 kg
Approximate Surface Area	: >120 m^2/g

Process Conditions

Operating Temperature Range	:	300 - 400°C
Operating Pressure	:	300 kg/cm ²
Normal Space Velocity	:	30,000 hr ⁻¹
Space Time Yield	:	> 1.3 at 360°C, 300 kg/cm ² and 30,000 SV.
Catalyst Life	:	more than one year (Expected life : > 2 years)

According to the above process conditions, the present experiments should be carried out at very high pressure (around 300 kg/cm²) and very high space velocity (around 30,000 hr⁻¹), the temperature range of interest being 300-400°C. Unfortunately, the maximum design pressure of the fabricated tubular reactor is only 50 atg.

Furthermore, the existing pressure relief valve, which has been installed to prevent excessive pressure buildup, tends to open automatically at pressures slightly above 40 atg. Thus, the permissible maximum pressure in the present study is quite low and the investigated pressure range is chosen to be from 20 to 40 atg.

With respect to space velocity,,it is felt that a space velocity of 30,000 hr⁻¹ is not only too high but also fails to provide any information on the effect of space velocity on methanol synthesis. It is expected that at low space velocities the yield of methanol will depend primarily on thermodynamic equilibria of the reversible methanol synthesis reaction ($\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$) and side reactions; whereas at high space velocities, the yield of methanol should depend primarily on the relative rates of the methanol synthesis reaction and the side reactions. Thus, it is

decided to vary the space velocity from 1600 to 16,000 hr^{-1} in this study. The upper-limit of 16,000 hr^{-1} is necessary to reduce the high cost of synthesis gas required in this study. Here the space velocity is defined as the flow rate of synthesis gas (25°C, 1 atm) per unit volume of catalyst bed .

Since the maximum design temperature of the tubular reactor is 450°C, whereas the recommended process temperature ranges from 300 to 400°C, it is decided to use a similar temperature range, i.e. 280-300°C, in the present experimental investigation.

Three milli-liters of the above industrial catalyst is packed into the tubular reactor in this study. Table 6.1 summarizes the experimental conditions investigation

Table 6.1 Summary of Experimental Conditions

Pressure(atg)	GHSV(hr^{-1})	Temperature(°C)
20	1600	280-360
	3700	280-360
	6000	280-360
	13000	280-360
30	2400	300-380
	3500	280-360
	6700	280-360
	13000	280-360
40	1700	280-360
	3900	280-360
	7000	280-380
	16000	280-360

6.3 Analytical Technique

The technique of gas chromatography is used to analyze the product gases. It is equipped with a thermal conductivity detector (TCD), a MS-5A column and Porapak T column.

As an introduction, gas chromatography (GC) is a method of separating the components of a mixture. It involves two phases which are in contact. One phase is held stationary and the other (the mobile phase) moves over it. The mobile phase is a gas or vapor. In GC the stationary phase can be either a liquid or a solid. The stationary phase is poured into a long tube called column. The mobile phase flows through the void space in the column. As the carrier gas flows continuously through the column, the components of an injected sample are carried by it part of the time; the rest of the time they are attracted to and held immobile (adsorbed or absorbed) by the stationary phase. The longer a given component is held immobile, the longer it will take to come out of the column. If the stationary phase is chosen property, the sample components of interest will have different affinities for the stationary phase, will remain immobile for different lengths of time, and will exit at different times. Thus the sample components will have been separated from each other. A schematic diagram of the gas chromatographic system is shown in Figure 6.1.

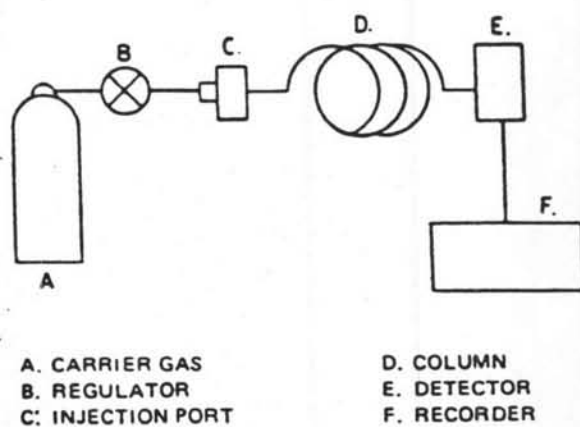


Figure 6.1 Schematic Diagram of a Gas Chromatographic System

6.4 Preparation of GC Calibration Curves

Preparation of GC calibration curves involves the injection of a number of standard samples, whose components and their concentrations should cover those expected of unknown samples. The operating conditions of the GC must be identical to those used when analyzing unknown samples.

In this way, the type of components in an unknown samples may be identified by compared the times it takes the peaks of the unknown sample to come out with those of known components in the standard sample. Furthermore, their concentrations in the unknown sample, can be estimated by comparing their peak areas with those of the known concentrations in the standard sample. The relation between the peak area and concentration of a known component is called a calibration curve.

Figure 6.2 is an example of the calibration curve obtained for carbon monoxide under the following conditions:

Gas chromatographic set	:	Shimadzu Model 8A
Column	:	Molecular Sieve 5A, 5-meter long
Column temperature	:	125°C
Injection port temperature	:	150°C
Detector type	:	Thermal Conductivity Detector (TCD)
Detector temperature	:	150°C

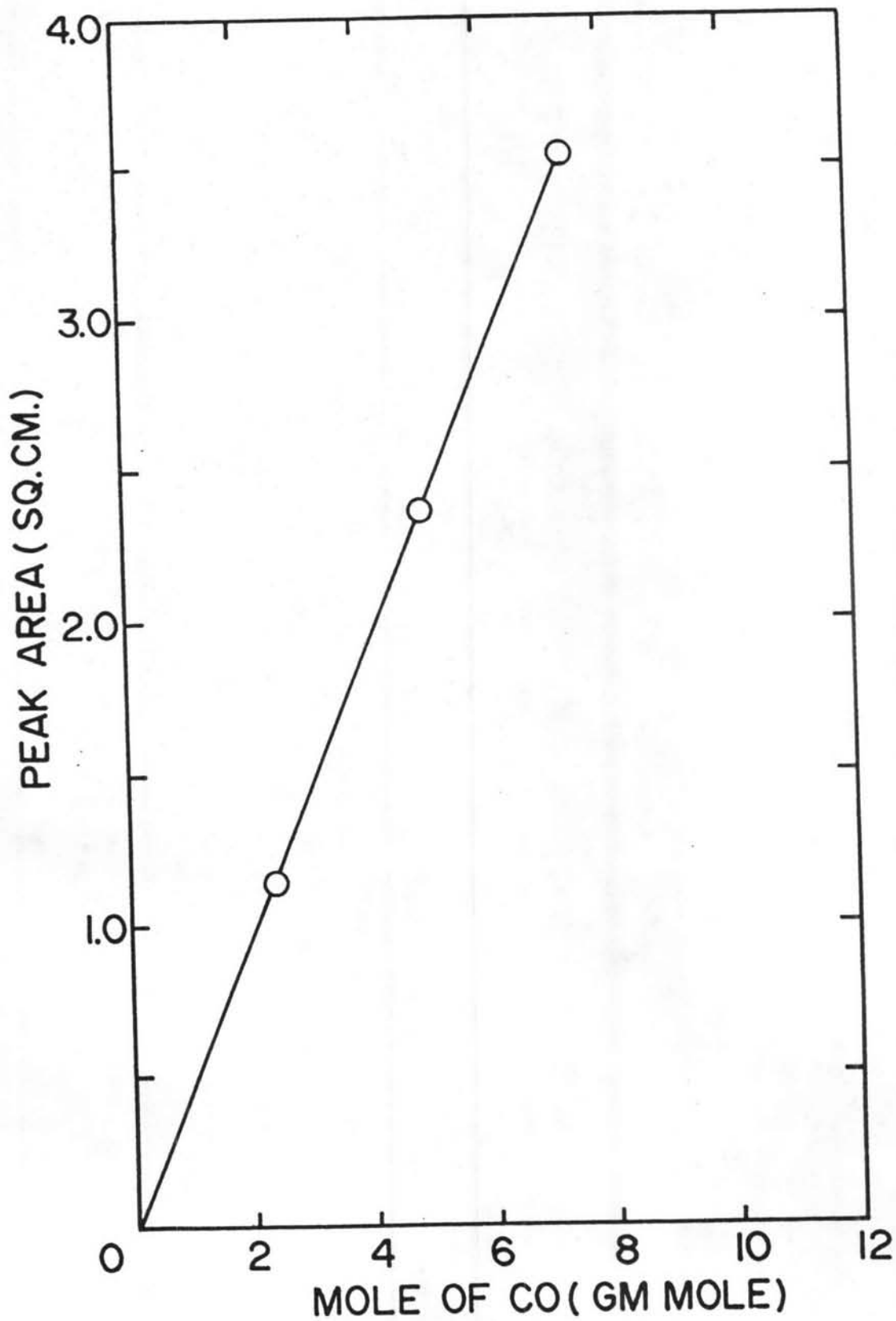


Figure 6.2 Calibration Curve of CO

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Carrier gas	: He
Carrier gas pressure	: 7.5 kg/cm ²
Carrier gas flow rate	: 32 ml/min
Current	: 60 mA

6.5 Experimental Results

The procedure of data analysis as well as an example of calculations of experimental results, is shown in detail in Appendix C. Appendix D also tabulates all analyzed experimental results. These are then plotted up for presentation in this section.

Figures 6.3-6.14 show the effects of temperature (280-380°C), pressure (20-40 atg) and gaseous hourly space velocity on total CO conversion (i.e. the amount of CO converted versus the amount CO present in the feed gas) and on product selectivities (i.e. the amount of CO reacted to form a specific product versus the total amount of converted CO). Figures 6.3-6.5 are for gaseous hourly space velocity (GHSV is defined here as the gaseous volume at 25°C, 1atm of synthesis gas (feed gas) fed per hour per unit volume of catalyst bed) around 1600 - 2400 hr⁻¹; Figures 6.6 - 6.8, for GHSV around 3500 - 3900 hr⁻¹; Figures 6.9 - 6.11, for GHSV around 6000 - 7000 hr⁻¹; and Figures 6.12 - 6.14 for GHSV around 13000 - 16000 hr⁻¹.

Figures 6.15 - 6.17 illustrate the effect of GHSV (3500 to 16000 hr⁻¹) on the space time yield of methanol in the temperature range of 280 - 380°C and pressure range of 20 - 40 atg. Similarly, Figures 6.18 - 6.20 show the effect of pressure (20 - 40 atg) on the space time yield of methanol in the temperature range of 280 - 380°C and GHSV range of 3500 - 16000 hr⁻¹.

6.6 Discussion of Experimental Results

Total CO Conversion in Methanol Synthesis

Figures 6.3 - 6.5 show how the relationship between total CO conversion and temperature is influenced by pressure in the case of low space velocity ($1600 - 2400 \text{ hr}^{-1}$). At 40 atg, total CO conversion gradually increases with temperature from 280 to 350°C , reaching a peak around 350°C . Total CO conversion then decreases against temperature above 350°C . As pressure decrease, the peak of total CO conversion appears to shift to a lower temperature. For example at 30 atg, and 20 atg, the peaks show up at 320°C and 300°C , respectively. In conclusion, the lower the pressure, the further the peak of total CO conversion shifts to the left.

In general, total CO conversion is found to decrease against increasing pressure. Since the present industrial methanol synthesis catalyst has not been designed for at low pressures (i.e. below 250 - 300 atg), hydrocarbon yields are found to be favored as pressure decreases from 40 to 20 atg in the present study. As a result, total CO conversion tends to decrease as pressure increases from 20 to 40 atg.

Figures 6.12 - 6.14 present the experimental results at high GHSV ($13000 - 16000 \text{ hr}^{-1}$). At 40 atg, total CO conversion is found to increase with temperature all the way to 360°C . As pressure decreases to 30 atg and 20 atg, the peak of total CO conversion shifts leftward to 345°C and 335°C , respectively. At high GHSV, total CO conversion appears to increase with increasing pressure because

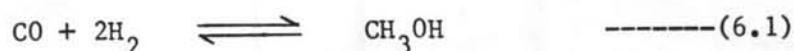
hydrocarbon yields remain nearly the same in the pressure range of 20 to 40 atg, while methanol yield always increases with pressure. Thus, total CO conversion increases as pressure rises from 20 to 40 atg.

Figures 6.6 - 6.11 show total CO conversion as a function of temperature with pressure as parameter at moderate GHSV. The effects of temperature and pressure on total CO conversion in Figures 6.6 - 6.8 are somewhat similar to those shown in Figures 6.3 - 6.5 for the case of low GHSV. From Figures 6.9 - 6.11, we see that total CO conversion at 30 atg is higher than at 20 and 40 atg, the peak of total CO conversion occurring around 340°C. At 20 and 40 atg, both corresponding peaks shift leftward to 300°C.

Methanol Selectivity

In theory and in practice, carbon monoxide and hydrogen can and do react to form products other than methanol. A list of possible side reactions is given in Table 6.2(2). An inspection of Table 6.2 reveals that the formation of paraffinic hydrocarbons (reactions 1-3,8) is favored thermodynamically over the formation of methanol at all temperatures. On the other hand, high pressures should have very favorable effect on reactions 4-7 and 9.

Now let's consider the methanol synthesis reaction



Since the reaction (6.1) is highly exothermic, its equilibrium constant K can be expected to decrease rapidly as temperature rises. Thus the equilibrium yield of methanol should decrease against

Table 6.2 Typical Side Reactions in Methanol Synthesis from Carbon Monoxide and Hydrogen.

Side reaction	ΔH_{25}°	ΔF_{25}°	ΔH_{327}°	ΔF_{327}°
(1) $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} (\text{g})$	-49,250	-33,970	-52,040	-17,270
(2) $2\text{CO} + 5\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6 + 2\text{H}_2\text{O} (\text{g})$	-82,960	-51,520	-87,585	-17,580
(3) $3\text{CO} + 7\text{H}_2 \rightleftharpoons \text{C}_3\text{H}_8 + 3\text{H}_2\text{O} (\text{g})$	-118,910	-71,095	-125,115	-20,830
(4) $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} (\text{g})$	-21,684	-5,900	-24,250	10,800
(5) $2\text{CO} + 4\text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 (\text{g}) + \text{H}_2\text{O} (\text{g})$	-49,250	-16,320	-52,850	18,720
(6) $2\text{CO} + 4\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} (\text{g}) + \text{H}_2\text{O} (\text{g})$	-61,190	-29,320	-64,610	4,520
(7) $3\text{CO} + 6\text{H}_2 \rightleftharpoons \text{C}_3\text{H}_7\text{OH} (\text{g}) + 2\text{H}_2\text{O} (\text{g})$	-98,800	-53,000	-103,660	-4,400
(8) $2\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{CO}_2$	-59,110	-40,780	-61,360	-21,220
(9) $3\text{CO} + 3\text{H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} (\text{g}) + \text{CO}_2$	-71,040	-36,140	-73,920	570
(10) $2\text{CO} \rightleftharpoons \text{C}(\text{s}) + \text{CO}_2$	-41,220	-28,640	-41,465	-15,730

temperature. On the other hand, the rate of reaction decreases rapidly as temperature drops. Thus a compromise in temperature is called for. Meanwhile, the equilibrium constant of methanol synthesis is favored by high pressure since the synthesis reaction involves a considerable volume contraction.

The above conclusions are confirmed by our simulation results. We clearly see from Figures 4.2 - 4.3 that the methanol synthesis rate gradually increases with temperature until a peak is reached at a certain temperature. Above this temperature, the rate starts to decline. Interestingly, as pressure decreases, the peak of methanol synthesis rate tends to shift to a lower temperature. Similarly, Figures 4.4 - 4.6 show the effects of temperature, pressure, GHSV on space time yield of methanol. We see from Figure 4.4 that as GHSV decreases, the maximum space time yield of methanol shifts to a lower temperature, and from Figures 4.5 , 4.6 that as pressure drops, the maximum space time yield of methanol also shifts leftward. Thus the combined effects of high GHSV and high pressure is found to shift the maximum space time yield of methanol to a high temperature. On the contrary, the maximum space time yield of methanol will be found at a relatively low temperature at low GHSV and low pressure.

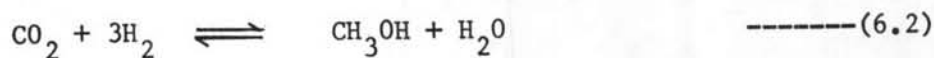
In the present work, methanol synthesis experiments are carried out at in the temperature range of 280 - 380°C as recommended by the catalyst manufacturer. The maximum pressure, however, is only 40 atg, a relatively low value compared to the recommended value of 300 atg; whereas the GHSV ranges from 1,600 - 16,000 hr^{-1} , still rather low when compared to 30,000 hr^{-1} . Therefore, the maximum space time yield of methanol appears to have shifted

below the above temperature. This partly explains why methanol selectivity in the present study rapidly decreases as temperature increases from 280°C to 360°C, as seen from Figures 6.3 - 6.5 for the case of low GHSV. In fact, thermodynamic consideration also clearly reveals that methanol yield should decrease as pressure falls.

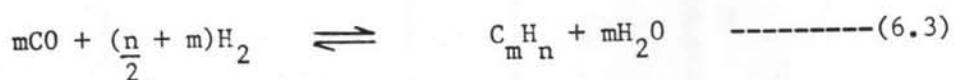
Figures 6.6 - 6.14 show that the effect of temperature on methanol selectivity at moderate to high GHSV is more complex within the pressure range of 20 - 40 atg.

Nevertheless, the effect of temperature may generally be divided into two sub-ranges for discussion. In the lower temperature sub-range, we see that methanol selectivity generally decreases as temperature increases. On the other hand, methanol selectivity tends to rise instead with temperature after temperature reaches the upper sub-range.

The tendency of methanol selectivity to decrease against temperature in the lower sub-range may be explained from thermodynamic and other considerations as in the case of low GHSV. The unexpected effect of temperature on methanol selectivity in the upper temperature sub-range, however, needs further elaboration. It is speculated that the unexpected increase in methanol selectivity is caused by hydrogenation of CO₂ to methanol according to the reaction



At relatively low temperatures, the above reaction should be negligibly slow when compared to the rate of hydrogenation of CO to methanol. At high temperatures, the role of CO₂ hydrogenation could be more visible. If this speculation is true, then we should observe a drop in CO₂ selectivity against temperature within the upper sub-range. Two other related side reactions are as follows :



Reaction (6.4) indicates that CO₂ must first be formed from CO and H₂O; whereas, before that H₂O must be formed from reaction (6.3).

From Figures 6.6 - 6.14 we see that total hydrocarbon selectivity remains very high within the upper temperature sub-range, even though it tends to decrease slightly as temperature increases. This means that there is ample supply of H₂O via reaction (6.3). This in turn appears to enhance the production of CO₂ via reaction (6.4), as we see from the figures that CO₂ selectivity is not only relatively high but also tends to rise with temperature within the upper sub-range. The ready availability of CO₂ (as well as H₂O) then accelerates the production of methanol via reaction (6.2). This finally helps to explain why methanol selectivity is observed to rise, though slightly, in the upper temperature sub-range.

Carbon Dioxide Selectivity

For the case of low GHSV, Figures 6.3 - 6.5 show that

- 1) at 40 atg CO₂ selectivity generally increases with temperature until reaching a peak at 350°C, after which it begins to decrease

against temperature, 2) at 20 atg, CO_2 selectivity is relatively high even at low temperatures (around 300°C), although at 40 and 30 atg, CO_2 selectivity is quite low at temperatures below 280°C . and 3) at temperatures below 300°C , CO_2 selectivity generally is favored by increasing pressure, whereas at high temperature, CO_2 selectivity does not vary with pressure (20 - 40 atg).

Figures 6.6 - 6.14 show that for the cases of moderate and high GHSV, CO_2 selectivity tends to increase with temperature in the range of $280-360^\circ\text{C}$ at 20 - 40 atg.

Total Hydrocarbon Selectivity

By "hydrocarbons" we mean all forms of hydrocarbons (methane, ethylene, etc.) that are observed during methanol synthesis.

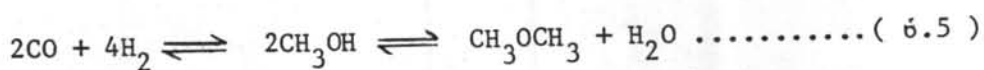
Figures 6.3 - 6.5 show that for the case of low GHSV total hydrocarbon selectivity increases with temperature in the range of $280 - 340^\circ\text{C}$, then decreases against increasing temperature. It generally decreases against pressure.

Figures 6.12 - 6.14 show that for the case of high GHSV, total hydrocarbon selectivity at 40 atg increases with temperature and peaks at 300°C before decreasing against temperature. As pressure increases from 20 to 30 atg, total hydrocarbon selectivity increases. It however decreases when pressure increases to 40 atg.

Figures 6.6 - 6.11 show that total hydrocarbon selectivity for the case of moderate GHSV is similar to the case of high GHSV (Figures 6.12 - 6.14)

Dimethyl Ether (DME) Selectivity

Figures 6.3-6.5 show that, for the case of low GHSV, though DME selectivity is enhanced by high pressure, its absolute value is quite small when compared to methanol selectivity in the low temperature range (280-310°C). It is speculated that most DME comes from dehydration of methanol, as follows



At high GHSV, DME is not detected, most probably because the residence time is too short for methanol to dehydrate further to DME.

Space Time Yield of Methanol

When methanol selectivity and total CO conversion are both high, the space time yield of methanol automatically is high. Figures 6.15-6.17 show the effect of temperature and GHSV on the space time yield (STY) of methanol. It is obvious from these figures that the space time yield of methanol is a strong function of temperature, rising at first with temperature up to a certain temperature before falling against temperature. We see from Figures 6.15-6.17 that STY of methanol also increases with GHSV. Similarly, it is enhanced by pressure, as seen in Figure 6.18-6.20. These general conclusion are in good agreement with the simulation results shown in Figures 4.4-4.6

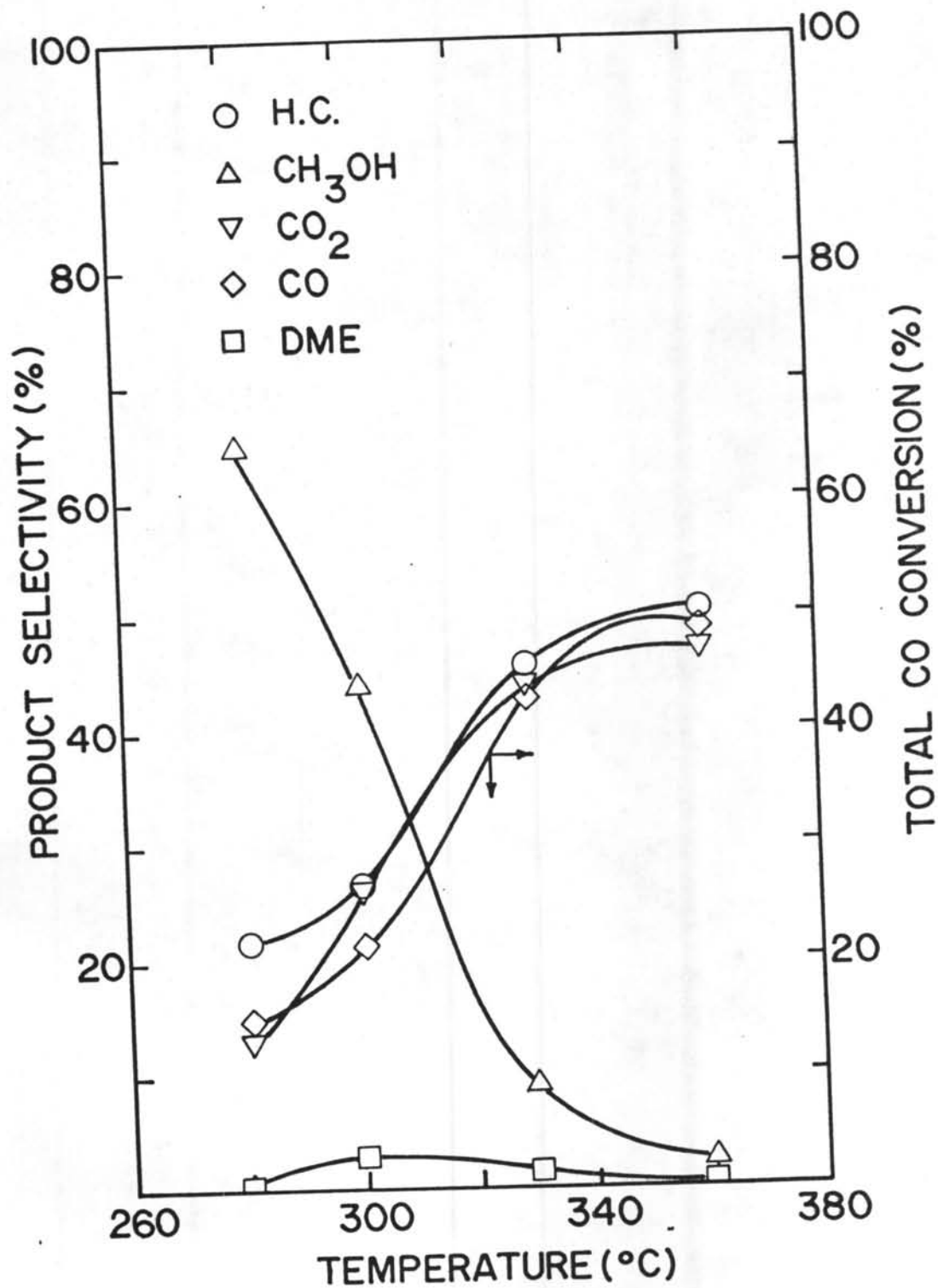


Figure 6.3 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 40 atg, 1700 hr⁻¹)

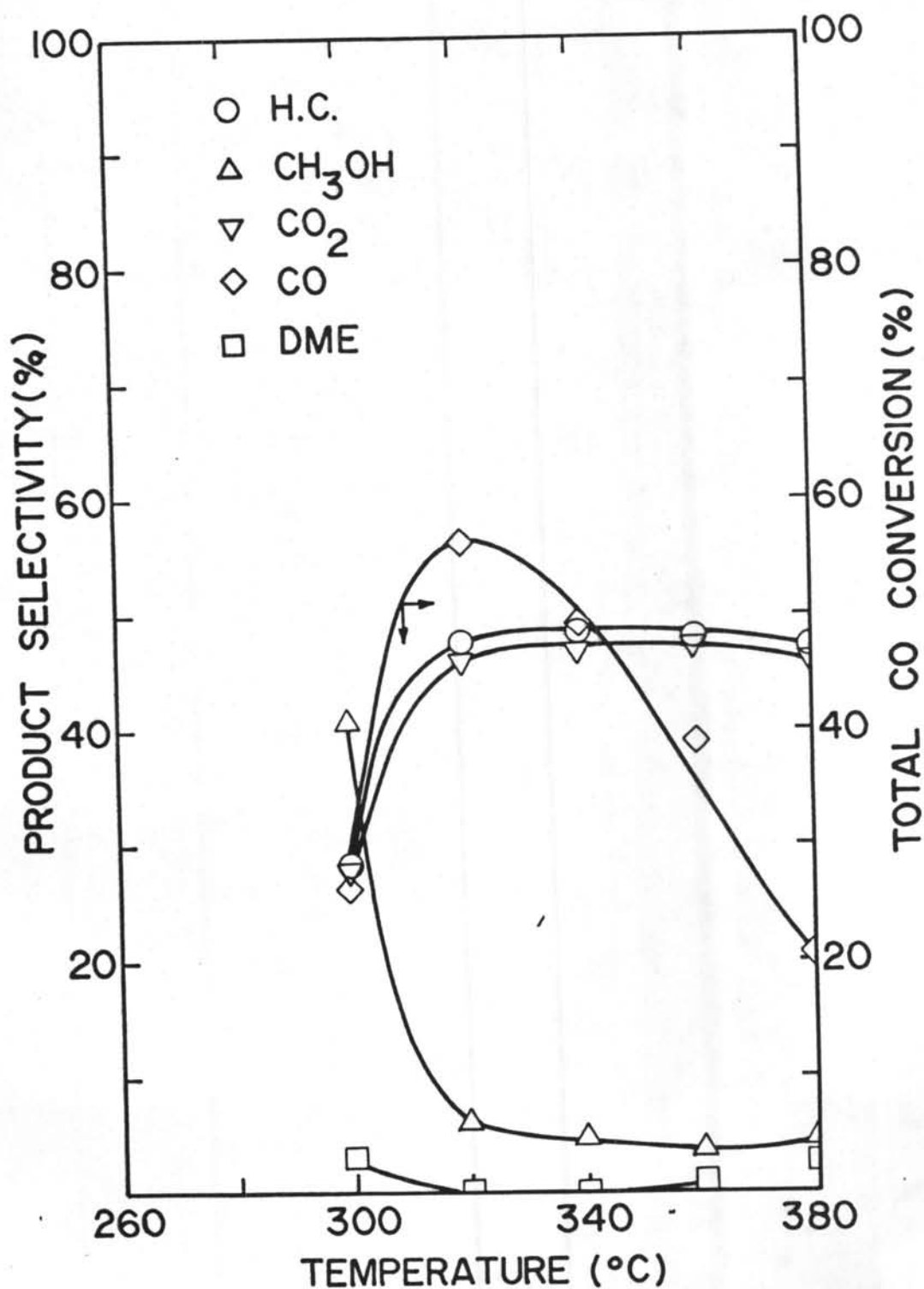


Figure 6.4 Effect of Temperature (300 to 380°C) on Total CO Conversion and Product Selectivities (at 30 atg, 2400 hr⁻¹)

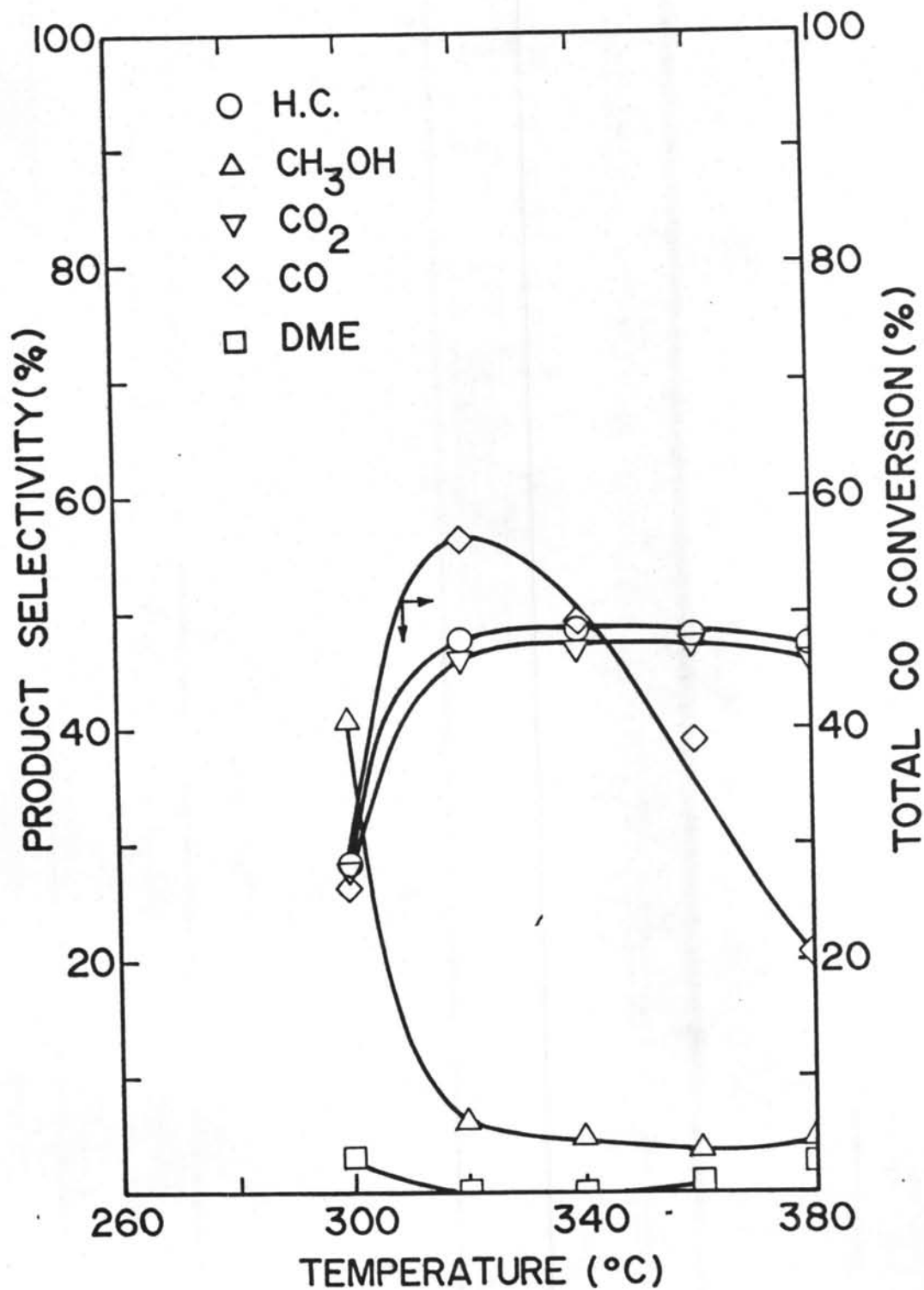


Figure 6.4 Effect of Temperature (300 to 380°C) on Total CO Conversion and Product Selectivities (at 30 atg, 2400 hr⁻¹)

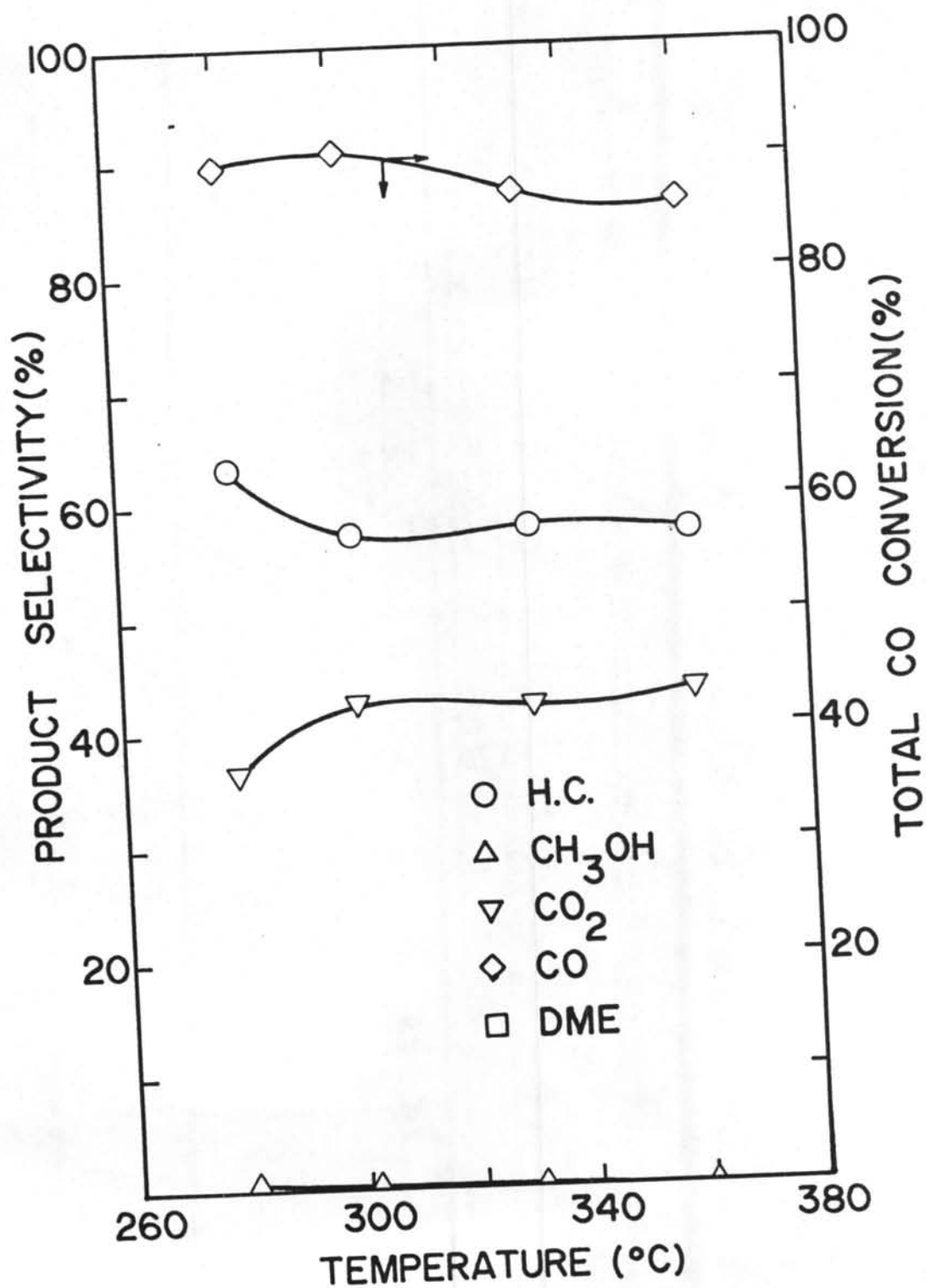


Figure 6.5 Effect of Temperature (280 to 360 °C) on Total CO Conversion and Product Selectivities (at 20 atg, 1600 hr⁻¹)

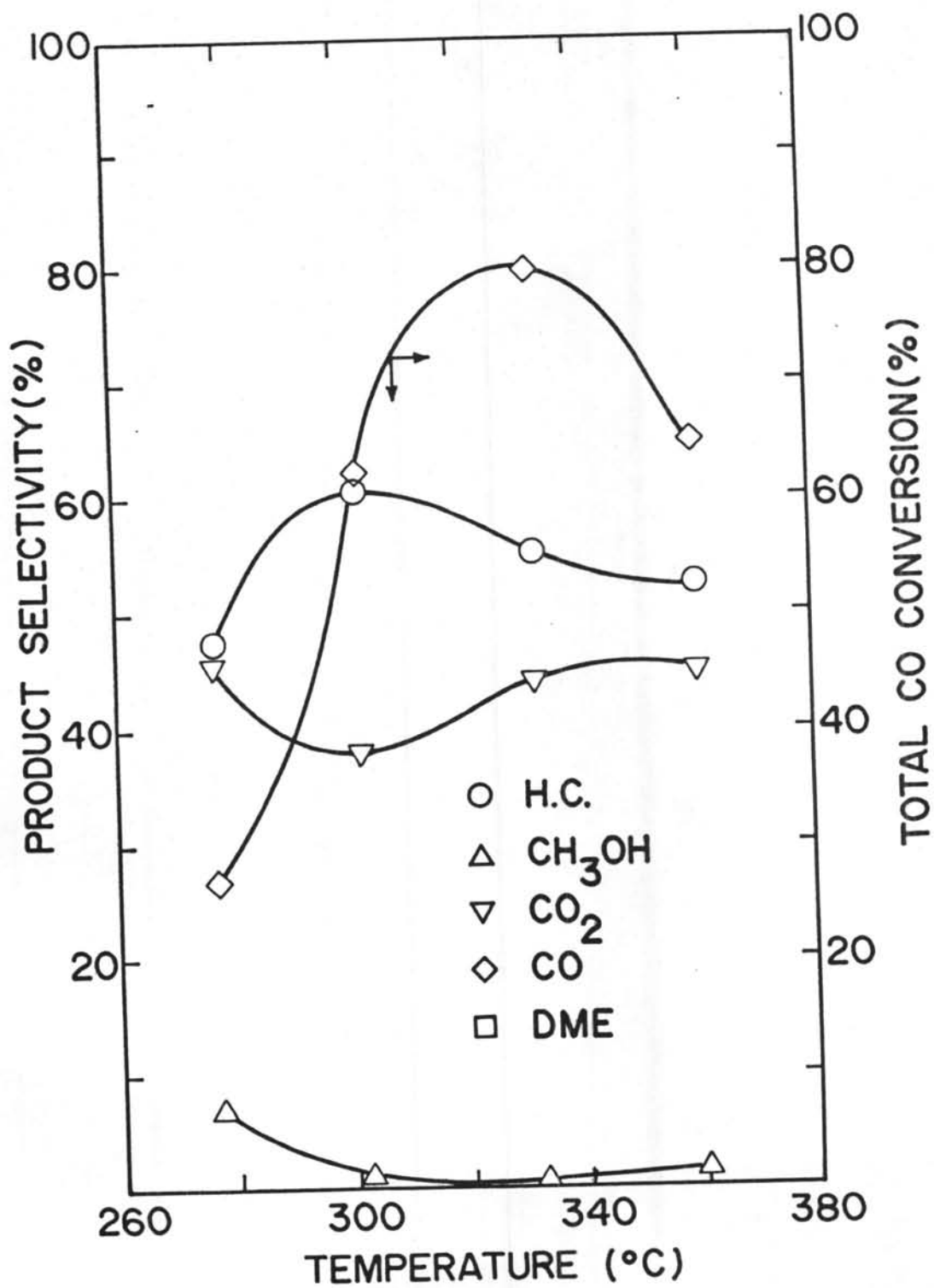


Figure 6.6 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 40 atg, 3900 hr⁻¹)

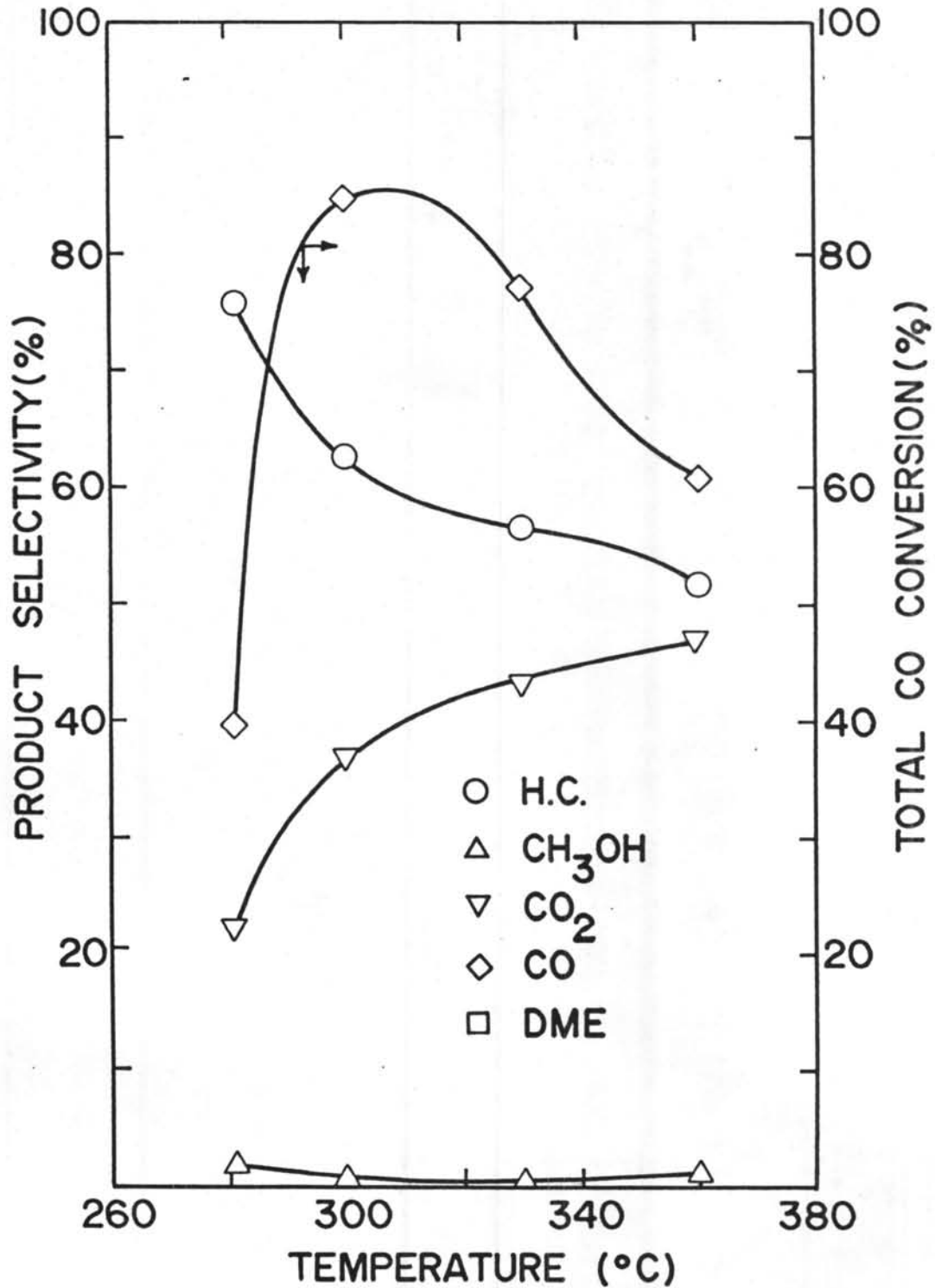


Figure 6.7 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 30 atg, 3500 hr⁻¹)

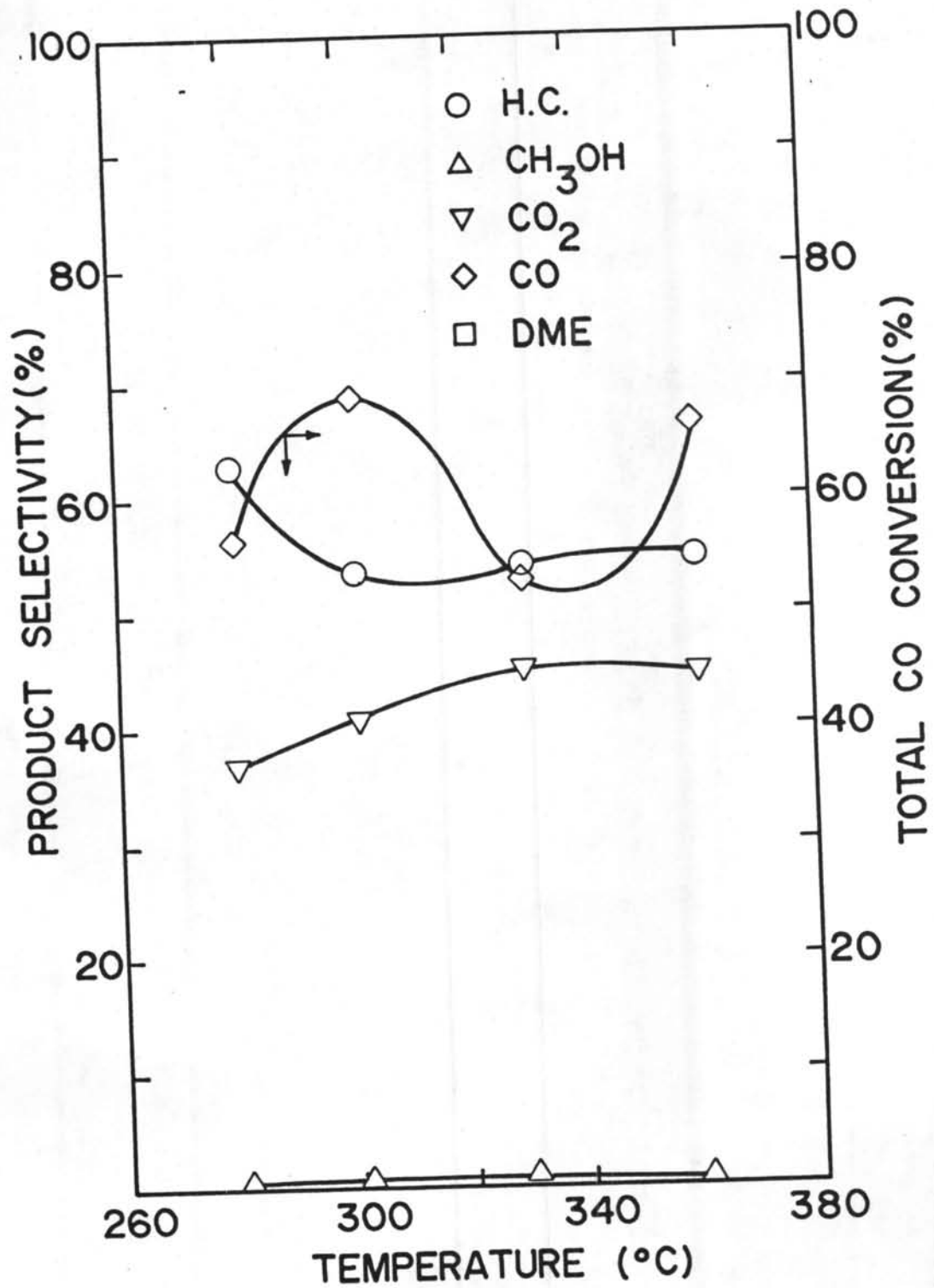


Figure 6.8 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 20 atg, 3700 hr⁻¹)

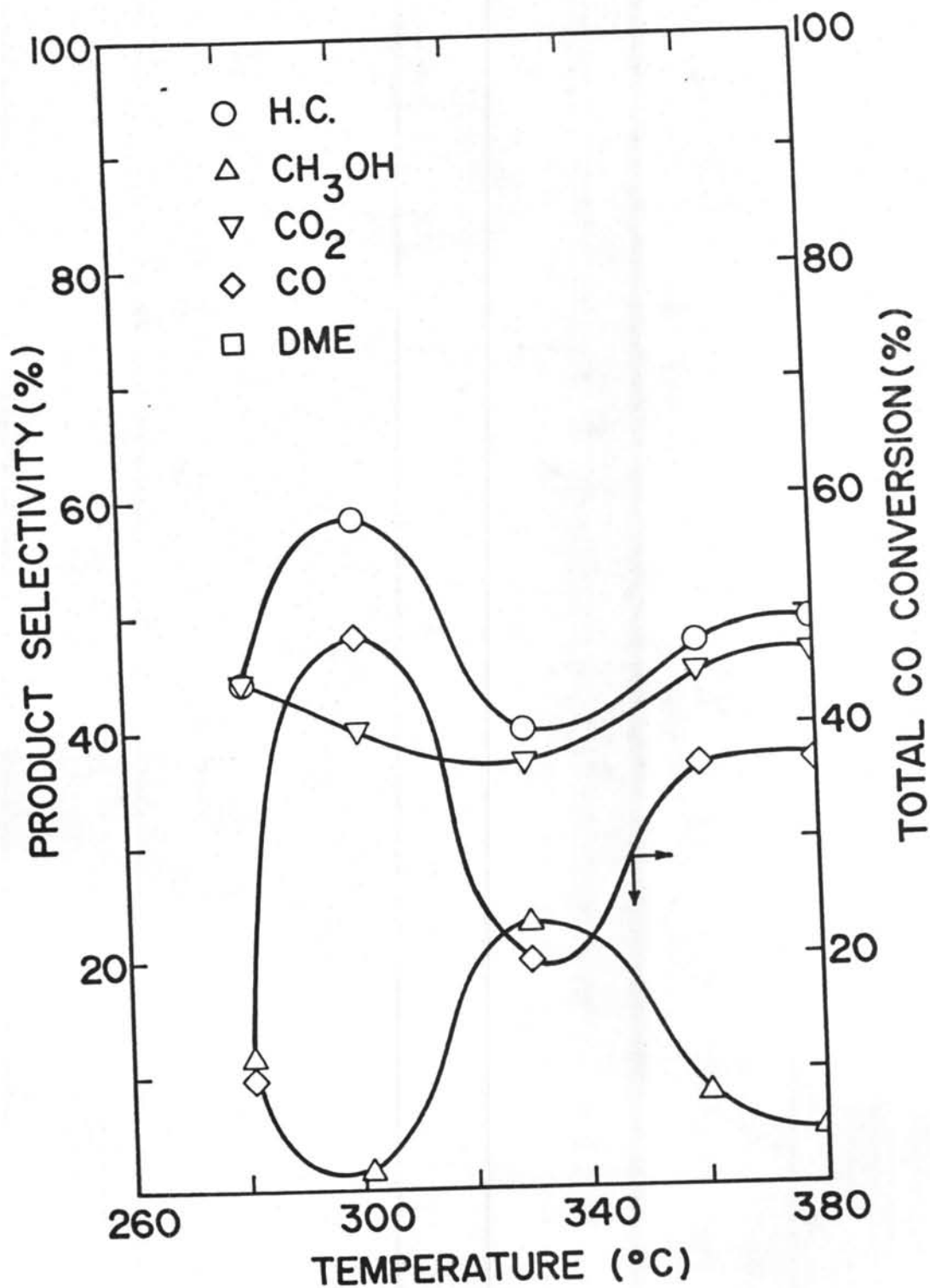


Figure 6.9 Effect of Temperature (280 to 380°C) on Total CO Conversion and Product Selectivities (at 40 atg, 7000 hr⁻¹)

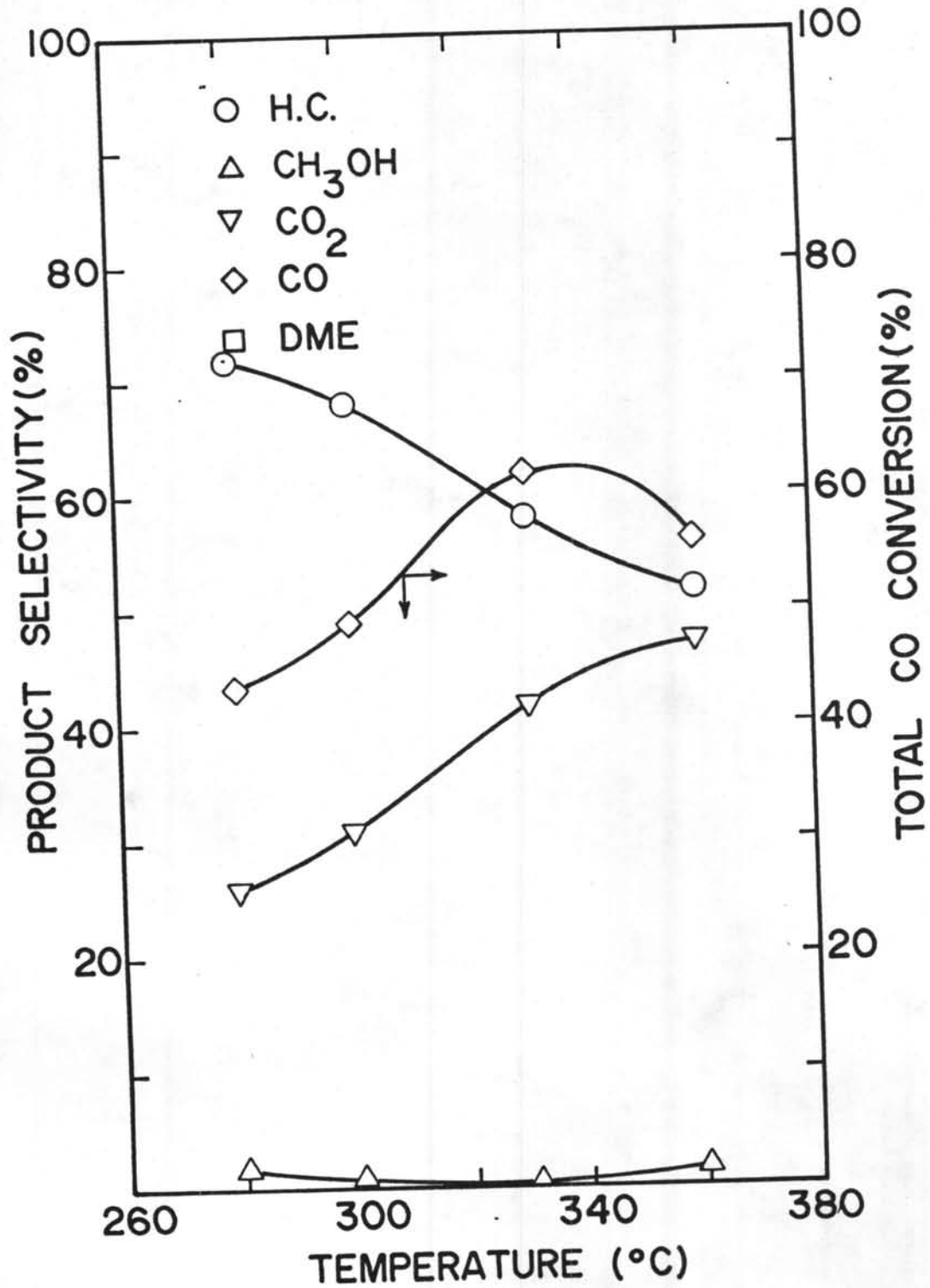


Figure 6.10 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 30 atg, 6700 hr⁻¹)

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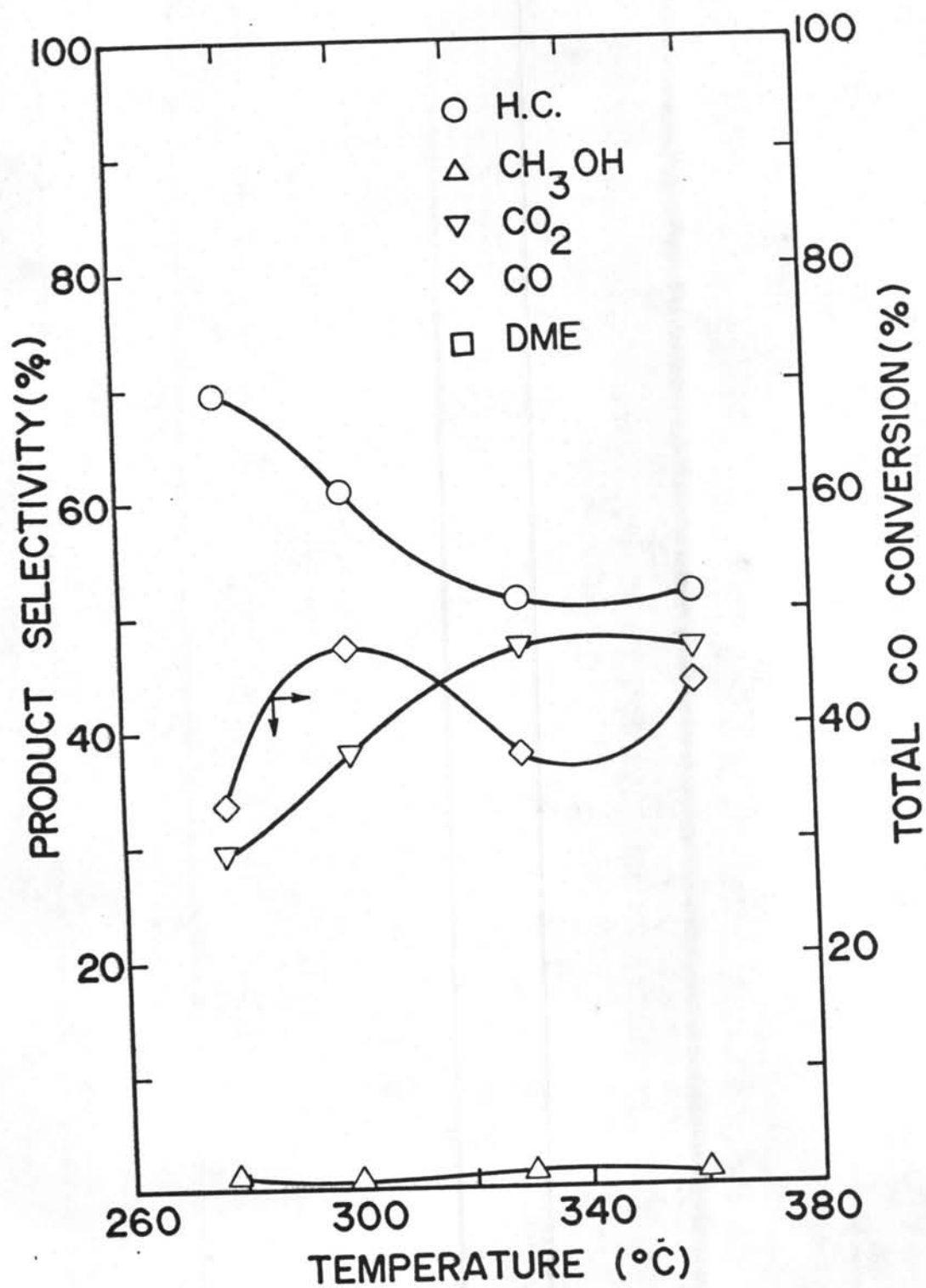


Figure 6.11 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 20 atg, 6000 hr⁻¹)

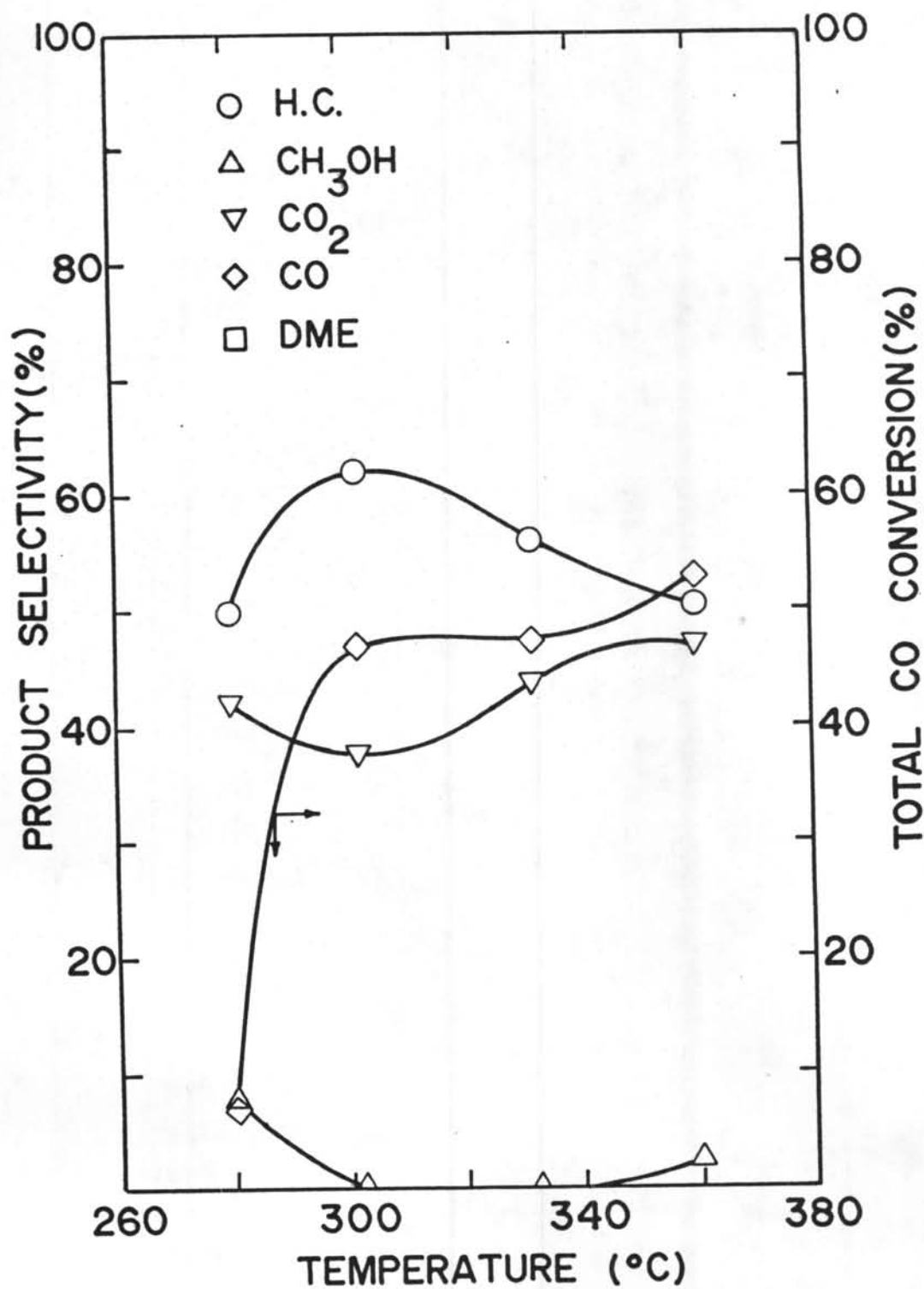


Figure 6.12 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 40 atg, 16000 hr⁻¹)

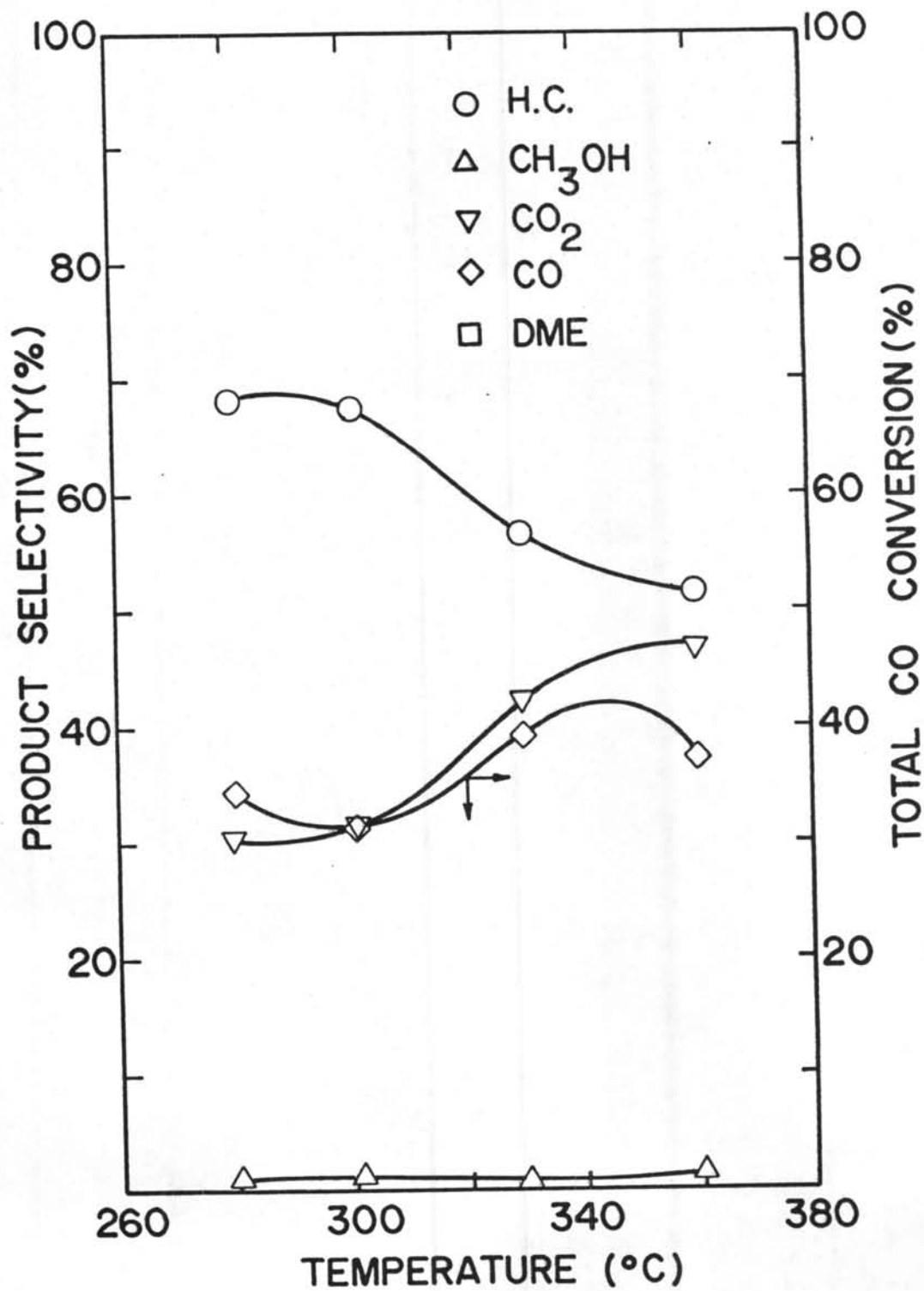


Figure 6.13 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 30 atg, 13000 hr⁻¹)

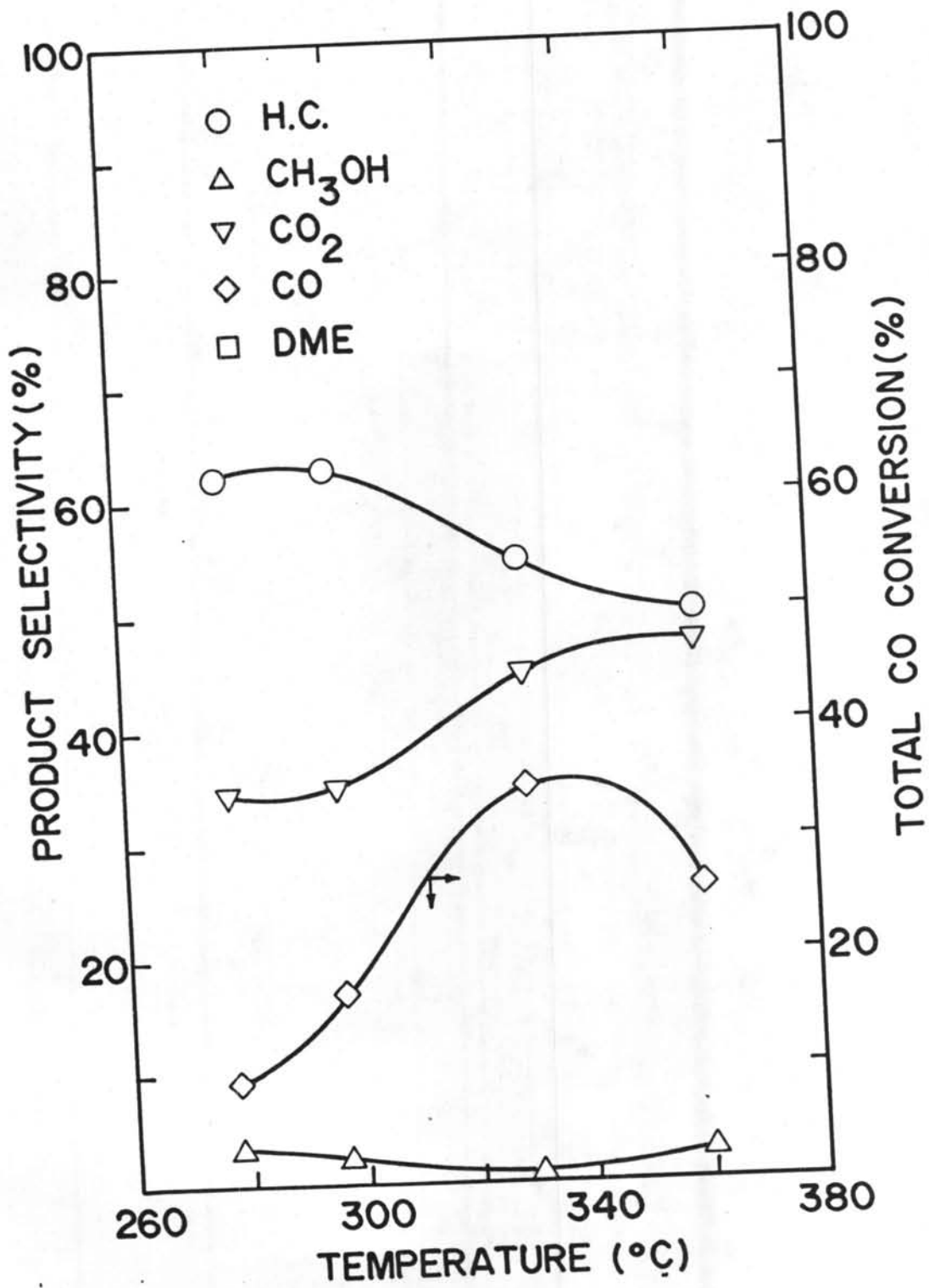


Figure 6.14 Effect of Temperature (280 to 360°C) on Total CO Conversion and Product Selectivities (at 20 atg, 13000 hr⁻¹)

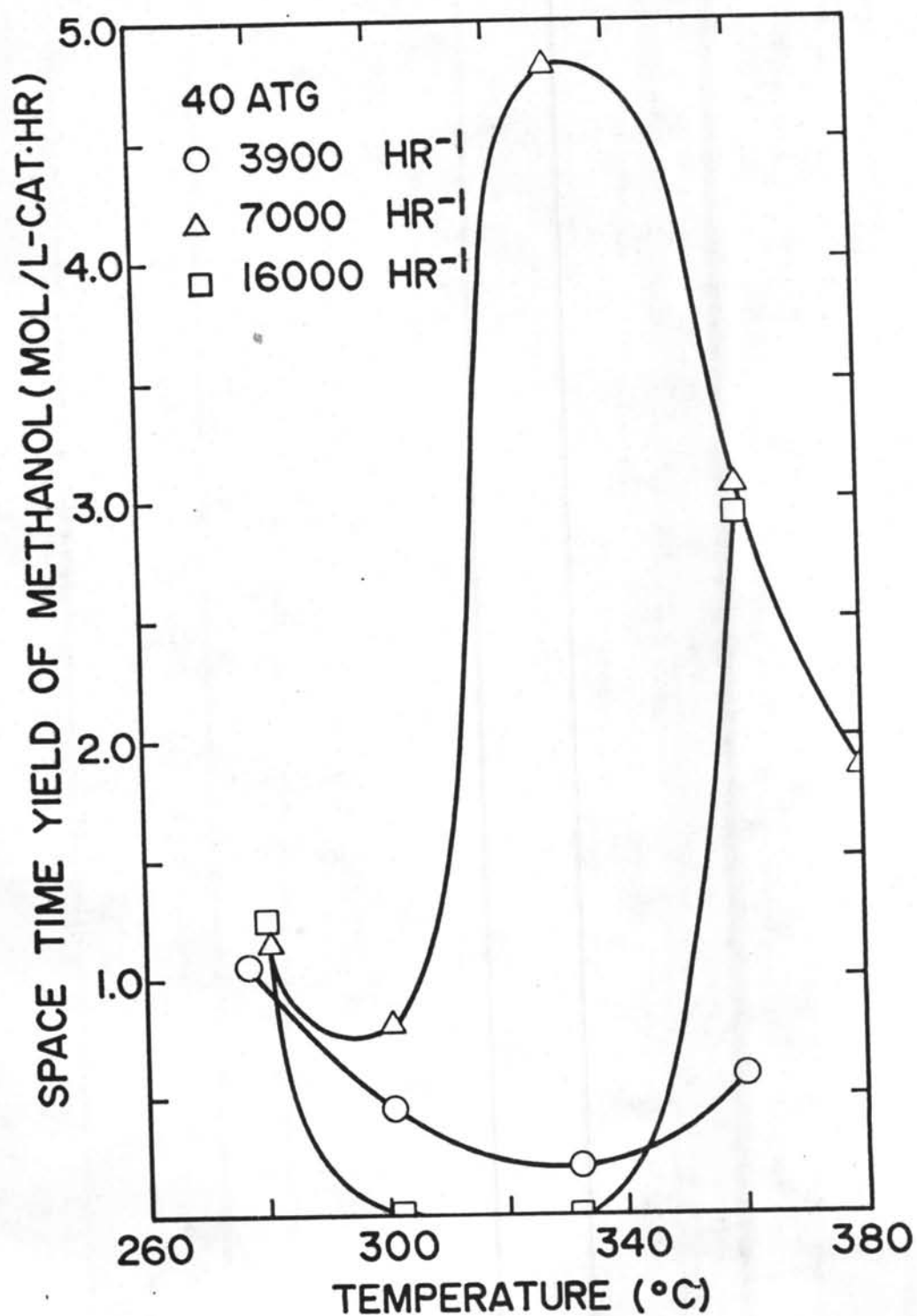


Figure 6.15 Effects of GHSV (3900 to 16000 hr⁻¹) and Temperature (280 to 380°C) on Space Time Yield of Methanol (at 40 atg)

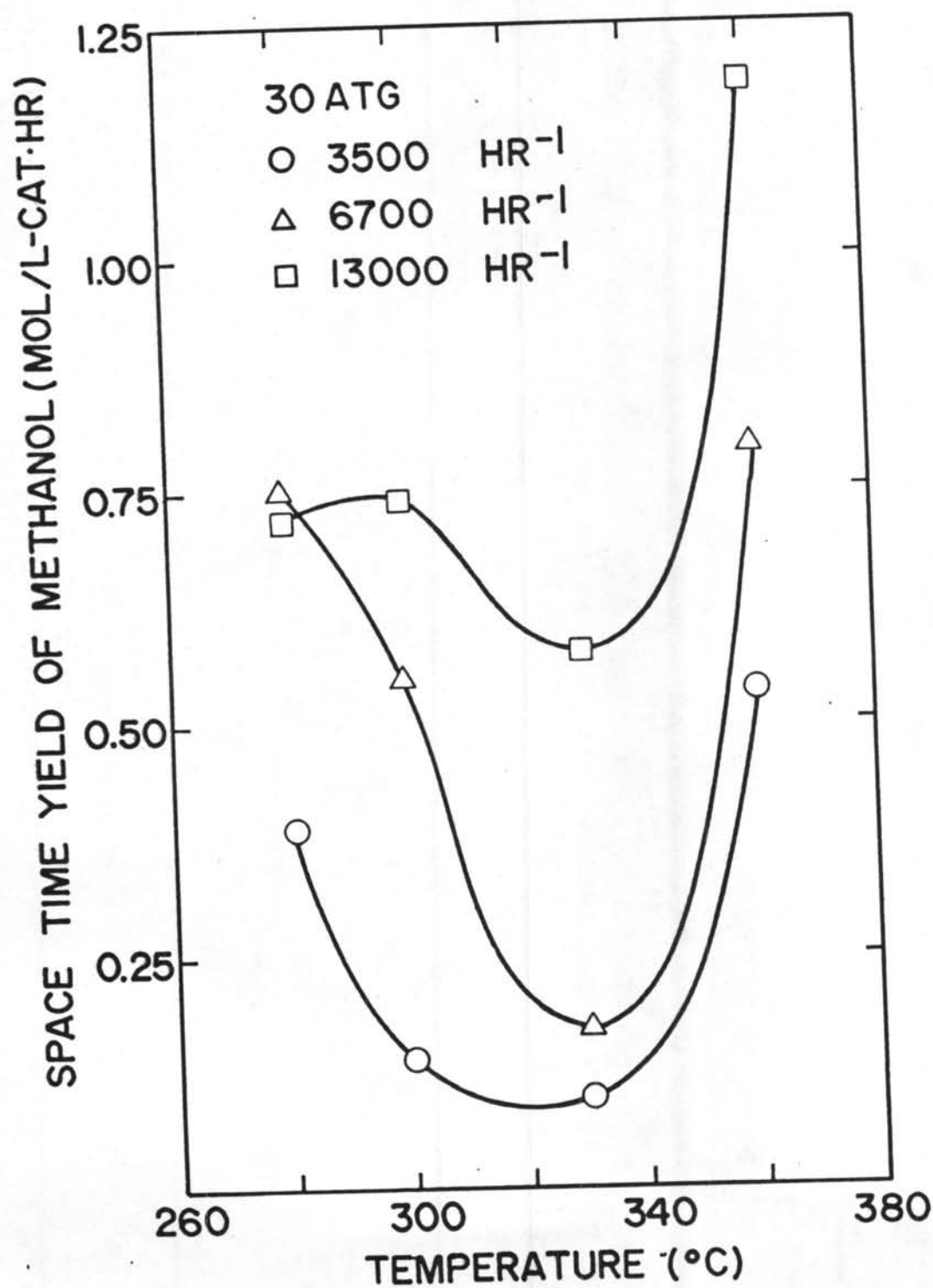


Figure 6.16 Effects of GHSV (3500 to 13000 hr⁻¹) and Temperature (280 to 360°C) on Space Time Yield of Methanol (at 30 atg)

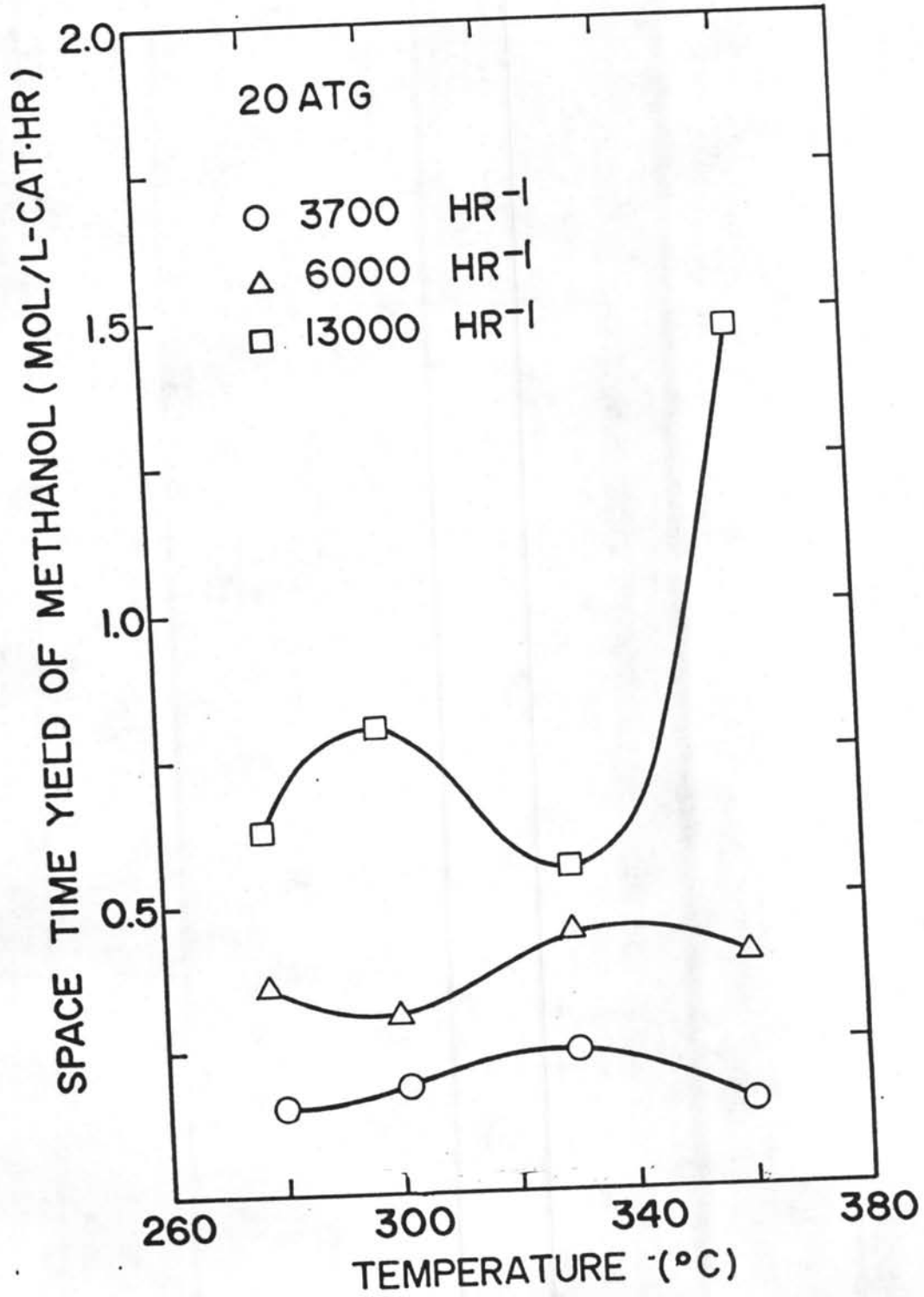


Figure 6.17 Effects of GHSV (3700 to 13000 hr⁻¹) and Temperature (280 to 360°C) on Space Time Yield of Methanol (at 20 atg)

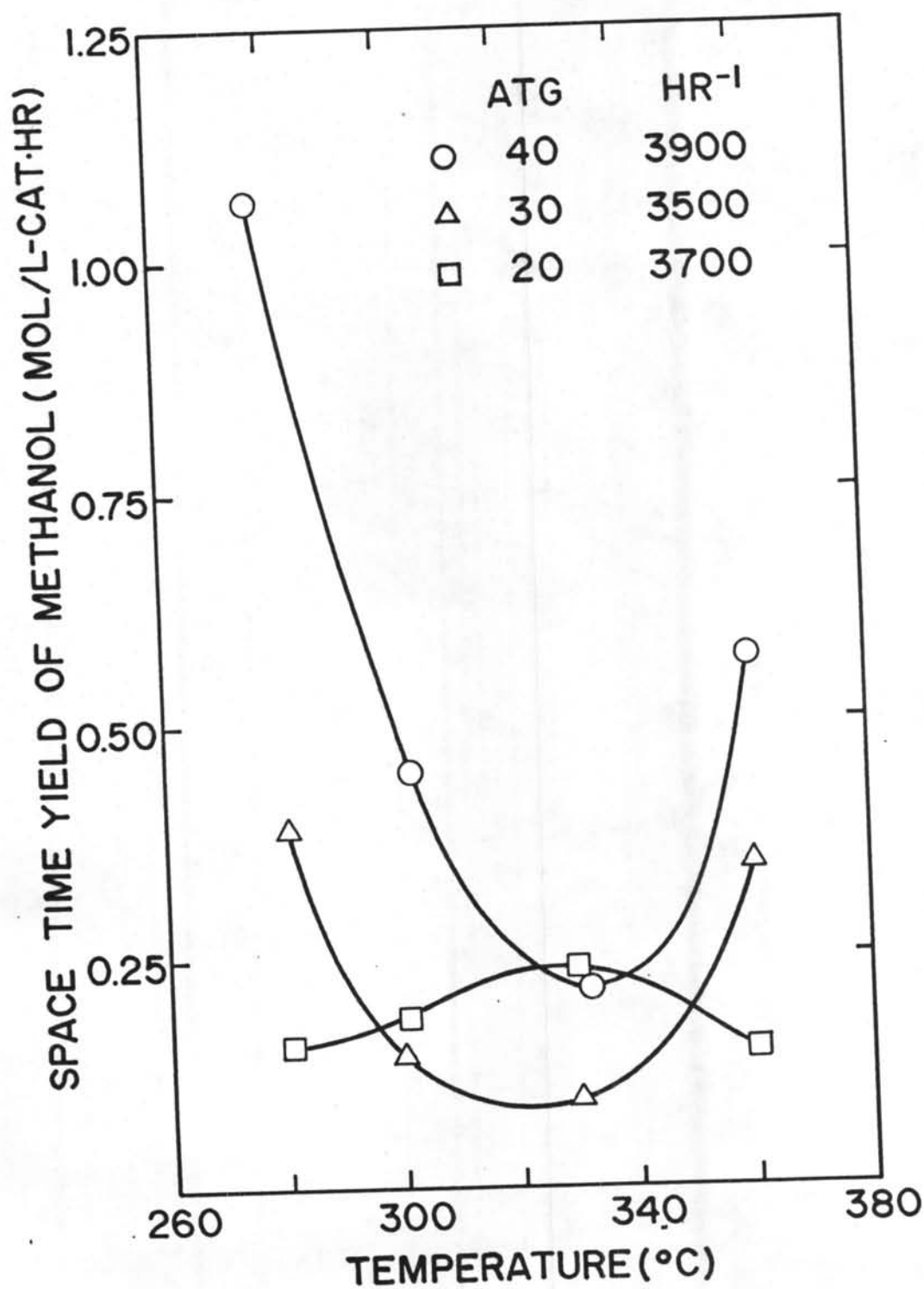


Figure 6.18 Effects of Pressure(20 to 40 atg) and Temperature (280 to 360°C) on Space Time Yield of Methanol (3500 to 3900 hr⁻¹)

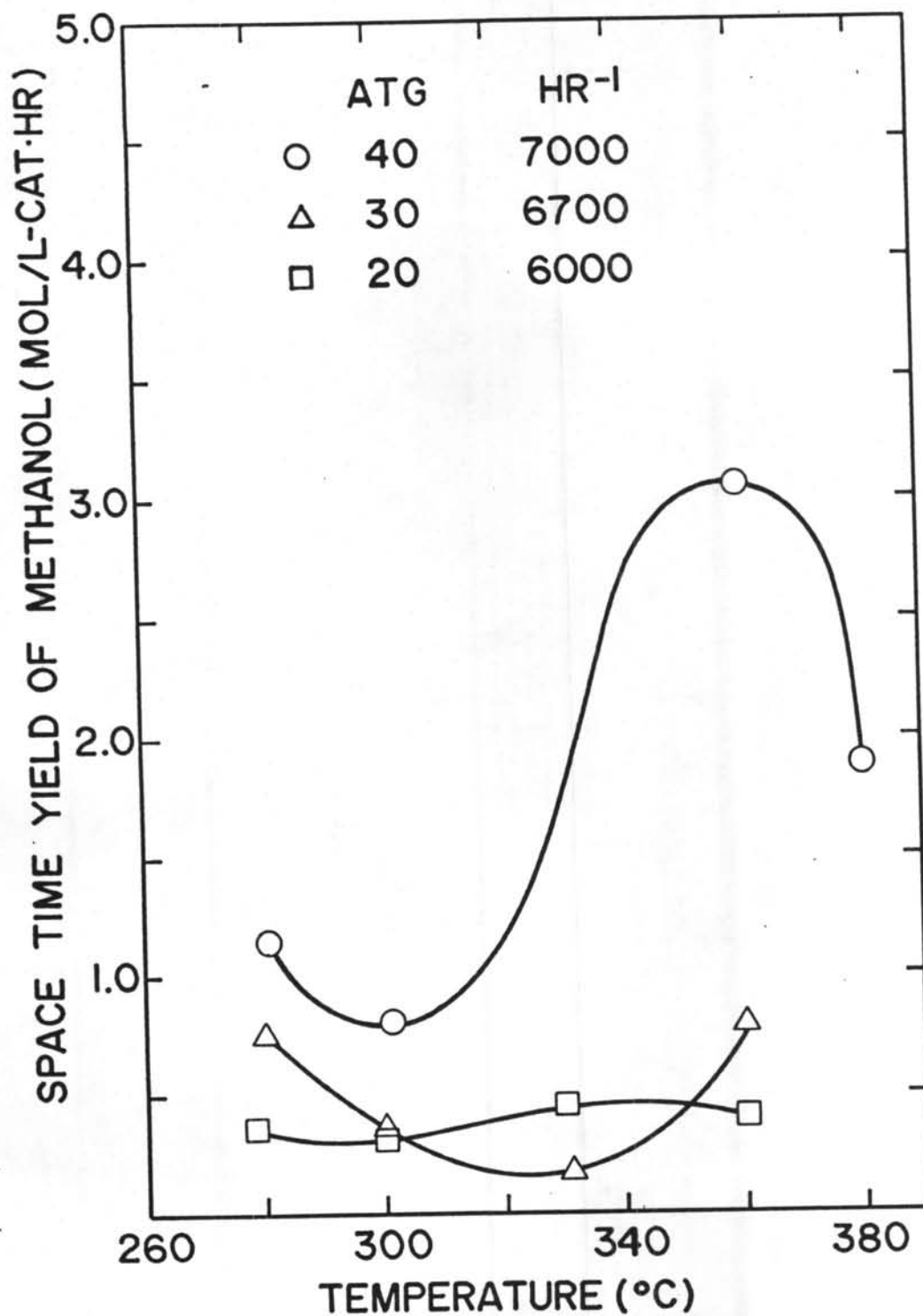


Figure 6.19 Effects of Pressure (20 to 40 atg) and Temperature (280 to 380 °C) on Space Time Yield of Methanol (6000 to 7000 hr⁻¹)

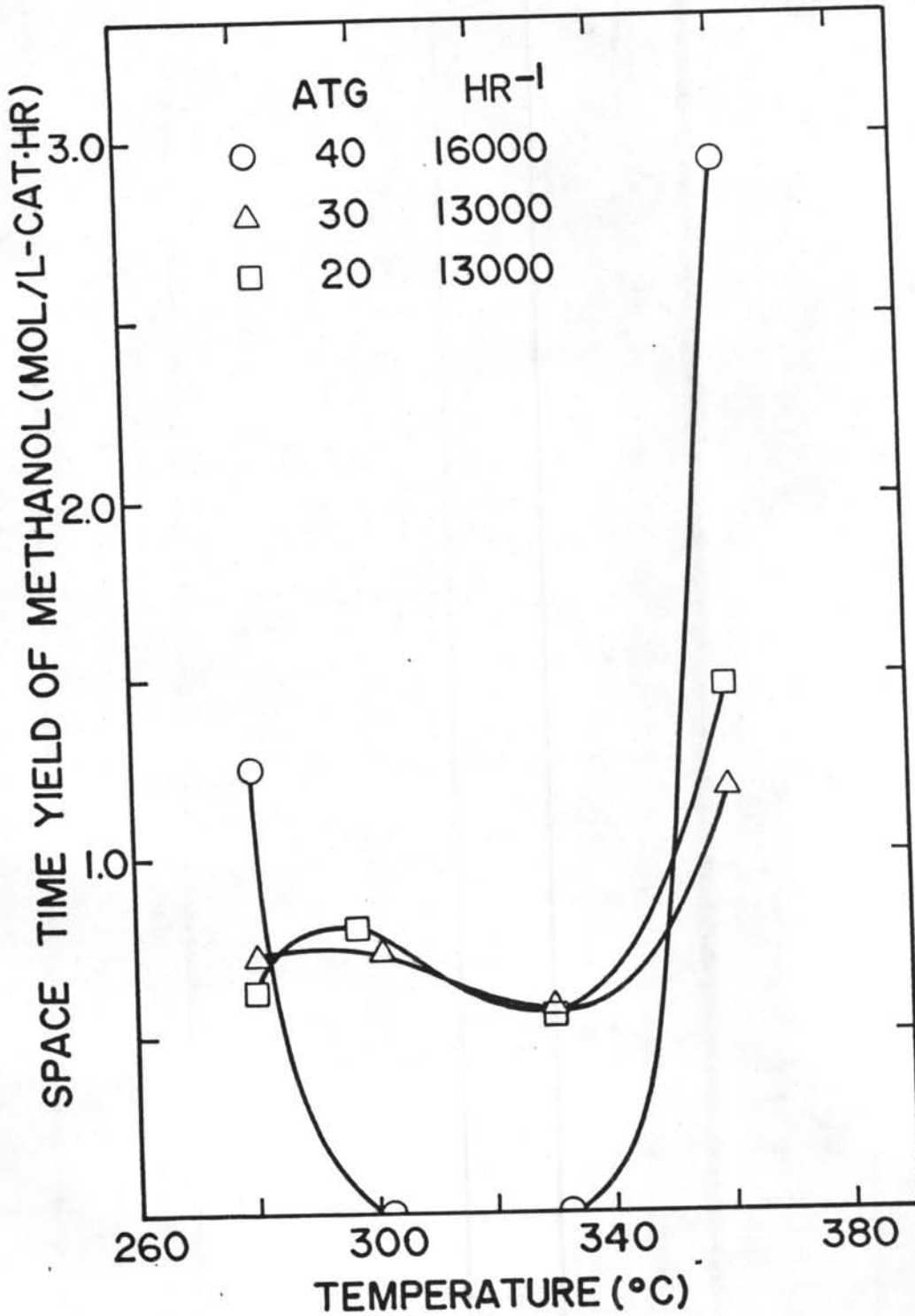


Figure 6.20 Effects of Pressure (20 to 40 atg) and Temperature (280 to 360 °C) on Space Time Yield of Methanol (13000 to 16000 hr⁻¹)

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