

CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Analytical Method

The Gas Chromatographic technique was used for analysing the outlet gas. First, a number of preliminary test runs of gas chromatographys were carried out to search for the appropriate condition for analysing the expected products from alcohol synthesis. Concurrently several runs of the synthesis reaction were carried out to yield preliminary results on the types of products that may be synthesized. Then the appropriate standard gases and substances were selected for preparing the calibration curves for the chromatograms. Figs. 5.1 and 5.2 show samples of the chromatograms obtained under the appropriate conditions with the two gas chromatographys, i.e. Shimadzu GC-8A1T and GC-8A1F. Figs. 5.3-5.6 show the calibration curves for hydrogen, carbon monoxide, methanol and ethanol. Other calibration curves are show in Appendix D.

5.2 Experimental Results

Four factors are investigated in this work. One is the reaction pressure, when the pressure increases, it means that the concentrations and the mean residence time of the reactants increase. Consequently the rate of reaction "i" increases too, if the rate expression is $-r_i = k_i C_a^n C_b^m$ and $n, m > 0$. Another factor is the GHSV. Increasing the GHSV means that the mean residence time decreases. The accompanying result may be considered under two conditions, i.e. when the conversion is low

and when it is high. In the case of a low conversion, the total moles of the product stream nearly equals the total moles of the feed stream. Thus the residence time essentially varies inversely to the GHSV. While at a high conversion, the total moles of the product stream is significantly less than the feed stream. Thus the residence time of the reactants increases. The third factor investigated in the present work is the reaction temperature. Due to the presence of the temperature T in the exponential term of the Arrhenius law, the rate of reaction strongly depends on temperature. Increasing the temperature will exponentially increase the rate of reaction. On the other hand, the concentrations of the gaseous reactants slightly decrease as temperature increases. In addition the residence time slightly decreases. On the overall, however, the rate of reaction should increase as temperature increase. The last factor investigated is the ratio of CO to H_2 in the feed gas, while the other factors are held constant.

The procedure of experimental data analysis as well as a detailed example of the calculations for the analysis of the experimental results is shown in **Appendix B**. **Appendix C** tabulates all the analyzed experimental results. The results are shown graphically in this chapter.

Figs. 5.7-5.62 show all the major results of the experiments under various conditions, as shown in **Table 4.1**. In the case of rhodium catalyst, investigated were the effects of temperature, pressure, GHSV and the feed composition of $\text{CO}:\text{H}_2$ on the total conversion of carbon monoxide (% CO conversion), selectivity of ethanol (% Se_{EtOH}), selectivity of total alcohols (% $\text{Se}_{\text{tot. alc.}}$), selectivity of hydrocarbons (C_1-C_6 paraffins, % Se_{HC}), space time yield of ethanol (STY_{EtOH}), space time yield of total alcohols ($\text{STY}_{\text{tot. alc.}}$), and space time yield of hydrocarbons (C_1-C_6 paraffins, STY_{HC}). For the other two

catalysts namely, $\text{Co}_1\text{Cu}_1\text{Cr}_{0.8}\text{K}_{0.096}$ and $\text{Co}_1\text{Ba}_{0.05}\text{Ag}_{0.01}/\text{SiO}_2$, the effects of the feed composition of syngas were not investigated because the limitation of syngas supply and the lack of explosion-proof gas compressor led to too low syngas pressure.

5.3 Rhodium Catalyst ($\text{Rh}_1\text{Mn}_1\text{Fe}_{0.1}/\text{SiO}_2$)

5.3.1 CO Conversion



Figs. 5.7-5.8 show the effects of temperature on the total conversion of carbon monoxide at various pressures and GHSV's i.e. at 40, 60 atg with GHSV $2,000\text{ hr}^{-1}$ and 80 atg with GHSV 1,000, 2,000, 4,000, 8,000 hr^{-1} , when the mole ratio of feed $\text{CO}:\text{H}_2 = 1:2$, whereas **Figs. 5.9-5.10** are the results for another ratio of feed $\text{CO}:\text{H}_2$ at 1.25:1. In the first case, as expected, the CO conversion generally increases somewhat as temperature increases, although there is some deviation at 60 atg and temperature above 310°C . This may be because the synthesis reaction is not a single reaction but a number of competitive reactions are present. Furthermore reduction of catalyst may take place. Since the experiments is no carried out daily the activity of the catalyst may change. Apart from the effect of pressure, the CO conversion decreases as the contact time decreases. That is as the GHSV increases. The effect is consistent at each experimental point.

When the feed ratio of CO to H_2 changes to 1.25:1, it is found that the CO conversion generally increases as the temperature increases. One exception is the run at $P = 80$ atg and $\text{GHSV} = 8,000\text{ hr}^{-1}$, in while at temperature above 280°C the CO conversion appears to be constant and slightly decreases. The cause may be that when carbon exists in excess in the feed, the observed rate of reaction is limited by the mass transfer effect.

Thus, as the GHSV increases, the CO conversion follows suit. While at $\text{GHSV} = 8,000 \text{ hr}^{-1}$ and temperature above 280°C . The observed rate of reaction becomes limited by the rate of reaction on the catalyst surface. In any case a decrease in contact time results in a decrease in the CO conversion, which is consistent with previously mentioned effect at a low GHSV, e.g. at $2,000 \text{ hr}^{-1}$. Generally, the CO conversion increases as pressure increases.

5.3.2 Selectivity of Ethanol (Se_{EtOH})

Figs. 5.11-5.12 show the effect of temperature on ethanol selectivity at $P = 40, 60 \text{ atg}$ with $\text{GHSV} = 2,000 \text{ hr}^{-1}$ and at $P = 80 \text{ atg}$ with $\text{GHSV} = 1,000, 2,000, 4,000$ and $8,000 \text{ hr}^{-1}$ when the feed ratio of $\text{CO}:\text{H}_2 = 1:2$. Generally ethanol selectivity decreases as temperature increases, except at $\text{GHSV} = 8,000 \text{ hr}^{-1}$ and $P = 80 \text{ atg}$, in which selectivity of ethanol increases as temperature increases from 250°C to 280°C and then decreases. Generally as pressure increases, the selectivity of ethanol increases. It is obvious from Fig. 5.11 that at $P = 60 \text{ atg}$ and temperature above 280°C the selectivity of ethanol is less than at $P = 40 \text{ atg}$.

Figs. 5.13-5.14 are similar to Figs. 5.11-5.12 except that the ratio of CO to H_2 is 1.25:1. As expected when the temperature increases, the ethanol selectivity generally decreases, except for the results at $P = 80 \text{ atg}$ and $\text{GHSV} = 1,000 \text{ hr}^{-1}$, in which the selectivity of ethanol increases as the temperature increases from 250°C to 280°C . This might be that other reactions become more favorable, e.g. hydrocarbon formation, methanol synthesis or even reduction reaction. As mentioned in 5.3.3, it appears that mass transfer may be the rate determining step at a low GHSV. The ethanol selectivity generally decreases as

GHSV increases because the ethanol synthesis rate might be faster than others. However the effect of pressure on the selectivity has no easily discernible trend.

5.3.3 Space Time Yield of Ethanol (STY_{EtOH})

On **Figs. 5.15 -5.16** show the relation between the space time yield of ethanol and temperature at various pressures, in the case of **Figs.5.15**, and at various GHSV, in the case of **Fig. 5.16**. Both cases are for the feed ratio of CO to $H_2 = 1:2$. Generally the STY_{EtOH} increases as pressure increases and gives an optimum temperature around $310^\circ C$ for each pressure. The effect of pressure is not always clear-cut. The effect of GHSV on STY_{EtOH} is found to be positive at temperature above $310^\circ C$, particularly when GHSV is above $4,000 \text{ hr}^{-1}$. While the effect of GHSV's is not significant at low temperatures.

Figs. 5.17 - 5.18 show the relation of STY_{EtOH} vs. temperature at various pressures and GHSV's, respectively. The feed ratio of $CO:H_2$ is $1.25:1$. As mentioned earlier, at low GHSV's the reaction rate is controlled by diffusion. Hence the STY_{EtOH} increases as GHSV increases especially at temperatures below $280^\circ C$. For each GHSV, there exists an optimum temperature which generally shifts lower as GHSV increases. At $GHSV = 4,000 \text{ hr}^{-1}$, the optimum temperature is represented by a broad peak. This is quite favorable for industrial operation. Unfortunately, its yield is about half of the maximum yield obtained at $GHSV = 8,000 \text{ hr}^{-1}$. Generally as the pressure increases the STY_{EtOH} also increases, and there appears to be an optimum temperature at most pressures.

5.3.4 Selectivity of Total Alcohol ($Se_{tot. alc.}$)

Figs. 5.19-5.20 show the relation of total alcohol selectivity vs. temperature at various pressures and GHSV's when the feed ratio of $CO:H_2 = 1:2$. The total alcohol selectivity is obtained from the summation of methanol, ethanol, n-propanol and i-propanol selectivities. The selectivity of total alcohols generally decreases as the temperature and pressure increase. There are some deviations from the above trend. For example, at 40 atg and $310^\circ C$ the selectivity inexplicably increases as temperature increases and at temperature above $310^\circ C$ the selectivity at 60 atg is lower than at 80 atg. The effect of GHSV appears to be quite complex. Nevertheless, it can be said that the selectivity decreases as temperature increases particularly at the highest temperature ($340^\circ C$). Because many reaction steps are involved in the synthesis of the numerous alcohols, the overall characteristics may be quite difficult to arrive at.

Figs. 5.21-5.22 are similar to Figs. 5.19-5.20 but they are for the feed ratio of $CO:H_2 = 1.25:1$. The relation of GHSV vs. temperature shows a simpler pattern than above and generally the total alcohol selectivity decreases as temperature and GHSV increases. Except at $GHSV = 1,200 \text{ hr}^{-1}$, where a sinusoidal curve is observed at 40 atg. The effect of pressure on selectivity is negative. So the selectivity decreases as pressure increases. This conclusion however has some exceptions. For examples, a sinusoidal relation is observed at 40 atg, and an optimum temperature exists at 60 atg.

5.3.5 Space Time Yield of Total Alcohols ($STY_{tot. alc.}$)

Figs. 5.23-5.24 show the relation of the space time yield of total alcohols vs. temperature at various pressures and

GHSV's for the feed ratio of $\text{CO}:\text{H}_2 = 1:2$. Generally the $\text{STY}_{\text{tot. alc.}}$ increases as pressure decreases. This means that the effect of the selectivity on space time yield is greater than that of the conversion. Typically the space time yield of total alcohols increases with the temperature and reaches an optimum at a rather high temperature, ca. 340°C . However at 60 atg, the optimum temperature is at 310°C . Generally the space time yield of total alcohols increases with the GHSV, and likewise the optimum temperature increases as GHSV increases.

In Figs. 5.25-5.26, are similar to Figs. 5.23-5.24 excepted that the feed ratio of $\text{CO}:\text{H}_2$ equals 1.25:1. In the region of diffusion control, i.e. at GHSV below $4,000 \text{ hr}^{-1}$, the $\text{STY}_{\text{tot. alc.}}$ increases as GHSV increases. Generally a higher GHSV gives a lower optimum temperature. The effect of pressure on $\text{STY}_{\text{tot. alc.}}$ is such that a higher pressure gives a lower optimum temperature.

5.3.6 Selectivity of Hydrocarbons (% Se_{HC})

Although the main objective of this investigation is the synthesis of alcohols, the actual products consists of a wide distribution of hydrocarbons. They are mostly methane, ethane, propane, propylene and i-butane. Thus it is worthwhile to consider the hydrocarbons selectivity vs. temperature at various pressures, and GHSV's. As shown in Figs. 5.27-5.28 for the feed ratio of $\text{CO}:\text{H}_2 = 1:2$, the hydrocarbon selectivity typically increases along with the pressure and temperature. It may be that the hydrogenation reactions become favourable at higher temperatures. At 310°C and above the selectivity of hydrocarbons at 60 atg is less than that at 40 atg. The same trend is also found in the case of ethanol selectivity and total alcohols

selectivity. Generally a higher GHSV gives a lower selectivity. It usually increases with the temperature, except at GHSV $2,000 \text{ hr}^{-1}$, where a broad optimum temperature is observed.

For the feed ratio of $\text{CO}:\text{H}_2 = 1.25:1$, as shown in Figs. 5.29-5.30, the selectivity of hydrocarbons is exceptionally high at 80 atg. The effect of temperature on selectivity of hydrocarbons shows a sinusoidal pattern at pressures 40 and 80 atg, while at 60 atg it gives a optimum temperature at ca. 310°C . A sinusoidal pattern is also obtained at various GHSV's.

5.3.7 Space Time Yield of Hydrocarbons (STY_{HC})

Figs. 5.31-5.32 show the relation of space time yield of hydrocarbon vs. temperature at various pressures and GHSV's for the feed ratio of $\text{CO}:\text{H}_2 = 1:2$. Generally the STY_{HC} increases as the temperature and pressure increases. The effect of GHSV on STY_{HC} is such that the STY_{HC} increases with the GHSV and there appears an optimum GHSV around $4,000 \text{ hr}^{-1}$. Furthermore, STY_{HC} also increases with the temperature.

Figs. 5.33-5.34 are similar to Figs. 5.31-5.32 but they are for the feed ratio of $\text{CO}:\text{H}_2 = 1.25:1$. It is found that at 80 atg the STY_{HC} is significantly higher than at lower pressures, and the STY_{HC} increases with the temperature at all pressures. The effect of GHSV shows that the space time yield of hydrocarbon is diffusion controlled at a high temperature and reaction controlled at low temperatures. An optimum temperature appears at GHSV = $8,000 \text{ hr}^{-1}$.



5.4 Catalyst No. 2 ; $\text{CO}_2\text{Ba}_{0.05}\text{Ag}_{0.01}/\text{SiO}_2$

5.4.1 CO Conversion

Figs. 5.35-5.36 show the relation of carbon monoxide conversion vs. temperature at various pressures and GHSV's for the feed ratio of $\text{CO}:\text{H}_2 = 1.25:1$. Generally CO conversion increases with the temperature. Apparently the conversion of carbon monoxide decreases as pressure and GHSV increase. Some deviations are found at $2,000 \text{ hr}^{-1}$ and a temperature above 310°C , where conversion is lower. This may be attributed to the time history of the experimental work. The experiment is carried out at $2,000 \text{ hr}^{-1}$ on the first day and then carried out at $1,000 \text{ hr}^{-1}$ and $4,000 \text{ hr}^{-1}$ on the following days. The conversion for the latter two GHSV's is found to be nearly the same at each temperature.

5.4.2 Selectivity of Ethanol (% Se_{EtOH})

Figs. 5.37-5.38 show the selectivity of ethanol vs. temperature at various pressures and GHSV's. The feed ratio of $\text{CO}:\text{H}_2$ is $1.25:1$. At low temperatures, i.e. below 200°C , the selectivity of ethanol decreases as pressure increases. The trend is reversed at high temperatures. There seems to be an optimum temperature at each pressure, except for 60 atg. Likewise an optimum temperatures is observed at each GHSV.

5.4.3 Space Time Yield of Ethanol (STY_{EtOH})

In Figs. 5.39-5.40, the space time yield of ethanol vs. temperature is plotted at various pressures and GHSV's for the feed $\text{CO}:\text{H}_2 = 1.25:1$. Except for 60 atg, the pressure does not significantly affect the space time yield of ethanol. An optimum

temperature occurs in the same range, ca. 310°C , both at for 40 and 80 atg, and at GHSV 2,000 and $4,000\text{ hr}^{-1}$. Generally, at low temperatures, ca. $250\text{--}280^{\circ}\text{C}$, the trend is the reverse of that at temperature above 280°C , the result for $\text{GHSV} = 1,000\text{ hr}^{-1}$ shows a sinusoidal trend as temperature increases.

5.4.4 Selectivity of Total Alcohols ($\text{Se}_{\text{tot. alc.}}$)

Figs. 5.41-5.42 show the selectivity of total alcohols at various pressures and GHSV's. Below 310°C , the selectivity of total alcohols increases as temperature increases, and reaches an optimum temperature at ca. 310°C . An exception is at 60 atg where the selectivity of total alcohols decreases monotonically with the temperature. The selectivity of total alcohols at 250°C , 60 atg is higher than that of all other conditions. This same result is also observed for the selectivity of ethanol. The selectivity at low temperatures typically increases as GHSV increases. At $4,000\text{ hr}^{-1}$ the selectivity decreases monotonically with the temperature, whereas at other GHSV's it has an optimum temperature.

5.4.5 Space Time Yield of Total Alcohols ($\text{STY}_{\text{tot. alc.}}$)

From Fig. 5.43, it may be concluded that the space time yield of total alcohols generally increases with temperature and has an optimum temperature. A higher pressure gives a lower optimum temperature as well as a lower space time yield at the same temperature. Fig. 5.44 shows the relation of GHSV vs. temperature. A higher GHSV gives a higher optimum temperature for $\text{STY}_{\text{tot. alc.}}$.

5.4.6 Selectivity of Hydrocarbon (% Se_{HC})

Fig. 5.45 shows that the selectivity of hydrocarbon increases as pressure and temperature increases, except at 60 atg where an optimum temperature exists. The main hydrocarbons are methane, ethane and propane. As temperature increases the hydrogenation reaction and C-O bond breaking become more favorable. Also larger molecules are observed at higher temperatures. In Fig. 5.46, the selectivity of hydrocarbon generally increases as temperature increases at the same GHSV. There appears to be an optimum temperature at $1,000 \text{ hr}^{-1}$ and $4,000 \text{ hr}^{-1}$, but this is not evident at $2,000 \text{ hr}^{-1}$. If hydrocarbons synthesis is of interest the condition at $2,000 \text{ hr}^{-1}$, 340°C and 80 atg may be the best.

5.4.7 Space Time Yield of Hydrocarbon (STY_{HC})

Figs. 5.47-5.48 shows the relation of space time yield of hydrocarbons at various pressures and GHSV's. Generally the STY_{HC} increases with the temperature. At a temperature below 310°C , the STY_{HC} decreases as pressure increases from 60 atg to 80 atg. But the STY increases as pressure increases from 40 atg to 60 atg, especially at 310°C . The optimum temperature for STY_{HC} seems to decrease as GHSV increases. This can be seen at $GHSV = 4,000 \text{ hr}^{-1}$ and 310°C . A lower GHSV tends to shift the optimum temperature to a higher value. Furthermore the combustion reaction will complete with the synthesis reaction, as the temperature becomes relatively high.

5.5 Catalyst No. 3 (IFP type; $\text{Cu}_1\text{Co}_1\text{Cr}_{0.2}\text{K}_{0.095}$)

5.5.1 CO Conversion (X_{CO})

As seen in Figs. 5.49-5.50, the total CO conversion (X_{CO}) generally increases as the temperature increases, especially at temperatures above 310°C . At GHSV $2,000 \text{ hr}^{-1}$, the CO conversion increases along with the reaction pressure. On the other hand at $P = 75 \text{ atg}$, X_{CO} decreases as the GHSV increases from $1,000$ to $4,000 \text{ hr}^{-1}$. It is reasonable to assume that the combustion reaction becomes significant above 310°C . As expected from Le Chatelier's principle, ethanol synthesis is favored as the reaction pressure increased. Meanwhile an increase in the GHSV means that the contact time decreases. So only fast reactions would have sufficient time to take place.

5.5.2 Selectivity of Ethanol (Se_{EtOH})

As seen in Figs. 5.51-5.52 when the GHSV remains constant, the selectivity for ethanol tends to decrease as pressure increases. Meanwhile, at a constant pressure, the selectivity tends to increase as the GHSV increases. This means that at low pressures or high GHSV's, with the temperature being low, less by-reactions and thus less by-products occur, resulting in a higher selectivity for ethanol. On the other hand, at high temperatures, CO is more readily turned into CO_2 and there is less hydrogenation of CO to alcohols. Thus the selectivity for ethanol decreases rapidly in the high temperature range.

5.5.3 Space Time Yield of Ethanol (STY_{EtOH})

As seen in Figs. 5.53-5.54, the STY_{EtOH} generally increases with pressure. Furthermore the optimum temperature for STY_{EtOH} seems to shift lower as pressure increases. At $P = 75$ atg, the STY_{EtOH} decreases as the GHSV increases from 1,000 to 4,000 hr^{-1} . On the other hand optimum temperature for STY_{EtOH} tends to shift higher with an increase in GHSV.

5.5.4 Selectivity of Total Alcohols ($Se_{tot.alc.}$)

The selectivity of total alcohols tends to decrease as pressure increases. At $P = 75$ atg, the selectivity clearly decreases as the GHSV increases. It also decreases significantly at temperatures above $310^{\circ}C$. Most of the alcohols detected are methanol and ethanol (Figs. 5.55-5.56).

5.5.5 Space Time Yield of Alcohols ($STY_{alc.}$)

As seen in Fig 5.57-5.58, the space time yield of total alcohols increases with pressure, and there exists an optimum temperature, which shifts lower decreases as the pressure increases. At $P = 75$ atg, the optimum space time yield occurs at $GHSV = 2,000$ hr^{-1} and temperature around $310^{\circ}C$.

5.5.6 Selectivity of Hydrocarbon (Se_{HC})

The selectivity of hydrocarbon (C_1-C_6) at 75 atg decreases as the GHSV increases. The hydrocarbon selectivity monotonically increases as temperature increases. The main hydrocarbon was methane, which is synthesized according to the following reactions.



At very high pressures heavier hydrocarbons are observed more, while the combustion reaction becomes significantly (Figs. 5.59-5.60).

5.5.7 Space Time Yields of Hydrocarbons (STY_{HC})

The space time yield of hydrocarbons increases as temperature increases. At $P = 75$ atg the space time yield tends to decrease as GHSV increases up to 310°C , above which the trend is reversed (Figs. 5.61 - 5.62).

5.6 Overall Discussion for The Three Different Catalysts

5.6.1 $\text{Rh}_1\text{Mn}_1\text{Fe}_{0.1}/\text{SiO}_2$

The overall experimental results for the feed ratio of $\text{CO}:\text{H}_2 = 1:2$ are summarized in table E.1. As mentioned earlier an increase in the reaction pressure increase the contact time and the reactant concentrations, other conditions are being fixed.

Thus the rate of reaction will increase according to a typical expression

$$-r_1 = k_1 C_a^n C_b^m$$

when $n, m > 0$, and decrease if $n, m < 0$

It is found that there is an unconstrained optimum temperature at the following conditions : 40 atg and 60 atg with $\text{GHSV} = 2,000 \text{ hr}^{-1}$, and 80 atg with $\text{GHSV} = 1,000 \text{ hr}^{-1}$.

To considering the effect of pressure on STY_{EtOH} and $STY_{tot.alc.}$ at various pressures, i.e. 40, 60, and 80 atg, and the same GHSV, namely $2,000 \text{ hr}^{-1}$, the following data are the best results for STY_{EtOH} and $STY_{tot.alc.}$ at each pressure.

P (atg)	Temp ($^{\circ}\text{C}$)	STY_{EtOH} (mol/lit.cat.-hr)	$STY_{tot.alc.}$	STY_{EtOH} (g-atom/lit.cat.-hr)	$STY_{tot.alc.}$ (g-atom/lit.cat.-hr)
40	310	0.179	2.563	0.358	8.276
	340	0.124	2.543	0.248	10.061
60	310	0.168	1.917	0.336	5.620
80	310	0.265	1.734	0.530	4.133
	340	0.204	1.908	0.408	5.000

From the above data, it could be concluded that at the highest pressure ethanol synthesis is most favorable, meanwhile at the lowest pressure the synthesis of higher alcohols is most favorable.

In addition the effect of temperature on product distribution can be concluded from the results at 40 atg, between 310°C and 340°C . Obviously synthesis of higher alcohols is more favorable at the highest temperature.

Next consider the cases of 80 atg with GHSV = 2,000, 4,000, and 8,000 hr^{-1} , respectively. In all the three cases, a constrained optimum temperature for the synthesis of total alcohols shows up at the upper limit of the temperature range investigated. The maximum space time yield of ethanol and total alcohols is obtained at 340°C , GHSV = 8,000 hr^{-1} (80 atg). Their values are $STY_{EtOH} = 2.85 \text{ mole/lit.cat.-hr}$ (based on the moles of the products) and $STY_{tot.alc.} = 4.975 \text{ mole/lit.cat.-hr}$ (based on the moles of the products). While the respective values based on the grams atom of carbon in the products are 5.70 and 10.309 g-atom /lit.cat.-hr, respectively.

Obviously the main product at these conditions is ethanol, which is somewhat different from the above results conditions at a lower pressure. Thus it might be said that ethanol synthesis is favorable at a higher pressure, a higher temperature and a shorter contact time. When the temperature is very high and the contact time is not short enough, combustion of the "intermediate" products becomes favorable.

Of all the results obtained for the feed ratio of CO to $H_2 = 1:2$, the best STY_{EtOH} and best $STY_{tot. alc.}$ are 2.85 mole/lit.cat.hr, and 4.975 mole/lit.cat.-hr (based on the moles of the products). Both are obtained at 80 atg, GHSV 8000 hr^{-1} and $340^{\circ}C$. It might be said that at a lower pressure, the synthesis of higher alcohols is more favorable. On the other hand, at the same pressure and GHSV, a higher temperature is more favorable for the synthesis of higher alcohols. As stated above, at a higher pressure, more ethanol is synthesized, especially at a shorter contact time and a higher temperature.

Next consider the feed ratio of $CO:H_2 = 1.25:1$. The effects of pressure and temperature on $STY_{tot. alc.}$ are somewhat different from the case when the feed ratio is 1:2. At 40 atg, and 60 atg with GHSV 2,000 hr^{-1} , and at 80 atg with GHSV 1,200 hr^{-1} , the general trend is similar to that at 80 atg and GHSV = 2,000, 4000, and 8,000 hr^{-1} in the case of the feed ratio of $CO:H_2 = 1:2$. That is, a constrained optimum temperature tends to exist at the upper range of temperature investigated. However at the feed ratio of $CO:H_2 = 1.25:1$, an unconstrained optimum temperature is obtained at around $280^{\circ}C$ at the pressure = 80 atg and GHSV = 2,000, 4,000, and 8,000 hr^{-1} . The best $STY_{tot. alc.}$ for this feed ratio of $CO:H_2 = 1.25:1$ is obtained at 40 atg with GHSV = 2,000 hr^{-1} , and $340^{\circ}C$. The values are 3.965 mole/lit.cat.-hr (based on the moles of the products) and 13.384 g-atom/lit.cat.-hr (based on grams atom of carbon in the products),

respectively. It should be noted that less hydrocarbons and less combustion products are obtained at this optimum condition than in the case of the optimum $STY_{tot. alc.}$ obtained at 80 atg, GHSV 8,000 hr^{-1} , and 340°C. Thus there is a strong effect of the feed ratio of $CO:H_2$ on the product distribution and the appropriate condition for alcohol synthesis.

Focusing on an higher pressure and an higher GHSV for the feed ratio of $CO:H_2 = 1.25:1$, more combustion products are observed at the highest temperature. Also more hydrocarbons are observed.

5.6.2 $Co_1Ba_{0.05}Ag_{0.1}/SiO_2$ Catalyst ($CO:H_2 = 1.25:1$)

The results obtained from this catalyst are not satisfactory for alcohol synthesis, and the major products are hydrocarbons and combustion products. At a lower pressure, i.e. 40 atg, 60 atg with GHSV 2,000 hr^{-1} , and the feed ratio of $CO:H_2 = 1.25:1$, the alcohols are higher alcohols. Whereas at a higher pressure the major alcohols are methanol and ethanol.

The maximum $STY_{tot. alc.}$ is obtained at 40 atg, GHSV = 2,000 hr^{-1} and 310°C. The value is 1.909 mole/lit.cat.-hr (based on the moles of the products) and 3.949 gram-atoms/lit.cat.-hr (based on the grams atom of carbon in the products). In addition at the same conditions, an higher temperature yields more higher alcohols probably because the rates of reactions become fast enough for the production of a higher alcohols within the contact time.

5.6.3 $Co_1Cu_1Cr_{0.8}K_{0.096}$ Catalysts (IFP-type) ($CO:H_2 = 1.25:1$)

As in the case of the $Co_1Ba_{0.05}Ag_{0.1}/SiO_2$ catalyst, only one feed ratio of $CO:H_2 = 1.25:1$ is investigated. This

catalyst shows satisfactory results of alcohols synthesis comparable to the case of the $Rh_1Mn_1Fe_{0.1}/SiO_2$ catalyst. The results show that the higher the pressure, the more favorable the total alcohols synthesis. Generally, there is an unconstrained optimum temperature around $310^\circ C$ for each experiment. The maximum $STY_{tot. alc.}$ obtained at 80 atg, GHSV $2,000\ hr^{-1}$, $310^\circ C$ is 2.562 mole/lit.cat.-hr (based on the moles of the products) and 4.850 grams-atom/lit.cat.-hr. (based on the grams atom of carbon in the products). Less hydrocarbons and combustion products are observed at this condition.

5.7 Comments on Experimental Results

It is not surprising that numerous results do not exhibit a clear-cut and easily understand trend. Because of the continuous drop of pressure in the feed gas cylinder, after a sizable number of the experiments have been carried out the remaining pressure in the feed gas cylinder is significantly reduced, numerous strange or incongruous results can not be repeated for reconfirmation. Because the above synthesis ethanol and alcohols is accompanied by many side reactions in a complex way, yielding a large number of products, it is doubtful that the two GC's, Shimadzu GC-8A1T and GC-A1F, can completely analyze all trace and unusual products. Also the costs of the experimental and analytical as well as the feed equipment and the feed gas are very high. Furthermore the purchase of the syngas needs a long lead time because special permission from the military must be obtained before it may be imported into Thailand.

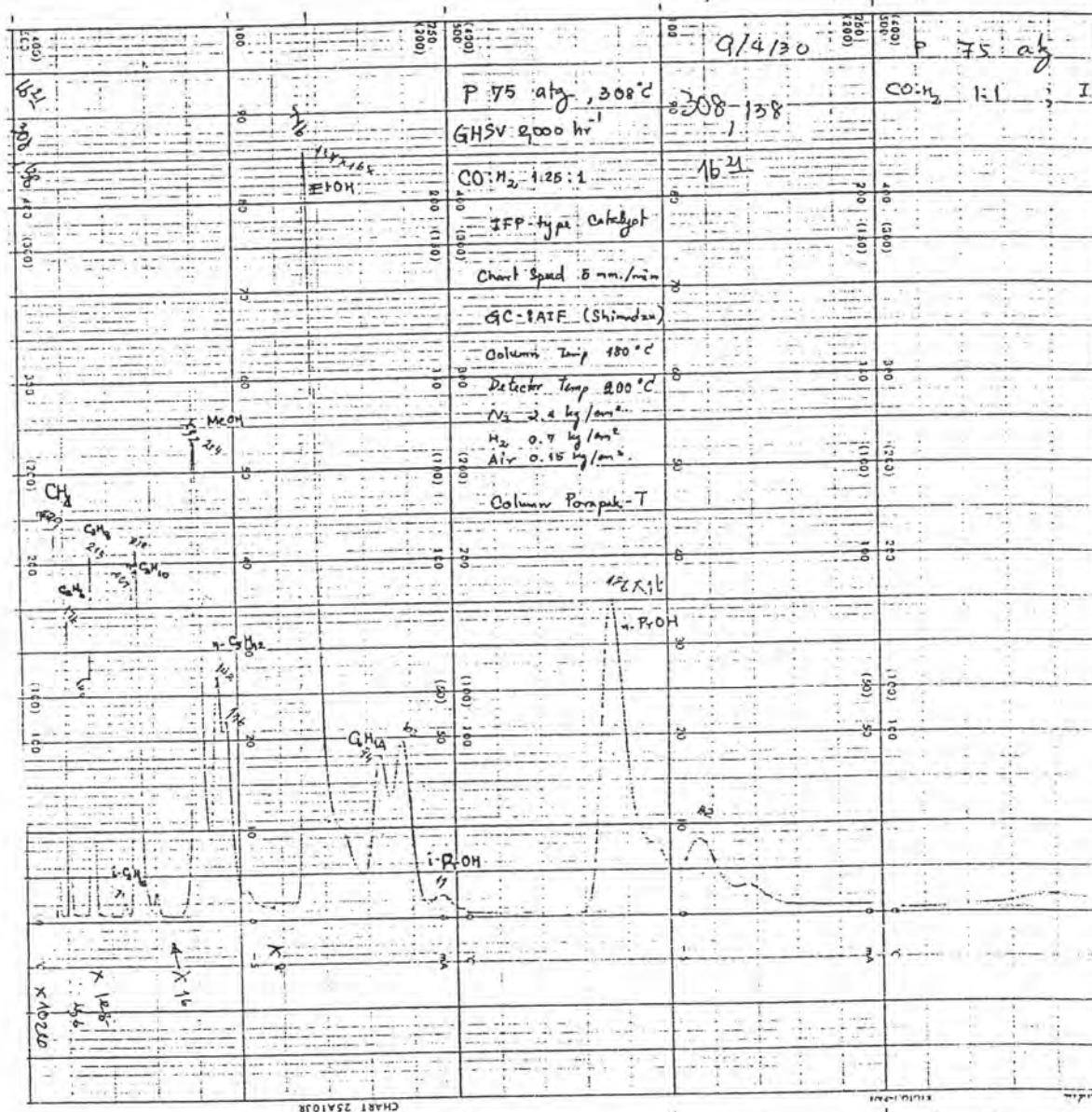


Fig. 5.1 An Example of Chromatograms of 1.0 ml wet gas sample, at 310°C, GHSV 2,000 hr⁻¹, 75 atg, at the feed ratio of CO:H₂ = 1.25:1, using Porapak-T column, Flame Ionized Detector.

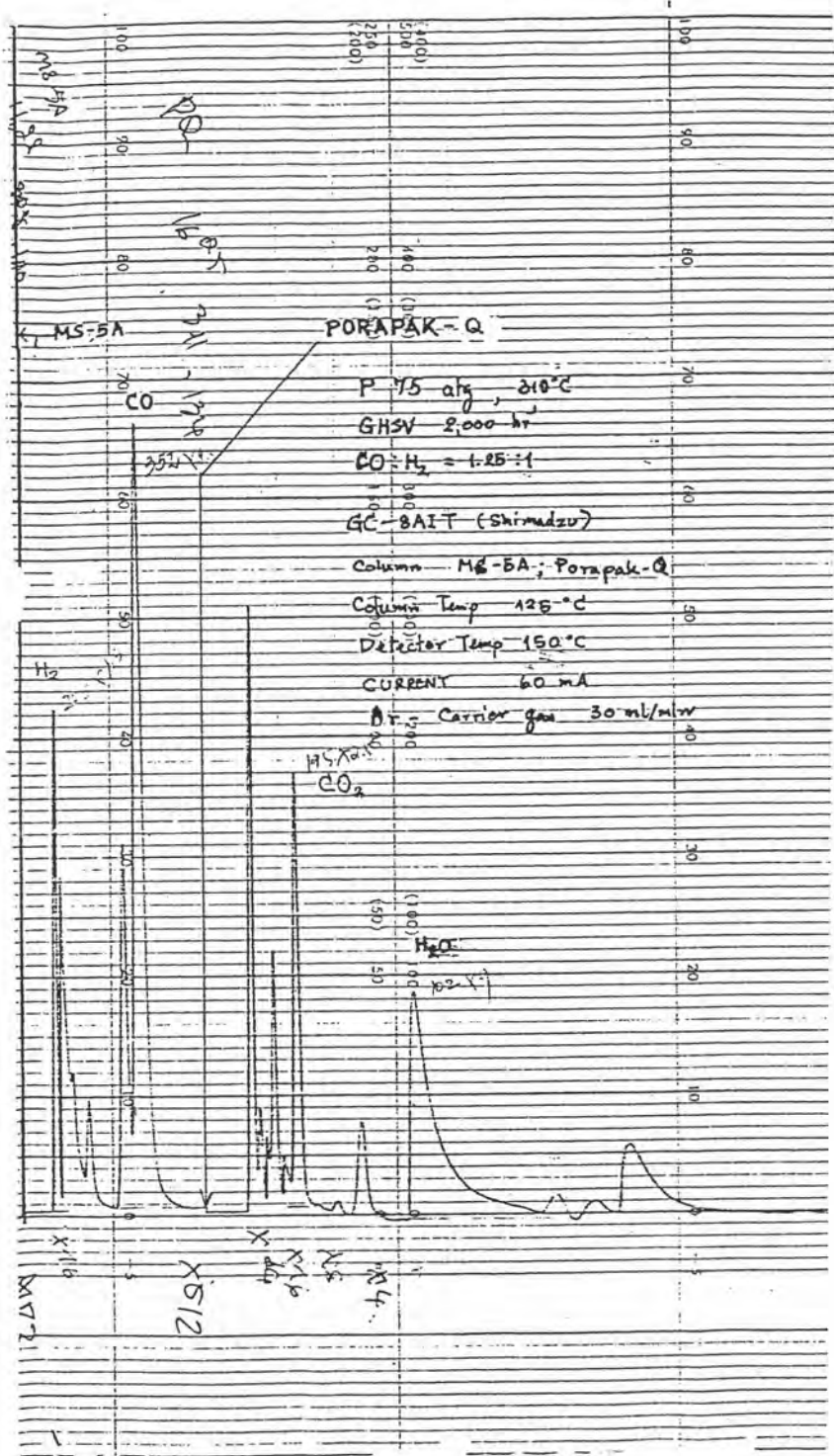


Fig. 5.2 Example of Chromatograms of 0.5 ml dry gas and 1.0 ml wet gas sample using MS-5A column and Porapak-Q column, respectively, and Thermal Conductivity Detector.

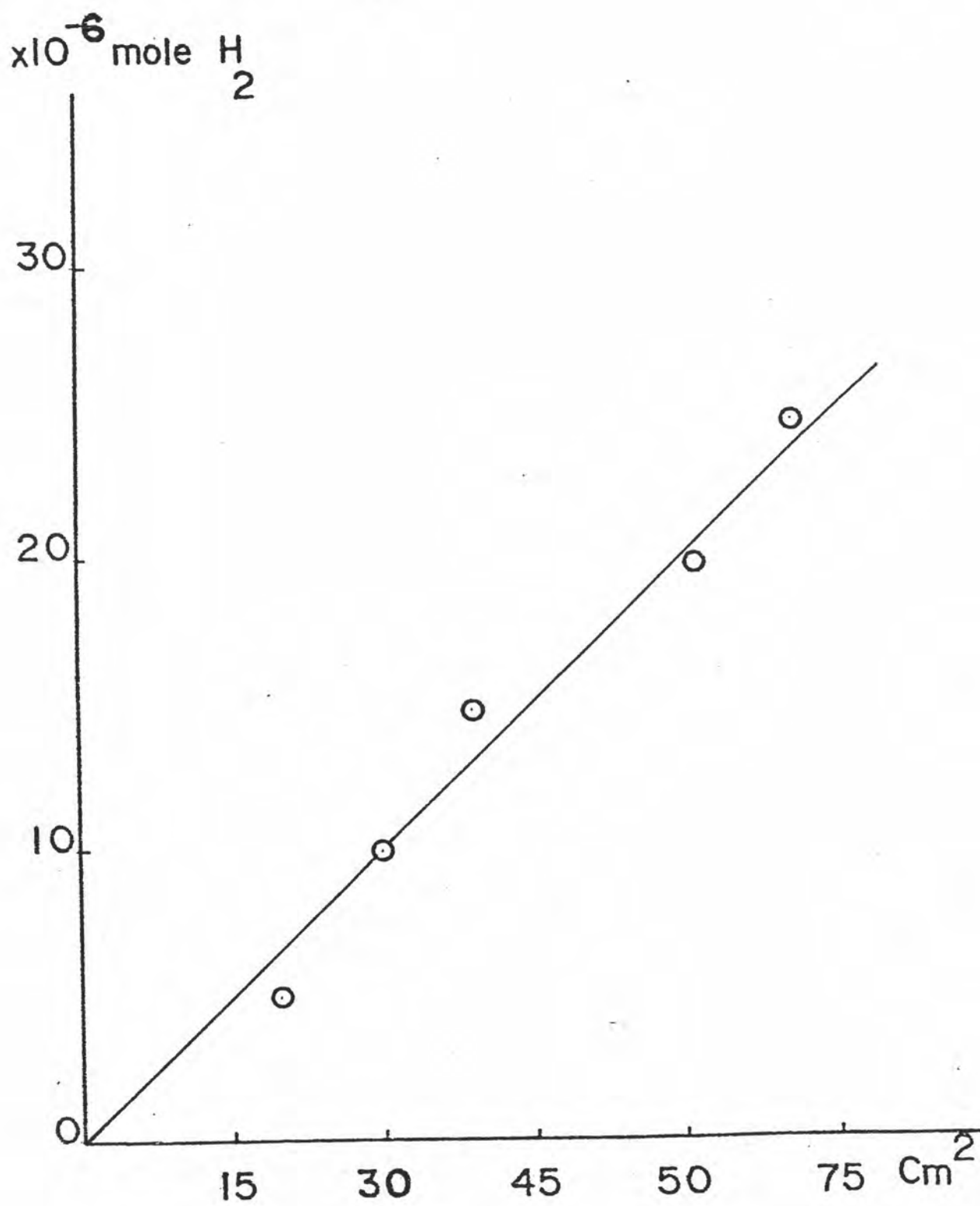


Fig. 5.3 Calibration Curve for H₂

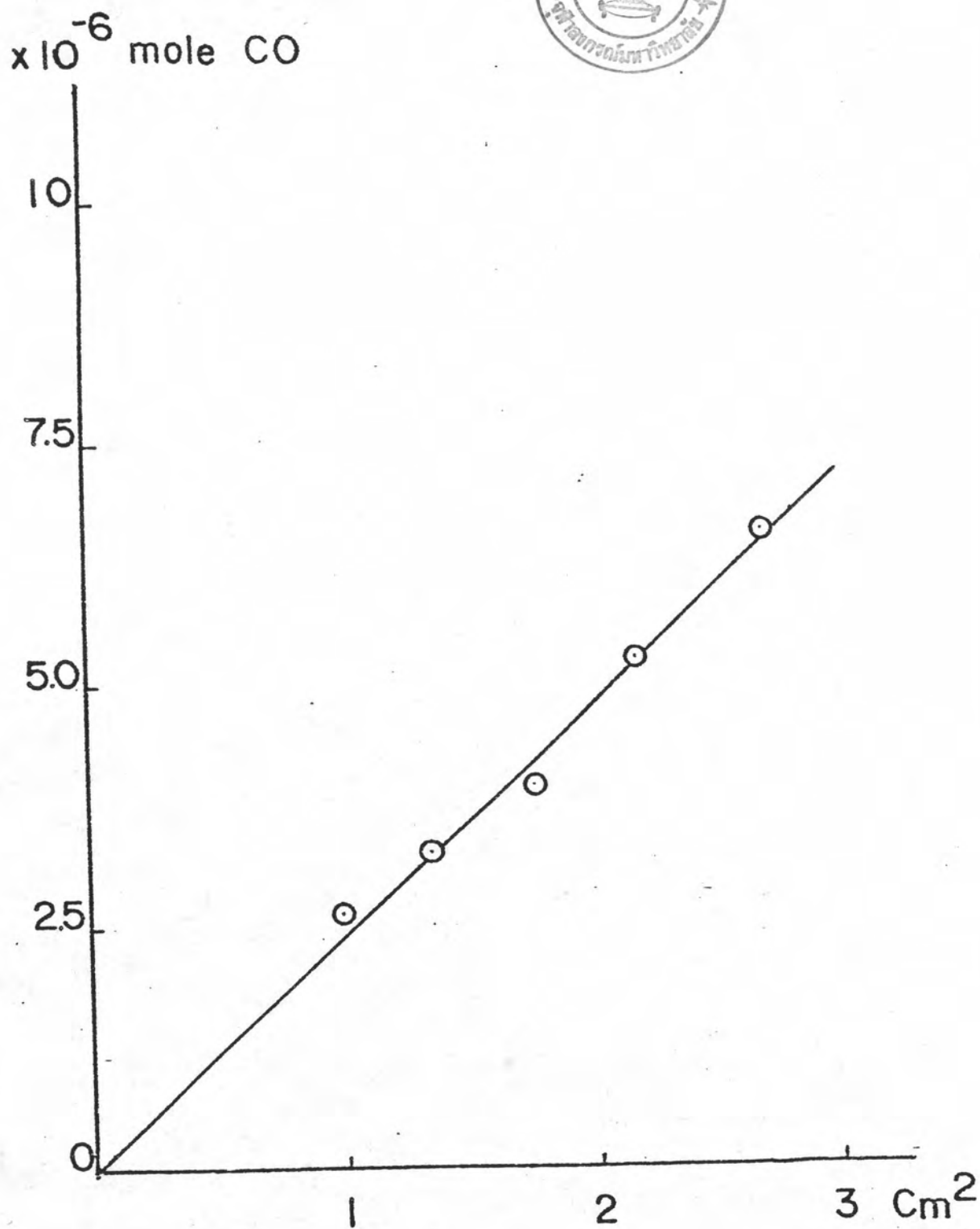


Fig. 5.4 Calibration Curve for CO

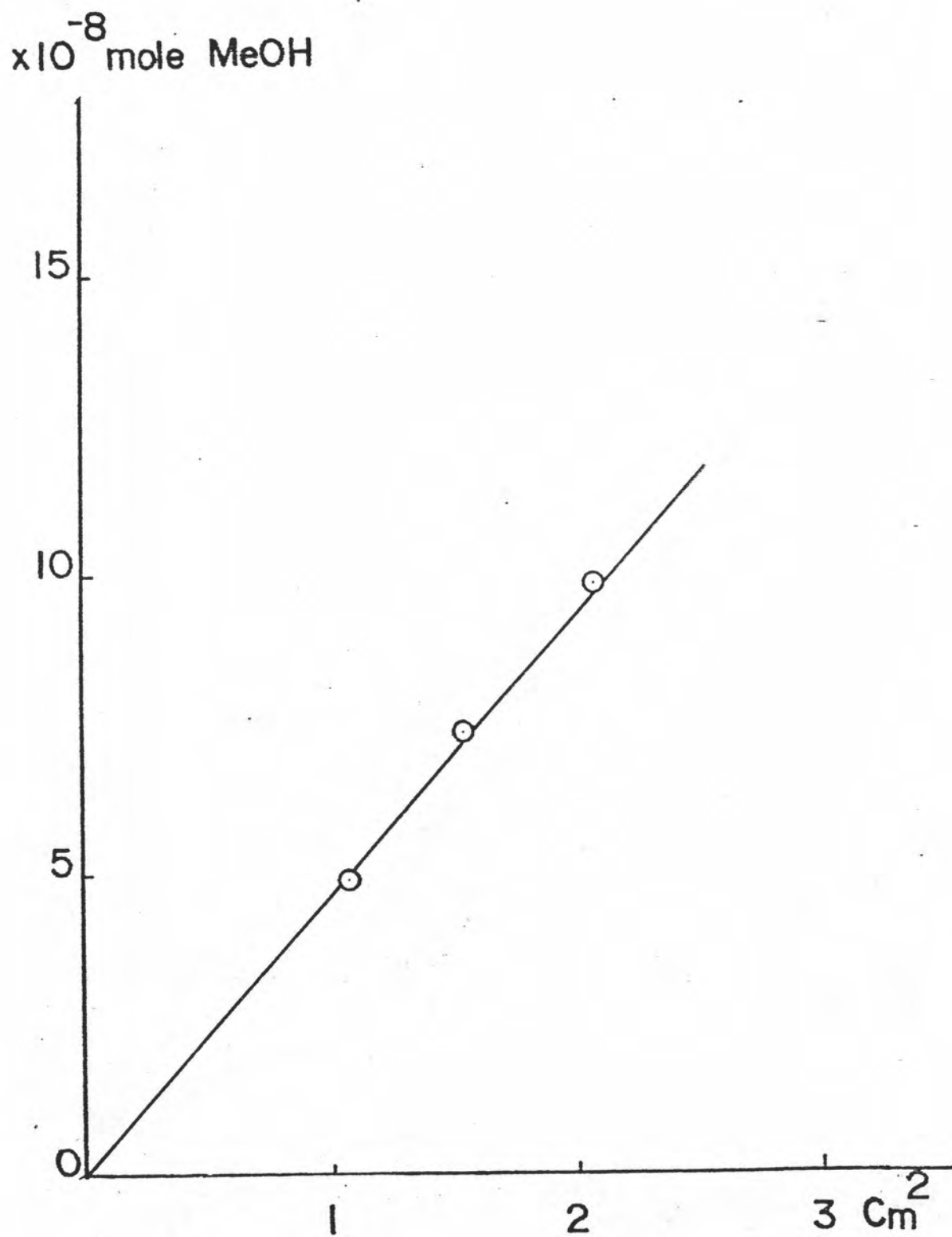


Fig. 5.5 Calibration Curve for MeOH

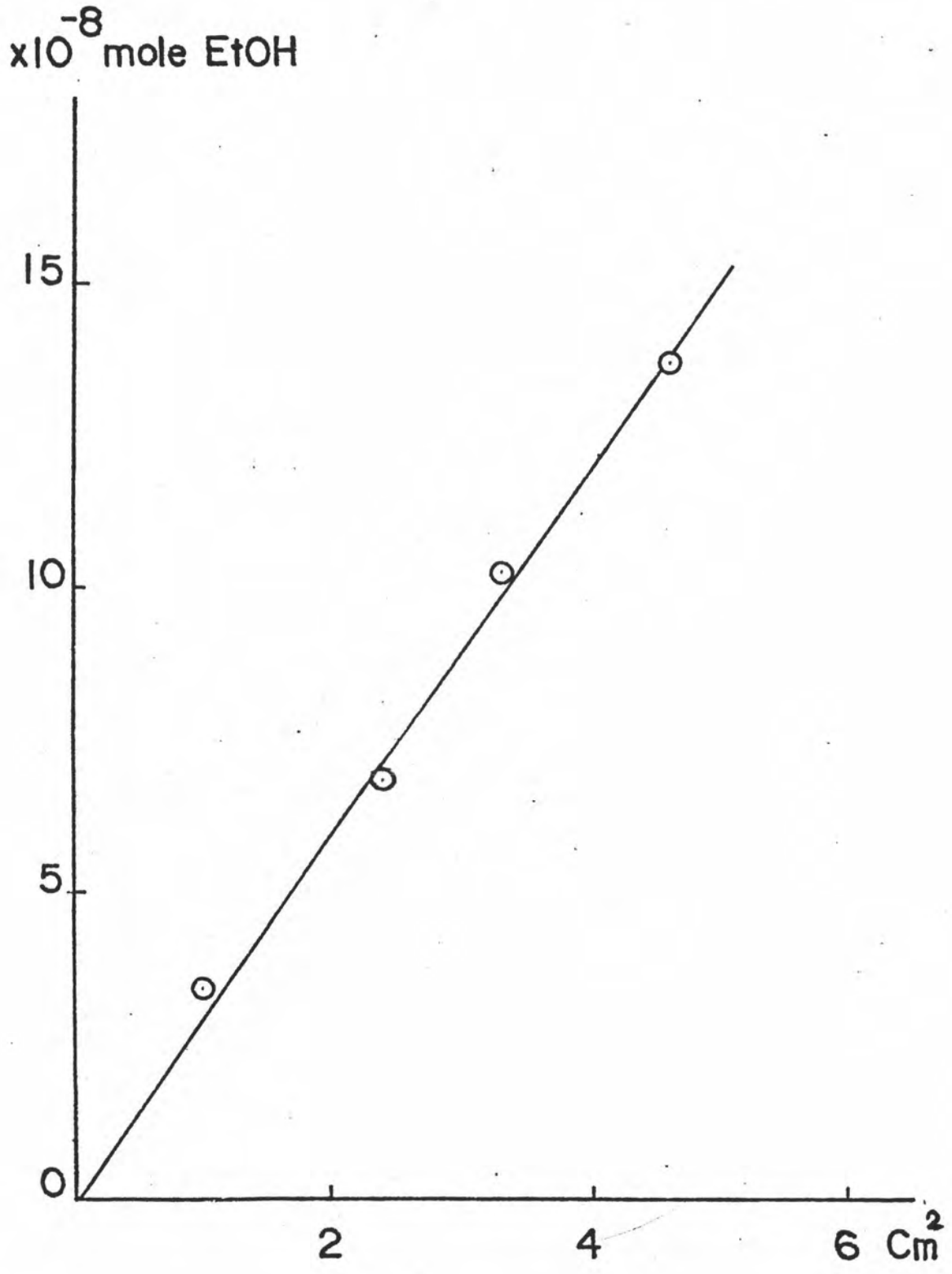
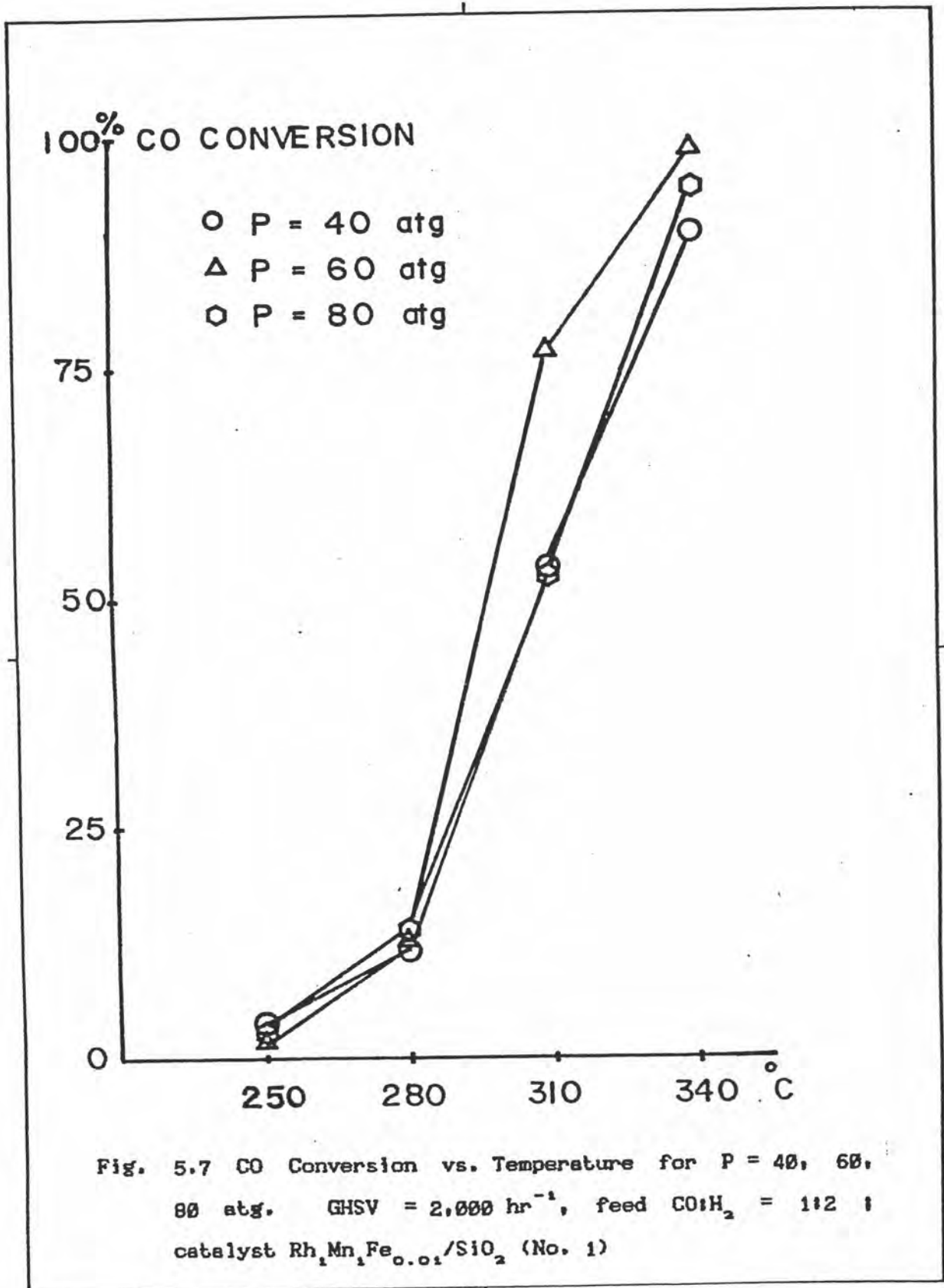
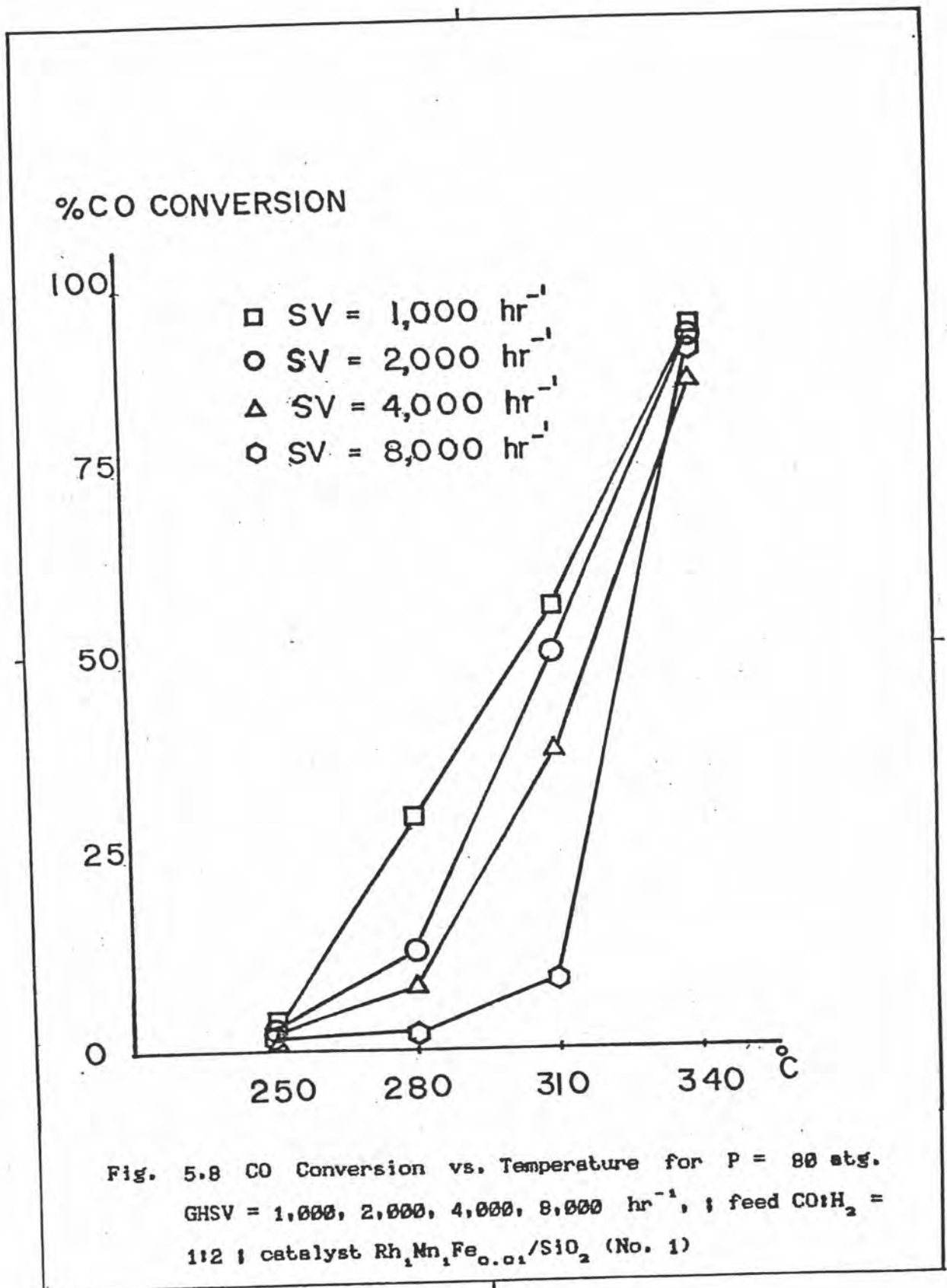
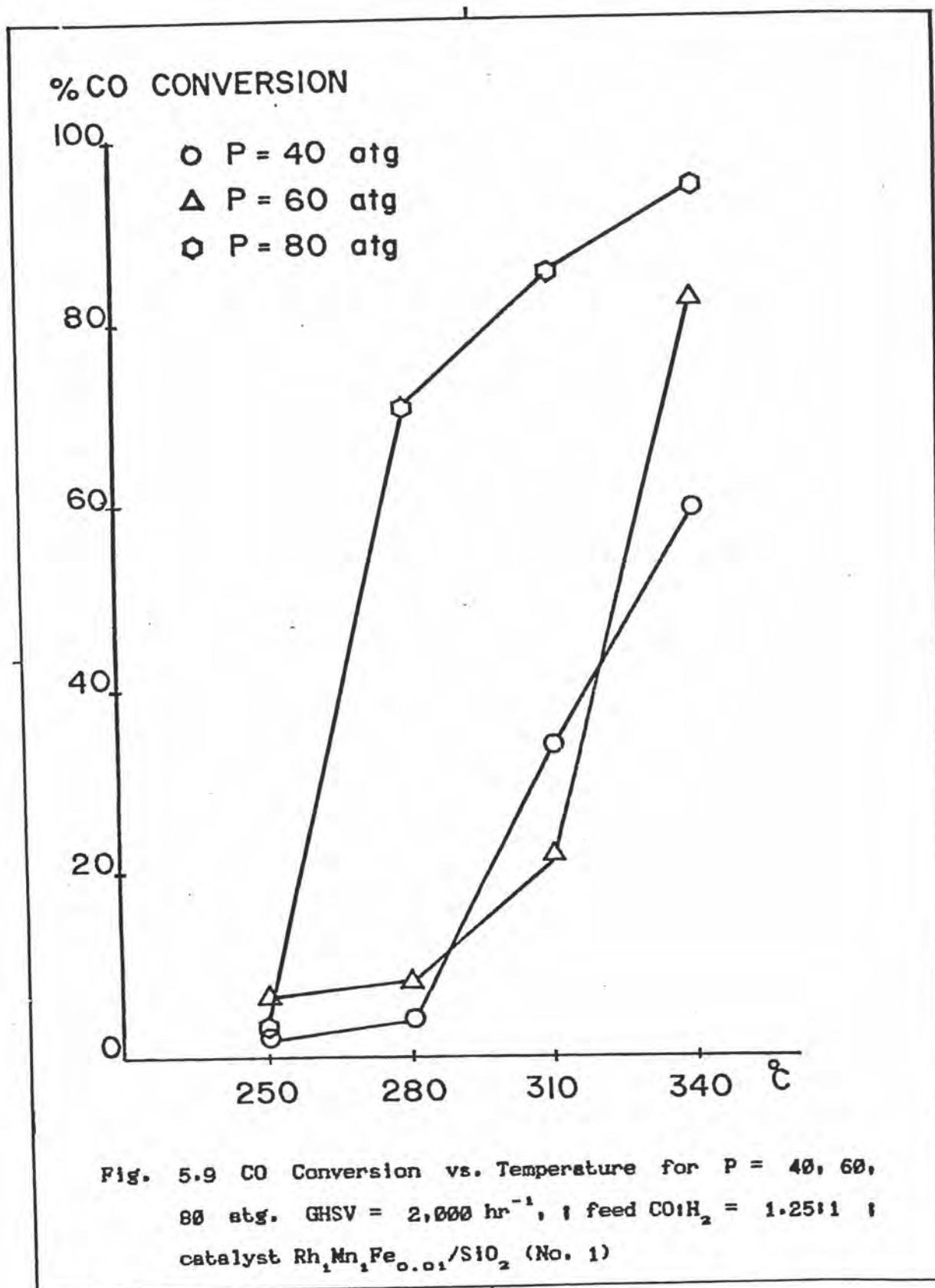
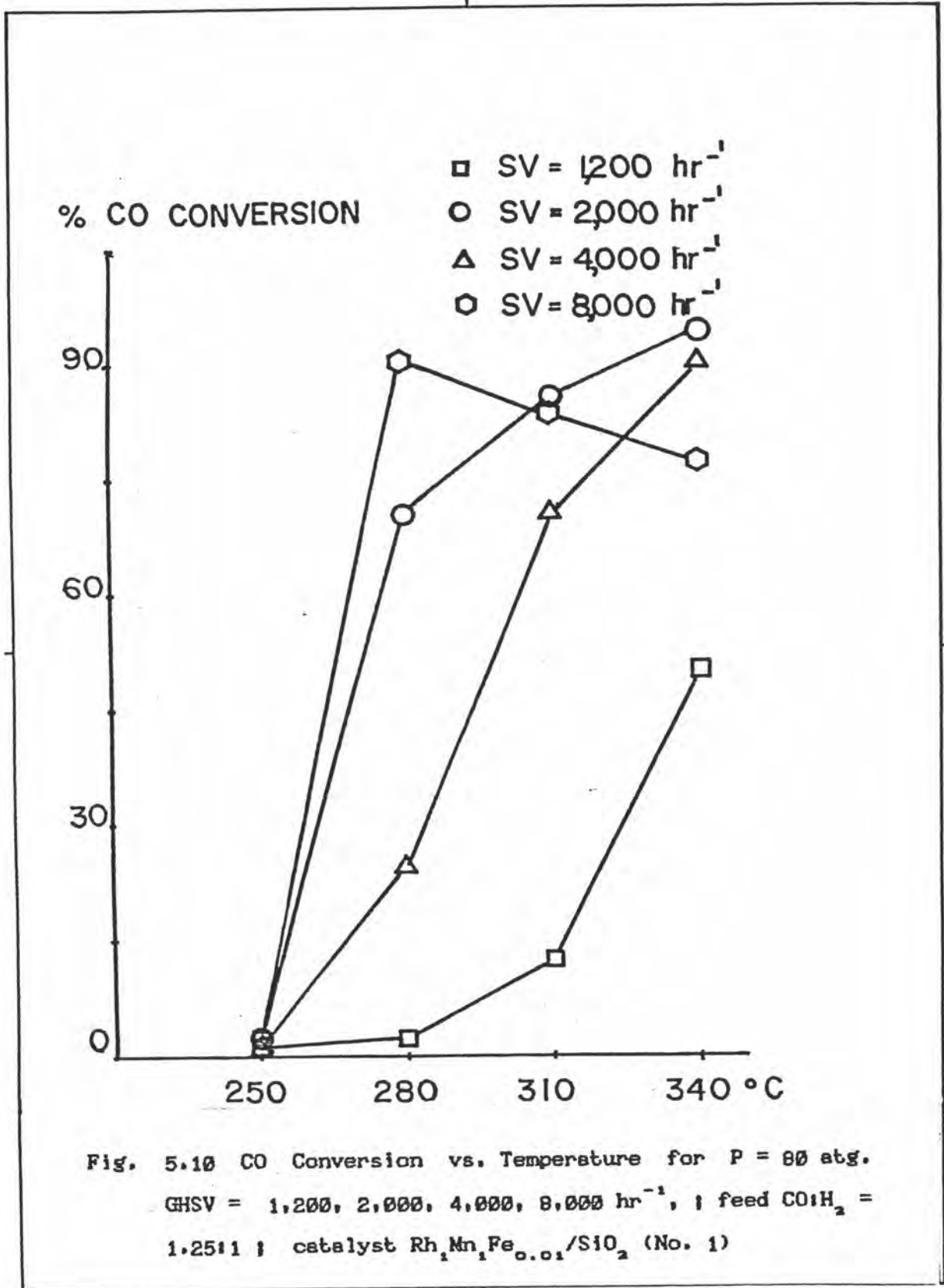


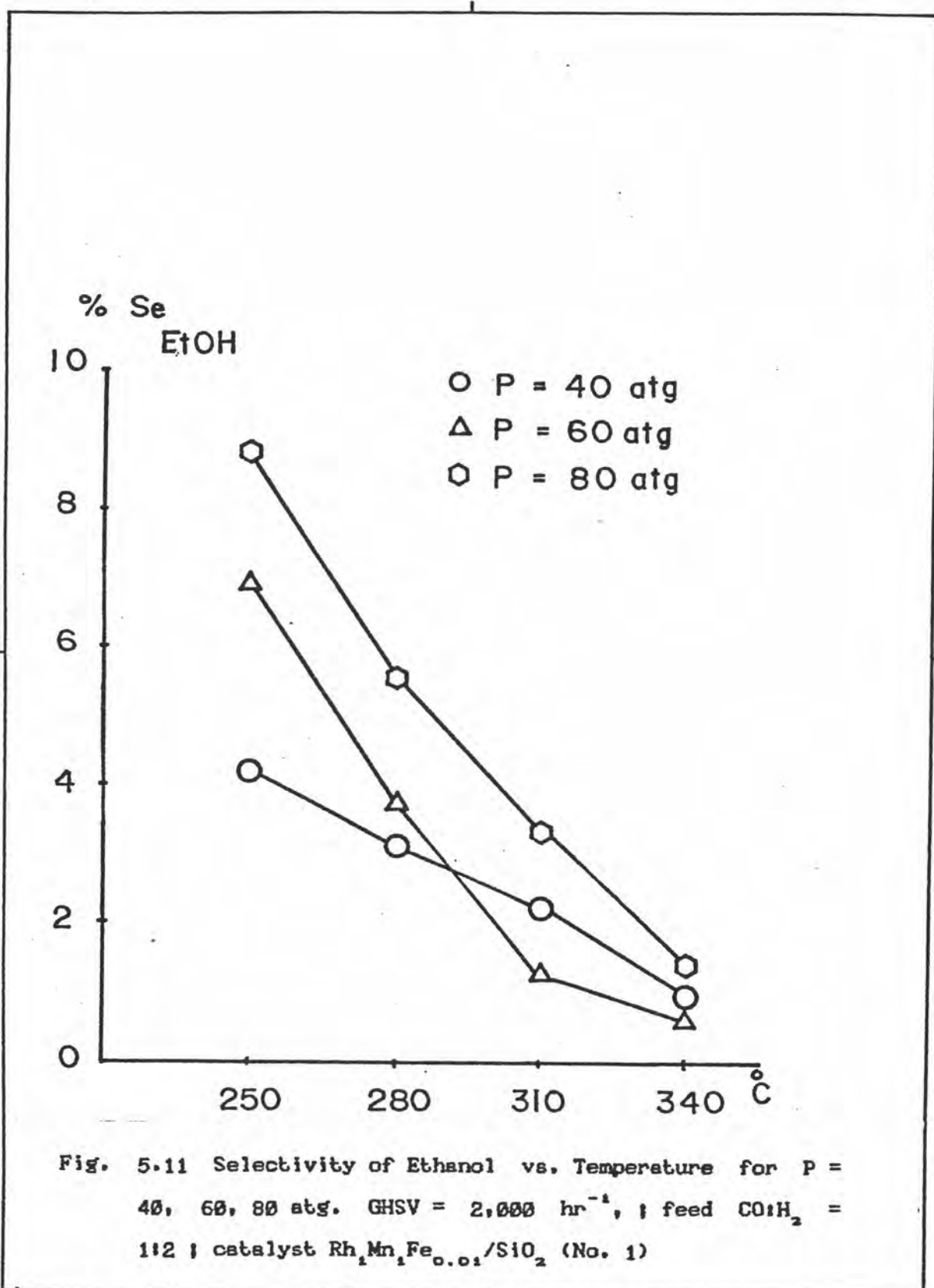
Fig. 5.6 Calibration Curve for EtOH

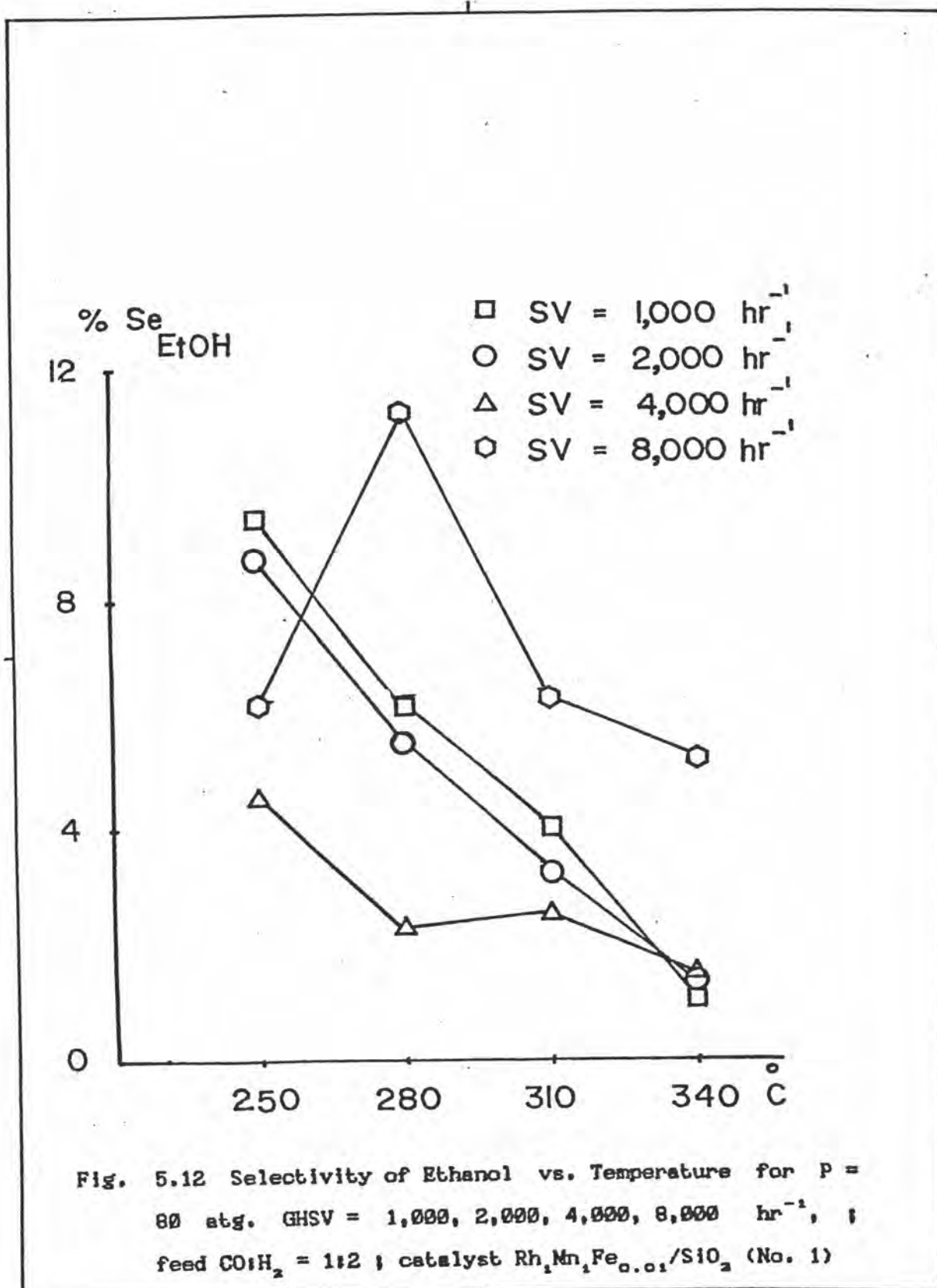












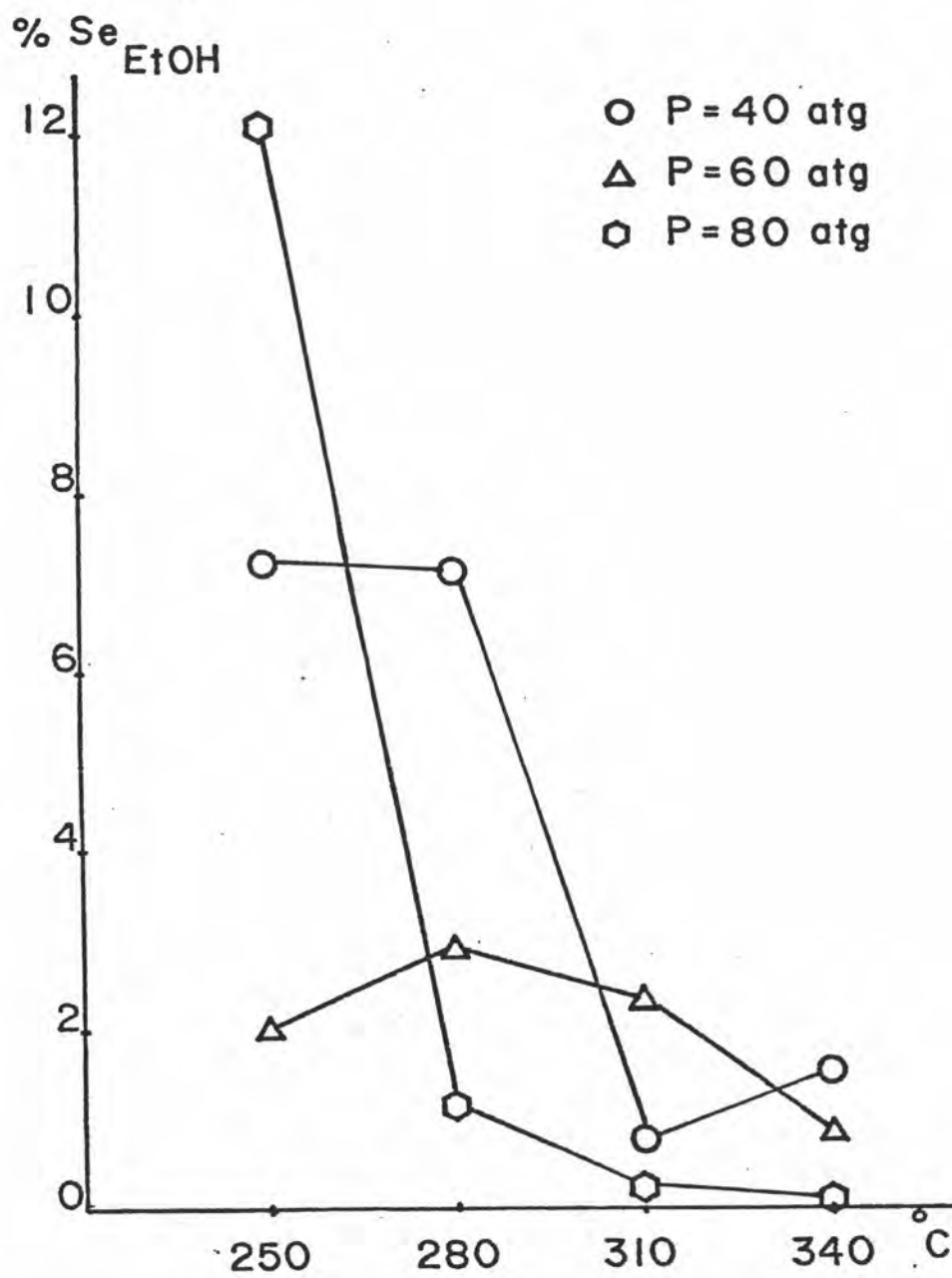
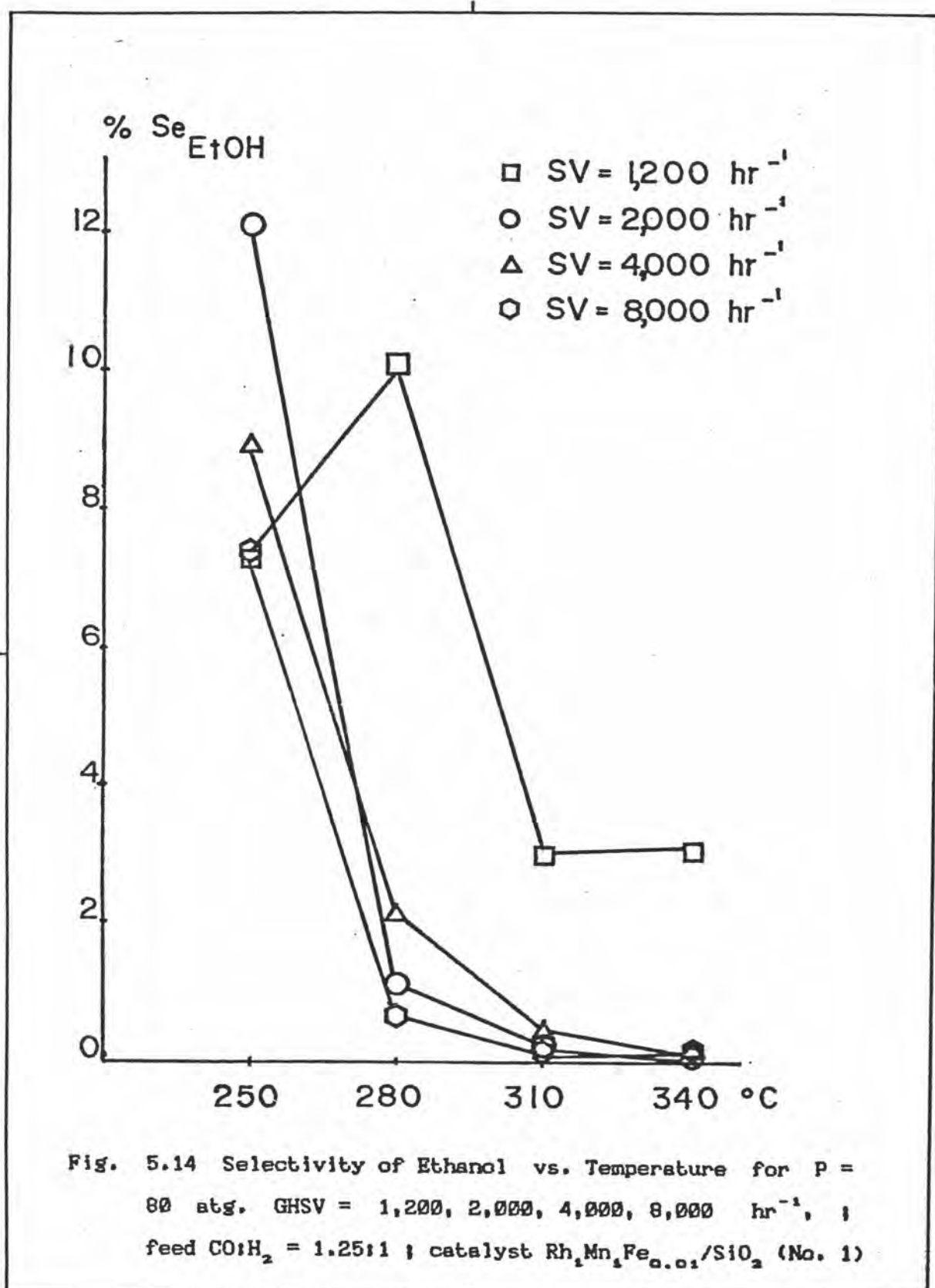
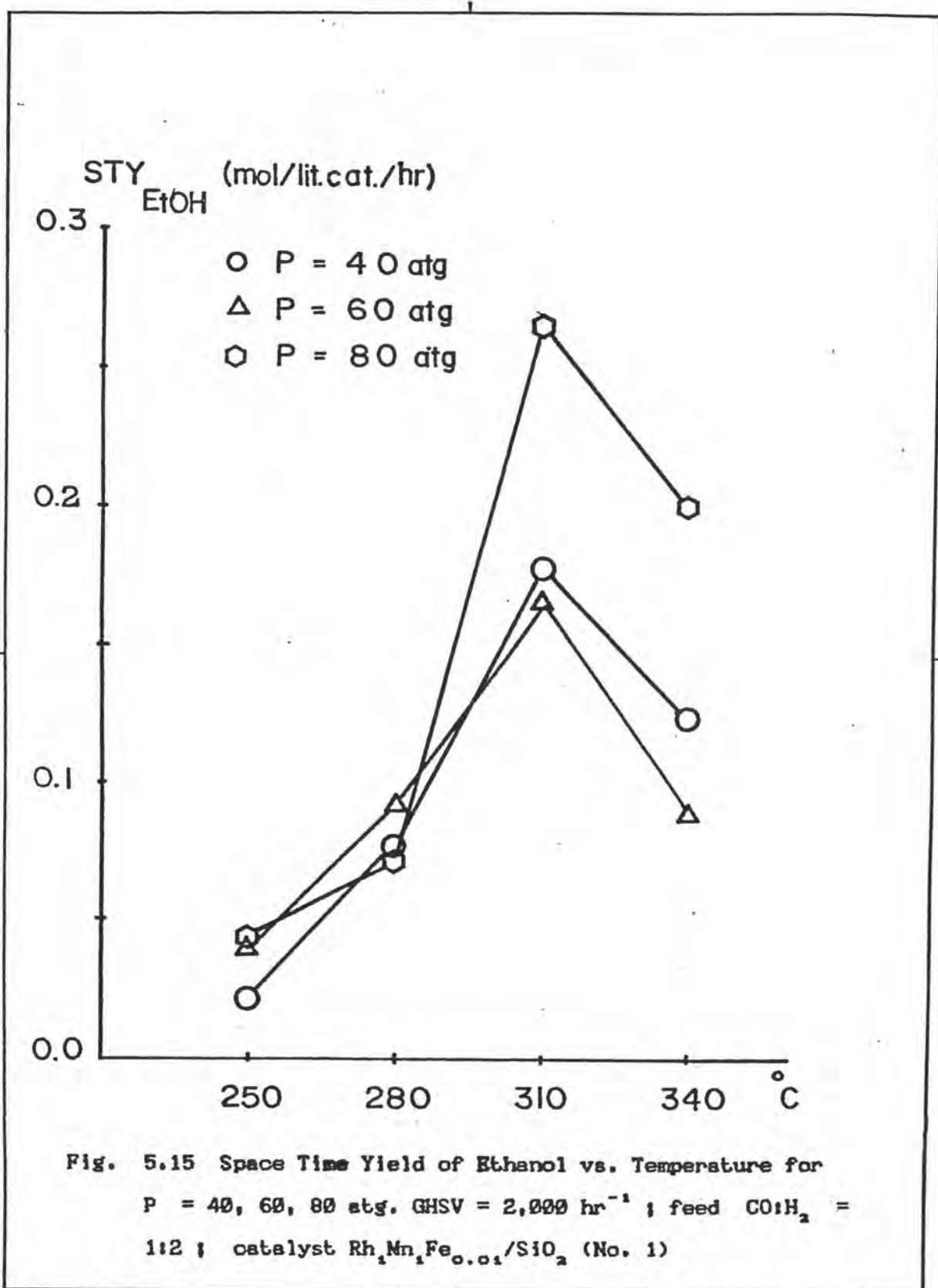
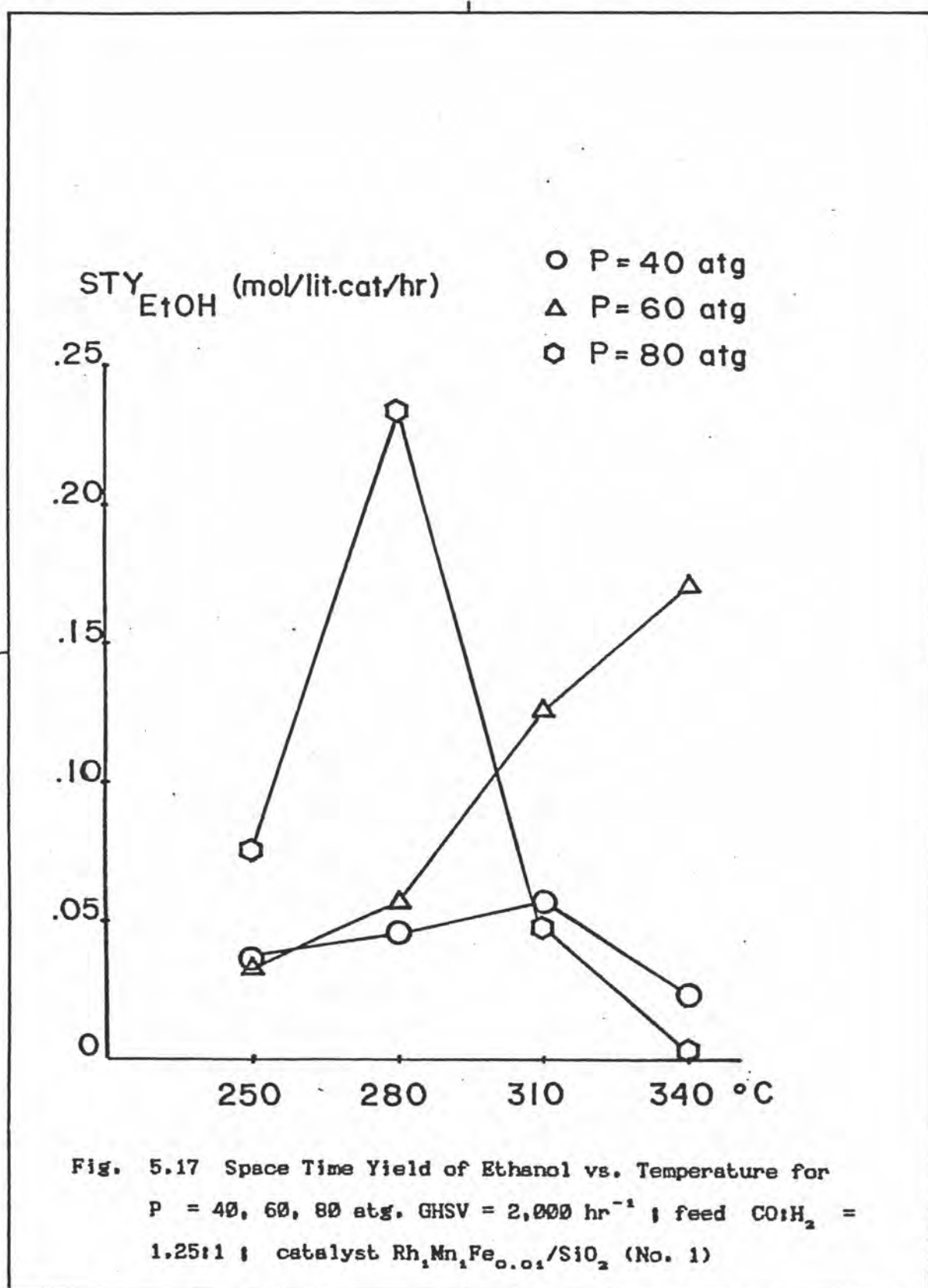
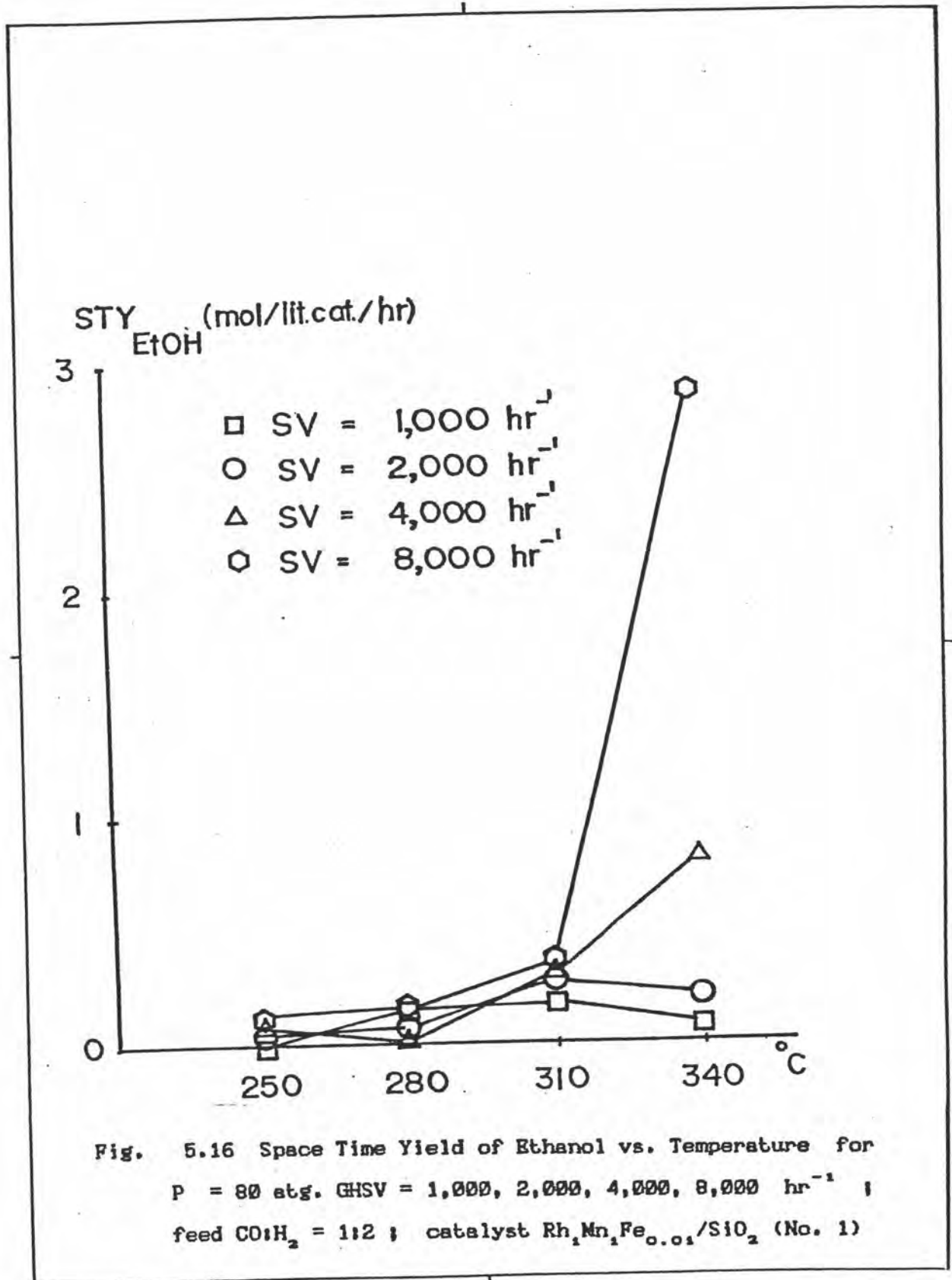


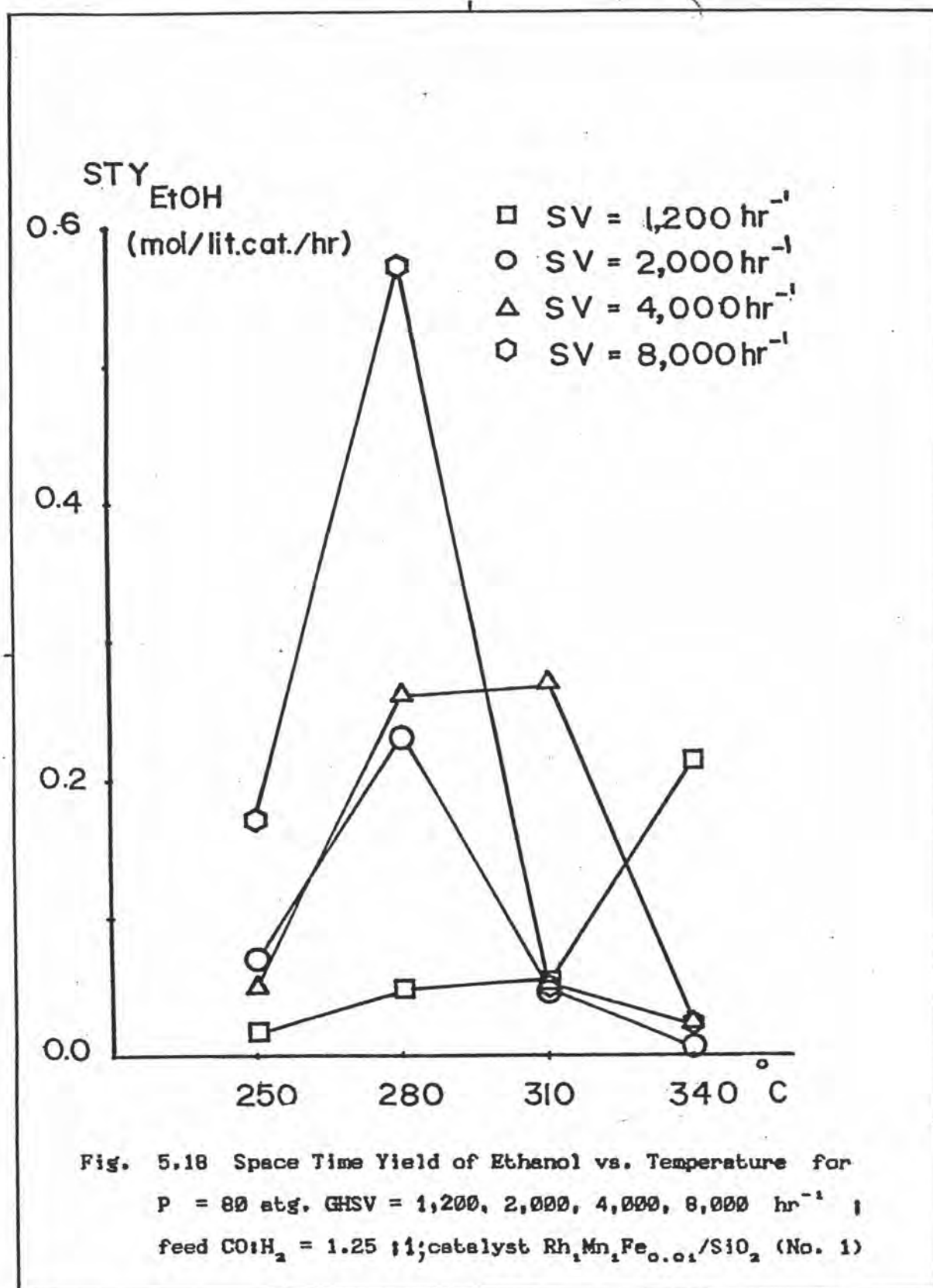
Fig. 5.13 Selectivity of Ethanol vs. Temperature for $P = 40, 60, 80$ atg. GHSV = $2,000 \text{ hr}^{-1}$, ; feed $\text{CO:H}_2 = 1.25:1$; catalyst $\text{Rh}_1\text{Mn}_1\text{Fe}_{0.01}/\text{SiO}_2$ (No. 1)

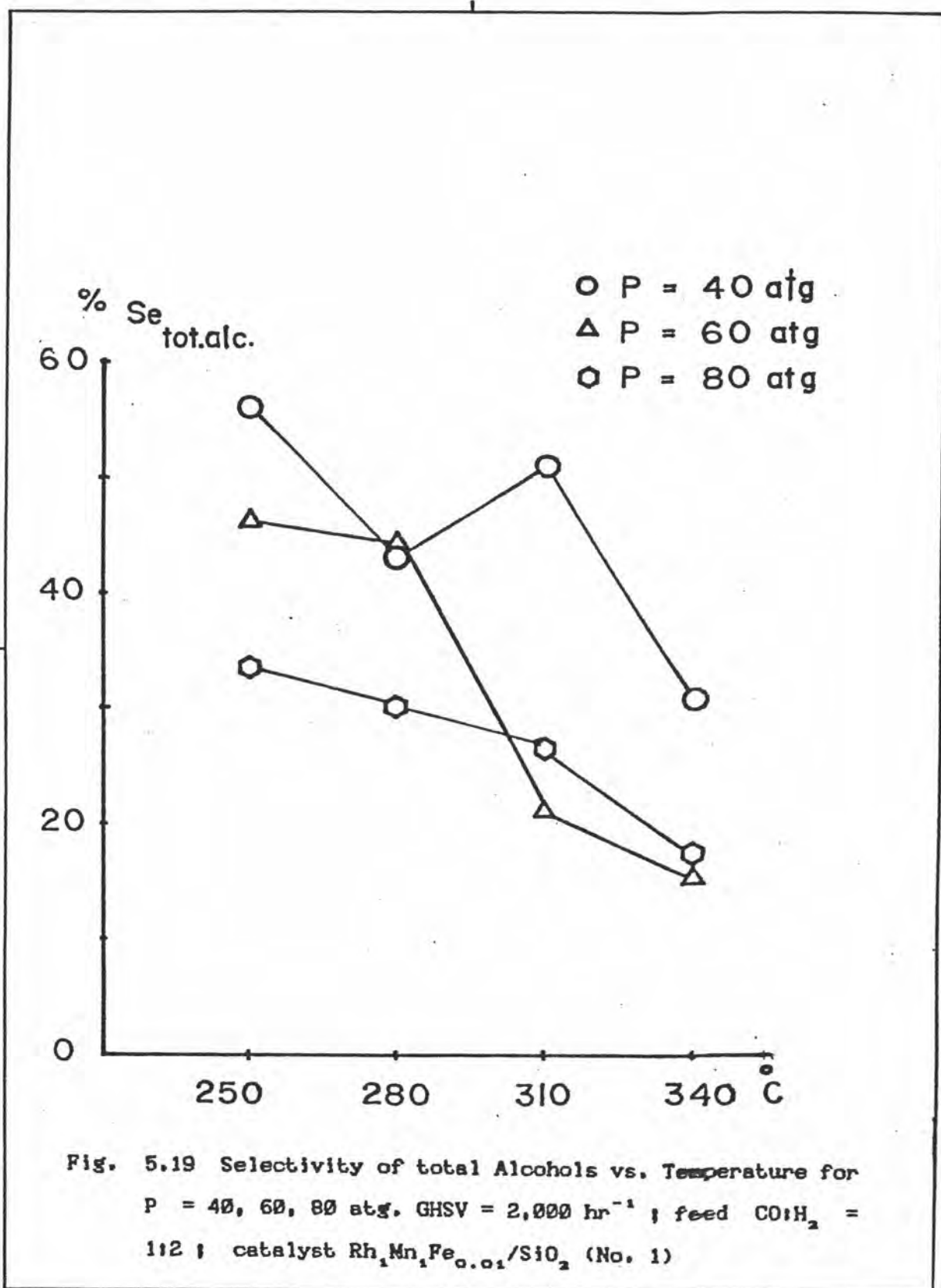


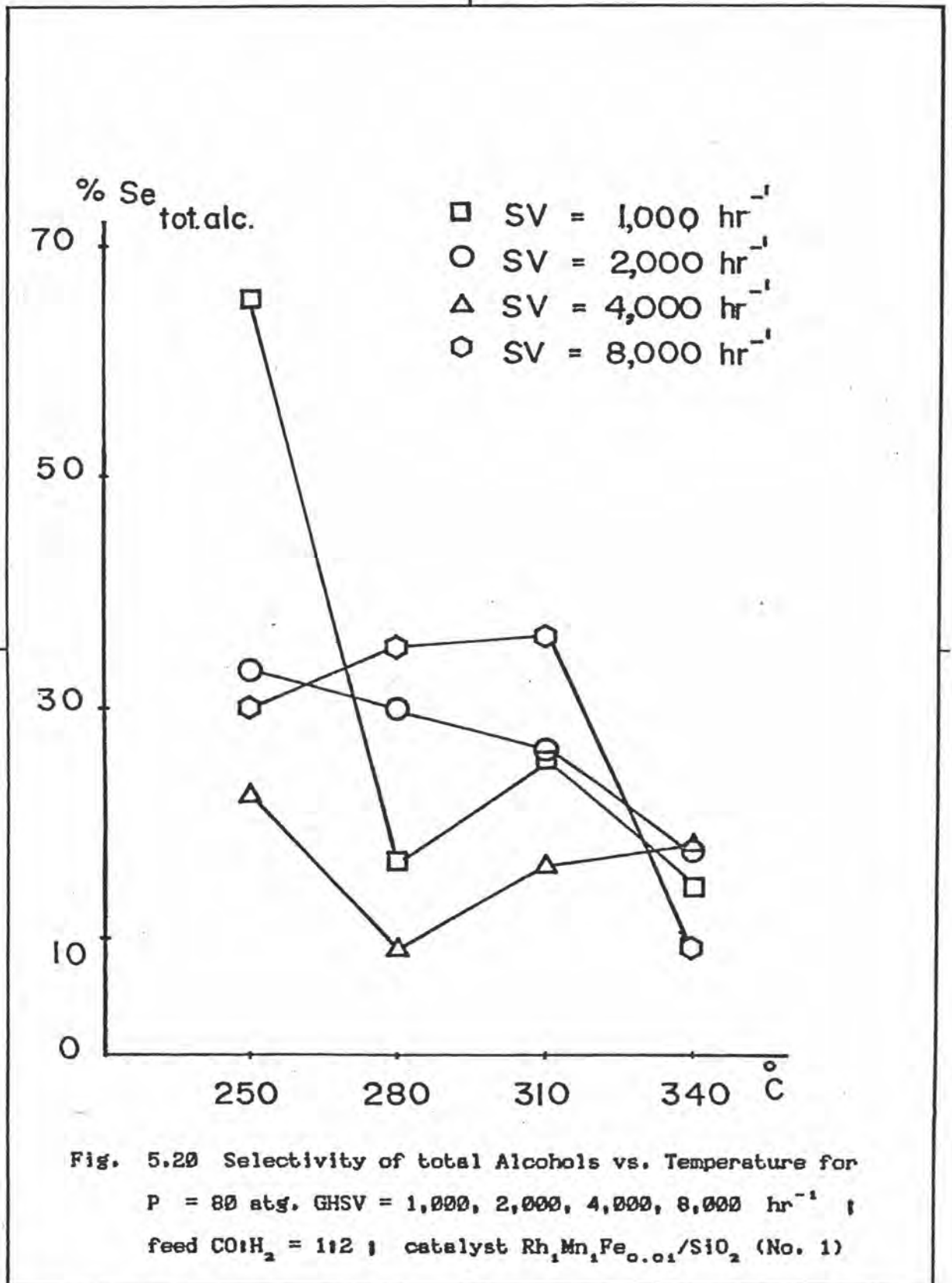


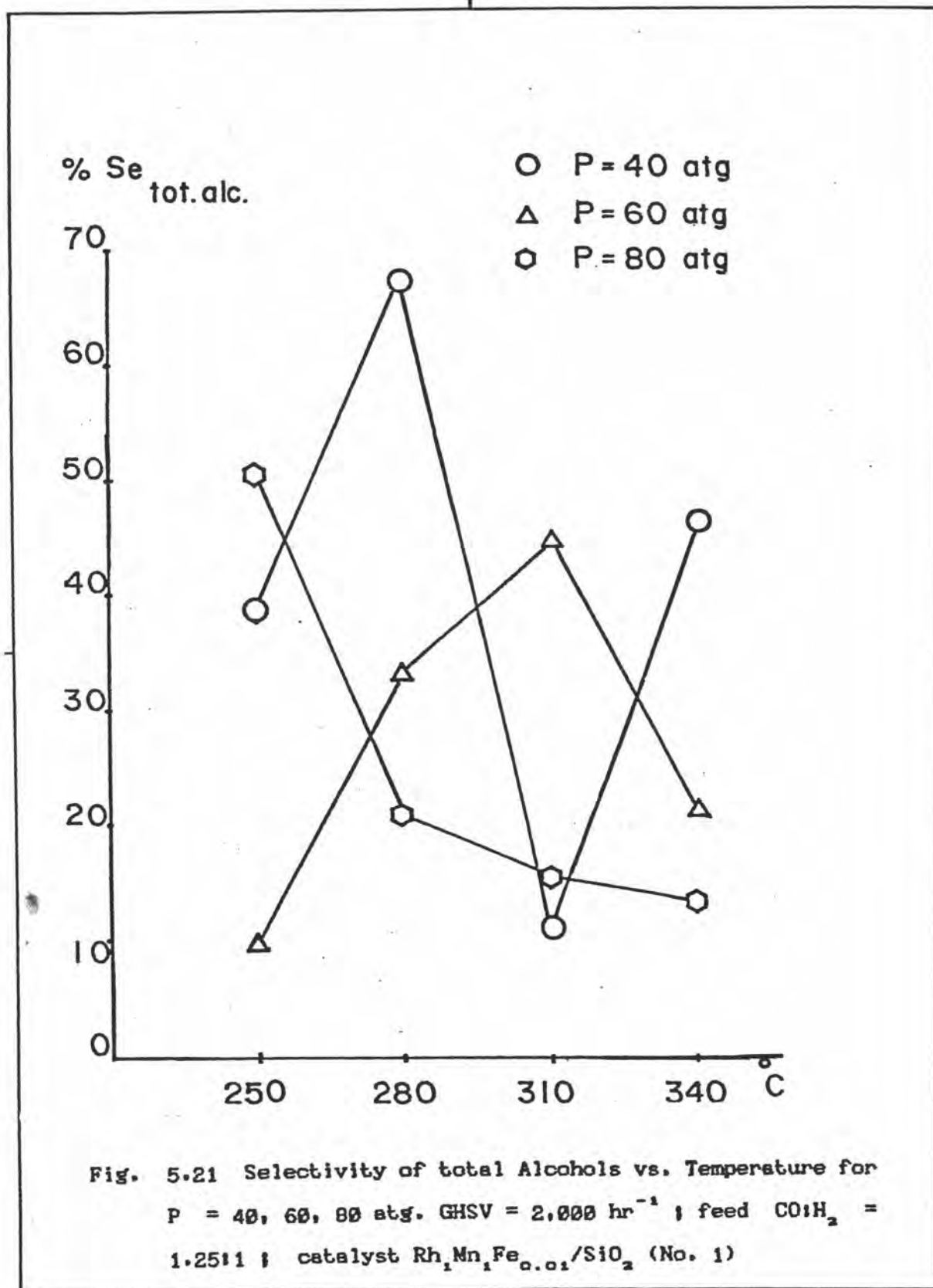












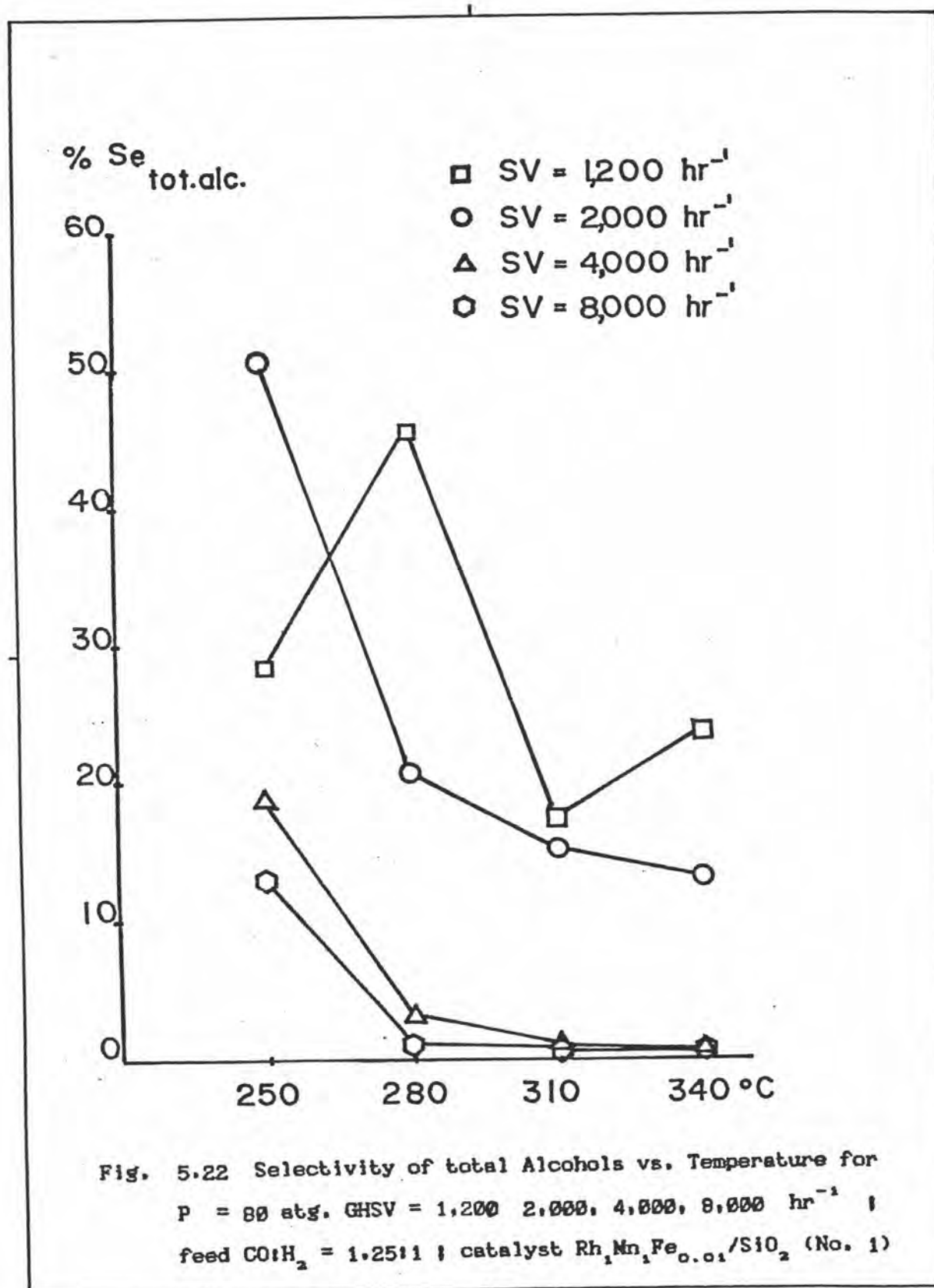
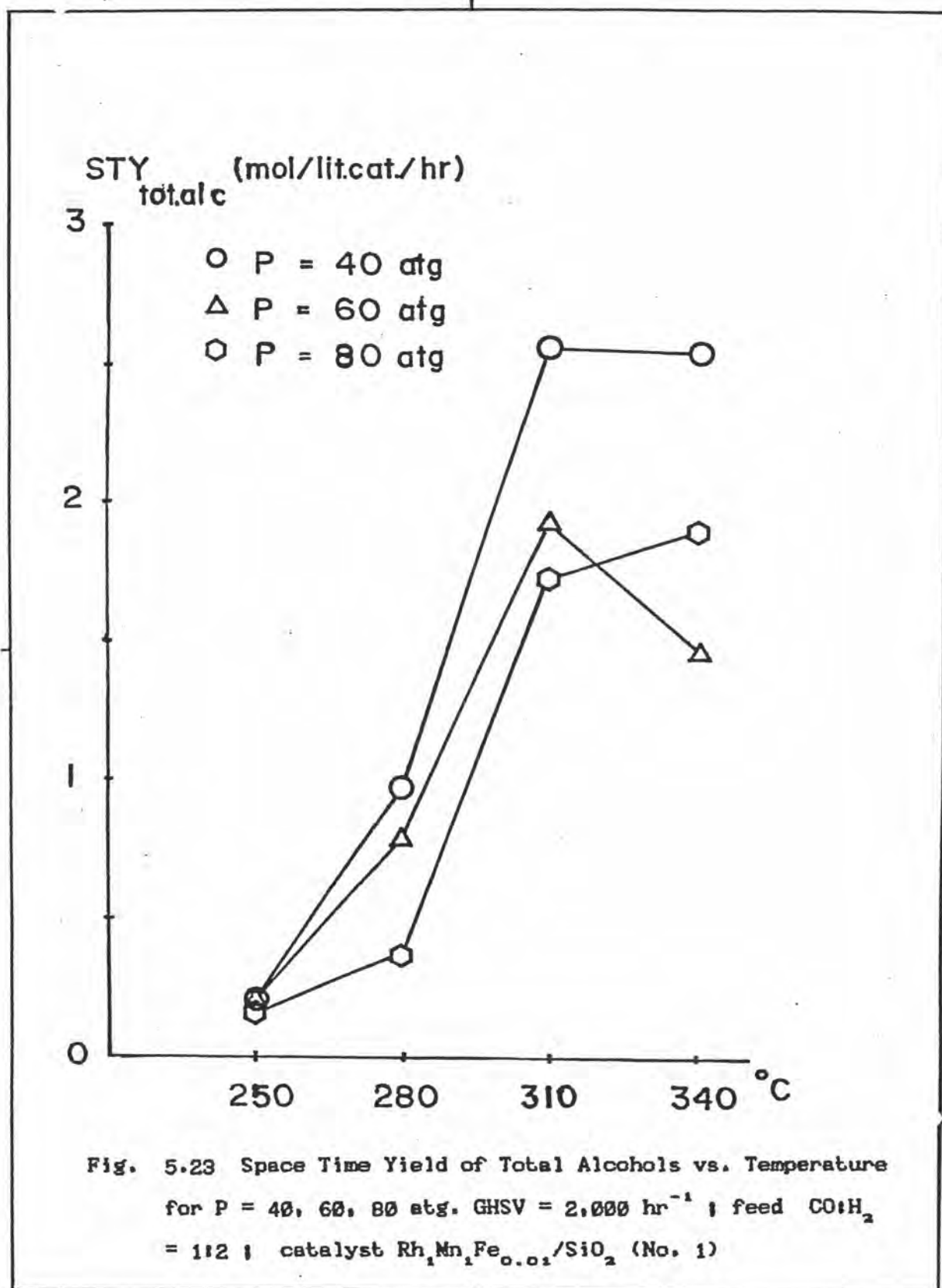


Fig. 5.22 Selectivity of total Alcohols vs. Temperature for
 $P = 80$ atg. GHSV = 1,200 2,000, 4,000, 8,000 hr⁻¹ ;
 feed CO:H₂ = 1.25:1 ; catalyst Rh₁Mn₁Fe_{0.01}/SiO₂ (No. 1)



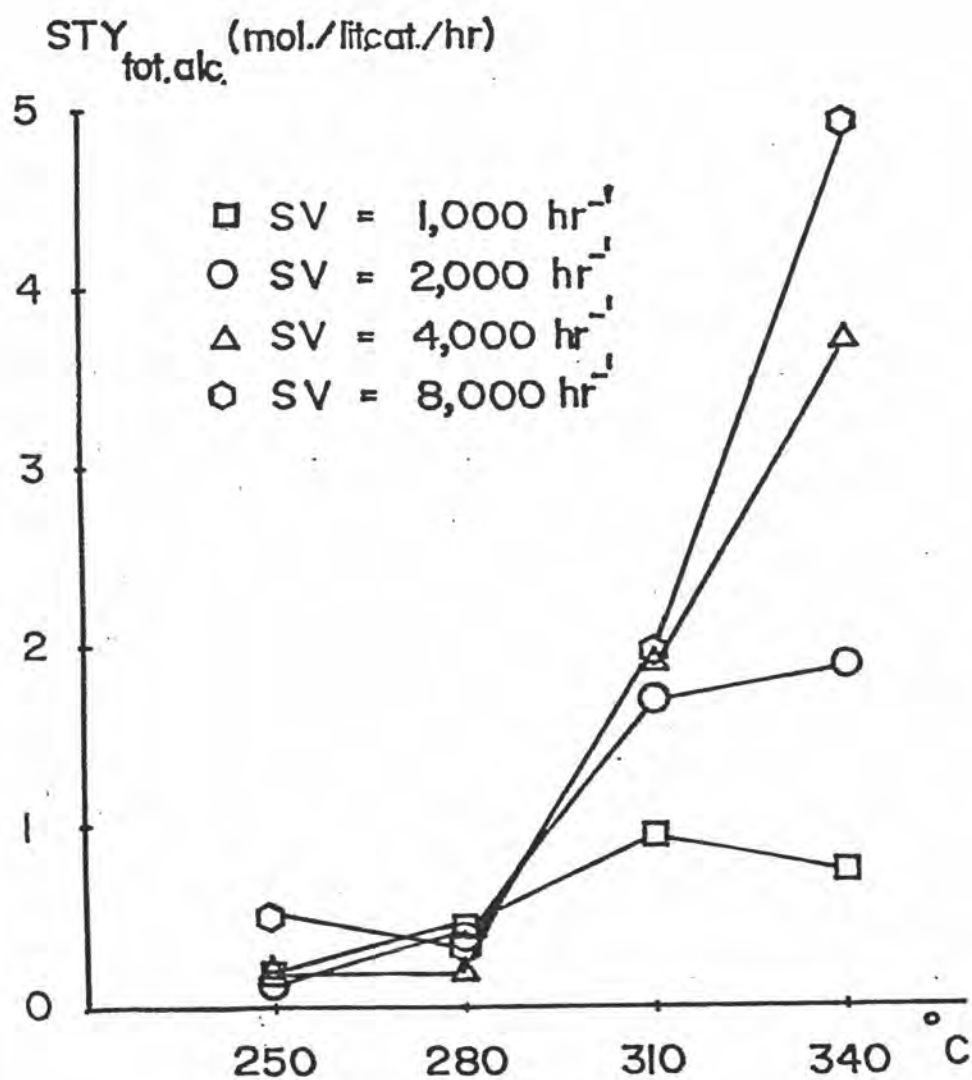
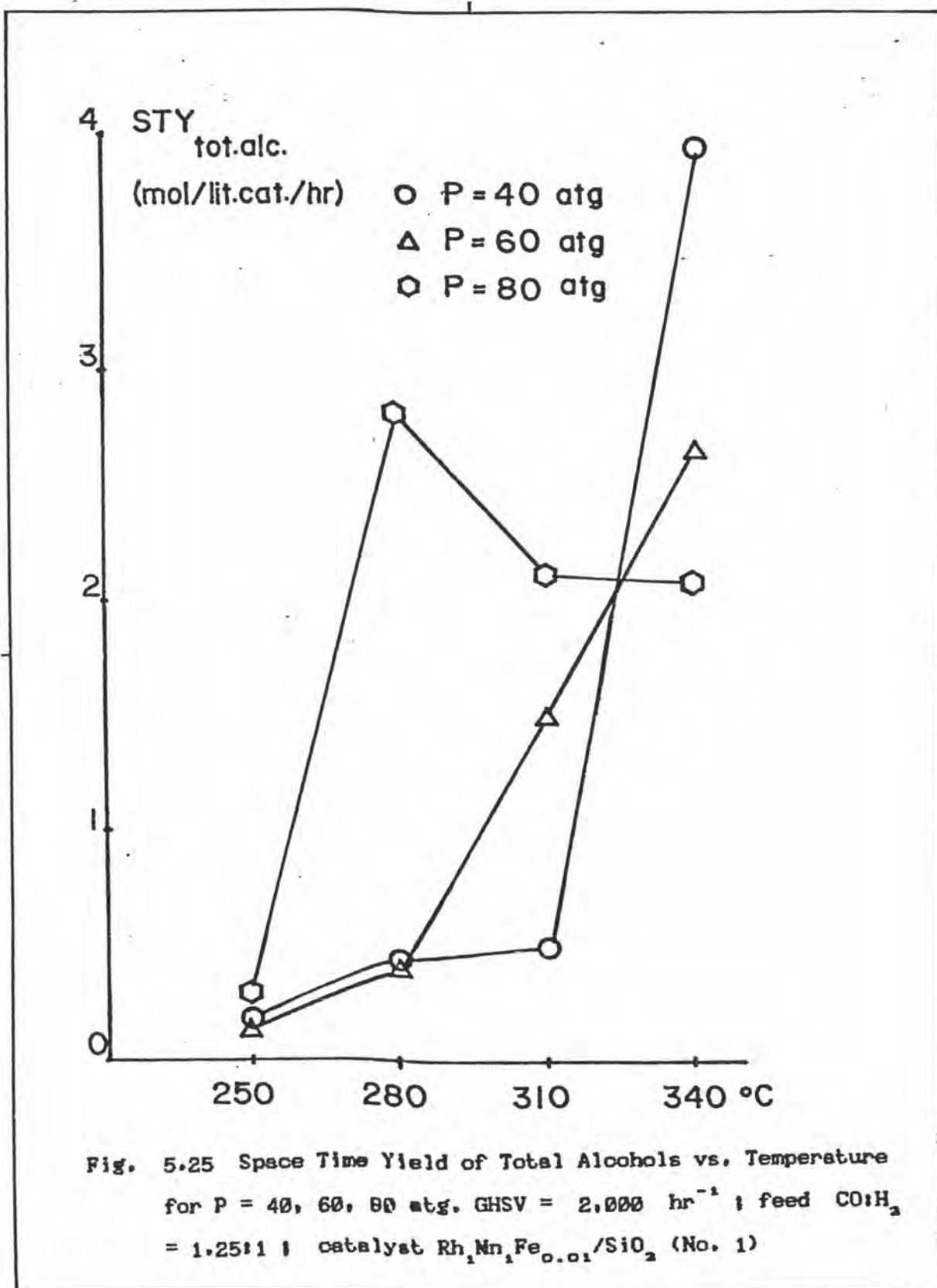
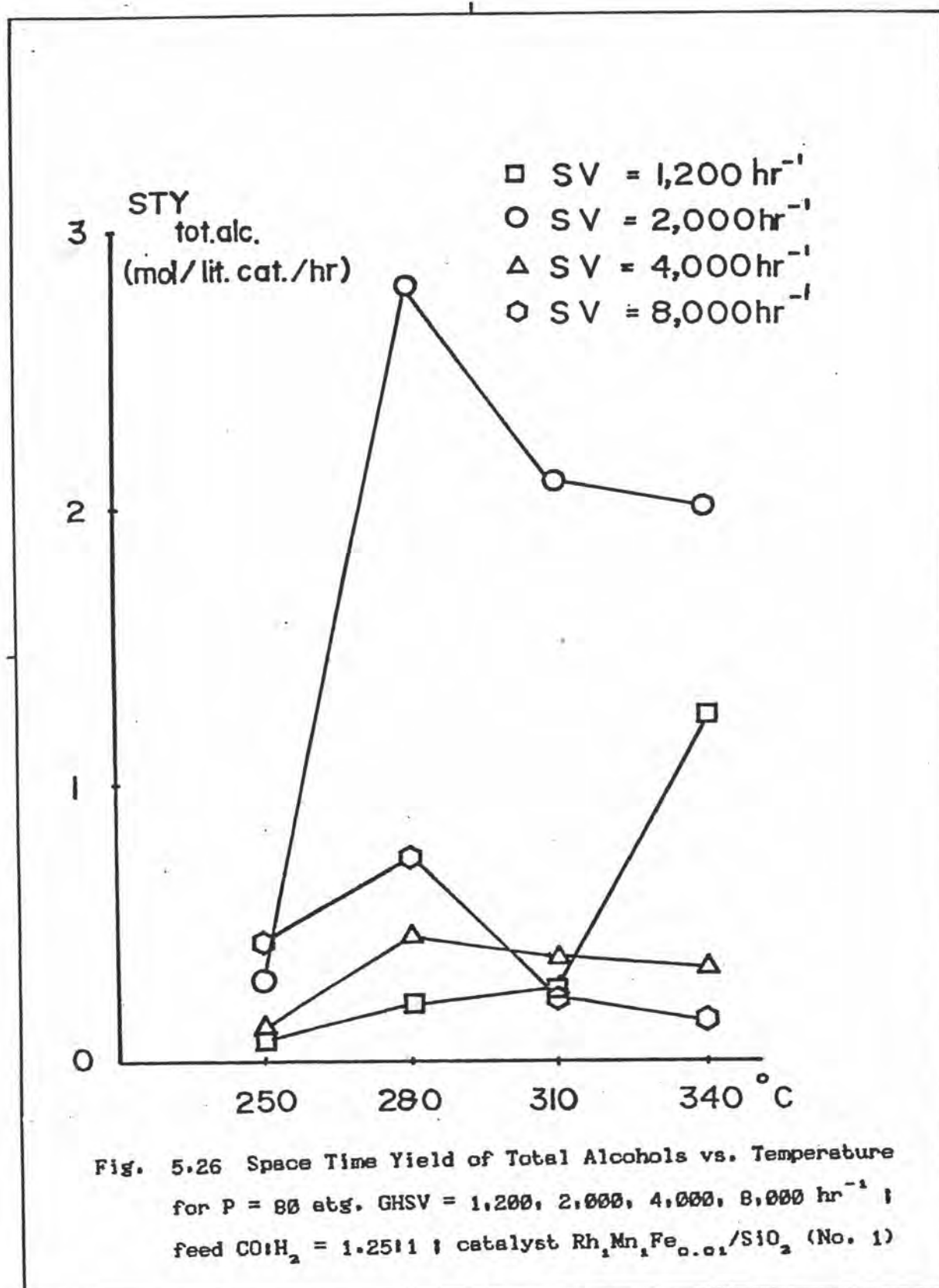
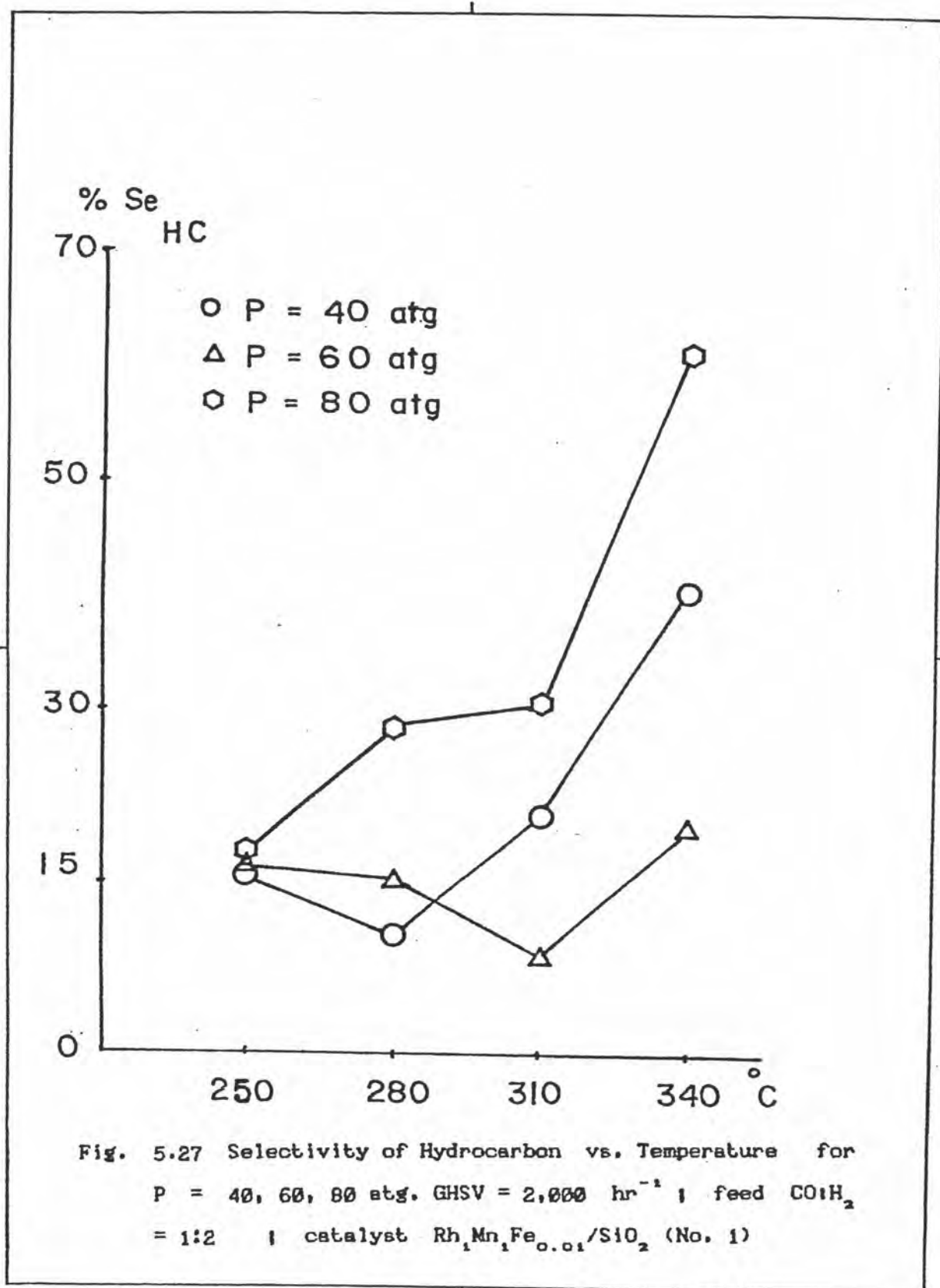
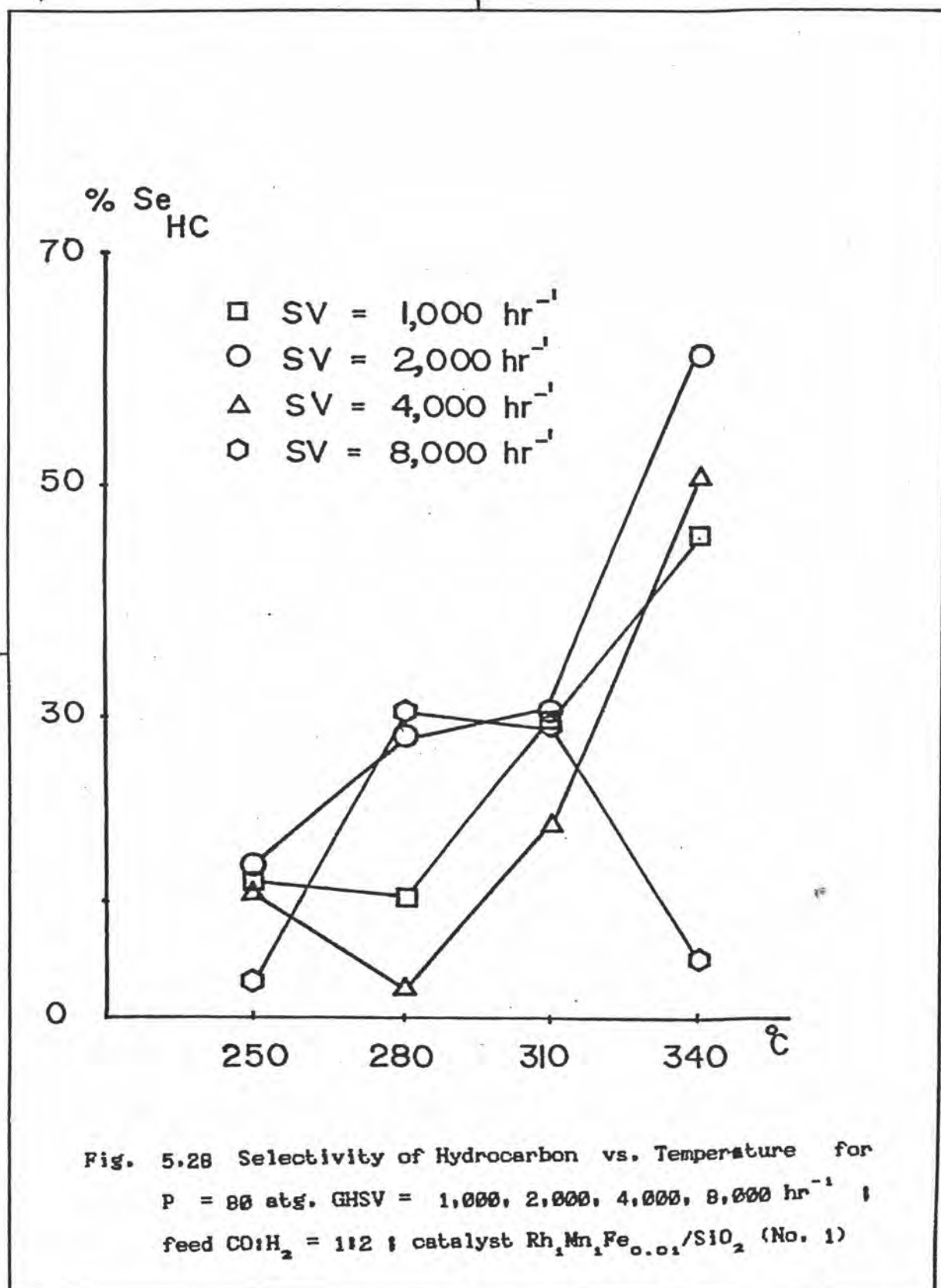


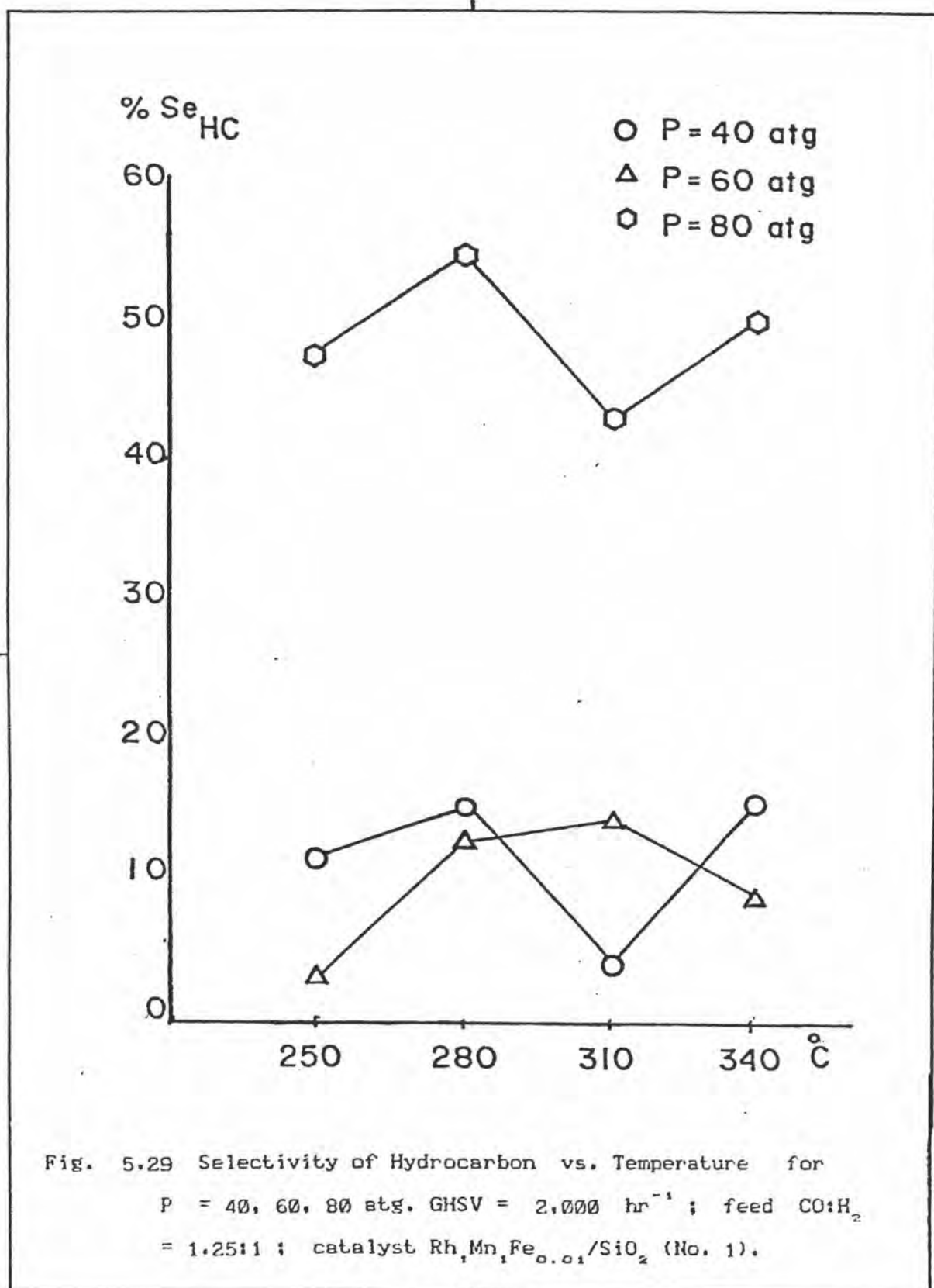
Fig. 5.24 Space Time Yield of Total Alcohols vs. Temperature for $P = 80$ atg. GHSV = 1,000, 2,000, 4,000, 8,000 hr⁻¹; feed $\text{CO}:\text{H}_2 = 1:2$; catalyst $\text{Rh}_1\text{Mn}_1\text{Fe}_{0.01}/\text{SiO}_2$ (No. 1)

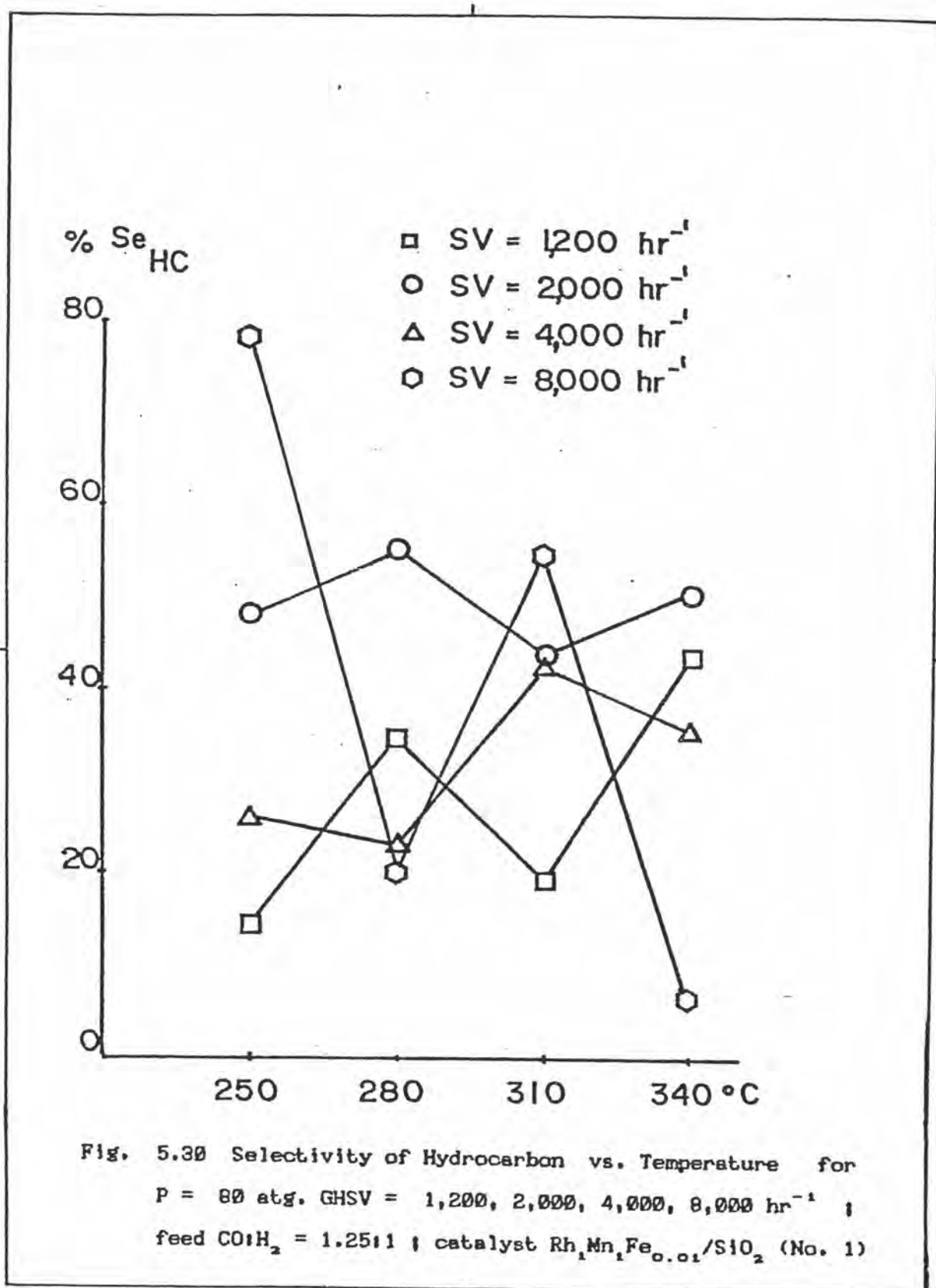


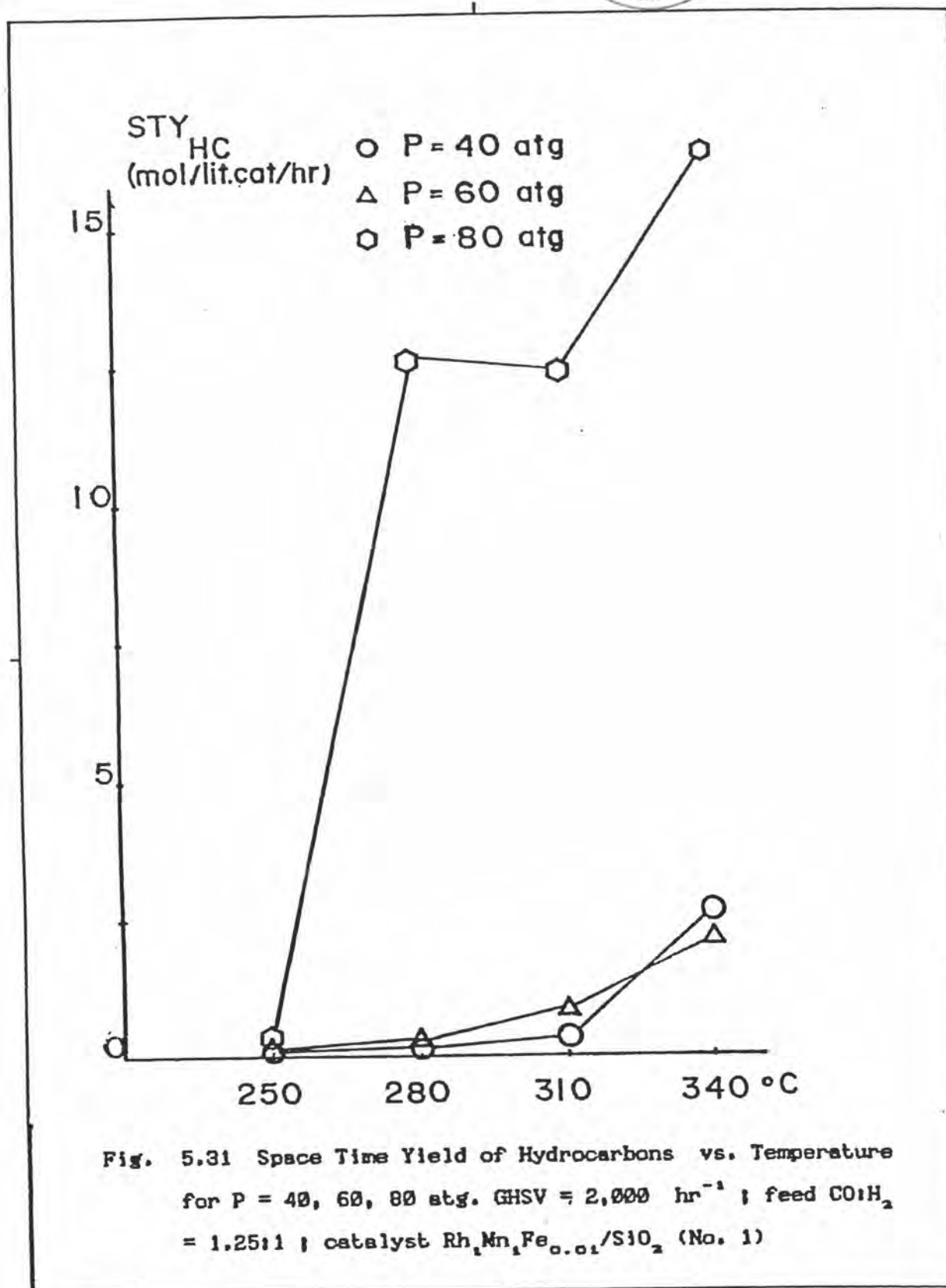


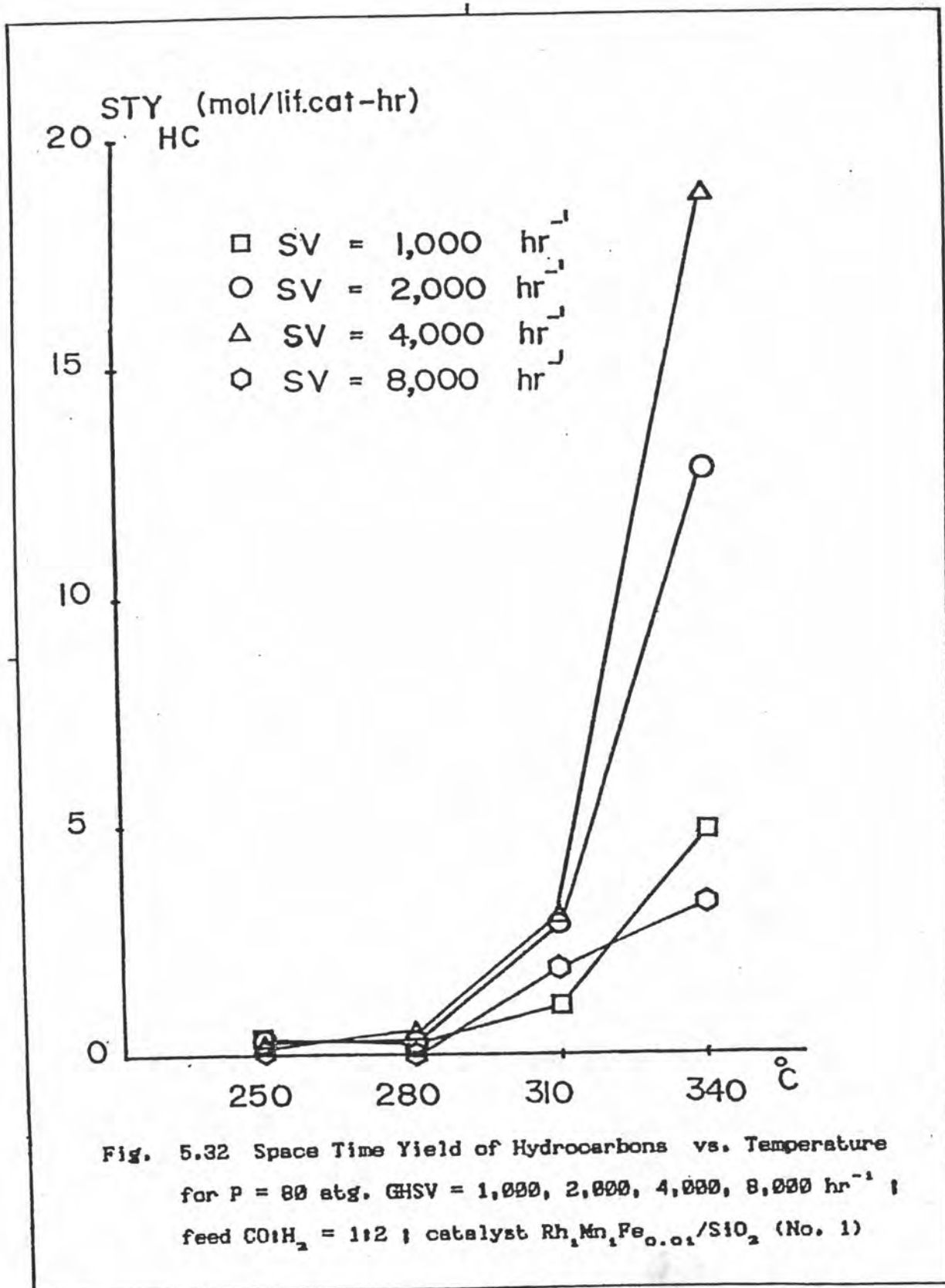


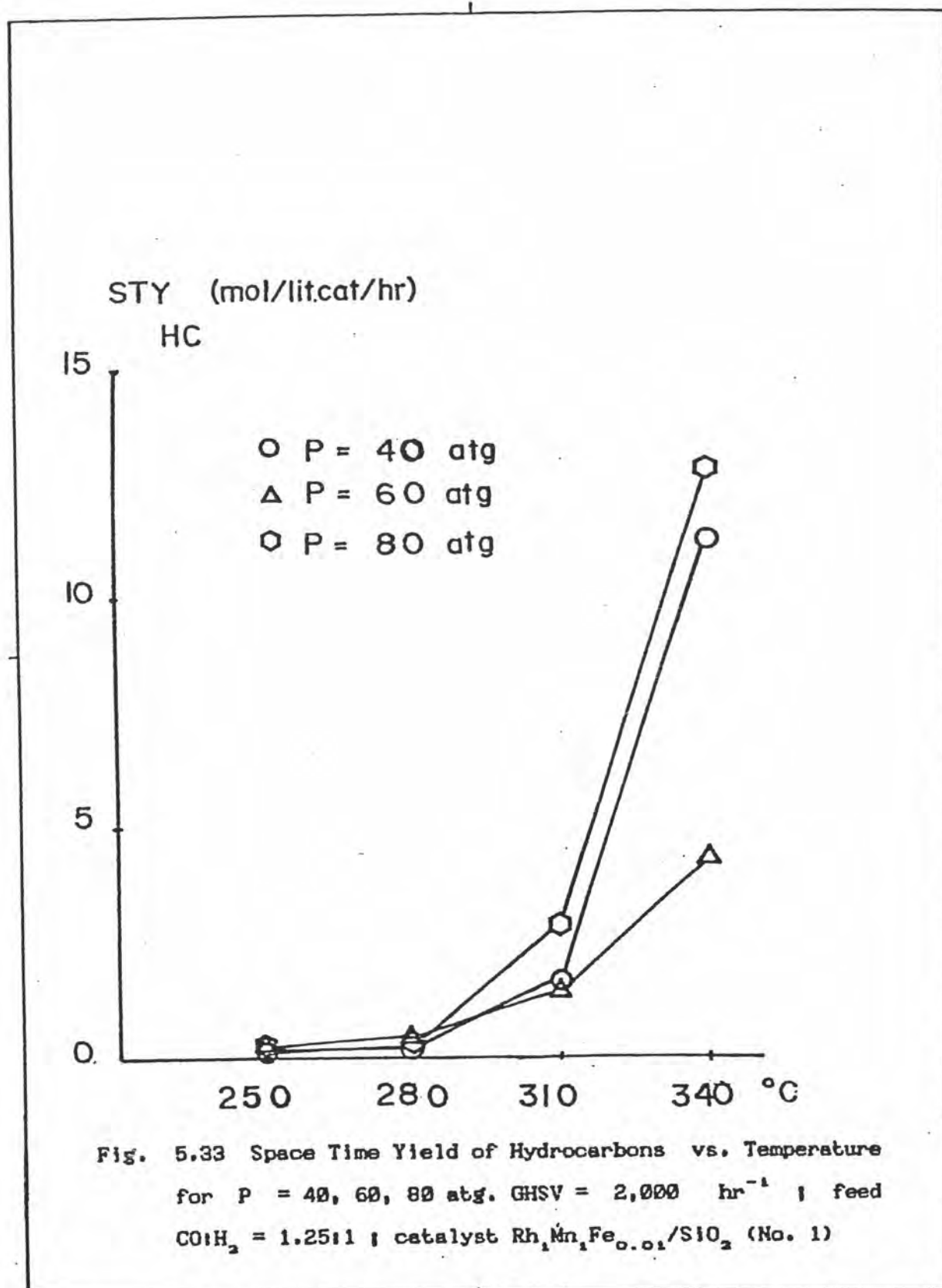


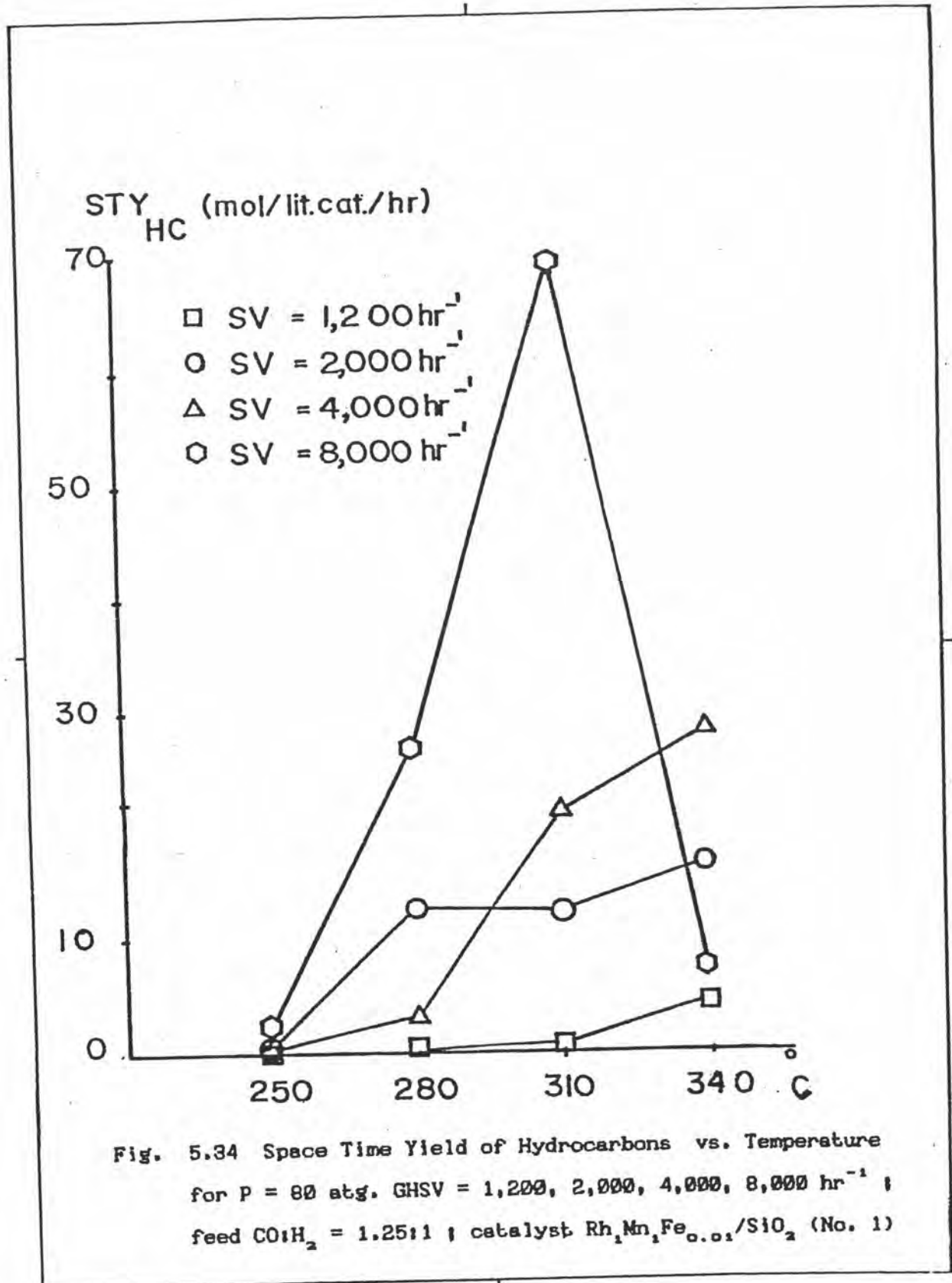


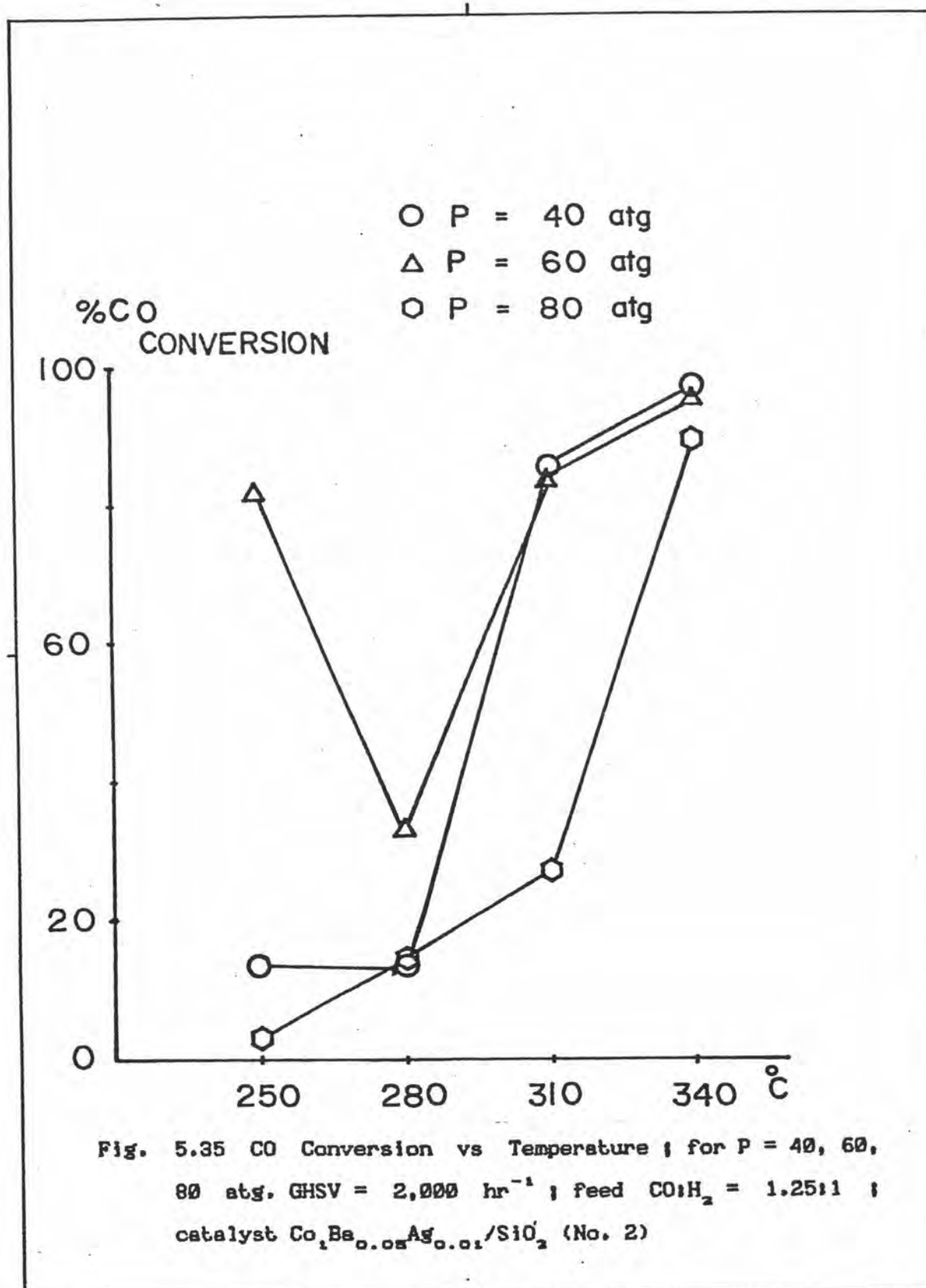


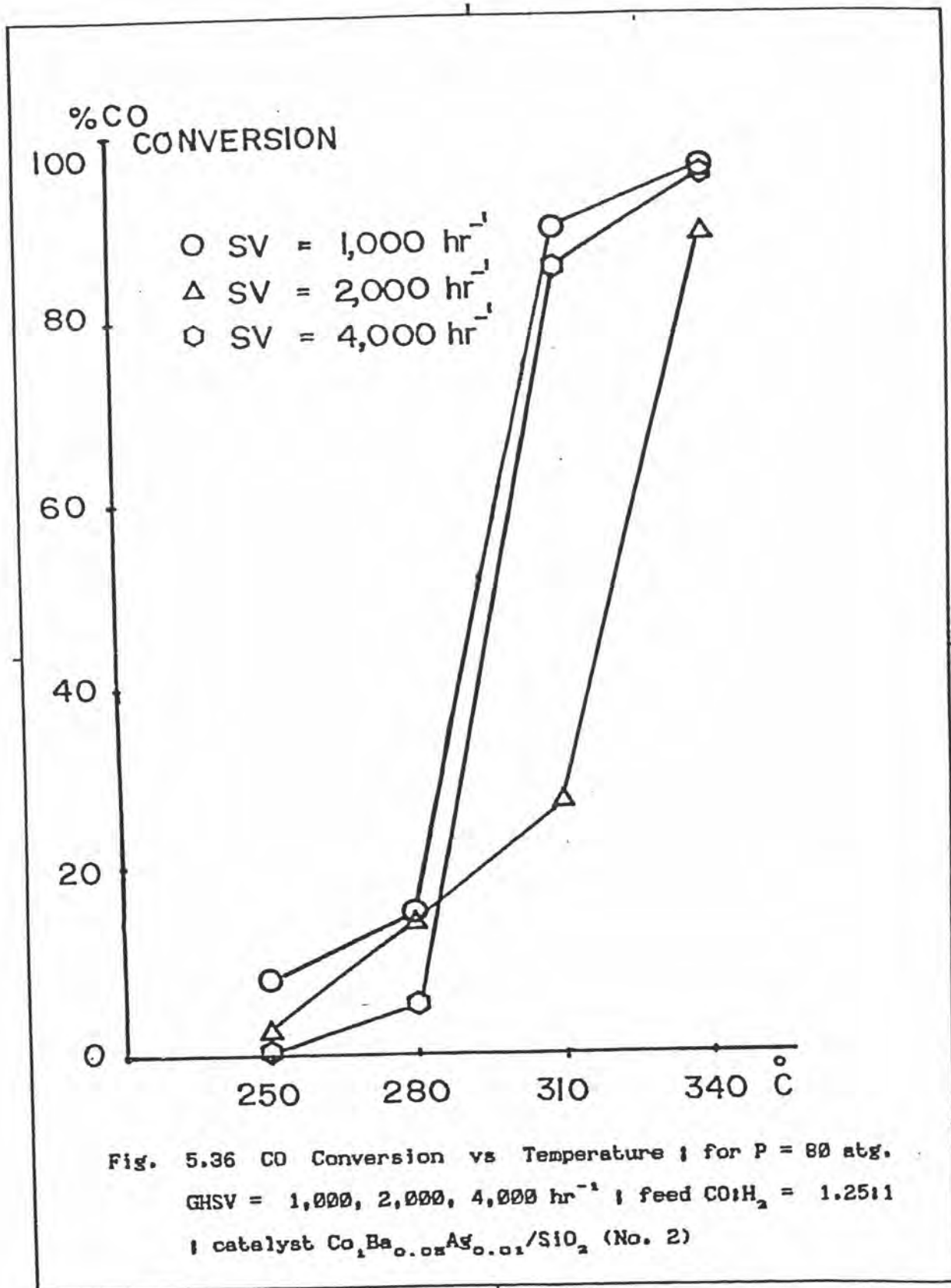


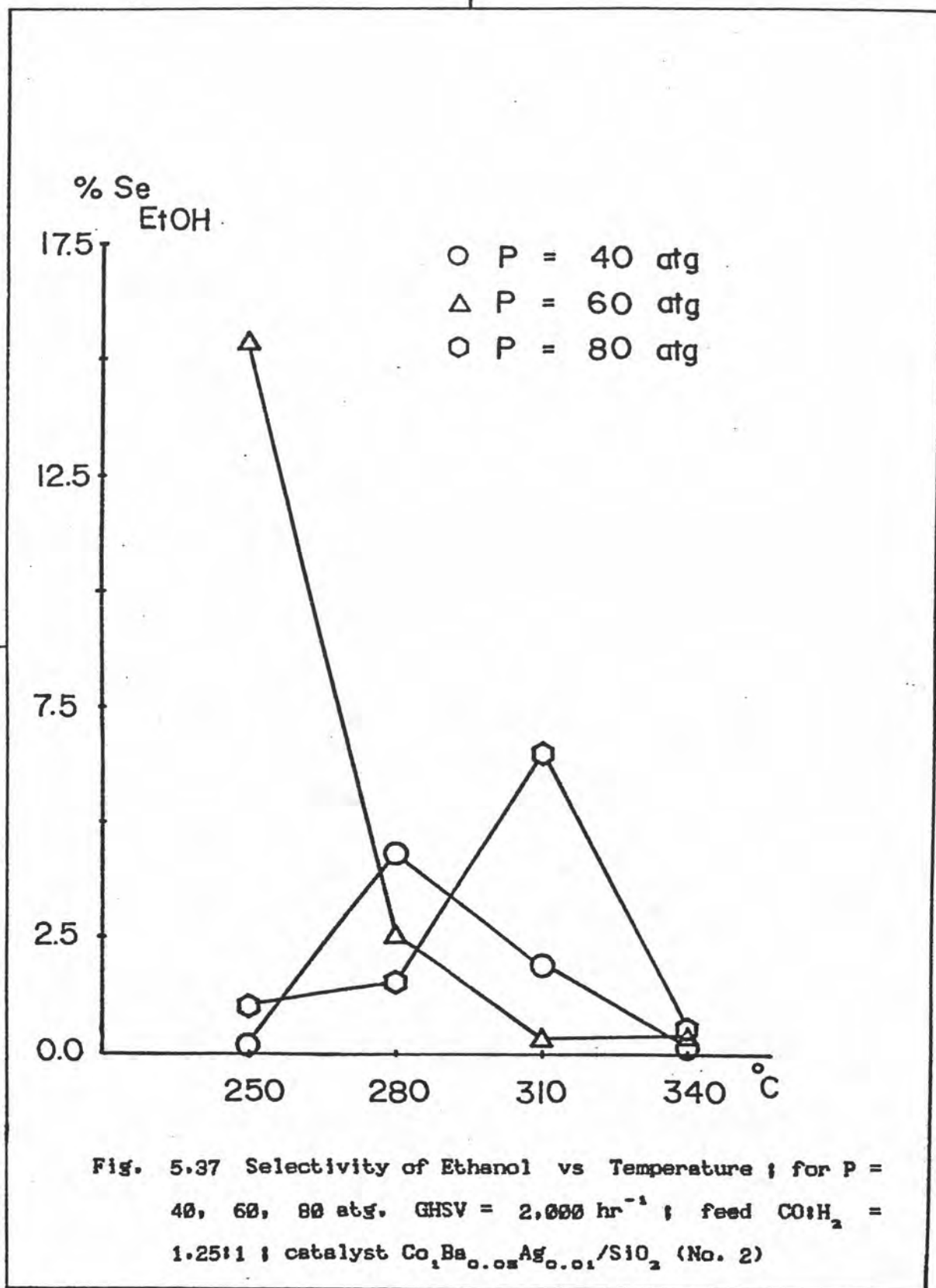


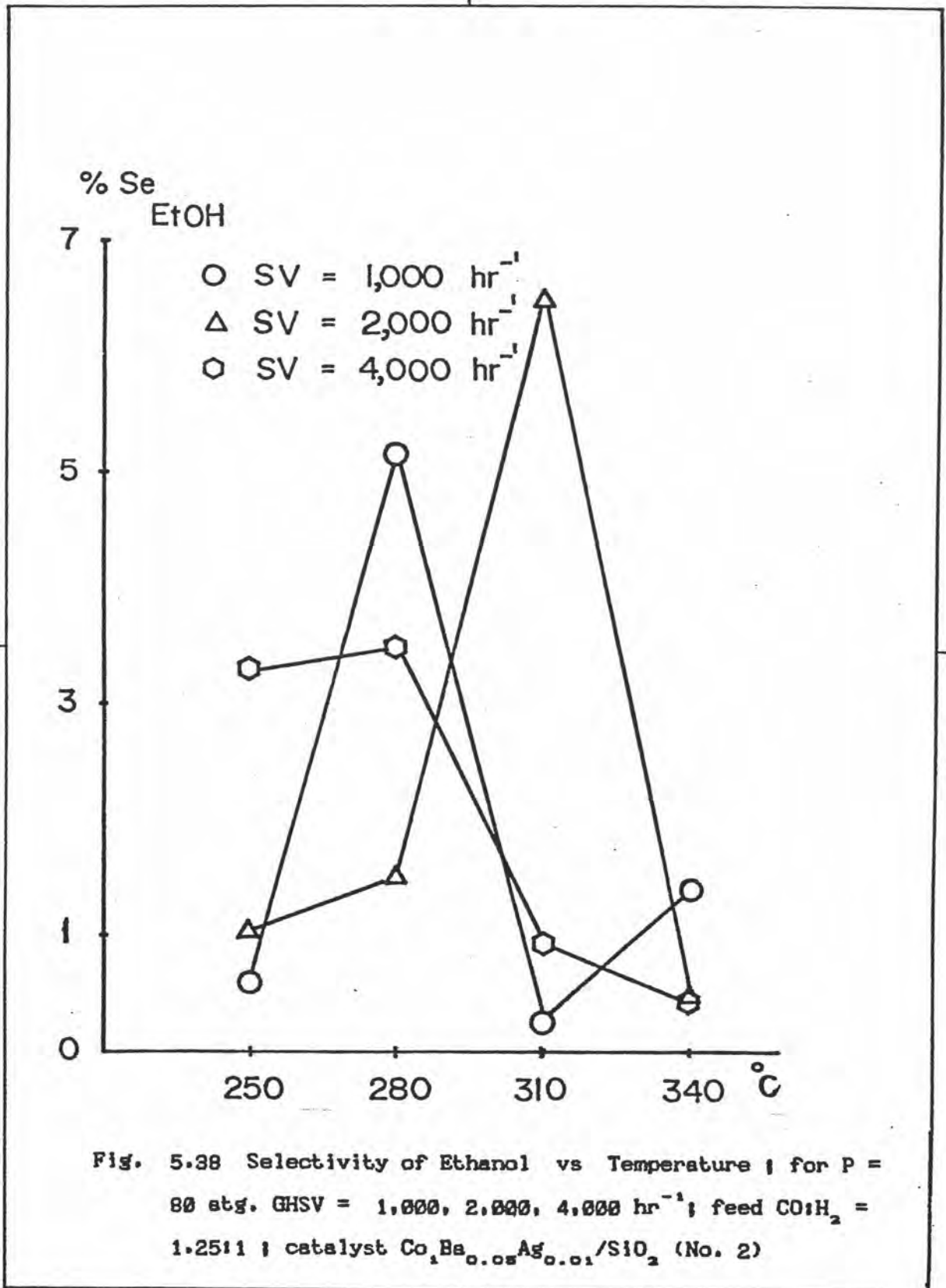


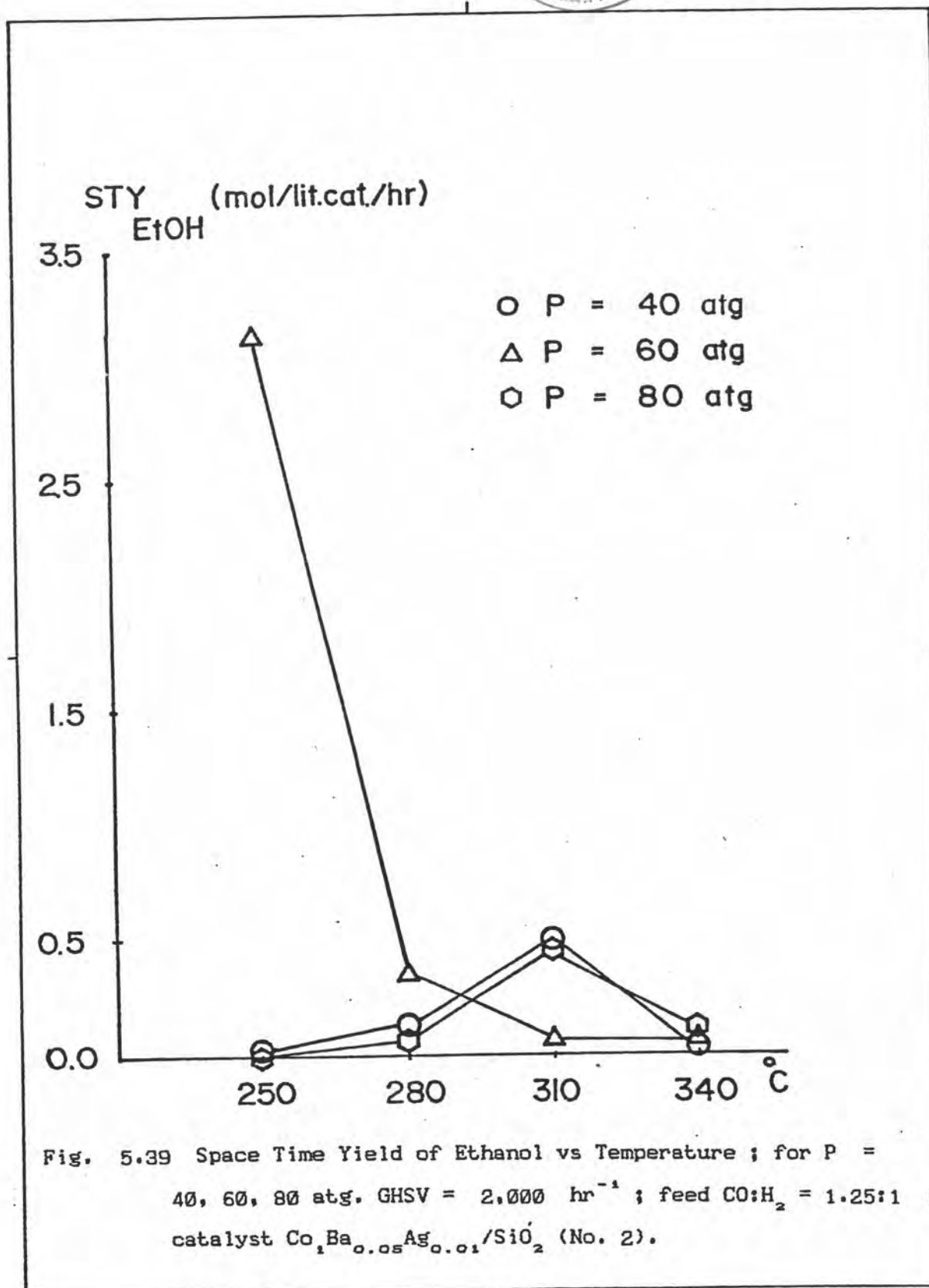


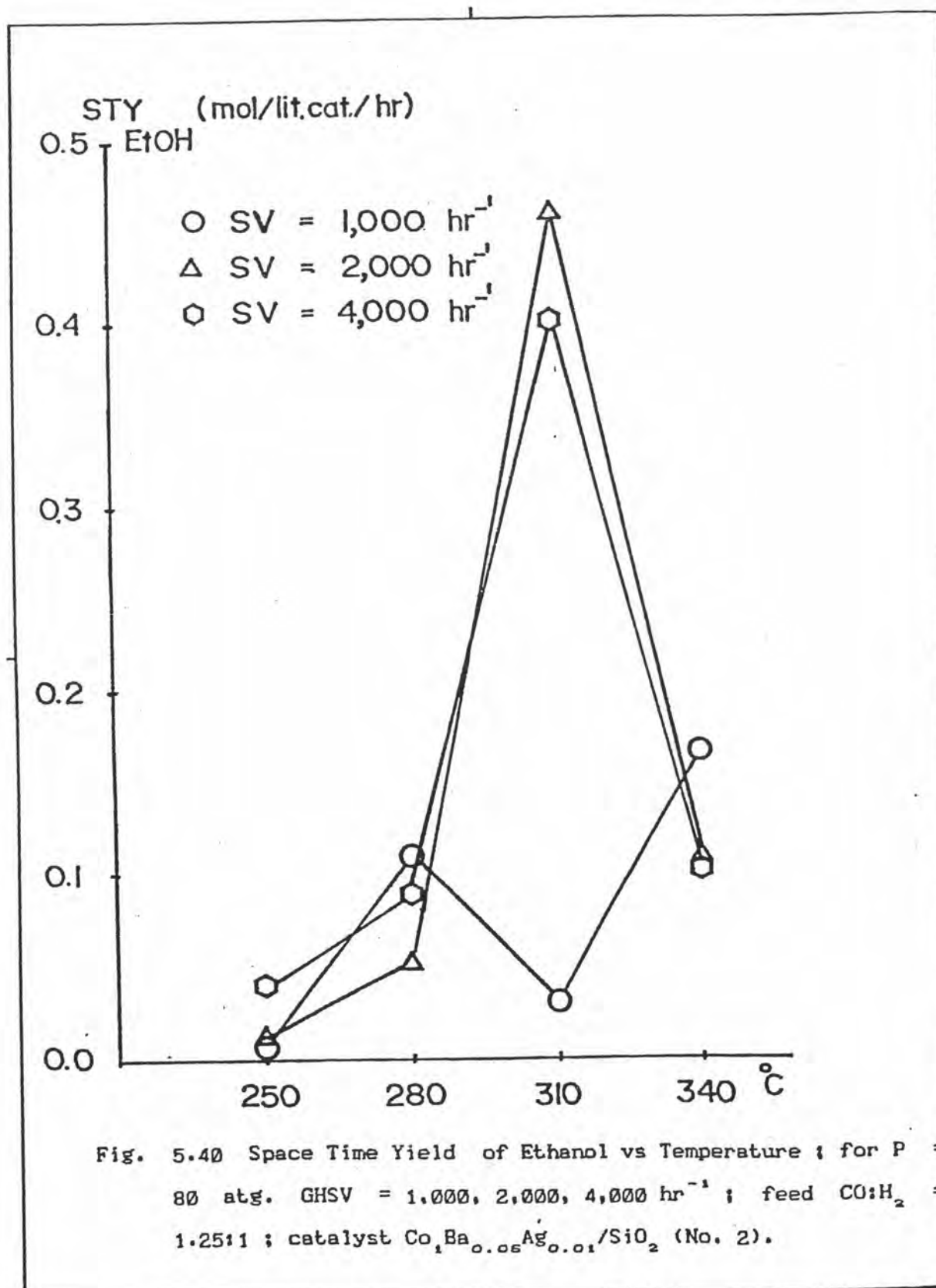












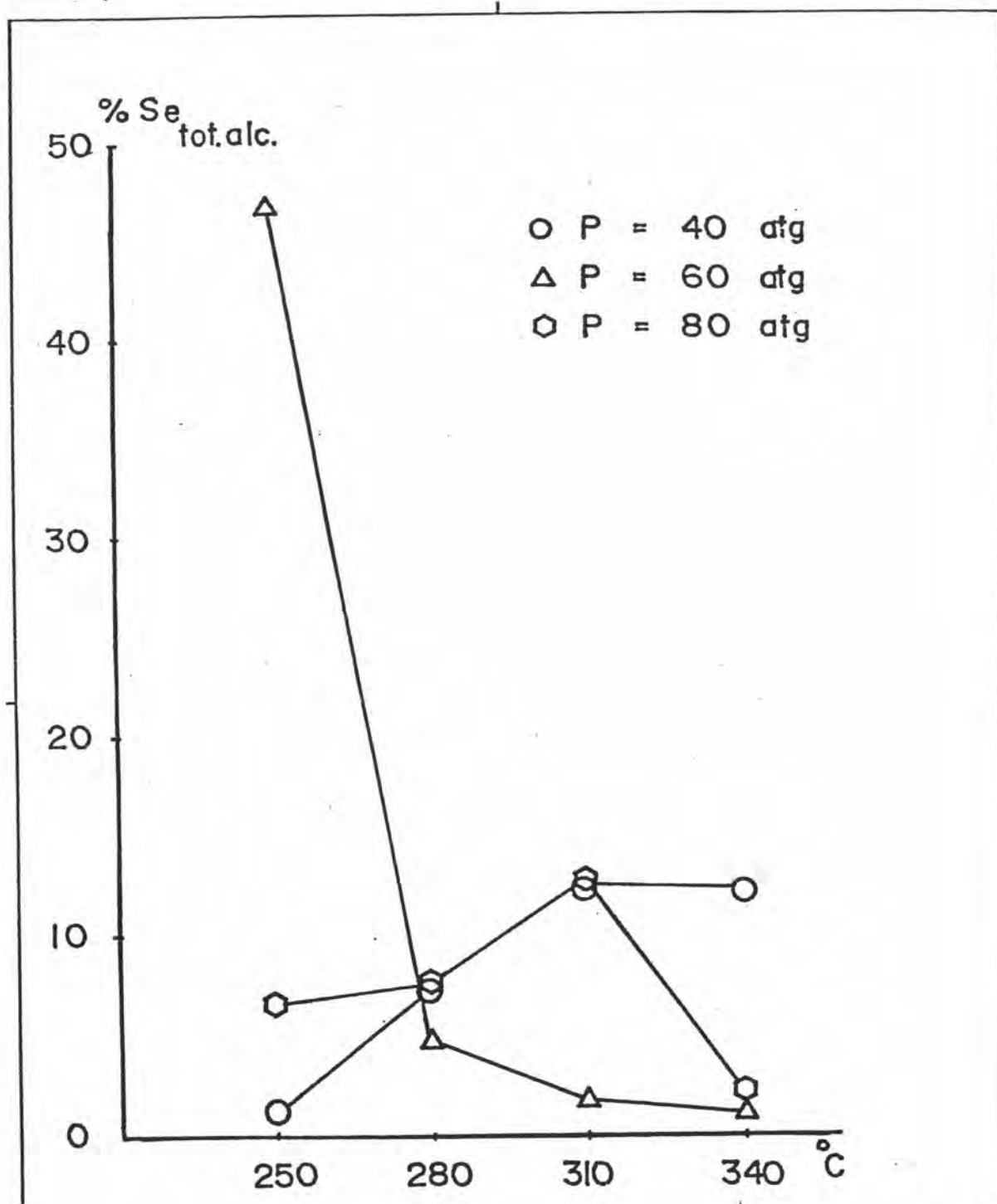
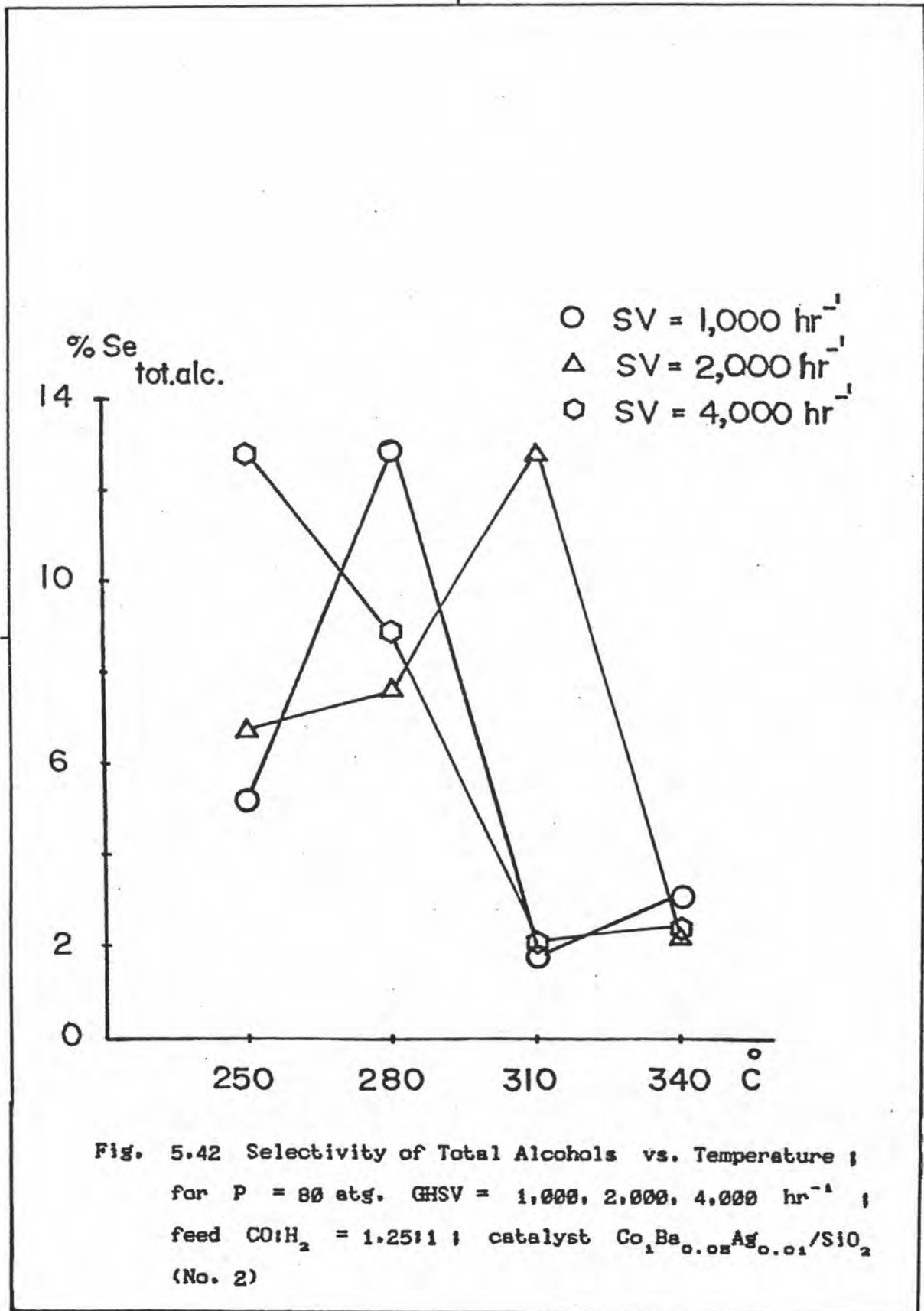


Fig. 5.41 Selectivity of Total Alcohols vs Temperature ;
 for $P = 40, 60, 80$ atg. $GHSV = 2,000 \text{ hr}^{-1}$; feed
 $\text{CO}:\text{H}_2 = 1.25:1$; catalyst $\text{Co}_1\text{Ba}_{0.05}\text{Ag}_{0.01}/\text{SiO}_2$ (No. 2)



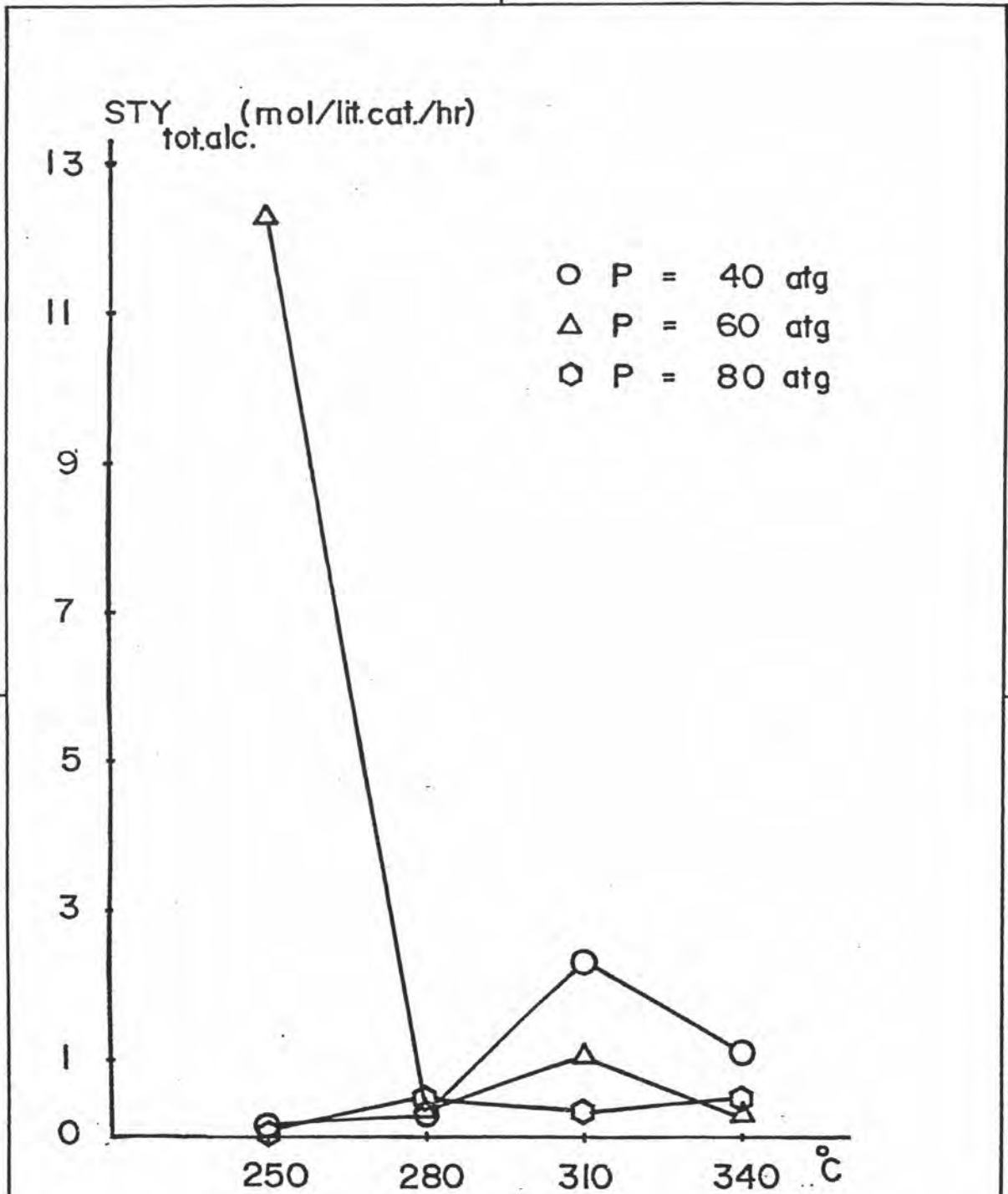
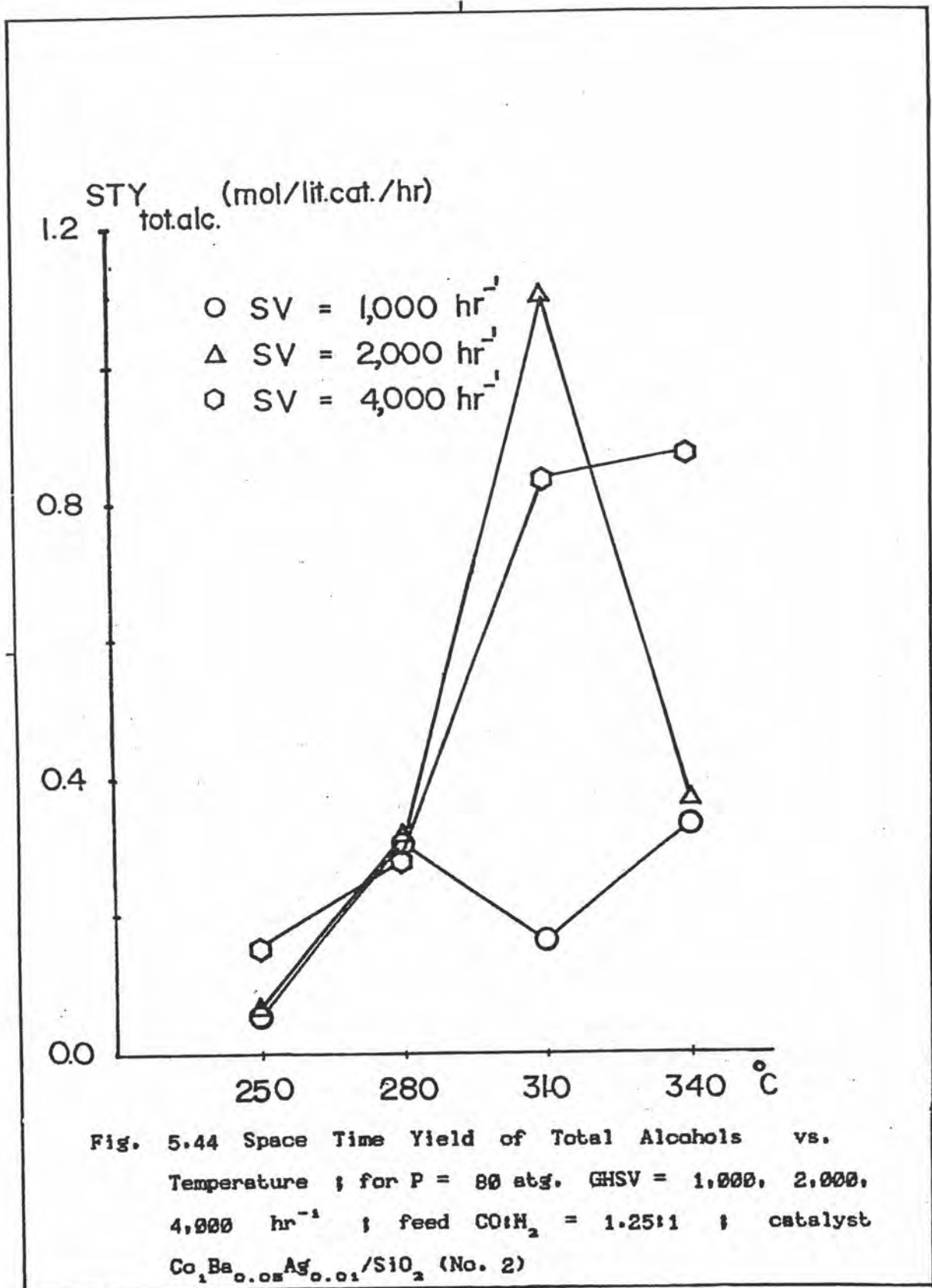
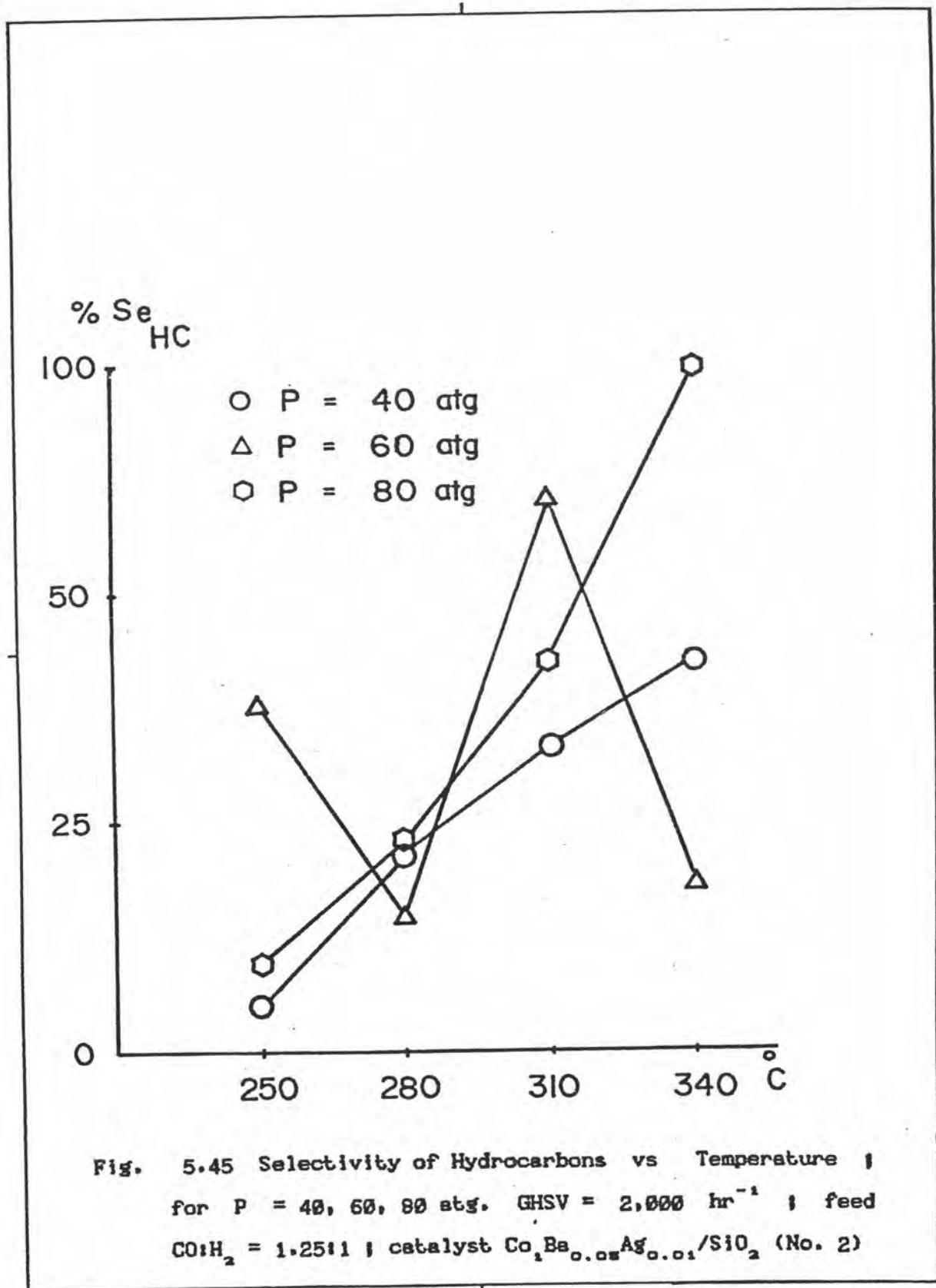
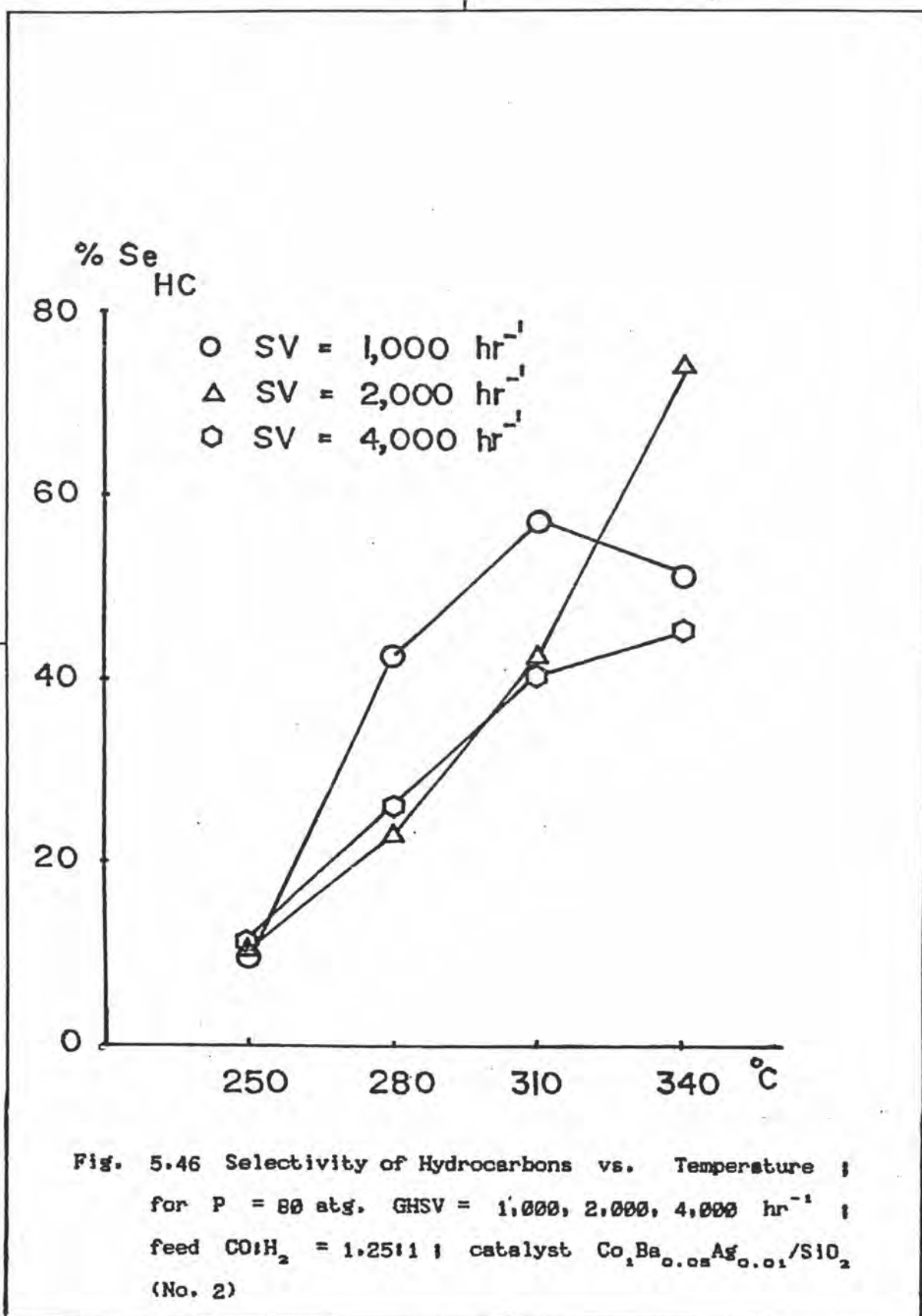
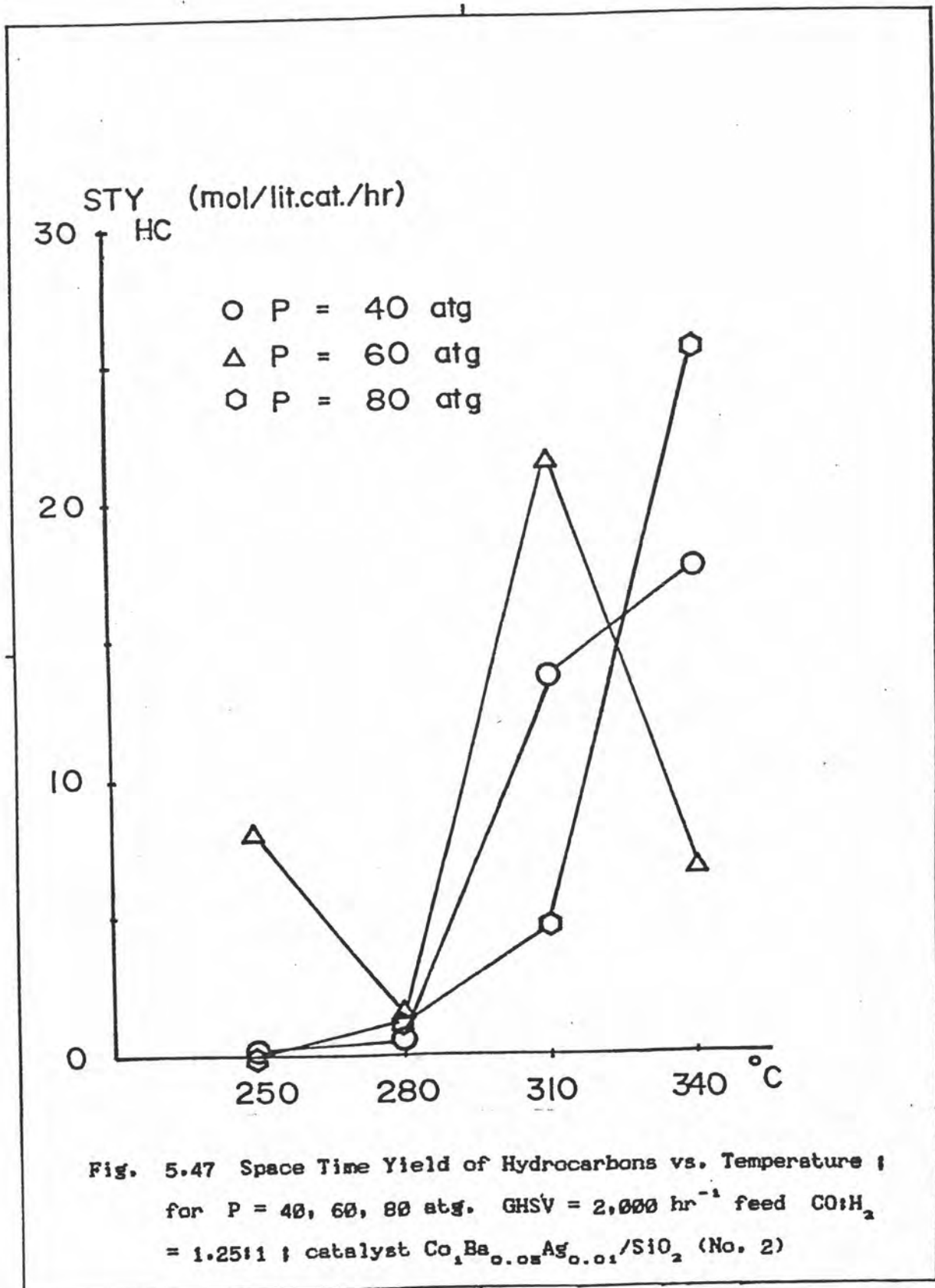


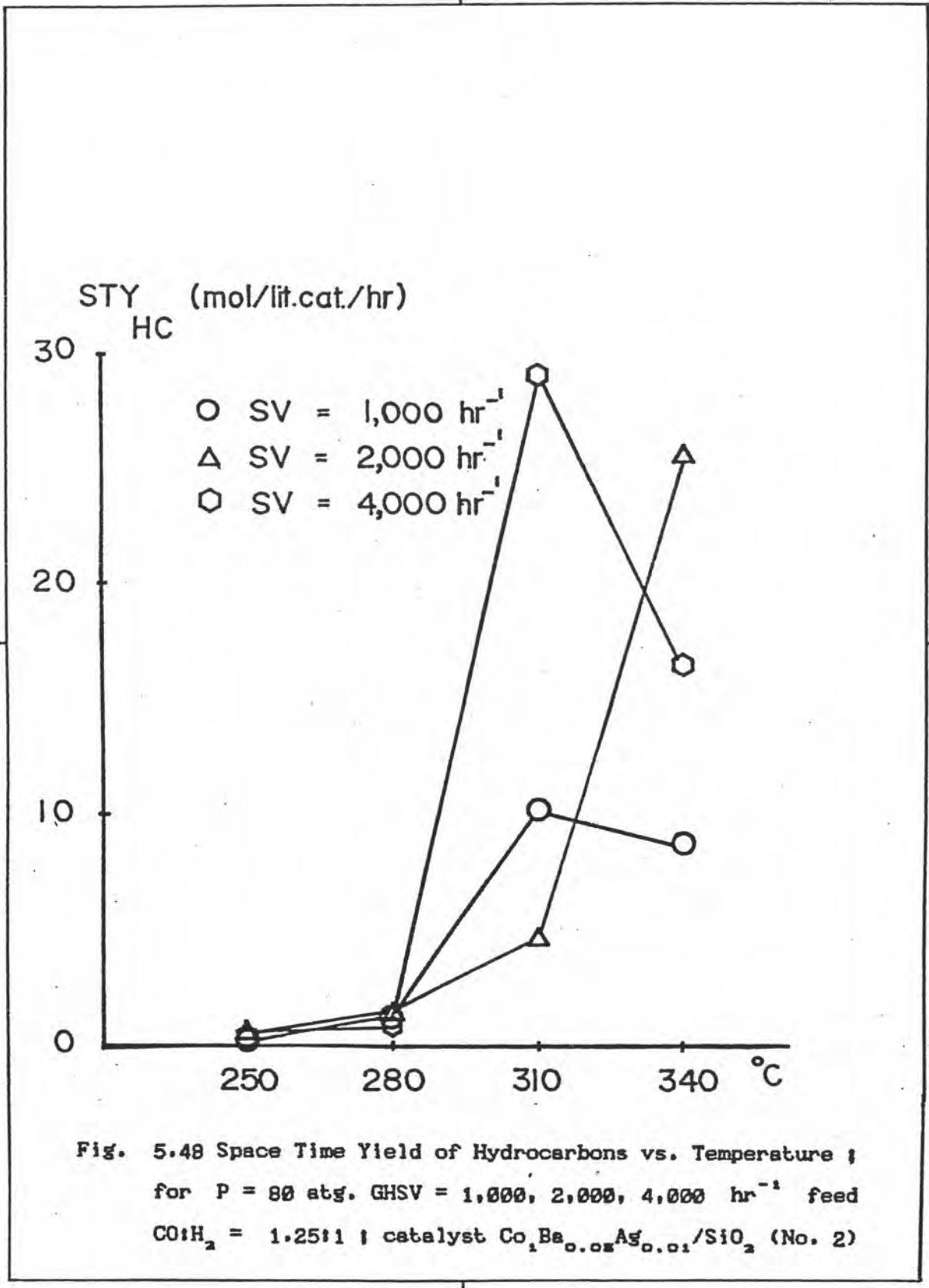
Fig. 5.43 Space Time Yield of Total Alcohols vs. Temperature ; for P = 40, 60, 80 atg, GHSV = 2,000 hr⁻¹ ; feed CO:H₂ = 1.25:1 ; catalyst Co₁Ba_{0.05}Ag_{0.01}/SiO₂ (No. 2)

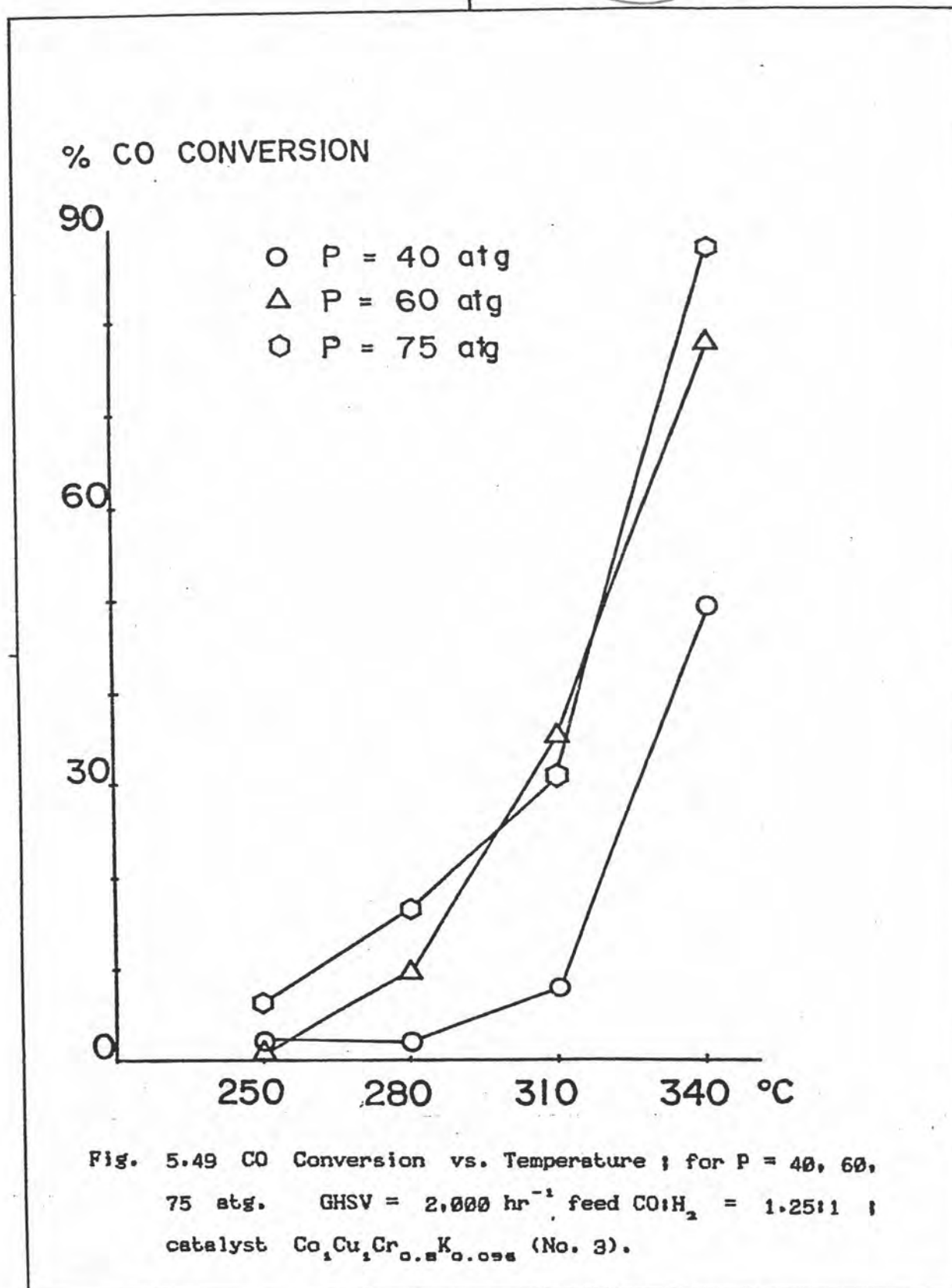


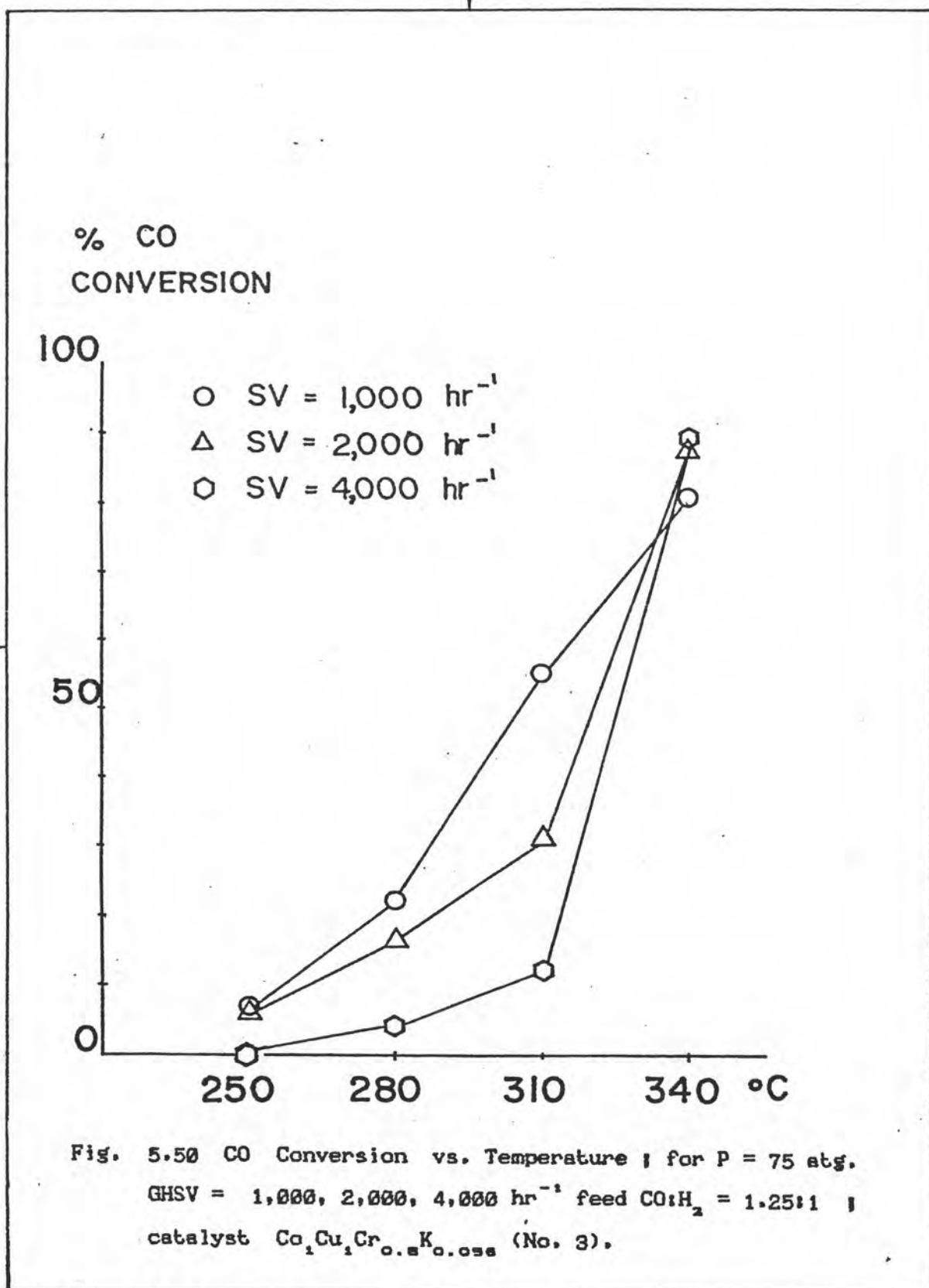












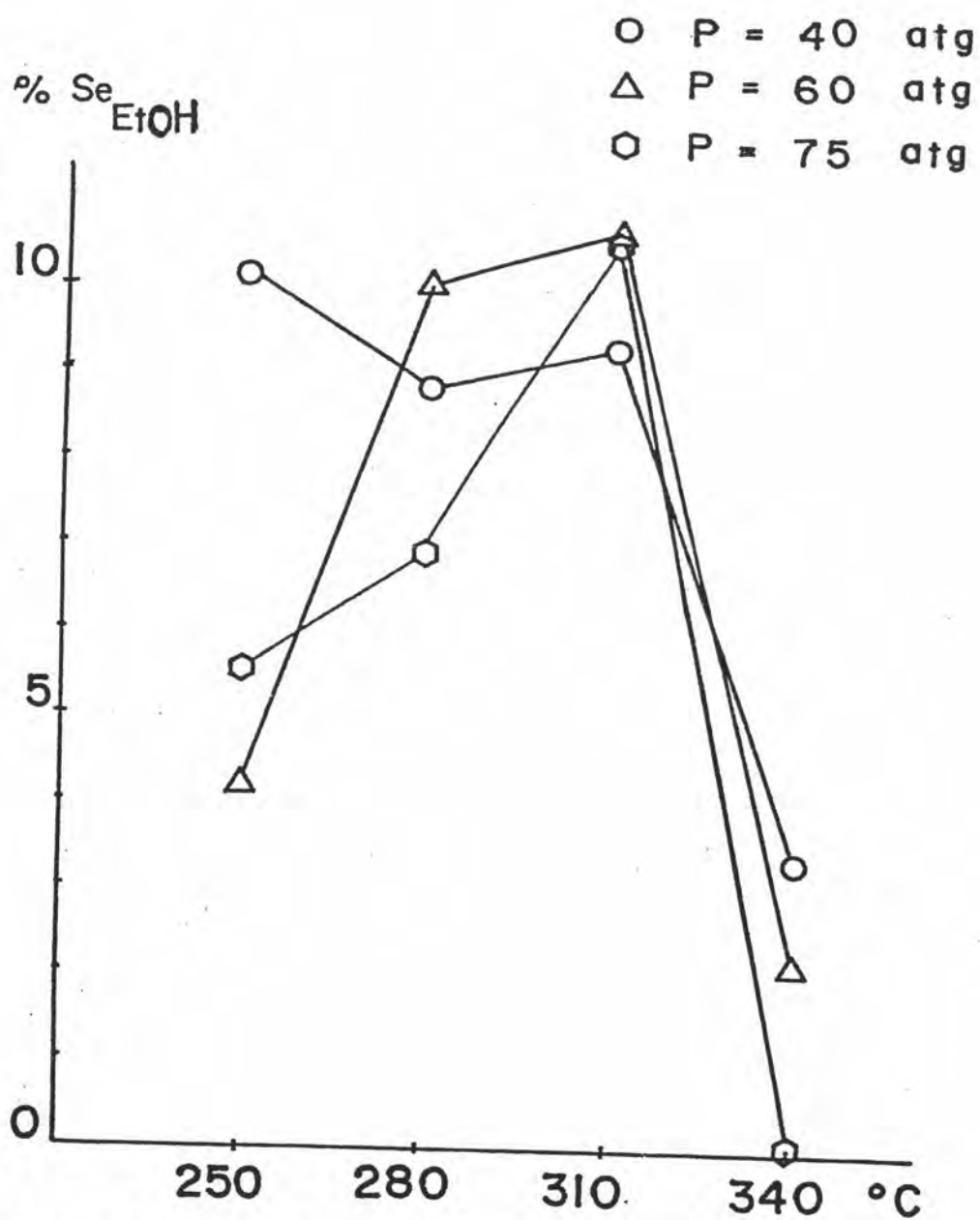
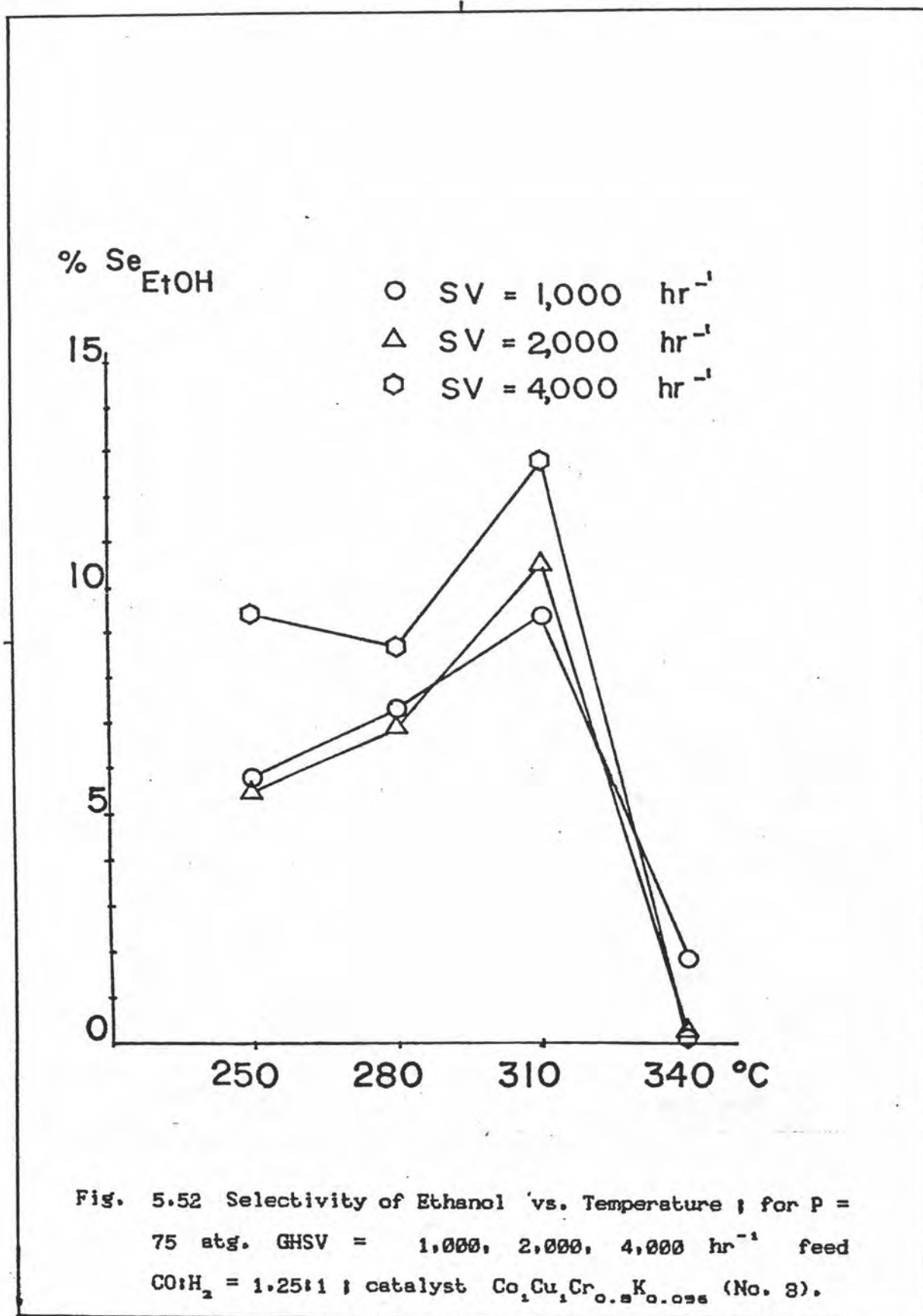
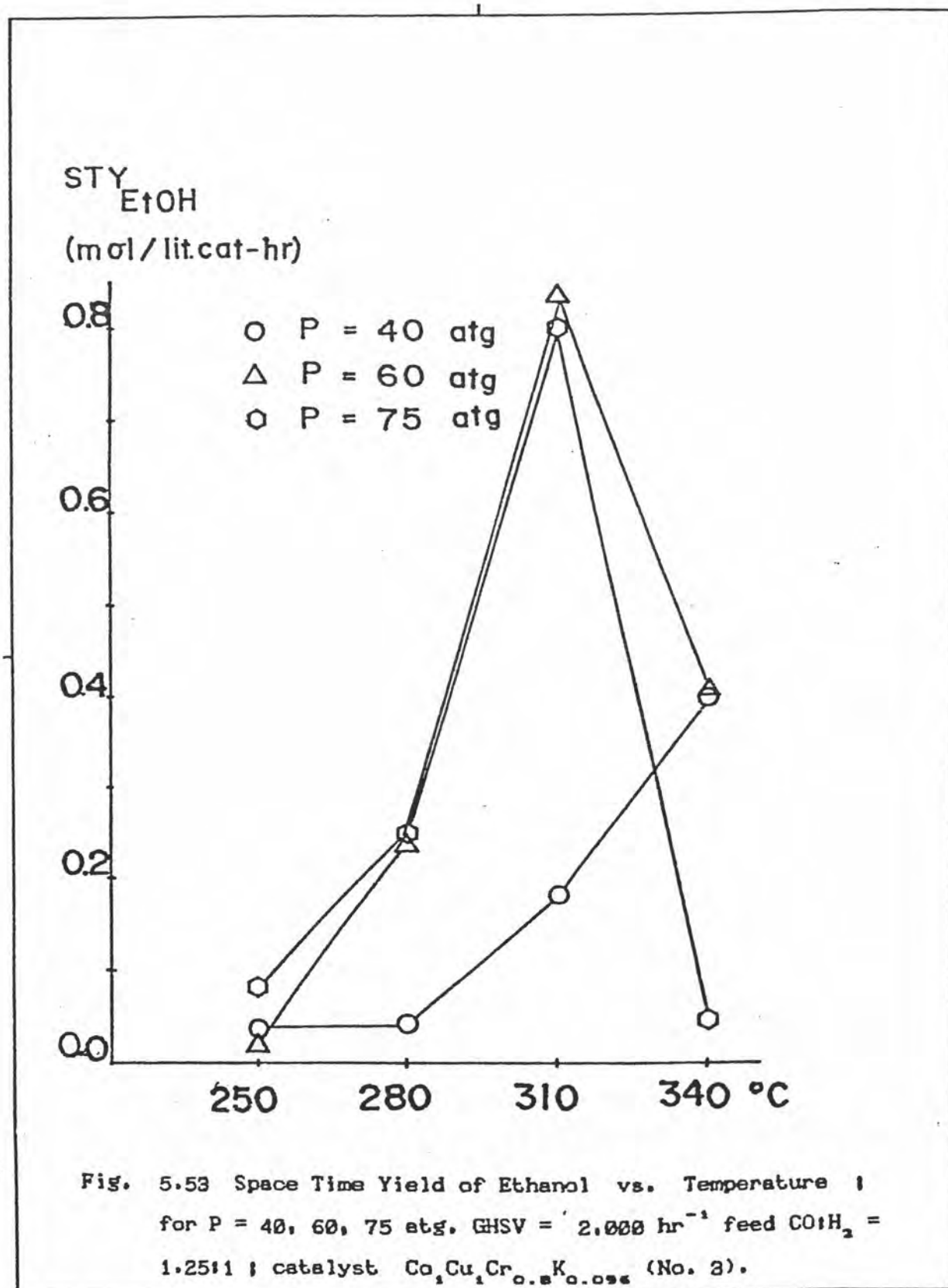
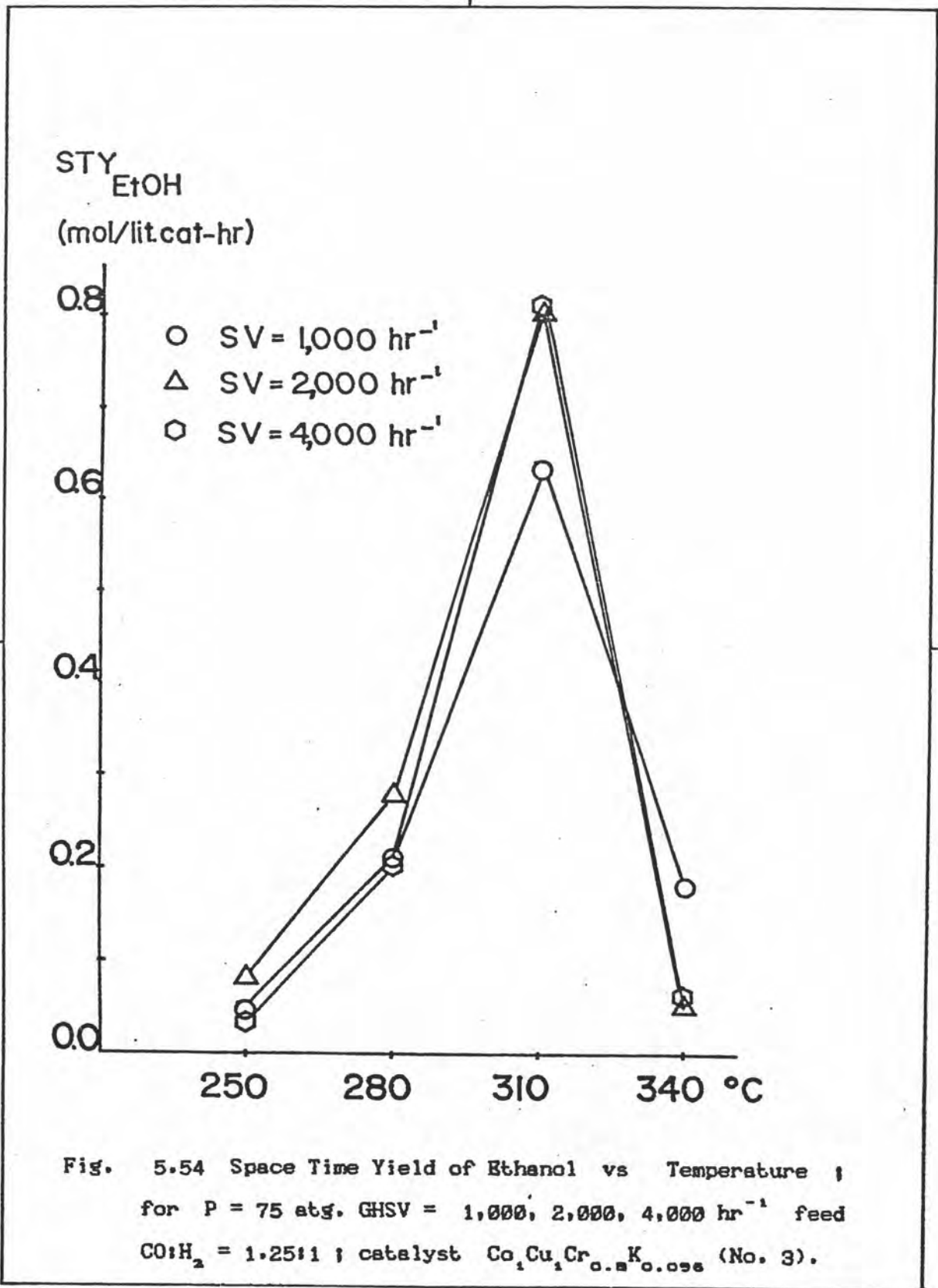
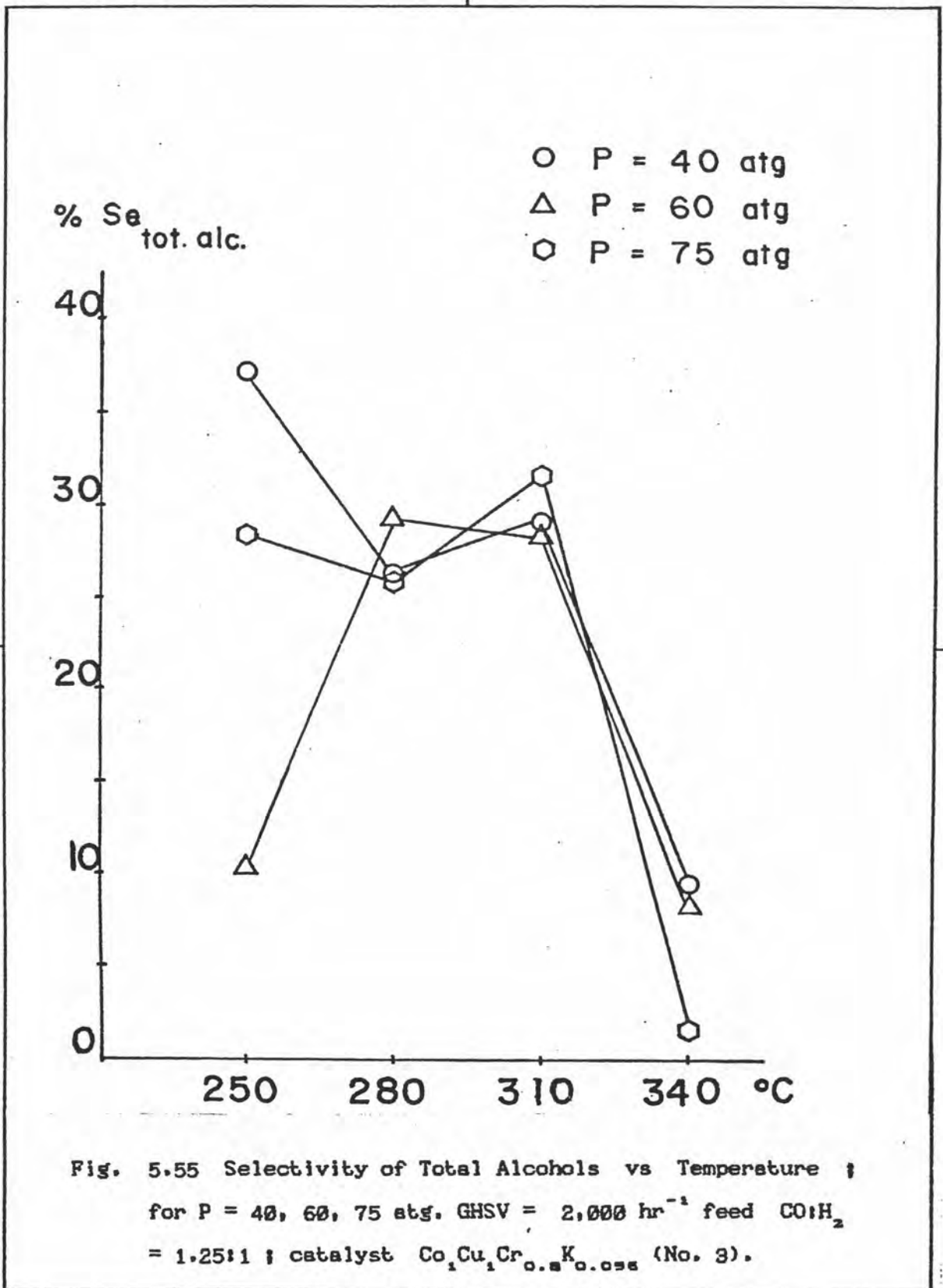


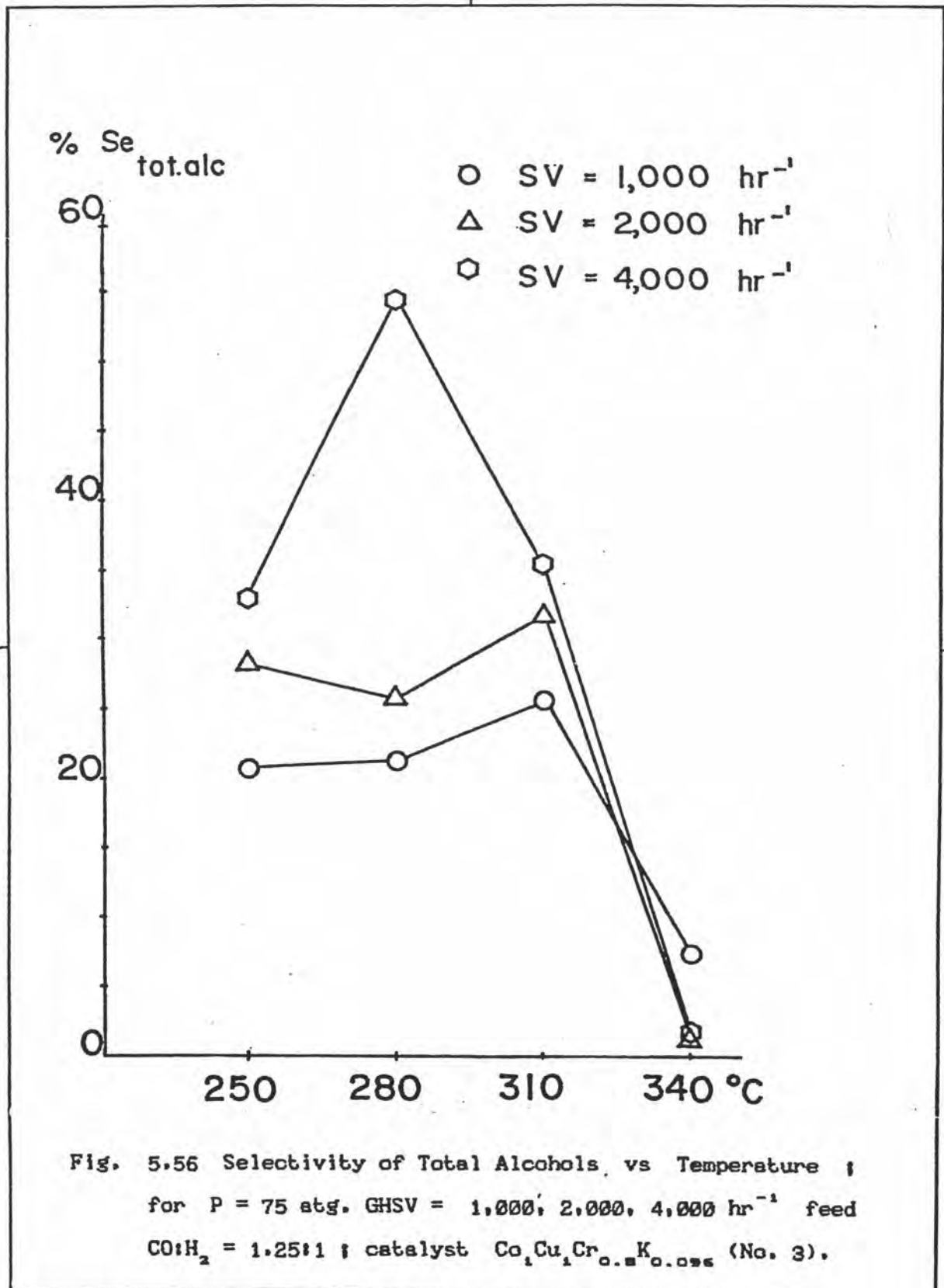
Fig. 5.51 Selectivity of Ethanol vs. Temperature ; for P = 40, 60, 75 atg. GHSV = $2,000 \cdot \text{hr}^{-1}$ feed $\text{CO}:\text{H}_2 = 1.25:1$; catalyst $\text{Co}_1\text{Cu}_1\text{Cr}_{0.5}\text{K}_{0.025}$ (No. 3).











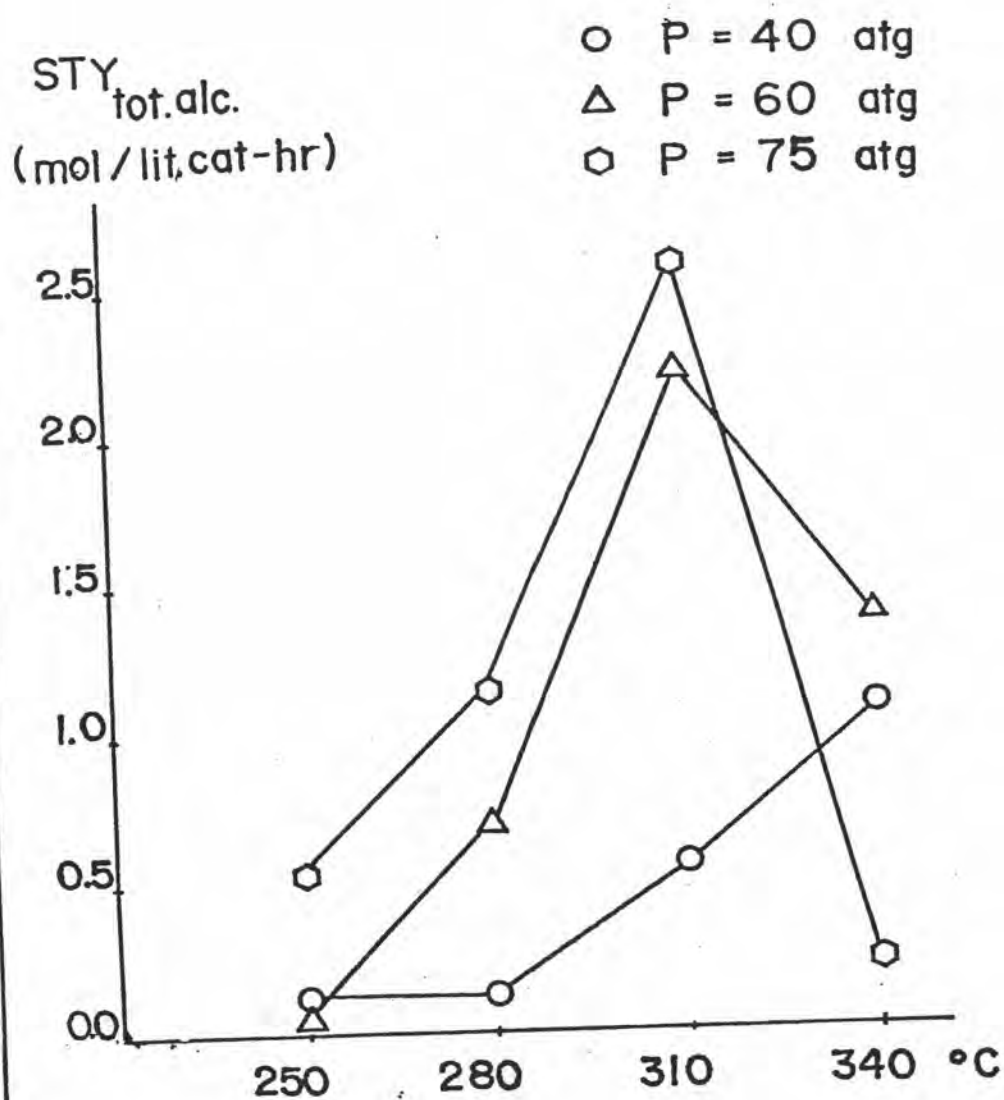
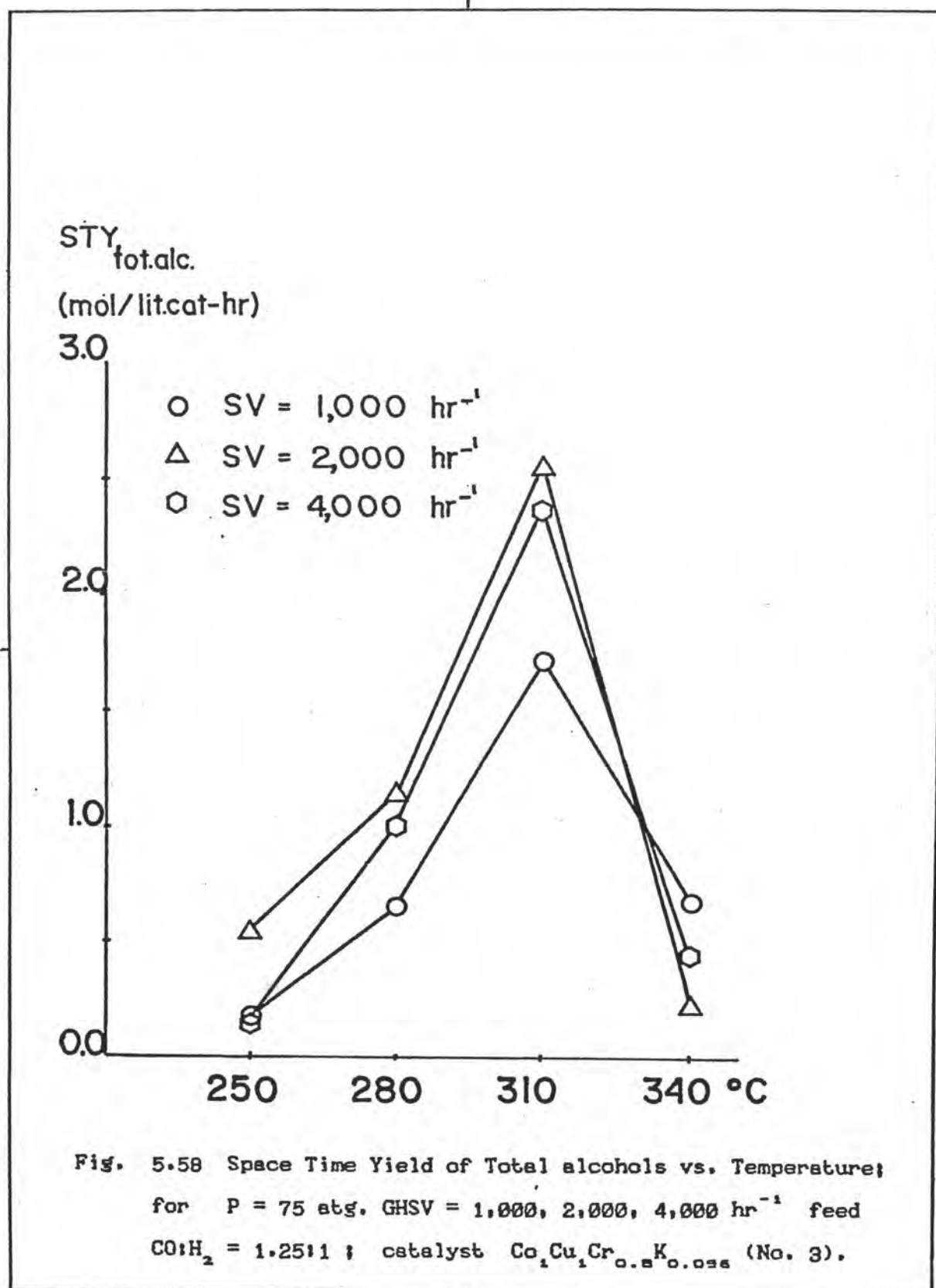
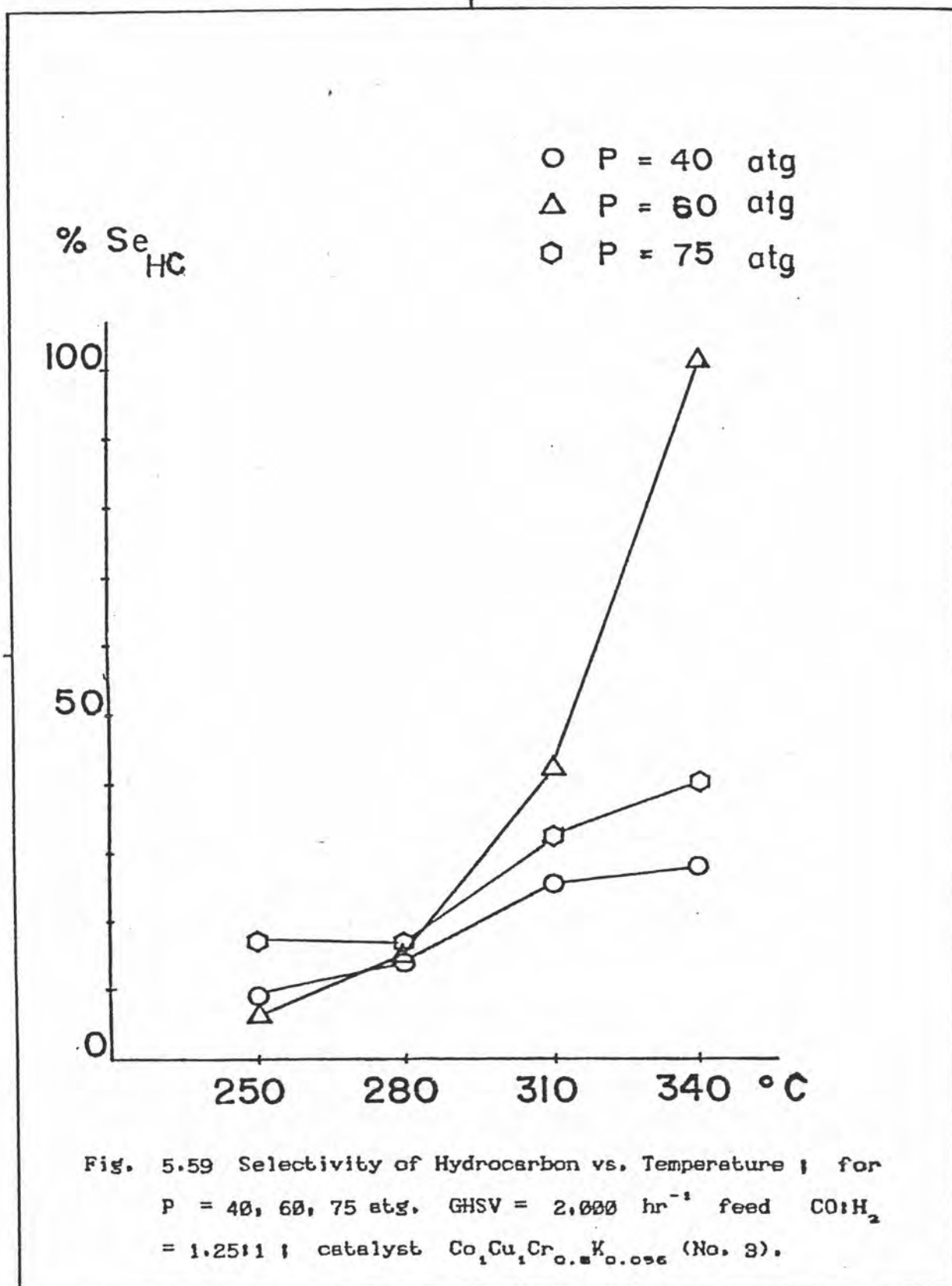


Fig. 5.57 Space Time Yield of Total alcohols vs Temperature ; for P = 40, 60, 75 atg. GHSV = 2,000 hr⁻¹ feed CO:H₂ = 1.25:1 ; catalyst Co₁Cu₁Cr_{0.5}K_{0.055} (No. 3).





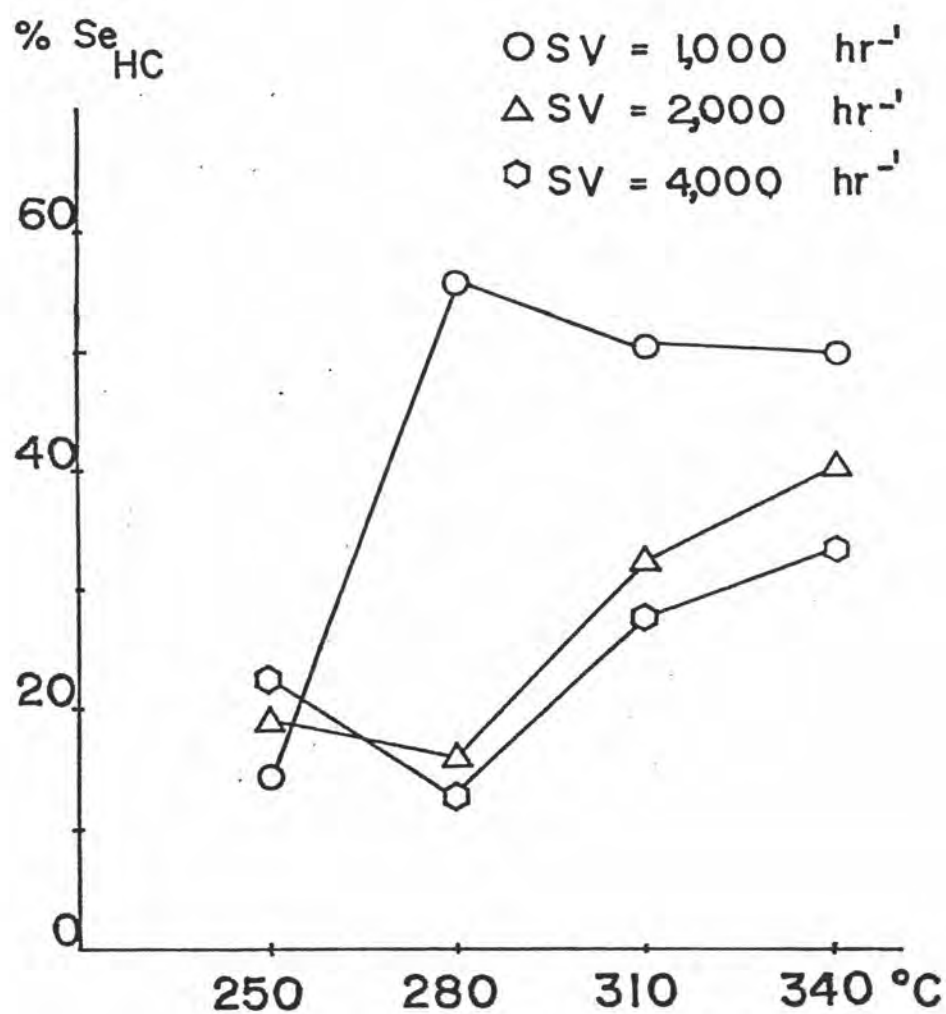
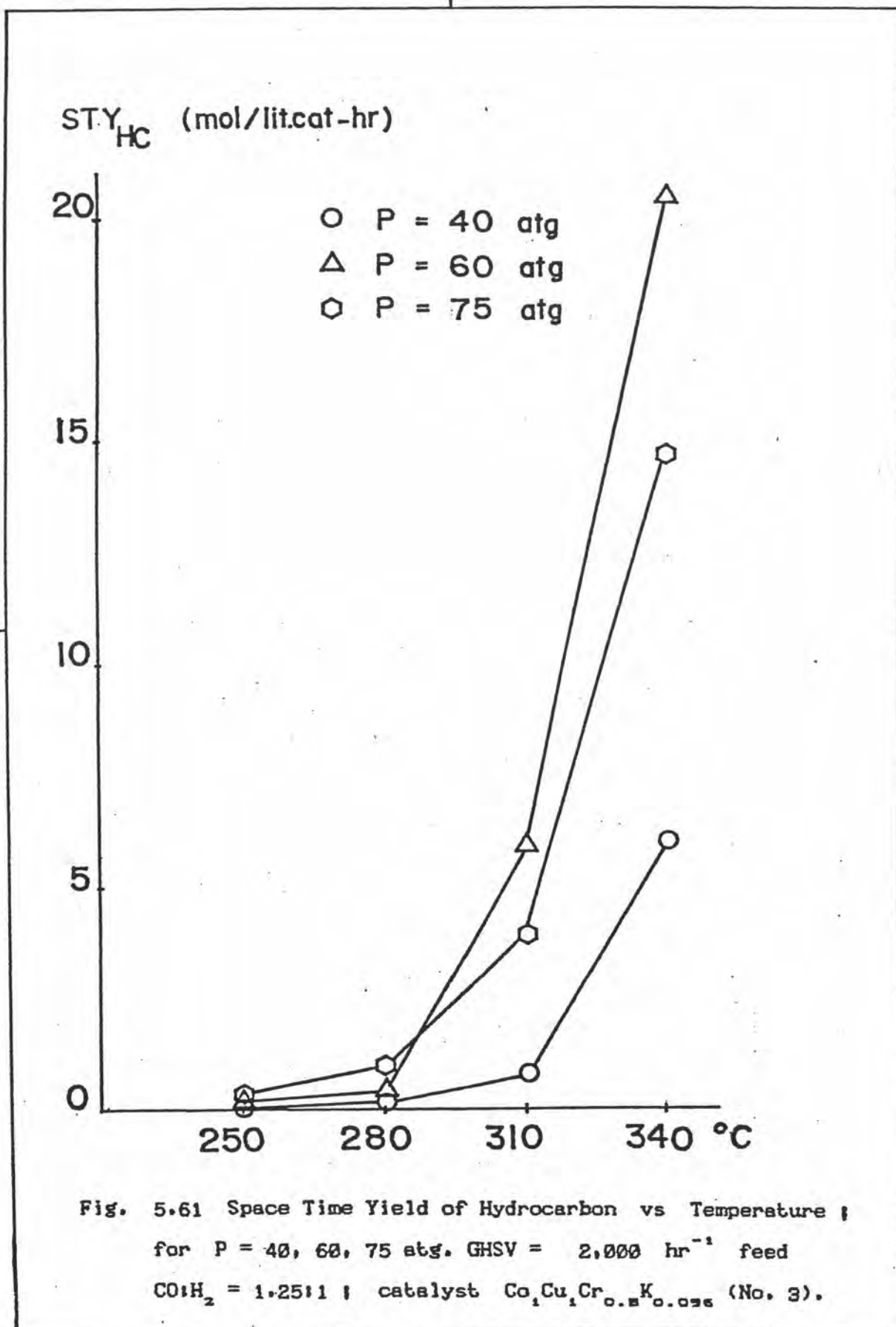
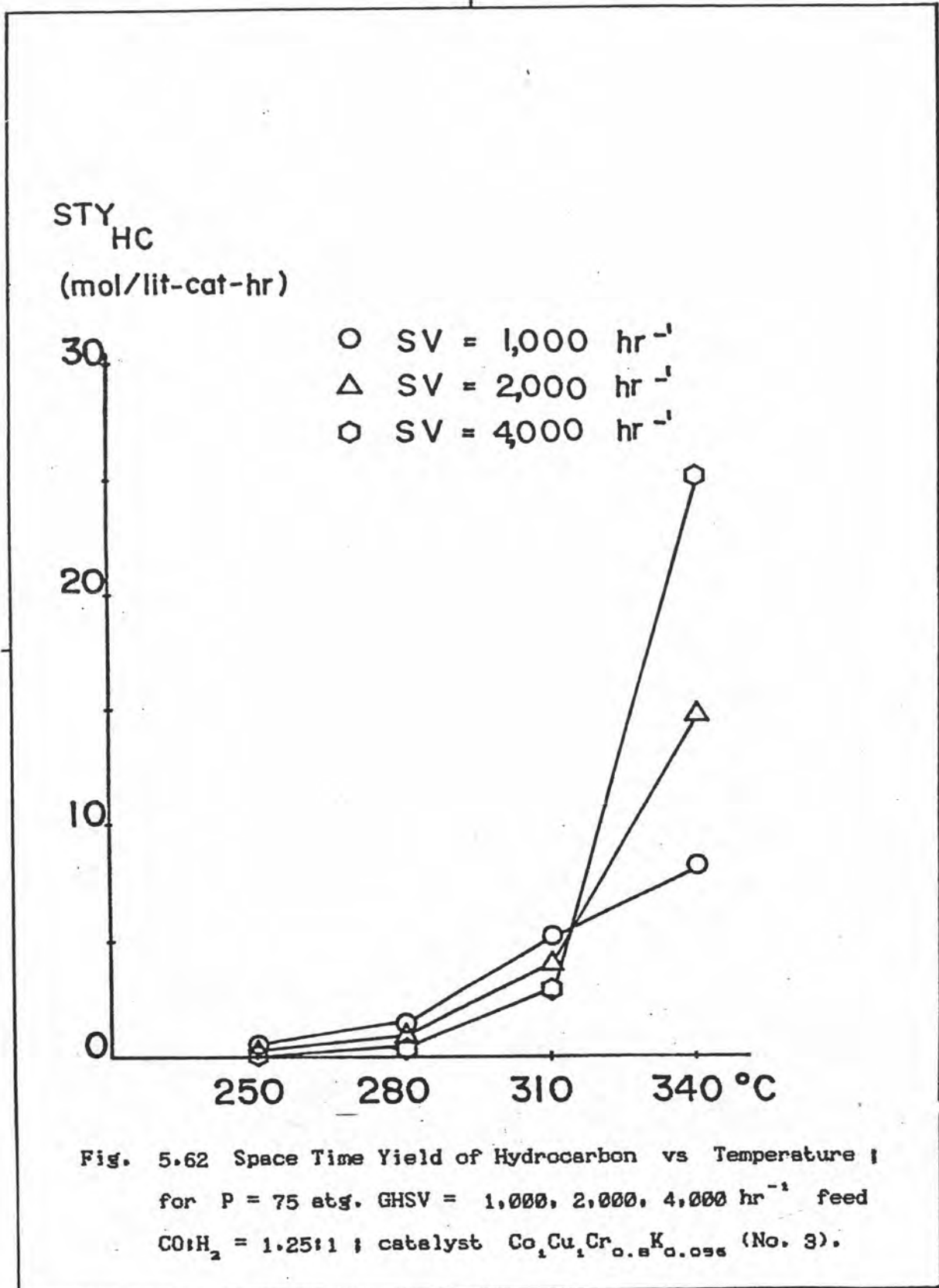


Fig. 5.60 Selectivity of Hydrocarbon vs. Temperature ; for
P = 75 atg. GHSV = 1,000, 2,000, 4,000 hr⁻¹ feed
CO:H₂ = 1.25:1 ; catalyst Co₁Cu₁Cr_{0.5}K_{0.055} (No. 3).





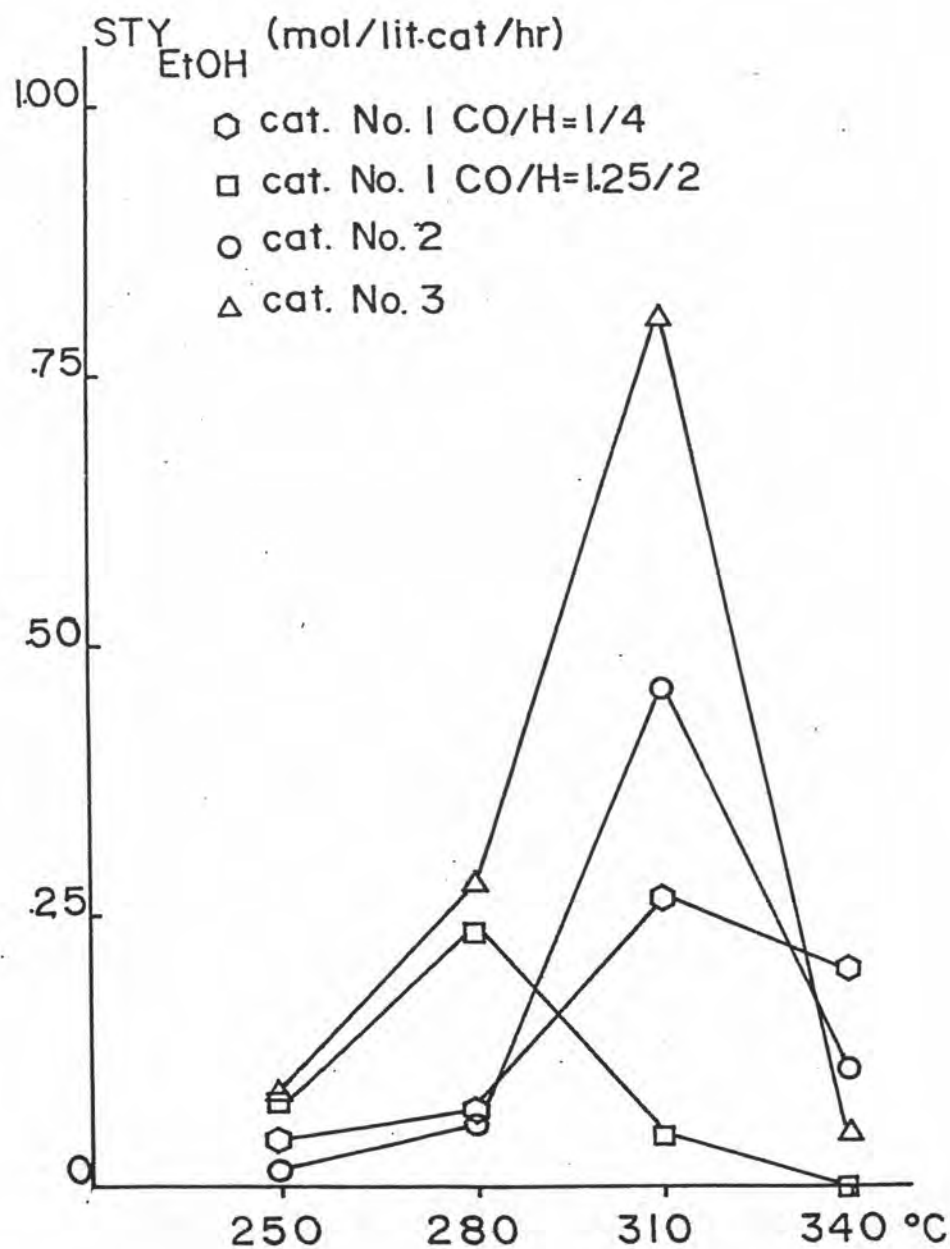


Fig. 5.63 Comparison of STY_{EtOH} vs. Temperature at $GHSV = 2,000 \text{ hr}^{-1}$, for Catalyst No. 1 at the feed ratio of $CO:H_2 = 1:4$, $P = 80 \text{ atg}$, and at the feed ratio of $CO:H_2 = 1.25:2$, $P=80 \text{ atg}$; Catalyst No. 2 at the feed ratio of $CO:H_2 = 1.25:2$, $P=80 \text{ atg}$; Catalyst No.3 at the feed ratio of $CO:H_2 = 1.25:2$, $P = 75 \text{ atg}$

