Catalytic Testing of the 12.5 wt% K/MoS_2 Catalyst. After the doping of this catalyst from liquid ammonia solution with metallic potassium was achieved using the apparatus shown in Figure 13, the catalyst was loaded into the reactor under argon and a flow of $H_2/CO = 0.99$ synthesis gas was initiated with GHSV = 7796 ℓ/kg cat/hr (no reductive pretreatment was employed). The reactor was then pressurized to 8.3 MPa and heated slowly to 245°C. The formation of alcohols was first seen at ≈200°C. The products in the exit gas were analyzed every 25-30 min using an on-line Hewlett-Packard 5890 Series II GC, and condensable products were also collected for analysis by GC/MS.

During the early period of testing of this catalyst at 245°C, a new analytical method was developed in which the GC thermal conductivity detector sensitivity was switched from low sensitivity to high sensitivity after the unreacted CO eluted as a peak. Hydrogen was not quantitatively analyzed. A correlation factor was found so that the space time yields of all of the oxygenated and hydrocarbon products could be accurately determined during the later stage of this testing.

Quantitative analytical data were obtained during the later period of catalytic testing (after 585 hr of continuous low temperature testing) at reactor tempertures of 245, 256, 265, and 295°C. The product selectivities and space time yields are presented in Figures 44-47. In Figure 44 only the alcohol and hydrocarbon selectivities are shown, although there were also small amounts of esters and aldehydes present in the reaction products. The selectivity toward hydrocarbons, principally methane, increased from ≈10 C mol% at 245°C to ≈19 C mol% at 295°C. As the reaction temperature was increased, the space time yield of the alcohol portion of the product significantly increased, as shown in Figure 46. Figure 47 shows that the large increase in productivity of alcohols upon increasing the temperture to 295°C can be attributed principally to the enhanced formation of methanol.

FIGURE 44. SELECTIVITY (C mol%) *vs* TEMPERATURE

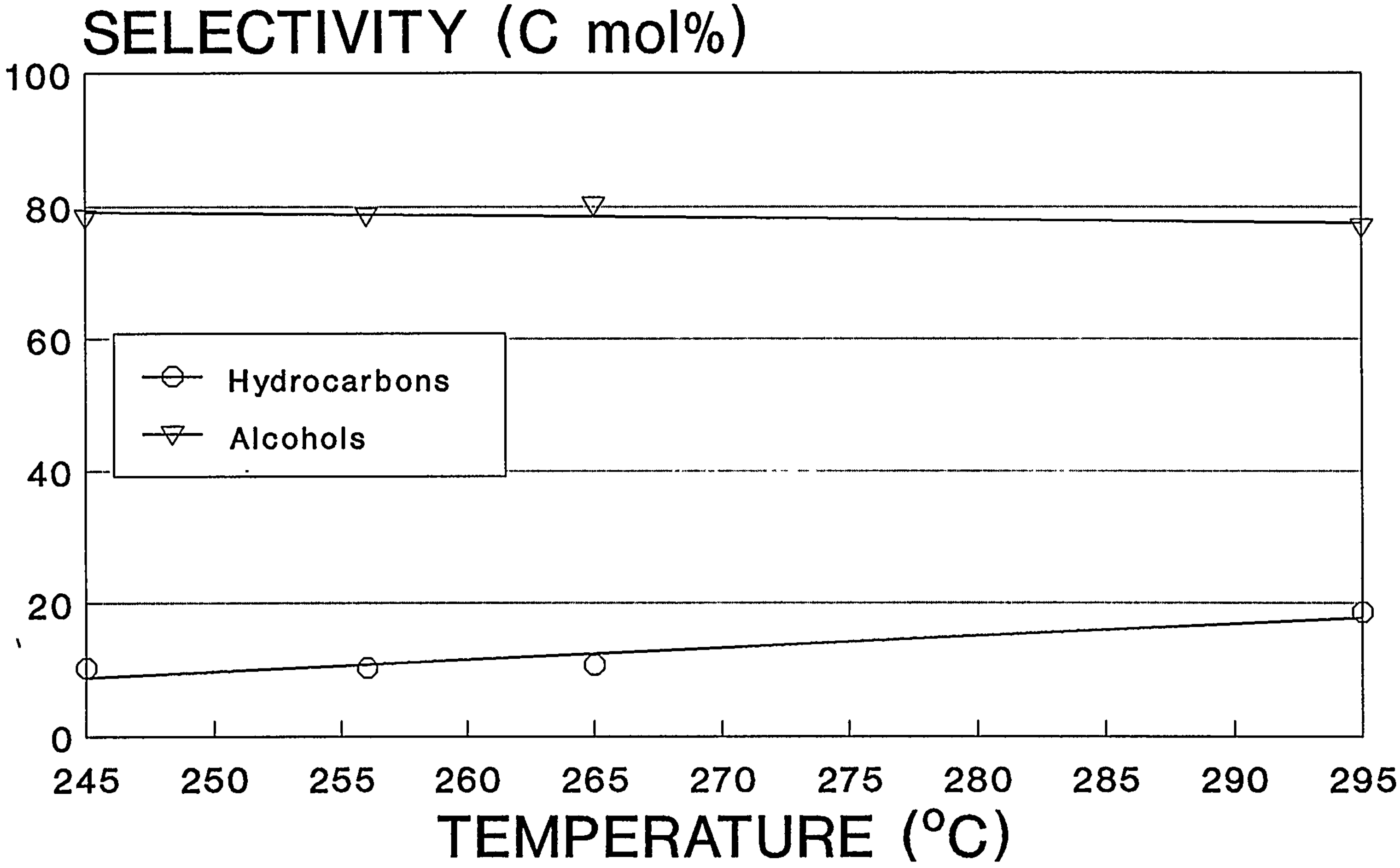


FIGURE 45. CO_2 SPACE TIME YIELD *vs* TEMPERATURE

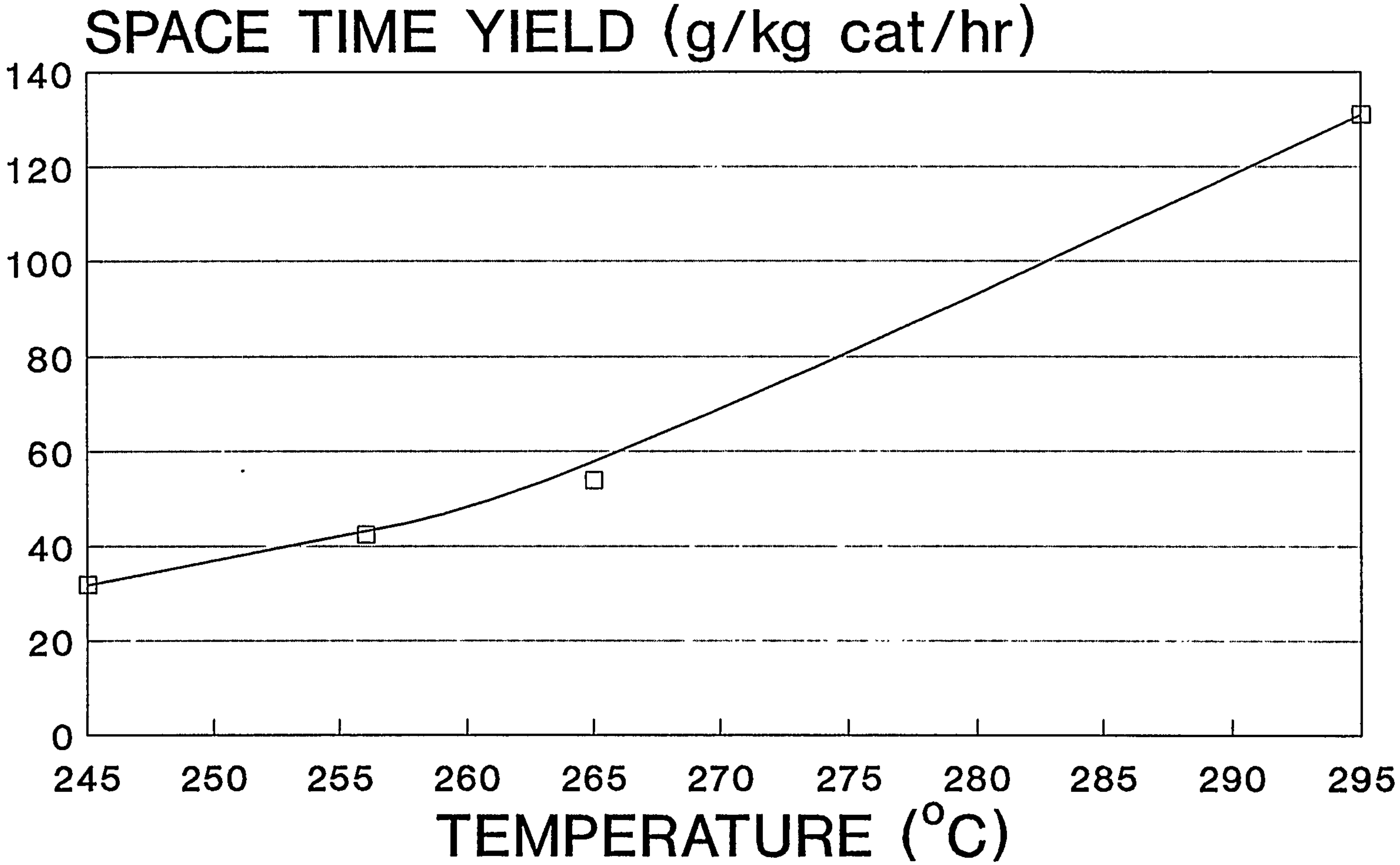


FIGURE 46. TOTAL ALCOHOL AND HYDROCARBON SPACE TIME YIELDS *vs* TEMPERATURE

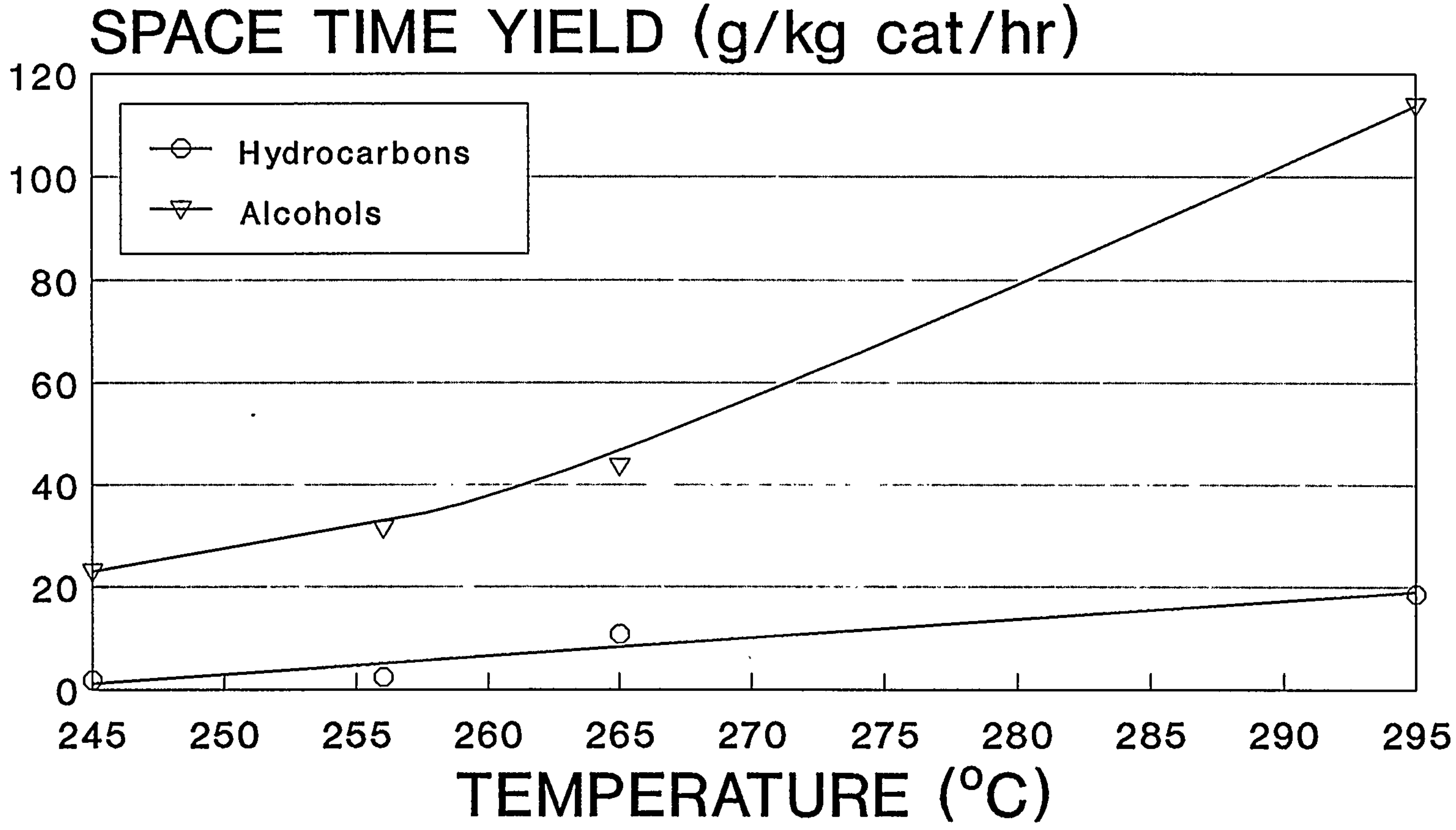
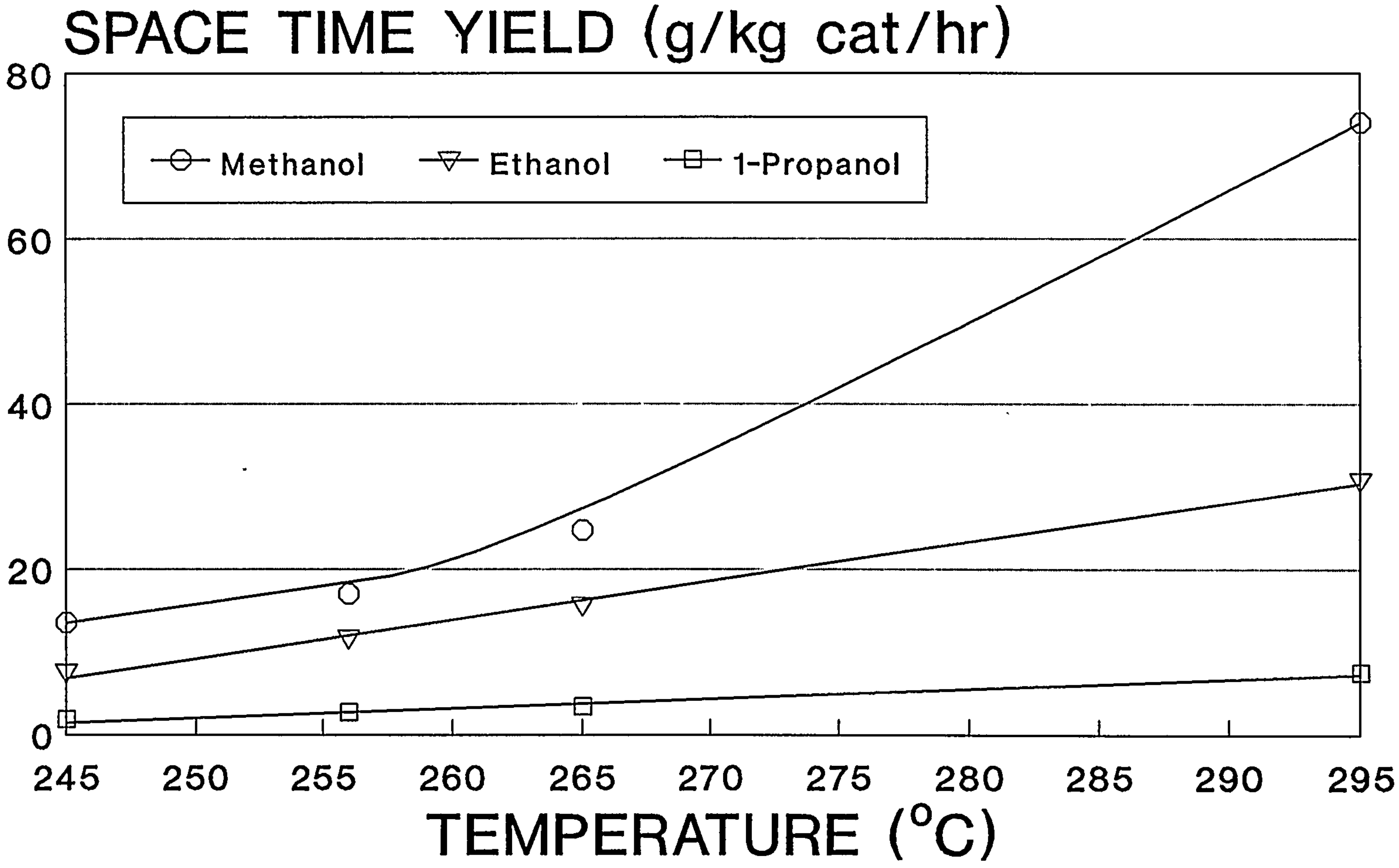


FIGURE 47. ALCOHOL SPACE TIME YIELDS *vs* TEMPERATURE



As the reaction temperature was increased, the converison level of CO increased, as shown in Figure 48, corresponding to 4 mol% CO conversion at 295°C. Figure 49 shows that as the temperature was increased, an apparent minimum in the methanol/C_2+ alcohol molar ratio, based on the moles of products formed, was observed. In contrast, the total alcohol/hydrocarbon molar ratio exhibited a linear dependence on the reaction temperature, as shown in Figure 50. This latter behavior was expected since more hydrocarbons were formed at higher reaction temperatures (see Figure 44), where most of the hydrocarbon product consisted of methane.

In this investigation, the promoted MoS_2 catalyst initially contained metallic potassium, and this experimental testing shows that alcohol synthesis catalysts can be successfully synthesized utilitizing this new preparation method. The catalytic results, where a total testing time of over 700 hr was utilized, show that a stable catalyst was obtained. Further characterization of this catalyst is needed.

Testing of the 10 wt% $CsOOCH/MoS_2$ Catalyst. Batch 3 MoS_2, with a surface area of 60 m^2/g, was doped with CsOOCH under vacuum, and then the dried catalyst was weighed and transferred to the reactor in air. A 1.1290 g portion of the 10% $CsOOCH/MoS_2$ catalyst was mixed with approximately 15 ml of 3 mm Pyrex beads. This mixture was then centered in a 316 stainless steel fixed bed reactor using additional quantities of the 3 mm Pyrex beads. After the reactor was reassembled, the catalyst was pretreated at 410°C for 1 hr under a flow of 2.04/97.96 H_2/N_2 vol% mixture at a flow rate of 60 ml/min. The reactor was then allowed to cool to room temperature overnight while maintaining the hydrogen/nitrogen flow. The gas flow was then changed to the H_2/CO = 1 synthesis gas reactant mixture, and the reactor was pressurized to 8.1 MPa, the gas hourly space velocity (GHSV) was adjusted to 7750 ℓ/kg cat/hr, and then heated at a steady rate

FIGURE 48. CO CONVERSION RATE (mol/kg cat/hr) *vs* TEMPERATURE

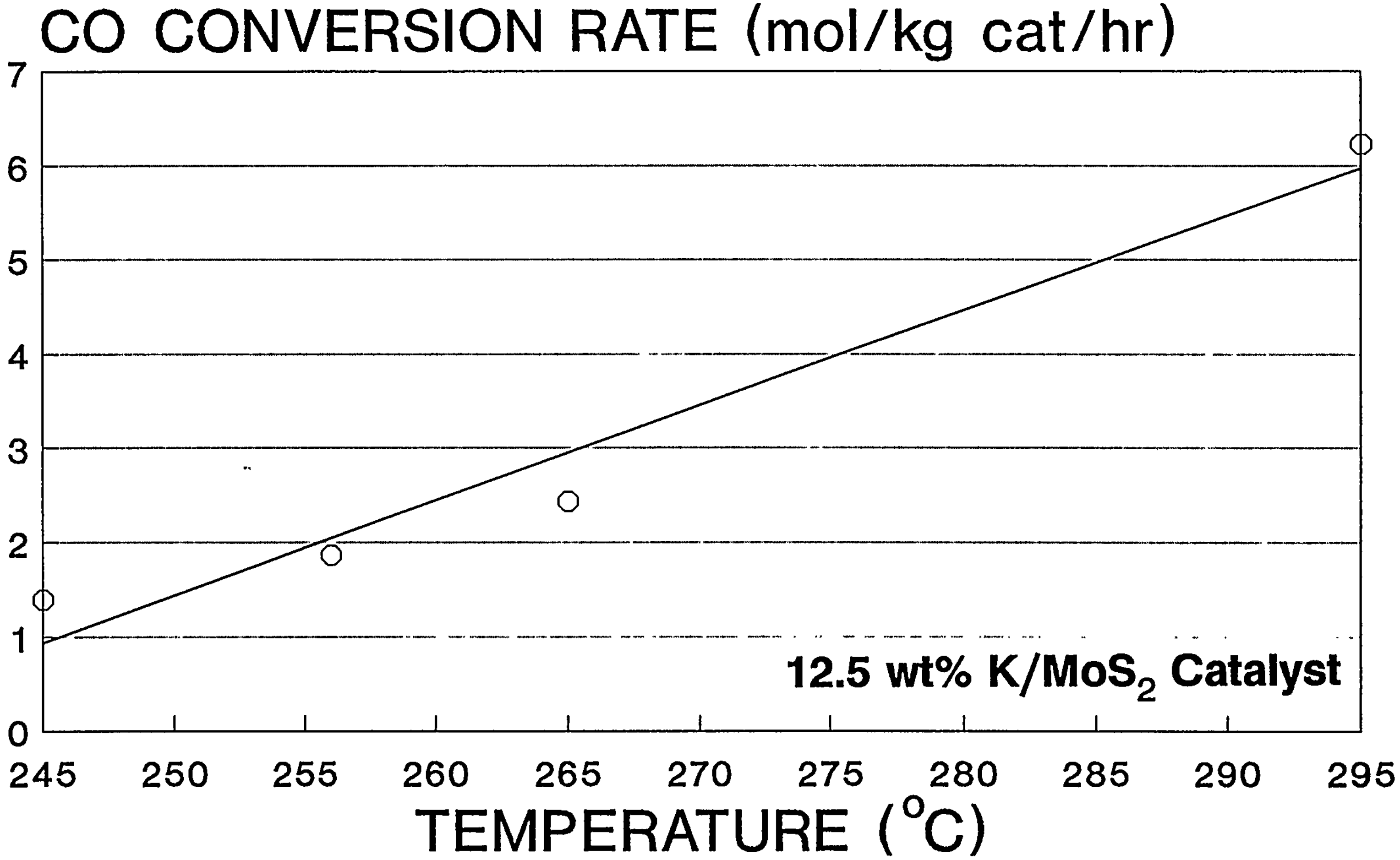


FIGURE 49. METHANOL/C_2+ ALCOHOL MOLAR RATIO *vs* TEMPERATURE

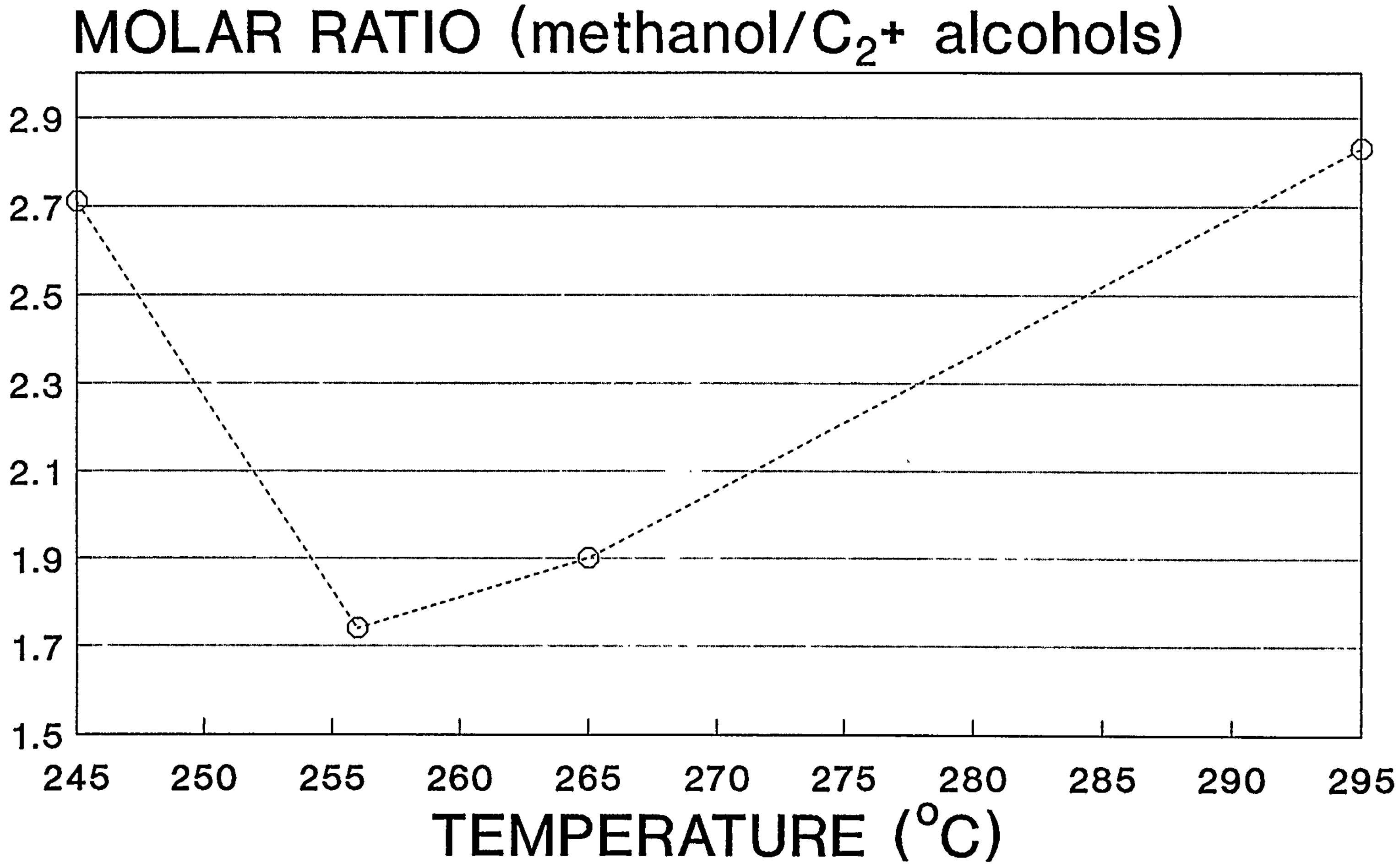
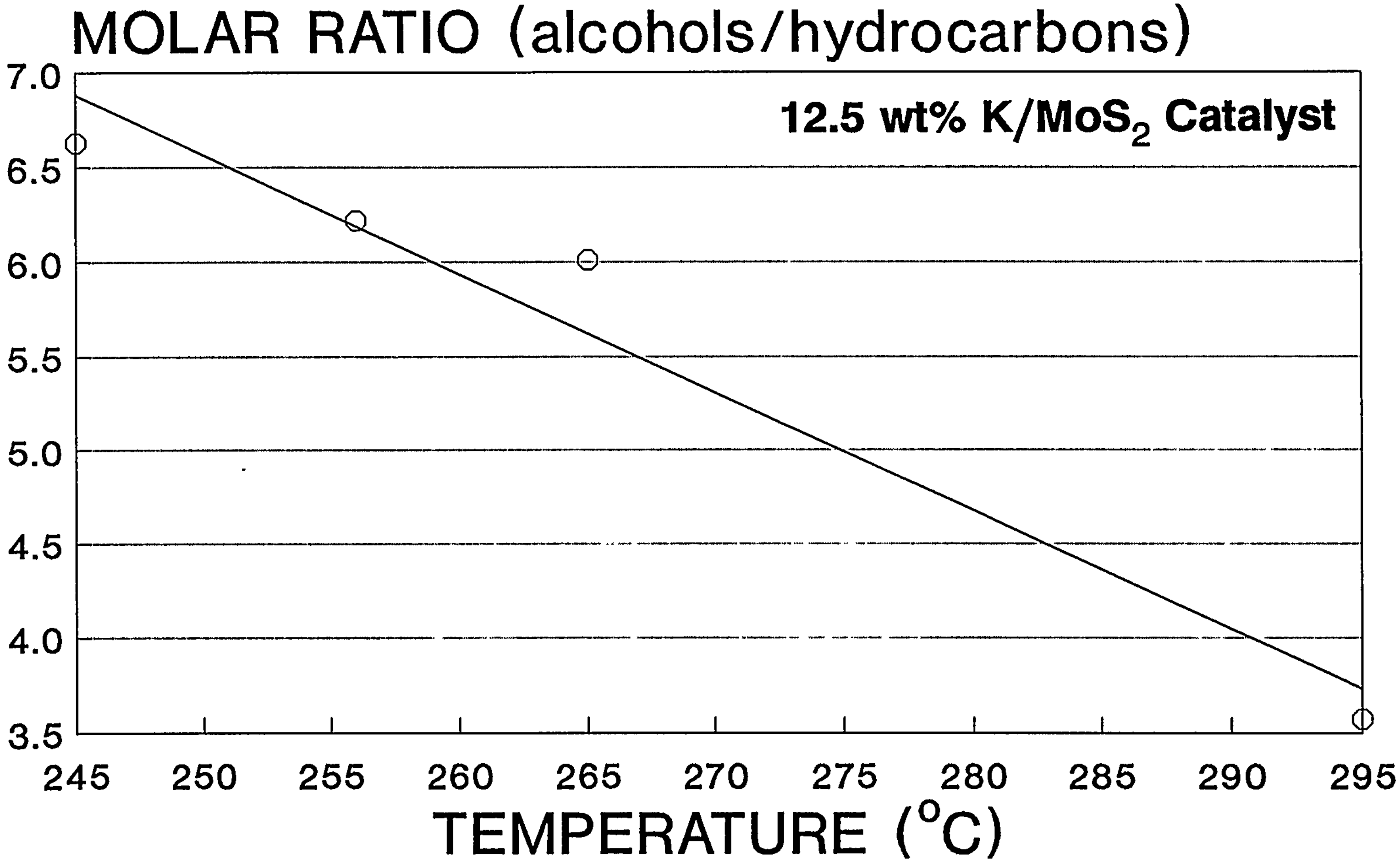


FIGURE 50. ALCOHOL/HYDROCARBON MOLAR RATIO *vs* TEMPERATURE



to the initial reaction temperature.

Catalytic testing was carried out in which two series of increasing reaction temperatures were utilized. These two sets of temperatures consisted of the following:

Temperature Set 1: 245, 256, 285, 295, 300, 308, 310, and 350°C, and.

Temperature Set 2: 265, 275, 288, 340, 285, and 245°C.

The second set of temperatures was run directly after the first set of temperature. It is pointed out that the higher reaction temperatures of 350 and 340°C are fairly severe conditions for alcohol synthesis catalysts. As will be shown in the figures in this report, there was a difference between the two sets of temperatures. This indicated that the catalyst deactivated over time. This was especially pronounced after lowering the temperature to 245°C at the end of the *second* temperature sequence. Indeed, while there was activity at this temperature at the beginning of the testing sequence, there was no activity observed at the end of the second reaction series that terminated at 245°C. The testing at each temperature was maintained at steady state for 6-24 hr, during which multiple analyses of the product stream were carried out. The catalytic response to a temperature change was immediate.

Some of the observed catalytic trends in terms of activity and selectivity are summarized here. Upon increasing the temperature according to **Temperature Set 1**, the productivity of methanol, which was the dominant product, proceeded through a broad maximum, as shown in Figure 51. As expected, the selectivity of the alcohols decreased as the temperature increased, while the selectivity of the hydrocarbons increased as the temperature increased for Temperature Set 1. These trends are shown in Figures 52 and 53 for the 285-350°C temperature range. Indeed, at 350°C the product selectivity was greatly shifted to the hydrocarbon, as shown in Figure 53. This behavior, however, was surprisingly

FIGURE 51. Product Space Time Yield vs Temperature (Set 1) at 8.1 MPa, 7750 l/kg cat/hr, H_2/CO = 1

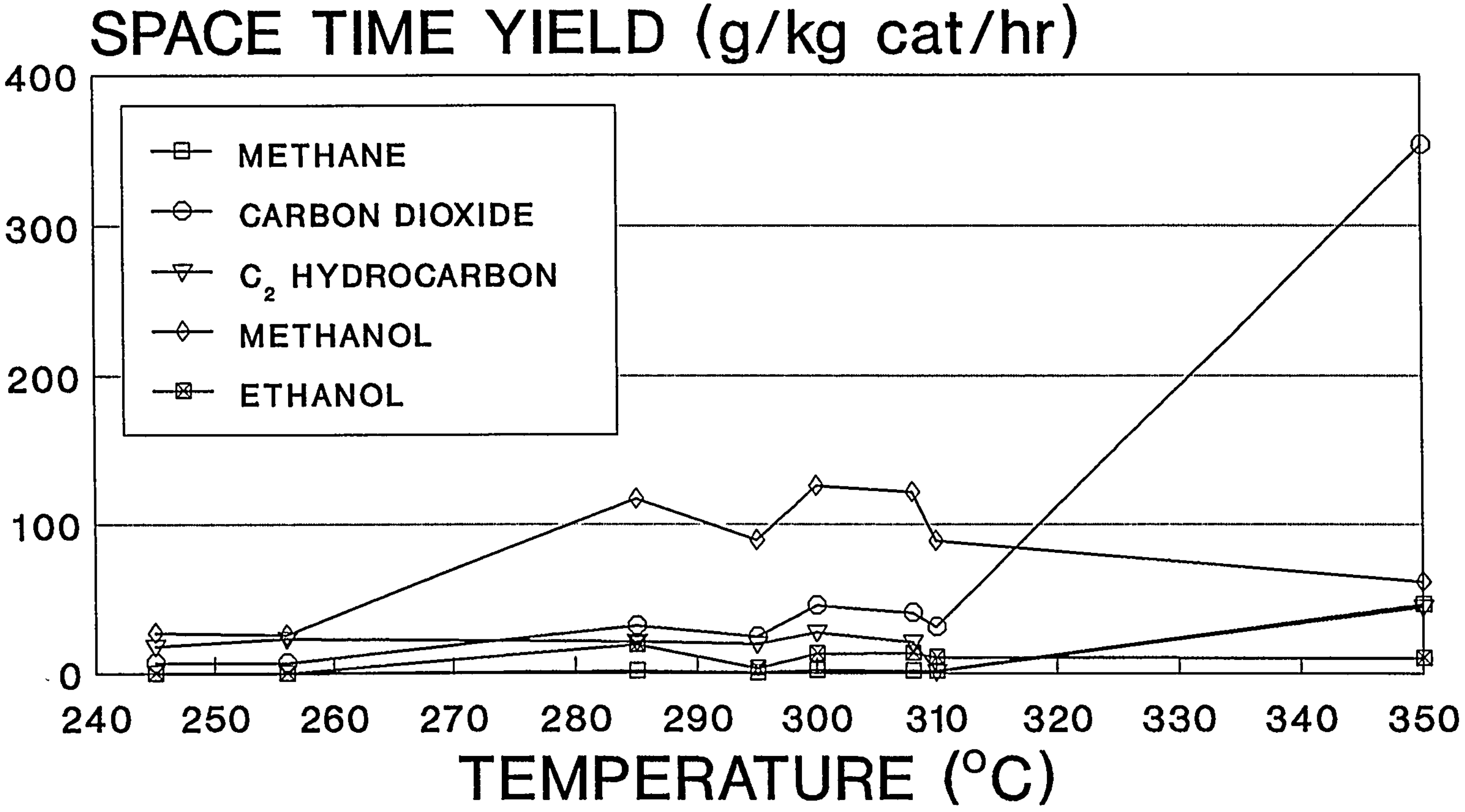


FIGURE 52. Selectivity vs Temperature (Set 1) at 8.1 MPa and GHSV = 7750 l/kg cat/hr with H_2/CO = 1

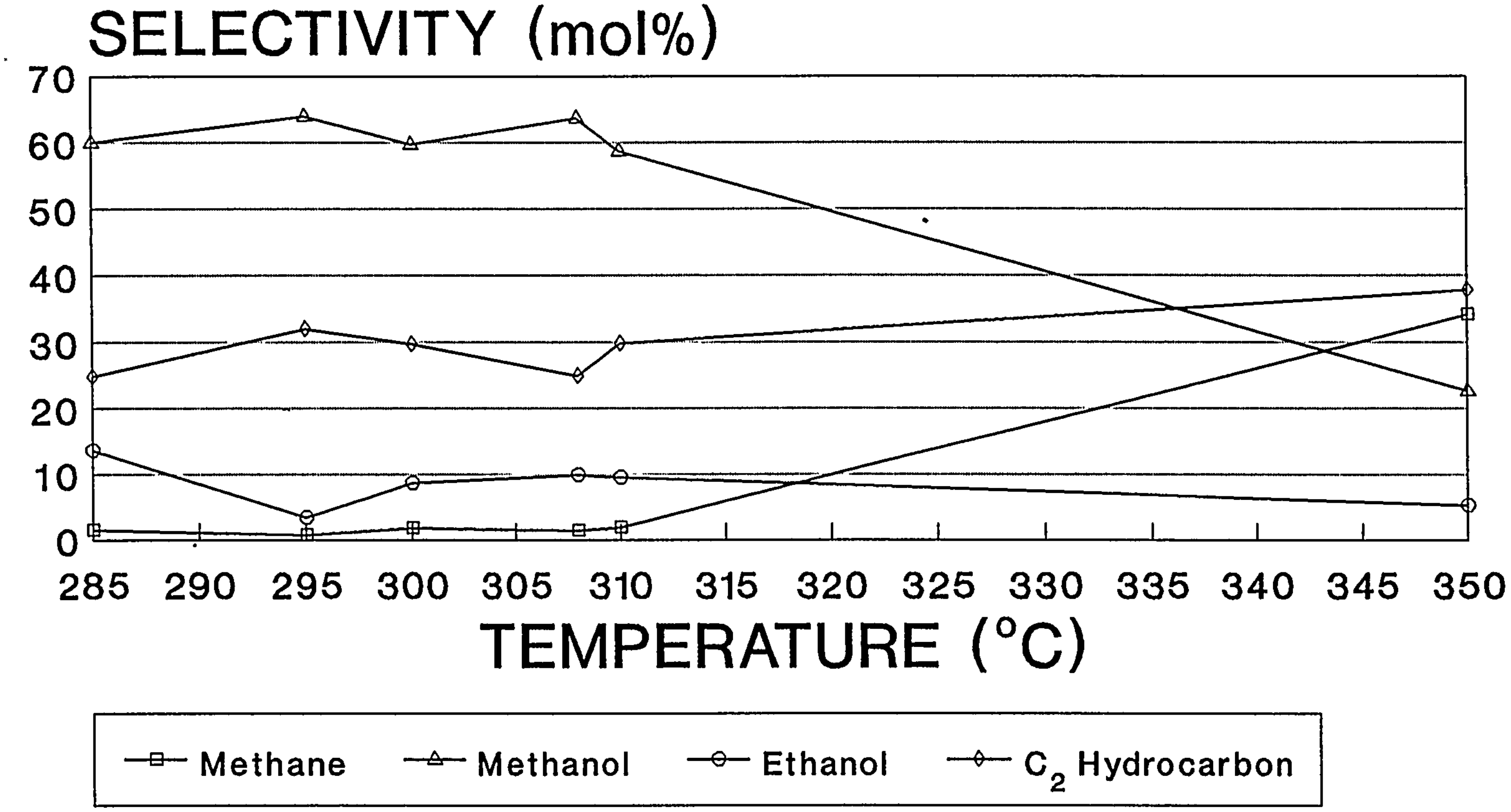
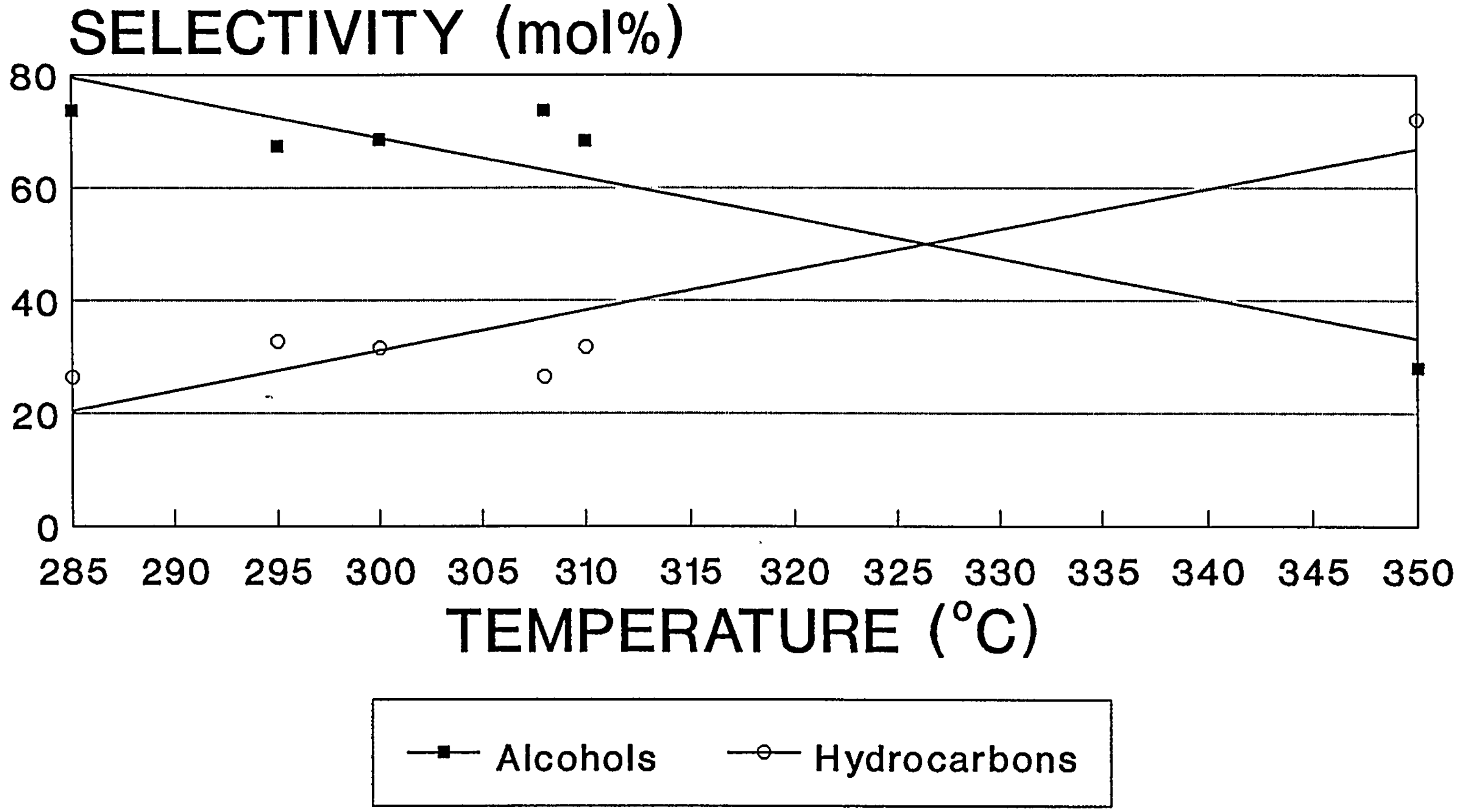


FIGURE 53. Selectivity vs Temperature (Set 1) at 8.1 MPa and GHSV = 7750 l/kg cat/hr with $H_2/CO = 1$



not observed during the Temperature Set 2 testing sequence. As the reaction temperature was progressively increased, the space time yield of methanol also increased, shown in Figure 54, and the selectivity trends were now reversed compared with the first set of experiments. As shown in Figures 55 and 56, the selectivity towards alcohols during the second set of experiments improved as the reaction temperature was increased. This is unexpected behavior for this catalyst. In each case, the selectivities were calculated on a CO- and CO_2-free basis.

Although there is scatter in the data, the conversion of CO in mol% and mol/kg cat/hr increased with increasing temperature for both series of experiments, as shown in Figures 57 and 58, respectively. The extent of deactivation of the $CsOOCH/MoS_2$ catalyst after the first testing sequence that reached 350°C is indicated in these figures, where the solid lines are computer-drawn trend lines that neglect the final 245°C data point (no activity). Of special interest is the alcohol productivity of this catalyst in terms of %yield and space time yield of the alcohols, and these are shown in Figures 59 and 60, respectively, as functions of the reaction temperature.

While the catalyst behavior in alcohol productivity as a function of temperature is of great interest (shown in Figure 60), correlation of the hydrocarbon/alcohol molar ratio during these experiments is also of interest. As shown in Figure 61, the product hydrocarbon/alcohol molar ratio was fairly constant in the 285-310°C temperature range during Temperature Set 1 testing but then increased above 1.0 when the reaction temperature was increased to 350°C. The latter point indicates an exceptionally large quantity of hydrocarbon products formed. However, under Temperature Set 2 conditions, the ratio decreased as the temperature increased (Figure 61). This latter observation is the opposite of the expected behavior, and it cannot be explained without further studies.

FIGURE 54. Product Space Time Yield vs Temperature (Set 2) at 8.1 MPa, 7750 l/kg cat/hr, $H_2/CO = 1$

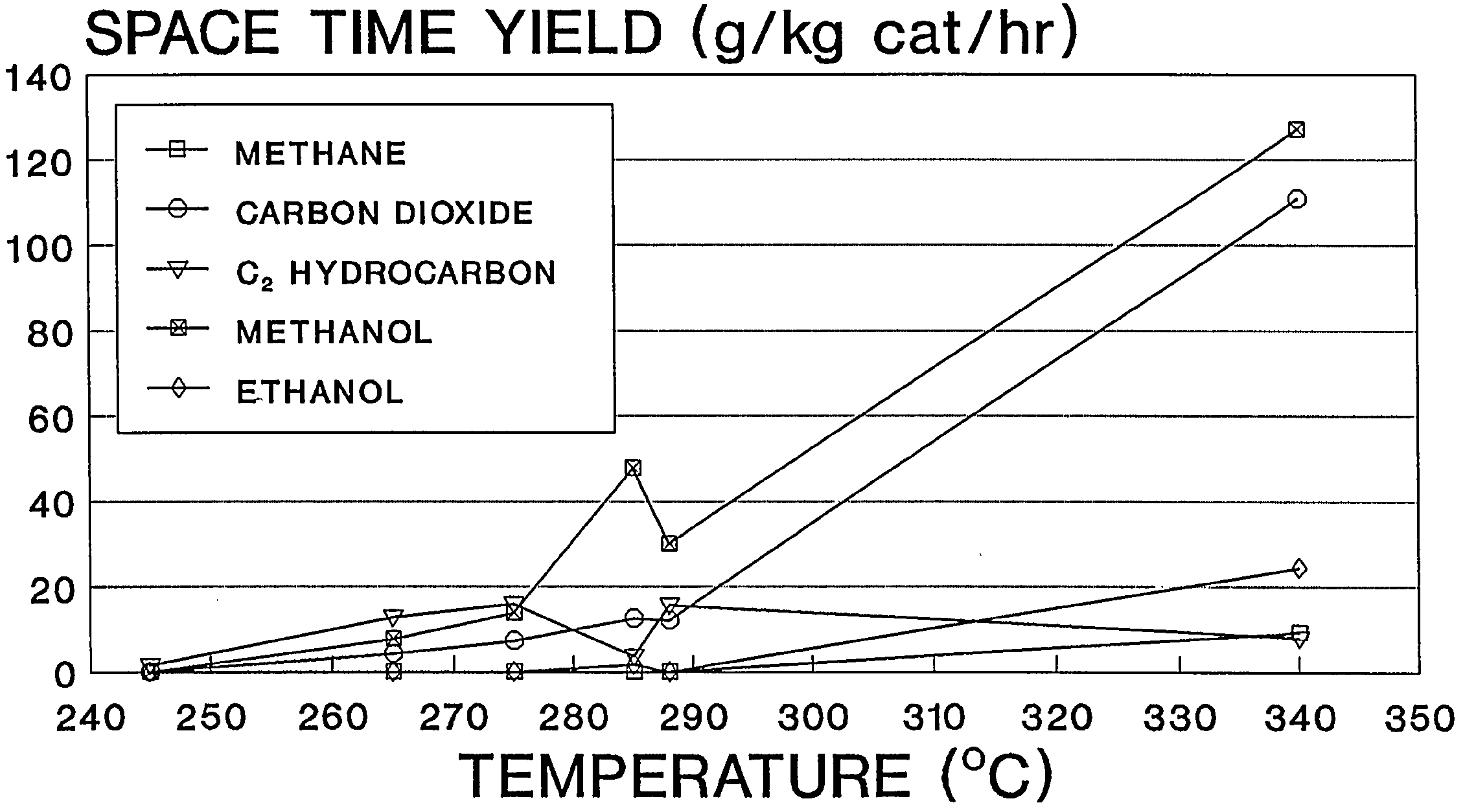


FIGURE 55. Selectivity vs Temperature (Set 2) at 8.1 MPa and GHSV = 7750 l/kg cat/hr with H_2/CO = 1

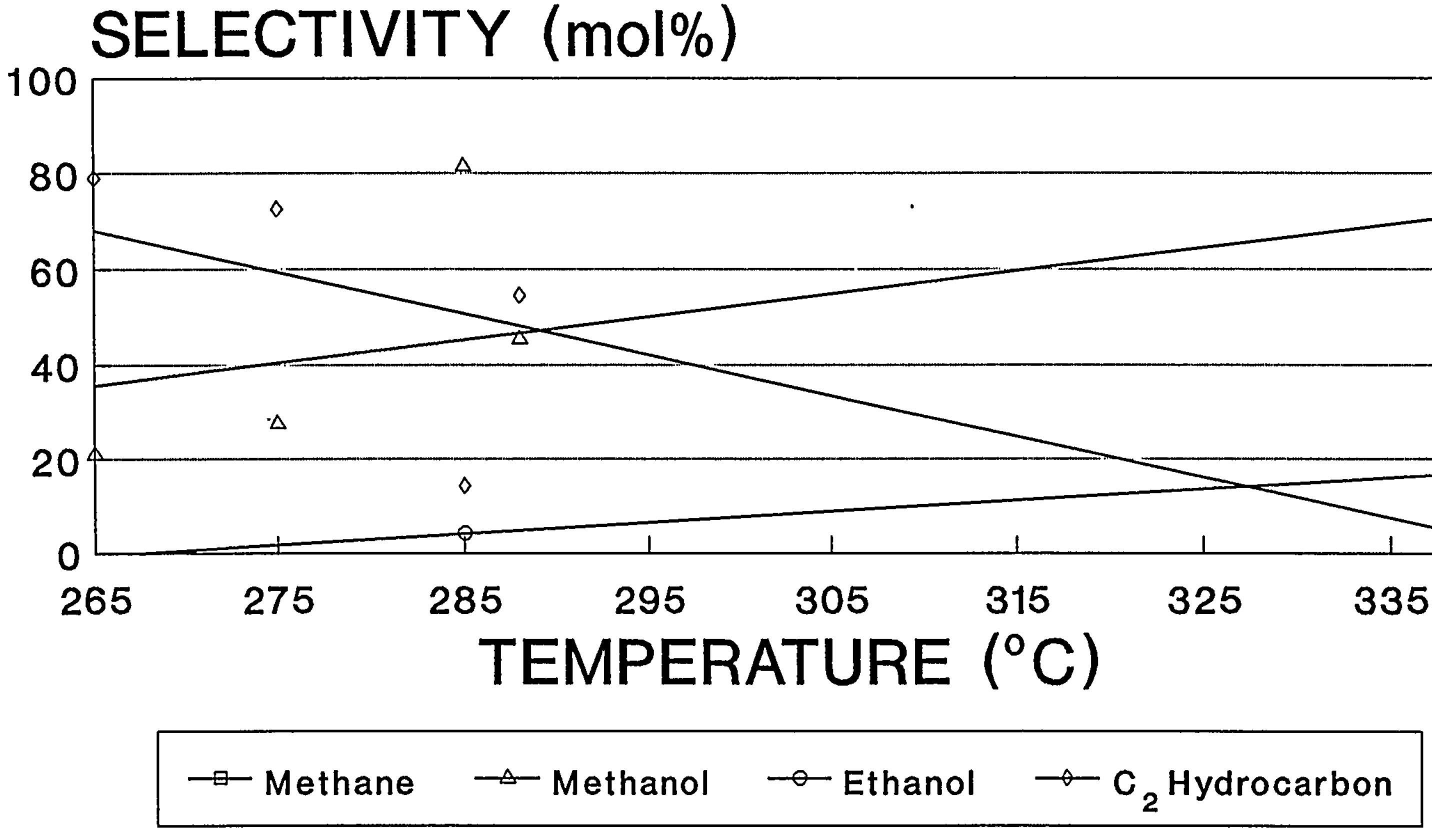


FIGURE 56. Selectivity vs Temperature (Set 2) at 8.1 MPa and GHSV = 7750 l/kg cat/hr with H_2/CO = 1

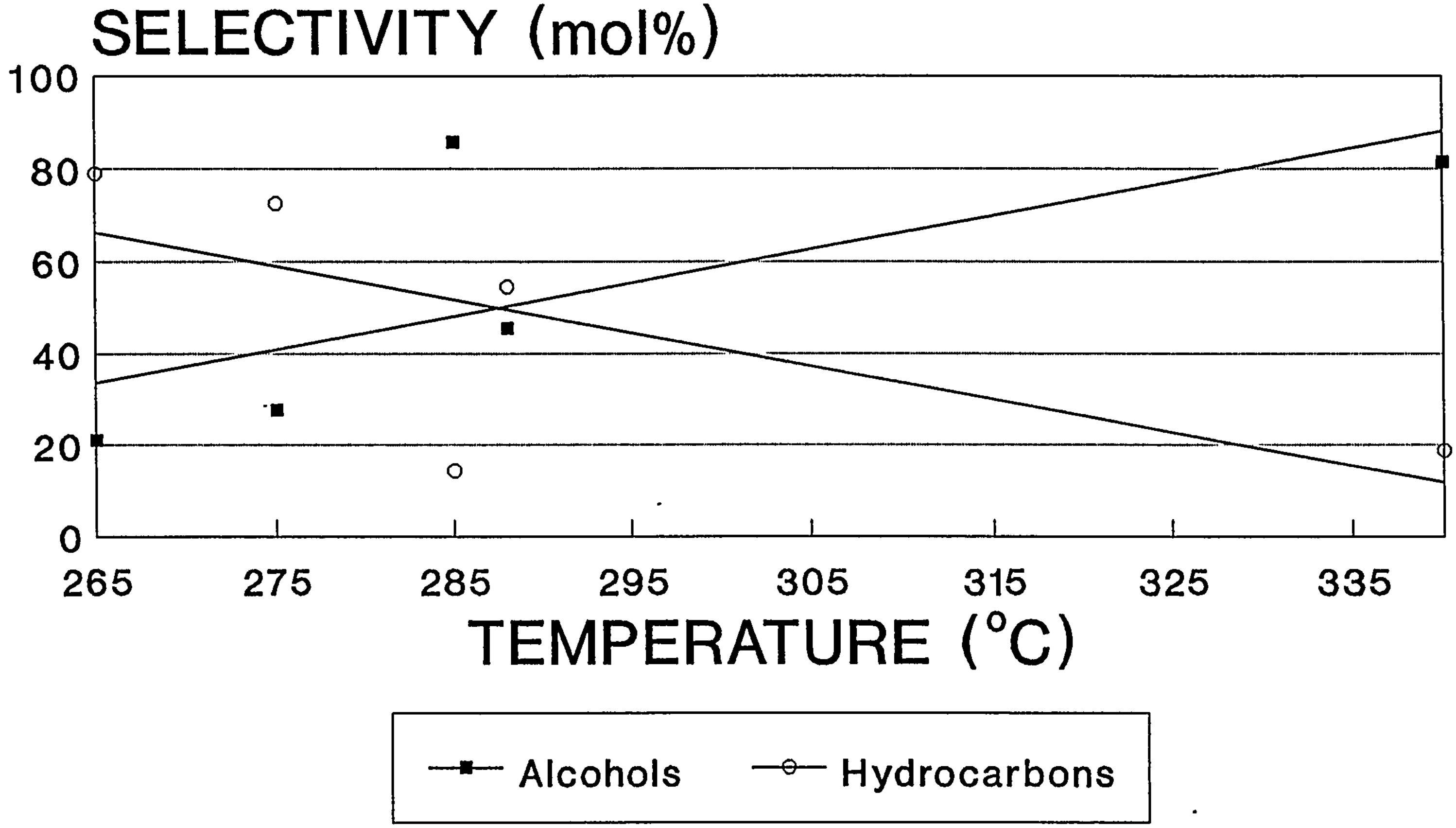


FIGURE 57. Conversion of CO in Mol% vs Reaction Temperature

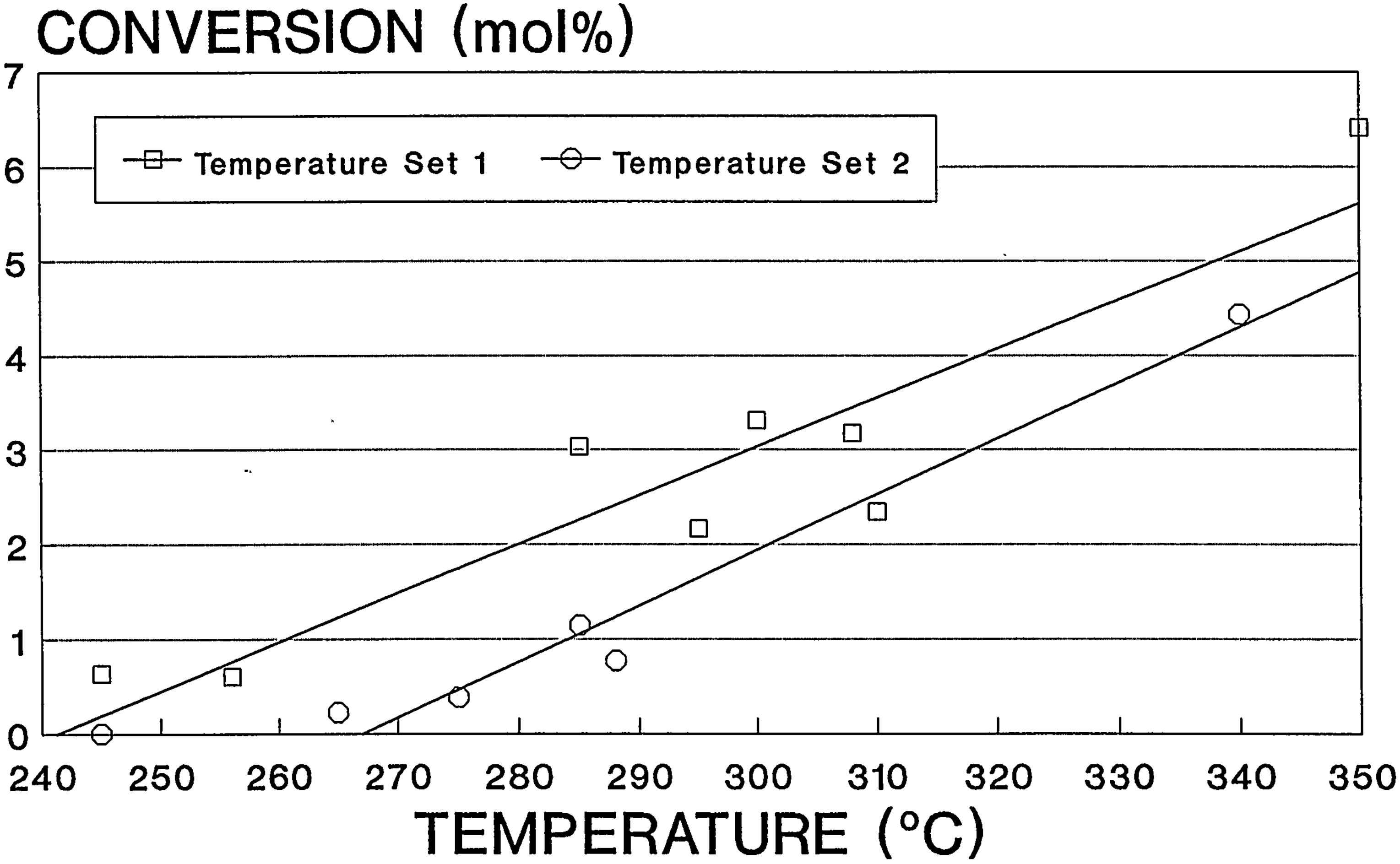


FIGURE 58. Conversion Rate of CO vs Reaction Temperature

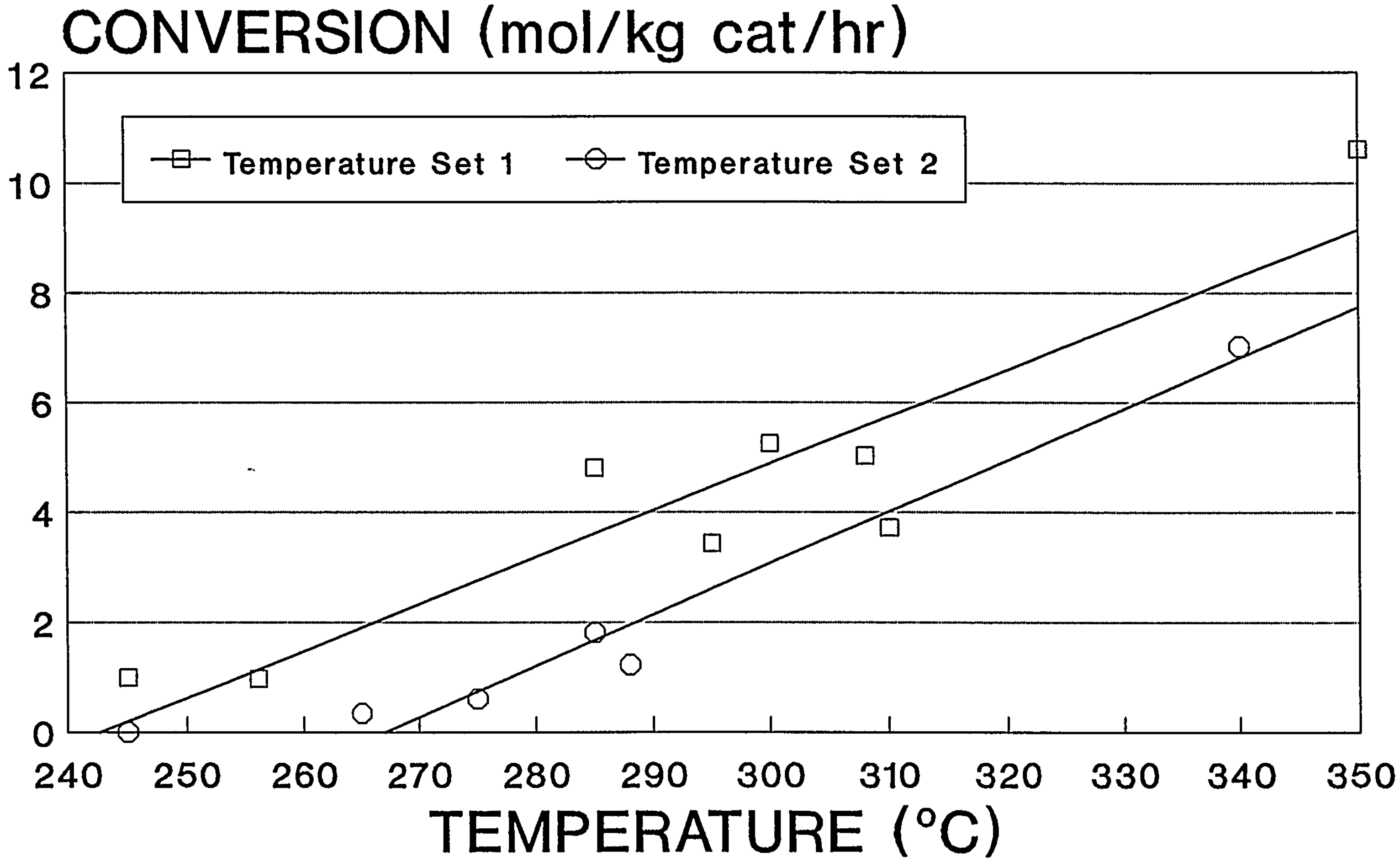


FIGURE 59. Total Alcohol % Yield vs Temperature at 8.1 MPa and GHSV = 7750 l/kg cat/hr with H_2/CO = 1

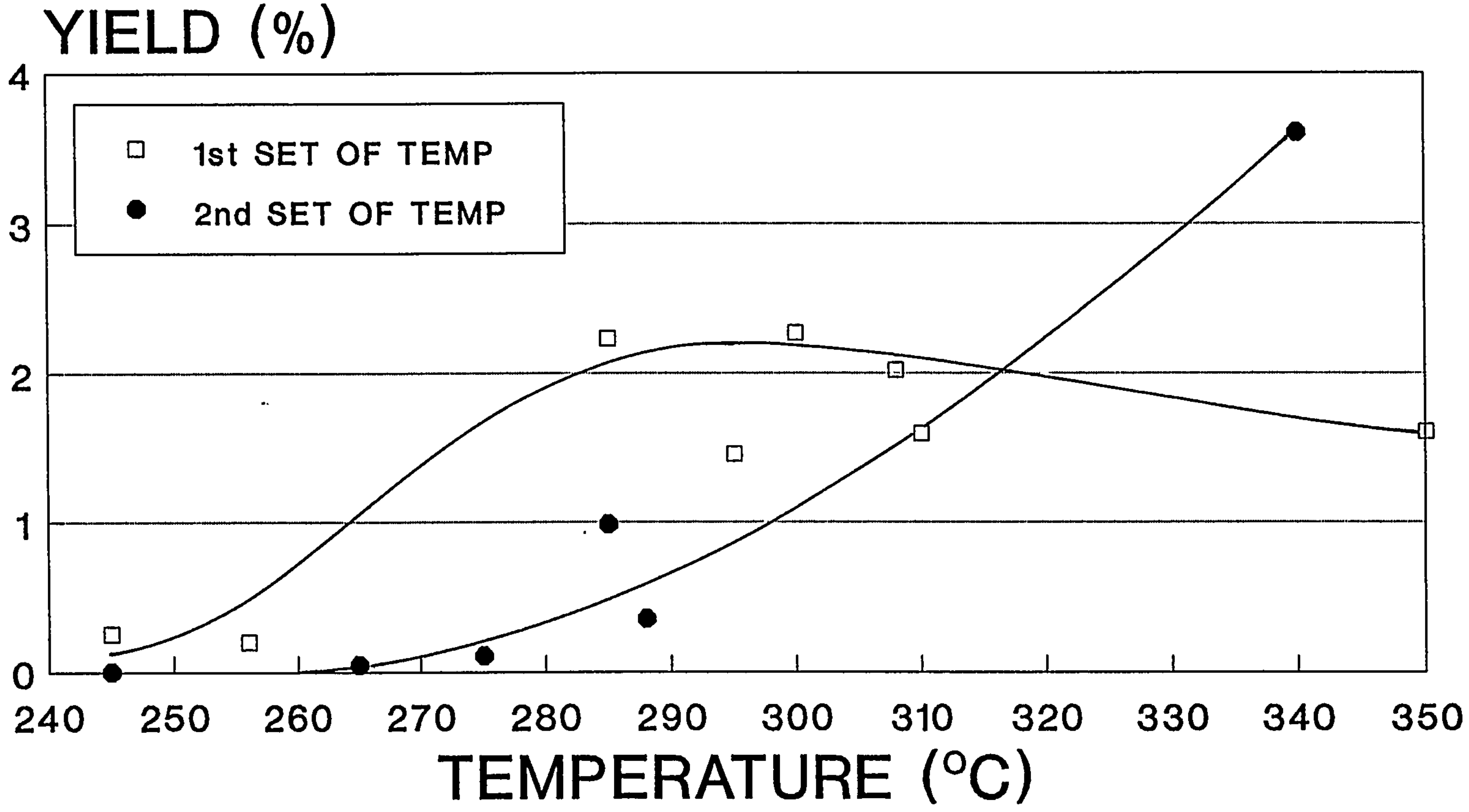


FIGURE 60. Total Alcohol Space Time Yield vs Temperature at 8.1 MPa and GHSV = 7750 l/kg cat/hr with H_2/CO = 1

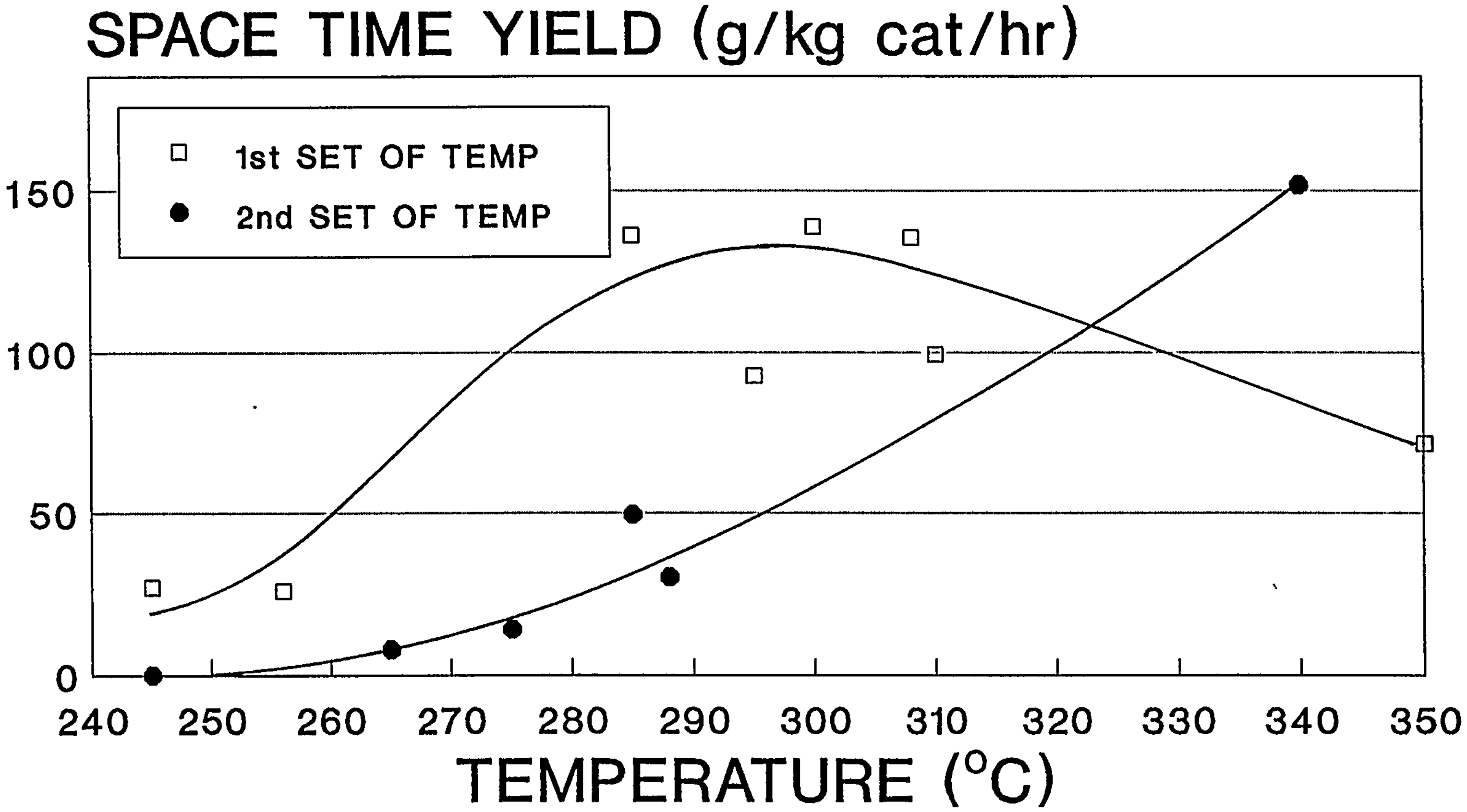


FIGURE 61. Hydrocarbon/Alcohol Molar Ratio vs Temperature from $H_2/CO = 1$ at 8.1 MPa and 7750 l/kg cat/hr