Catalytic Testing of Undoped Molybdenum Disulfide. In a nitrogen-filled glove bag, 1.6567 g of undoped MoS_2 from large Batch 1 (Pretreatment B) was mixed with ≈ 8 ml clean Pyrex beads and centered in the reactor. After connecting the reactor to the catalyst testing unit, the MoS_2 catalyst was reductively pretreated at 400°C with 2.04 vol% H_2/97.96 vol% N_2 (60 ml/min) for 1 hr at ambient pressure before testing.

Catalytic testing was carried out at a pressure of 8.1 MPa with a gas hourly space velocity (GHSV) of 7750 ℓ/kg cat/hr at the following temperatures 245, 255, 265, 275, 280, 300, and 320°C. For each temperature change, the reaction was allowed to reach steady state, and then testing was maintained under constant reaction conditions for 4 to 12 hr. As expected, the reaction over MoS_2 only produced hydrocarbons, water, and carbon dioxide. At lower temperatures, the major product was methane. As the reaction temperature was sequentially increased, higher molecular weight products were formed (up to C_6). Other trends that were seen included the observation that as the temperature was increased, the conversion of CO tended to increase, as can be seen in Figure 31. During this test, the CO_2/H_2O molar ratio also increased with increasing temperature, as shown in Figure 32. This increase in the CO_2/H_2O molar ratio occurred because the equilibrium of the water gas shift reaction, Equation 15, was shifted to the $H_2 + CO_2$ side as the temperature was increased.

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad (15)$$

Since C_1-C_6 hydrocarbon products were formed at the higher reaction temperatures, Schulz-Flory distribution plots were made for each of the higher temperatures used. These plots are shown in Figures 31-36. In constructing these graphs, Equation 16 was utilized and the log of the product concentration, given in terms of mol/hr, was plotted *vs* the carbon

FIGURE 31. CO Conversion (mol/kg cat/hr) vs Temperature Over MoS_2 at 8.1 MPa and GHSV = 7750 l/kg cat/hr

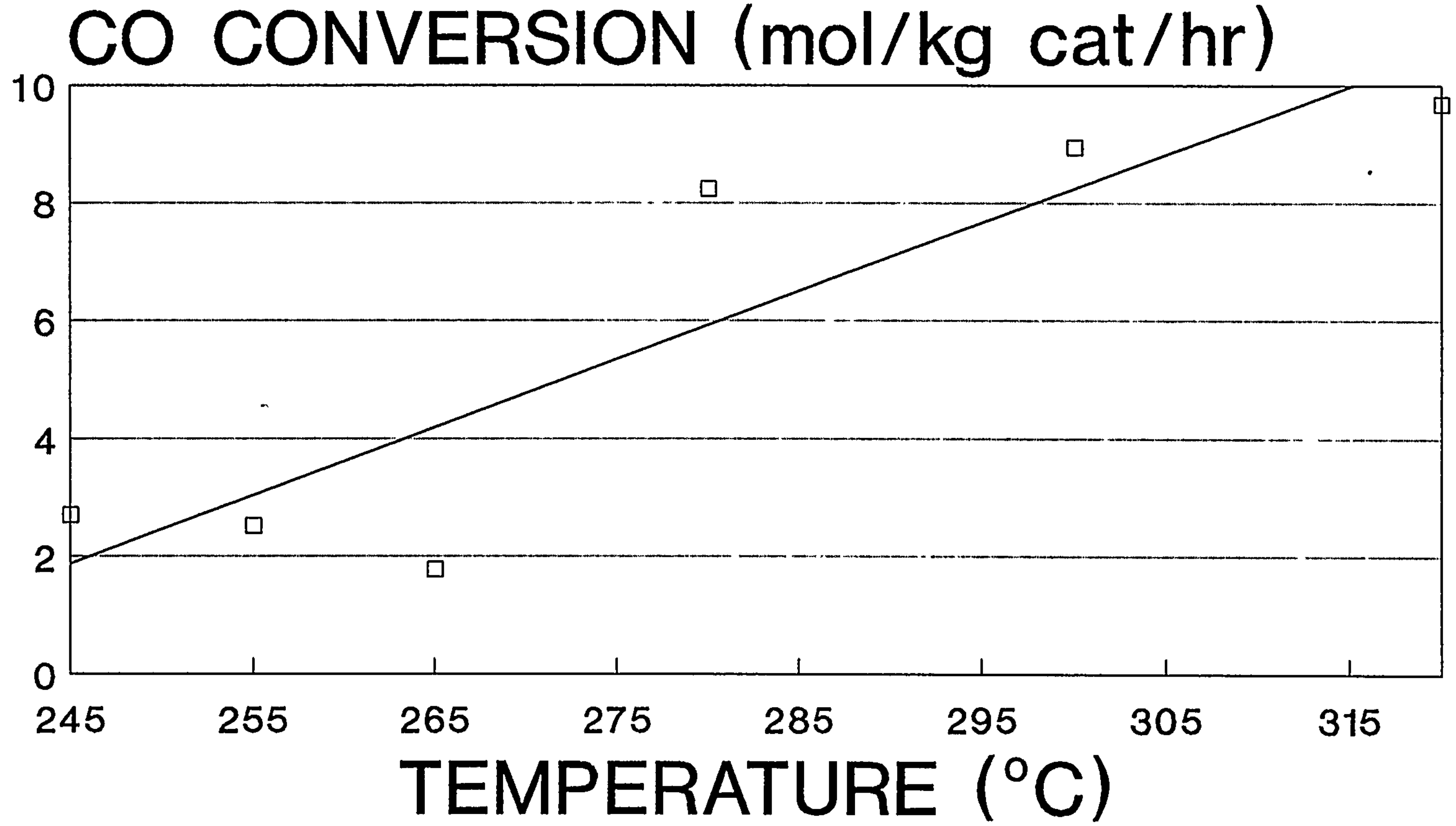


FIGURE 32. CO_2/H_2O Molar Ratio vs Temperature at 8.1 MPa and GHSV = 7750 l/kg cat/hr with H_2/CO = 1

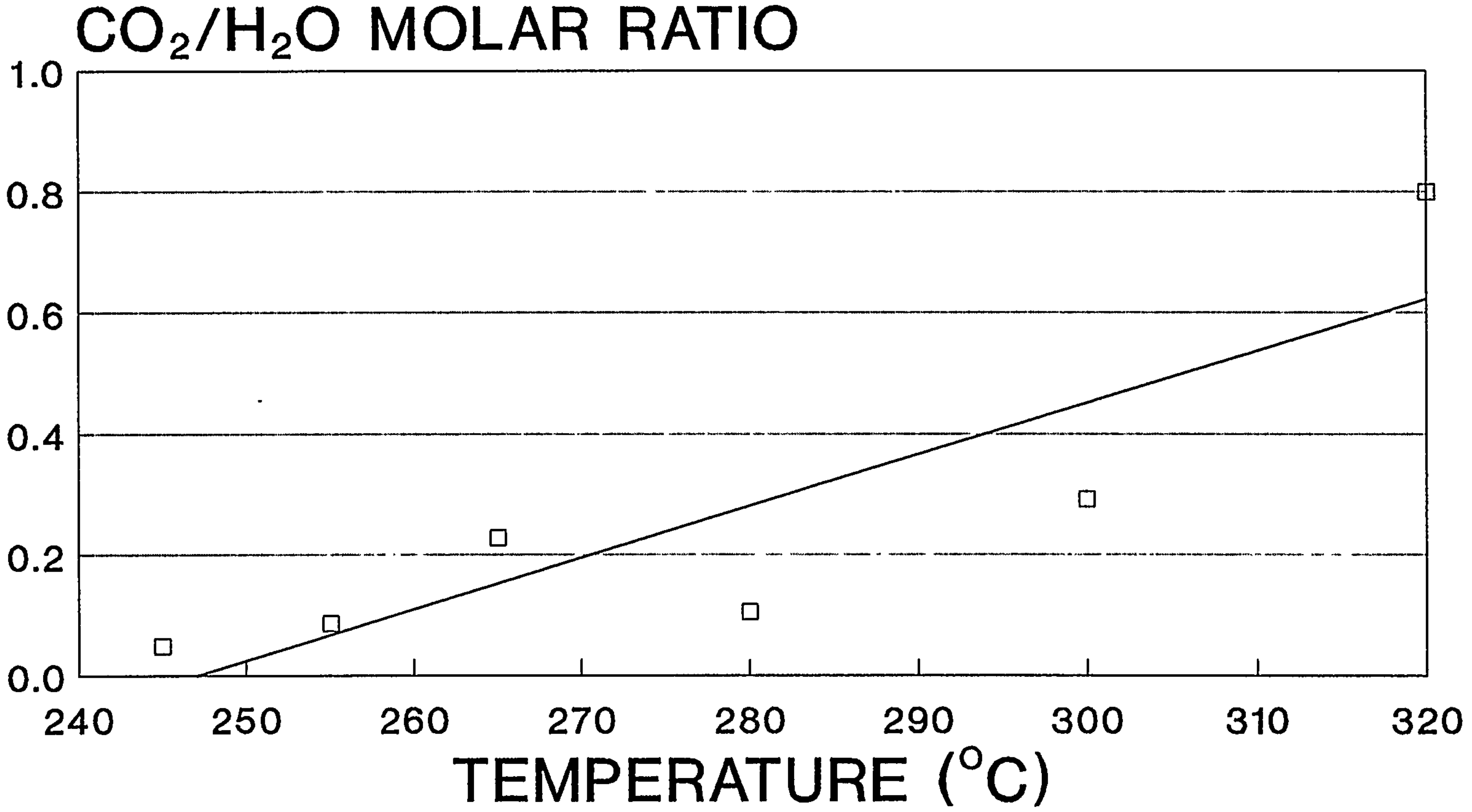


FIGURE 33. Schulz-Flory Plot for MoS_2 at 265°C, 8.1 MPa, and GHSV = 7750 l/kg cat/hr

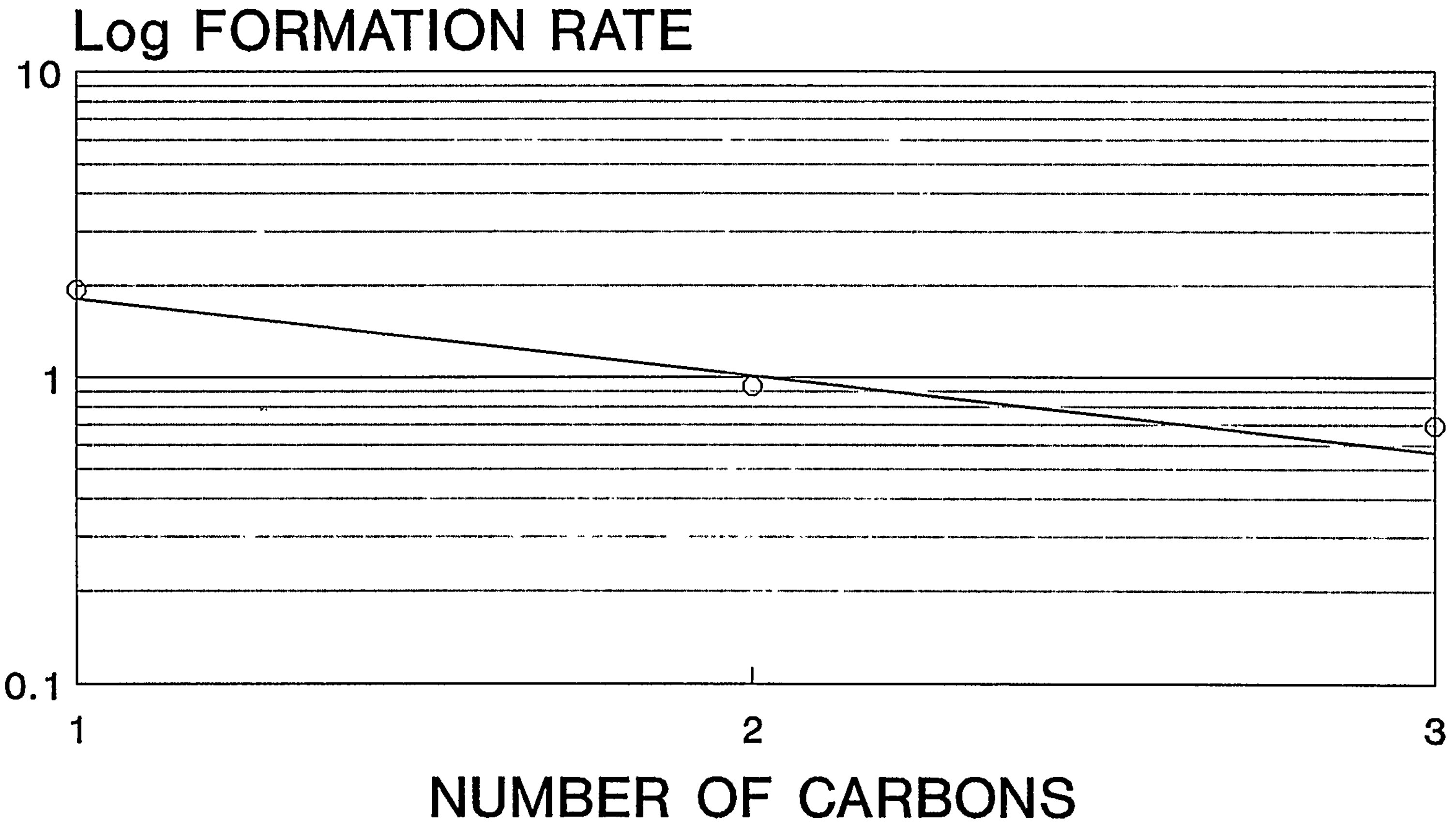


FIGURE 34. Schulz-Flory Plot at 280°C, 8.1 MPa,and GHSV = 7750 l/kg cat/hr

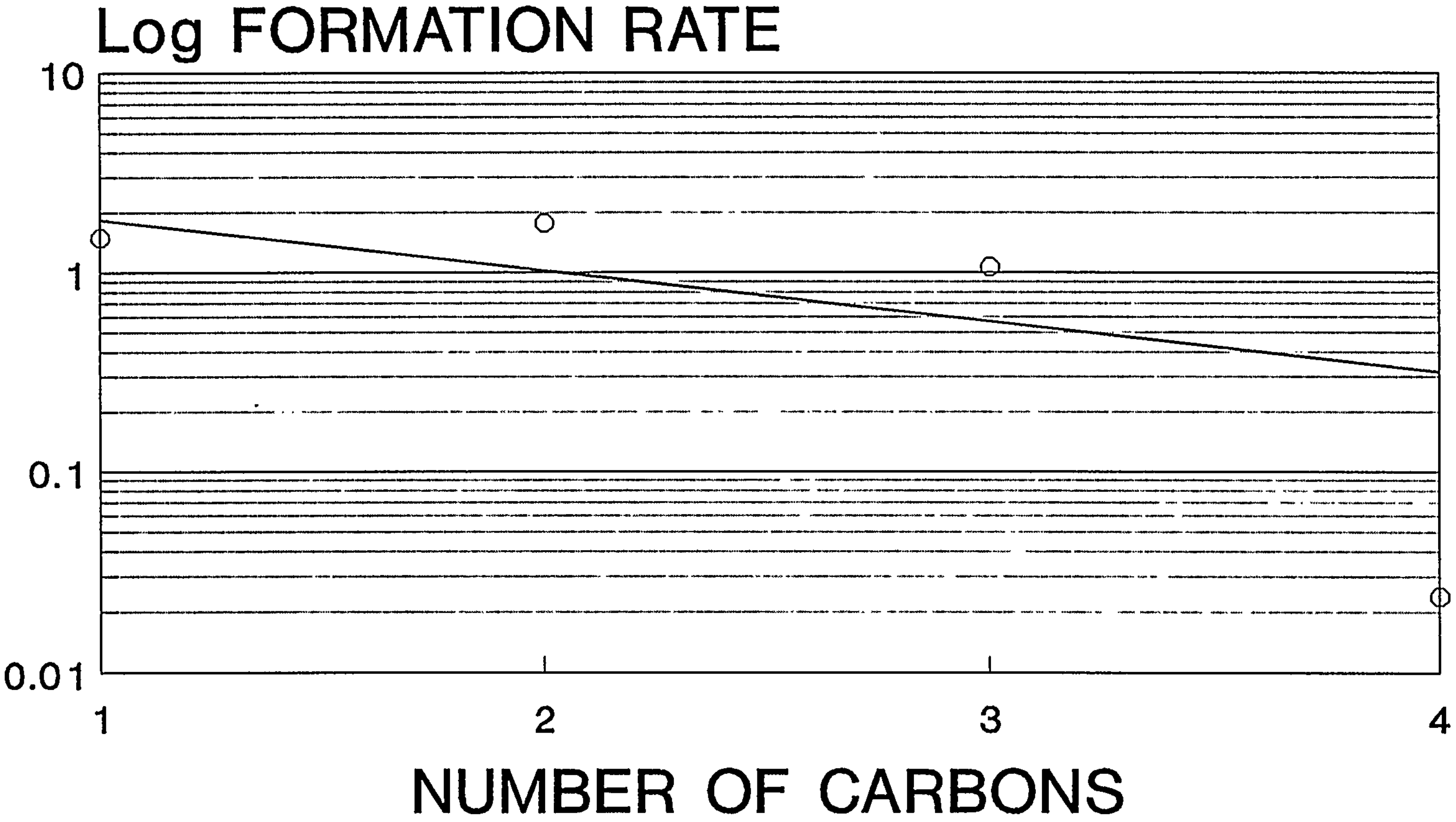


FIGURE 35. Schulz-Flory Plot at 300°C, 8.1 MPa,and GHSV = 7750 l/kg cat/hr

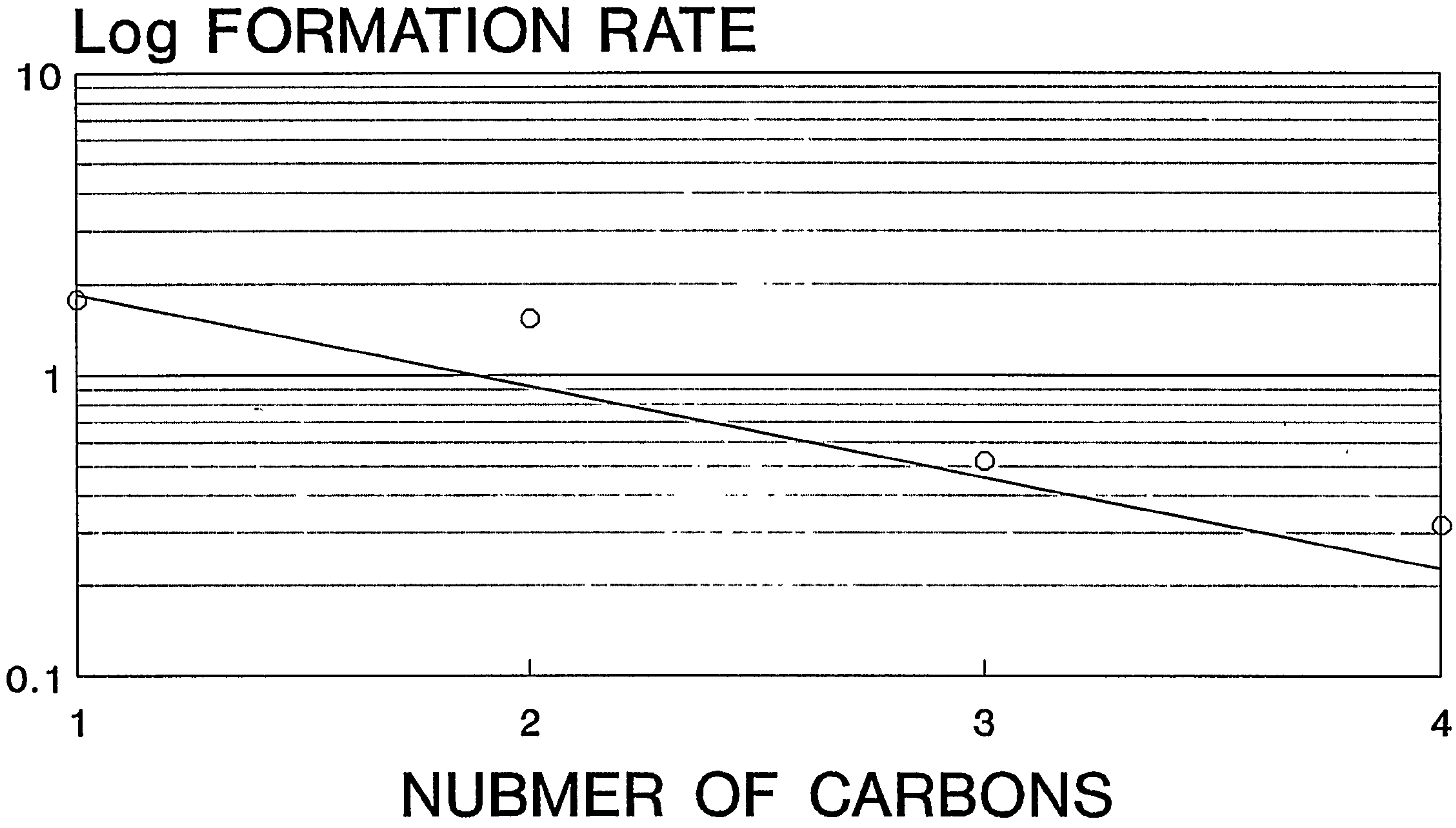
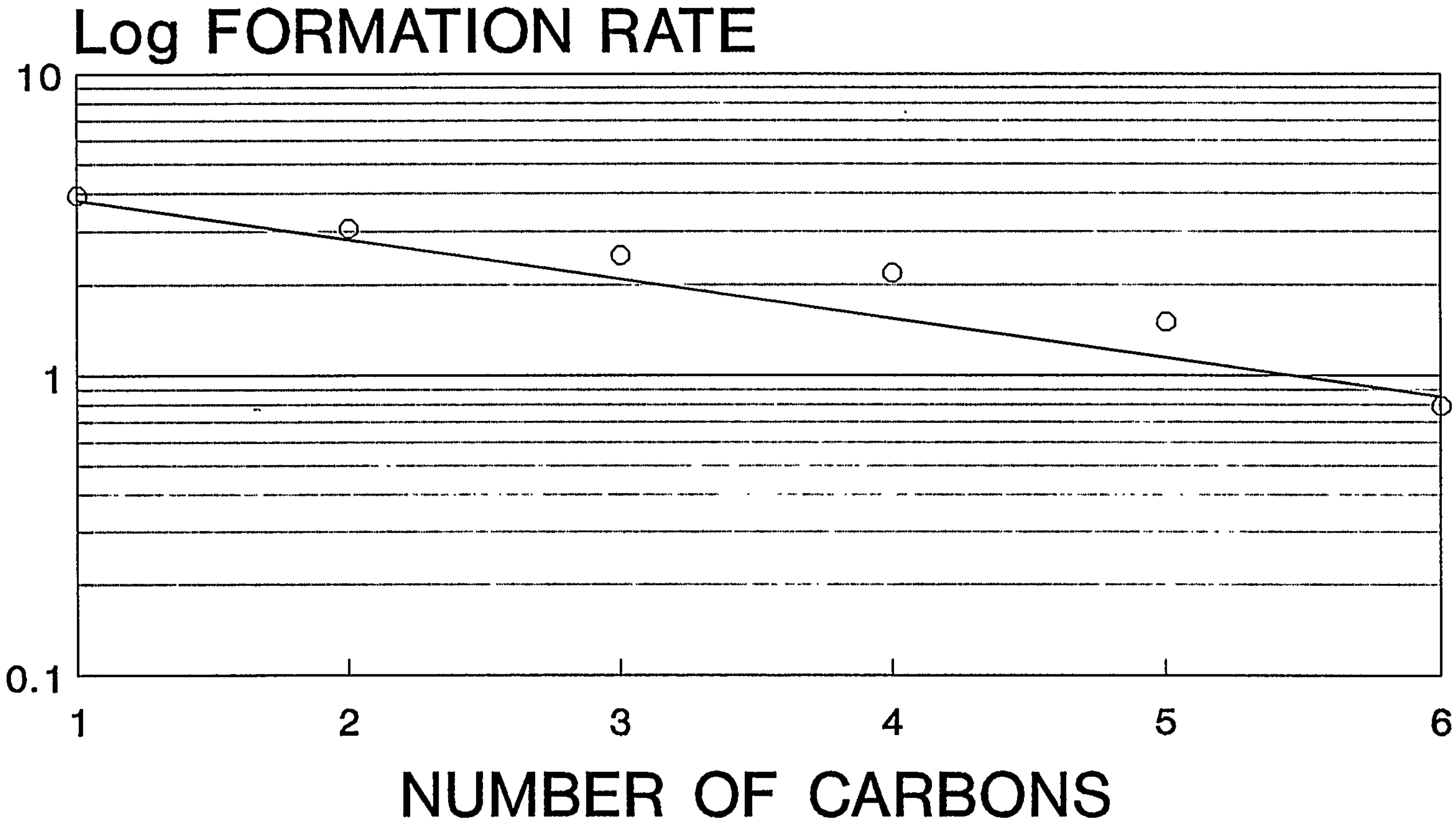


FIGURE 36. Schulz-Flory Plot for MoS_2 at 320°C, 8.1 MPa, and GHSV = 7750 l/kg cat/hr



number (n) of that product. For normal carbon-carbon bond formation *via* addition of a C_1 unit to a growing C_n carbon chain according to polymerization kinetics, this should give a straight line with a negative slope. The slope of the line expresses the probability of carbon chain growth and is designated as being equal to the log of α, where α is expressed as shown by Equation 17.

$$\log C_n = 2 \log (\ln \alpha) + n \log \alpha \tag{16}$$

$$\alpha = k_p/(k_p + k_t) \tag{17}$$

Equation 17 relates the probability that any intermediate carbon chain will grow by propagation rather than terminating *via* hydrogenation and desorption, where k_p is the rate for the propagation reaction and k_t is the rate of termination. The α value for each reaction was determined from the least squares best fit of the data at each reaction temperature from the Anderson-Schulz-Flory distribution of products. An appreciable scatter in the value of α was obtained, but no large variation of α was noted, as shown in Table 11. Table 12 shows that higher molecular weight products were produced at higher reaction temperatures, indicating that propagation was more likely at the higher temperatures. This can be seen in Figure 37, where the space time yields of all of the hydrocarbon products increased with increasing reaction temperature. However, there were appreciable variations in the C_2-C_4 product space time yields at the temperatures of 265, 280, and 300°C.

After the above tests were conducted, the temperature was decreased to 295°C, and methanol was injected into the inlet synthesis gas at a rate of 18 μl/min using the high pressure Gilson pump. This experiment was carried out to determine if the undoped MoS_2 catalyst would homologate the methanol into ethanol. No oxygenates were observed during the pumping of methanol. However, it was observed that the methanol was decomposed to carbon monoxide and hydrogen, and higher yields of hydrocarbons were obtained (Figure 38).

TABLE 11. Experimentally Determined Alpha Values

TEMPERATURE (°C)	SLOPE	ALPHA
265	-0.621	0.239
280	-0.508	0.310
300	-0.540	0.288
320	-0.589	0.258

TABLE 12. Product space time yields (g/kg cat/hr) of the hydrocarbons, carbon dioxide, and water formed over the updoped MoS_2 catalyst from H_2/CO = 1/1 synthesis gas.

TEMP (°C)	CH_4	C_2	C_3	C_4	C_5	C_6	CO_2	H_2O
245	23.2	0	0	0	0	0	3.6	45.2
255	15.3	0	0	0	0	0	5.8	40.5
265	12.0	2.2	3.4	0	0	0	8.8	23.3
280	20.7	72.4	20.5	2.6	0	0	16.1	92.4
300	57.9	3.0	8.8	7.3	0	0	44.6	91.8
320	303.9	75.6	30.4	19.8	5.2	1.2	87.0	65.3

FIGURE 37. Space Time Yield vs Temperature at 8.1 MPa and GHSV = 7750 l/kg cat/hr Over MoS_2

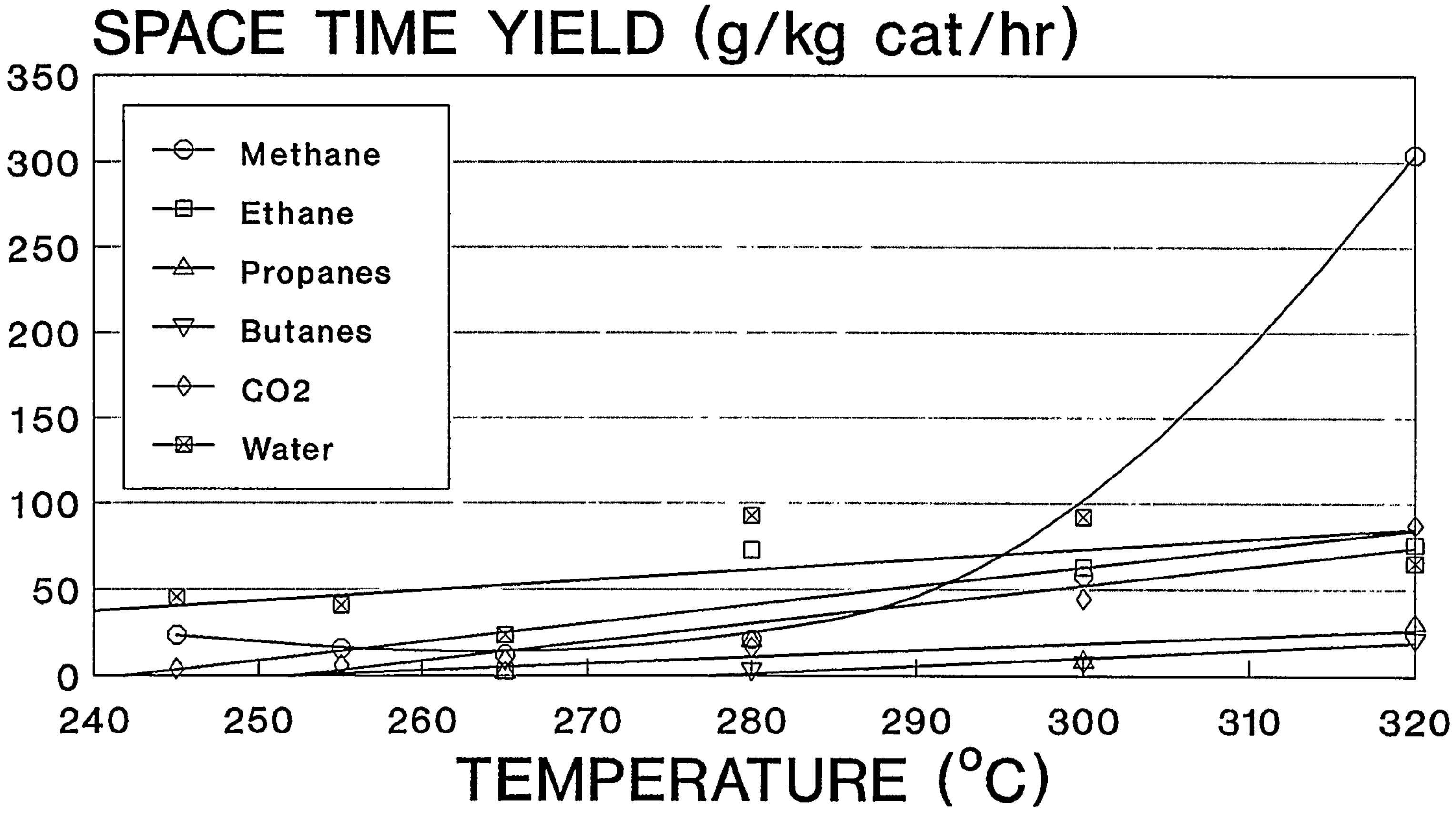
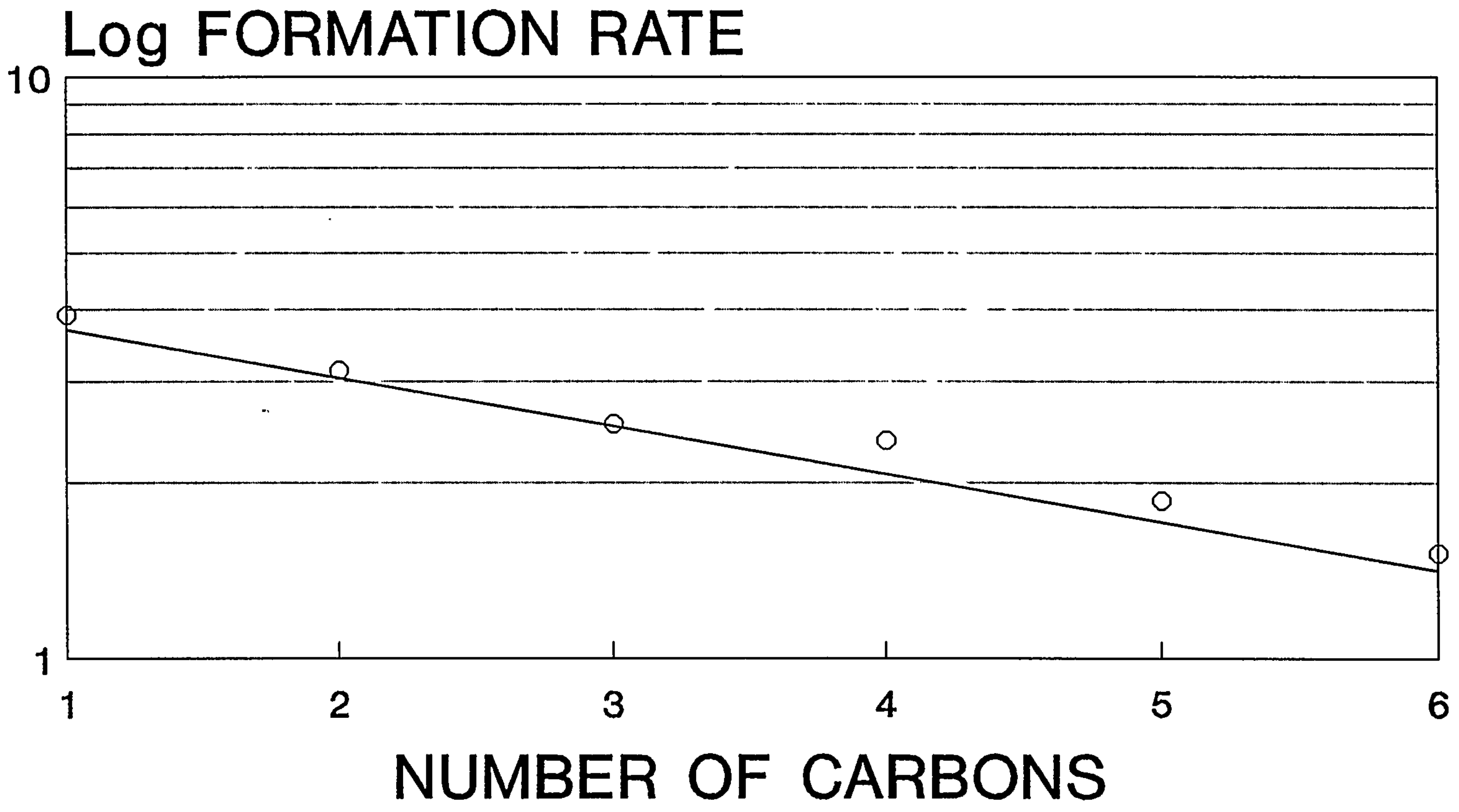


FIGURE 38. Schulz-Flory Plot for MoS_2 at 295°C, 8.1 MPa, and GHSV = 7750 l/kg cat/hr



Methanol Injected into the Synthesis Gas

__Testing of 13 wt% CsOOCH/MoS$_2$.__ This promoted catalyst was loaded into the reactor and pretreated in the same manner as described earlier for the undoped MoS$_2$. The testing was carried out at 8.1 MPa with $H_2/CO = 1$ synthesis gas at a GHSV of 7750 ℓ/kg cat/hr at 245, 255, 265, 275, 285, and 295°C. After this set of temperatures was run, the reaction was run at 245°C again to determine if there was any deactivation of the catalyst. As can be seen in Figure 39, which is a plot of the space time yield of methane *vs* time of testing, there was apparent deactivation at each of the higher reaction temperatures, as well as by comparing the initial test and the final test at 245°C. A plot of the total space time yield of oxygenates (alcohols + esters) exhibited very similar behavior, but there was more scatter in the experimental data at each temperature. The data in Figure 39 were collected during approximately 100 hr of continuous testing. Prior to Sample No. 94, the furnace was turned off and the reactor was allowed to cool to 245°C, at which point a rather constant reactor temperature of 245°C was maintained at the end of the experiment.

During this testing program at temperatures of 275°C and higher, apparent deactivation can be seen from the gradual decline in methane formation with time. The products that were formed in the reaction in appreciable yields in addition to methane were methanol, ethanol, propanol, ethyl formate, water, and carbon dioxide. The general trends that were followed by the catalyst were increasing selectivity of hydrocarbons, principally methane, and decreasing selectivity to alcohols with increasing temperature (Figure 40), which is also shown in Figure 41 where the hydrocarbon/alcohol molar ratio increased with increasing reaction temperature. As the temperature was increased, more higher alcohols were formed relative to methanol, and this is shown in Figure 42 where the methanol/C_2^+ oxygenated products molar ratio decreases with increasing temperature. As expected, the space time yields of the products increased with increasing reaction temperature (Figure 43).

FIGURE 39. Methane Productivity vs Time

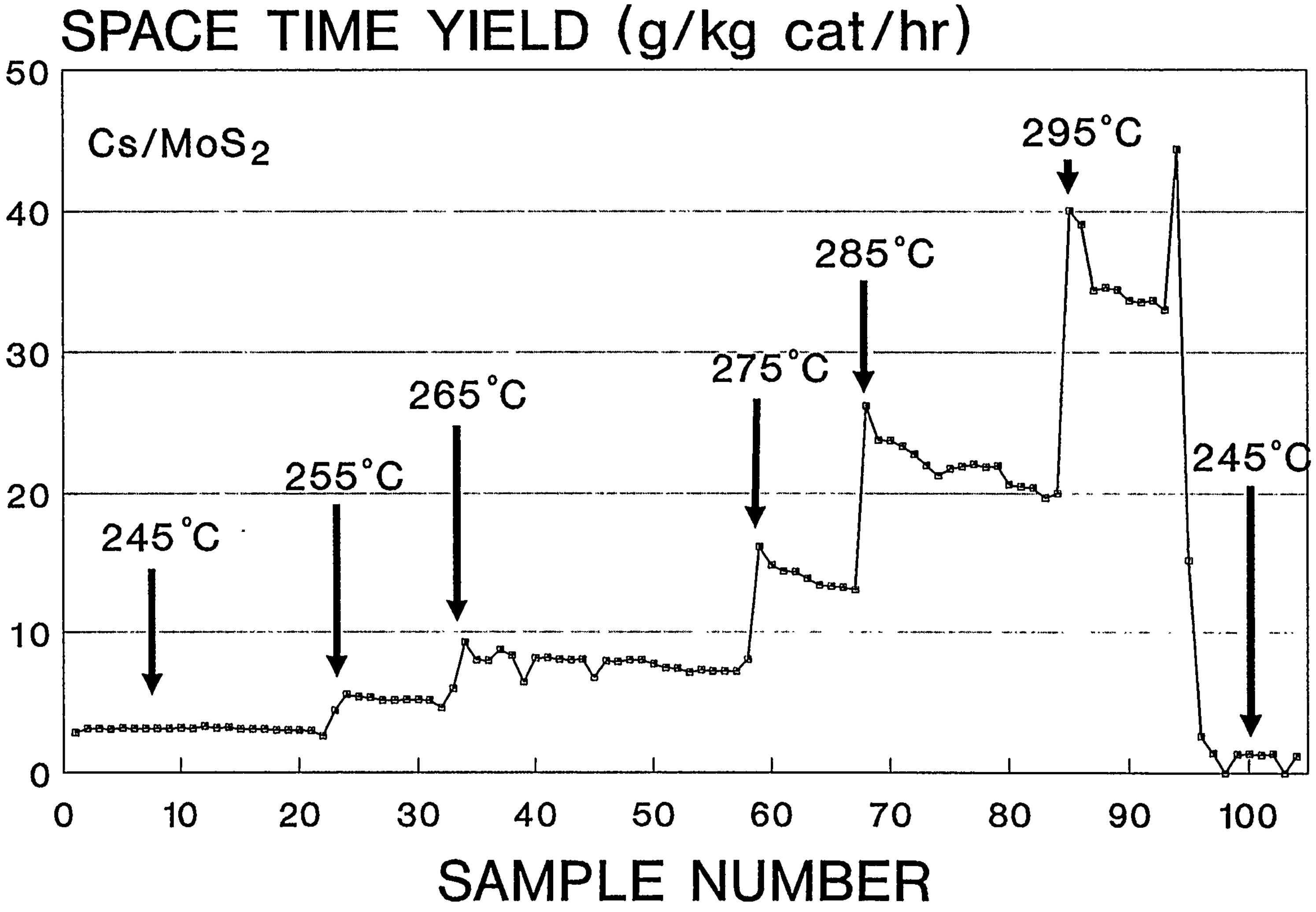


FIGURE 40. Selectivity vs Temperature Over the Cs/MoS_2 Catalyst

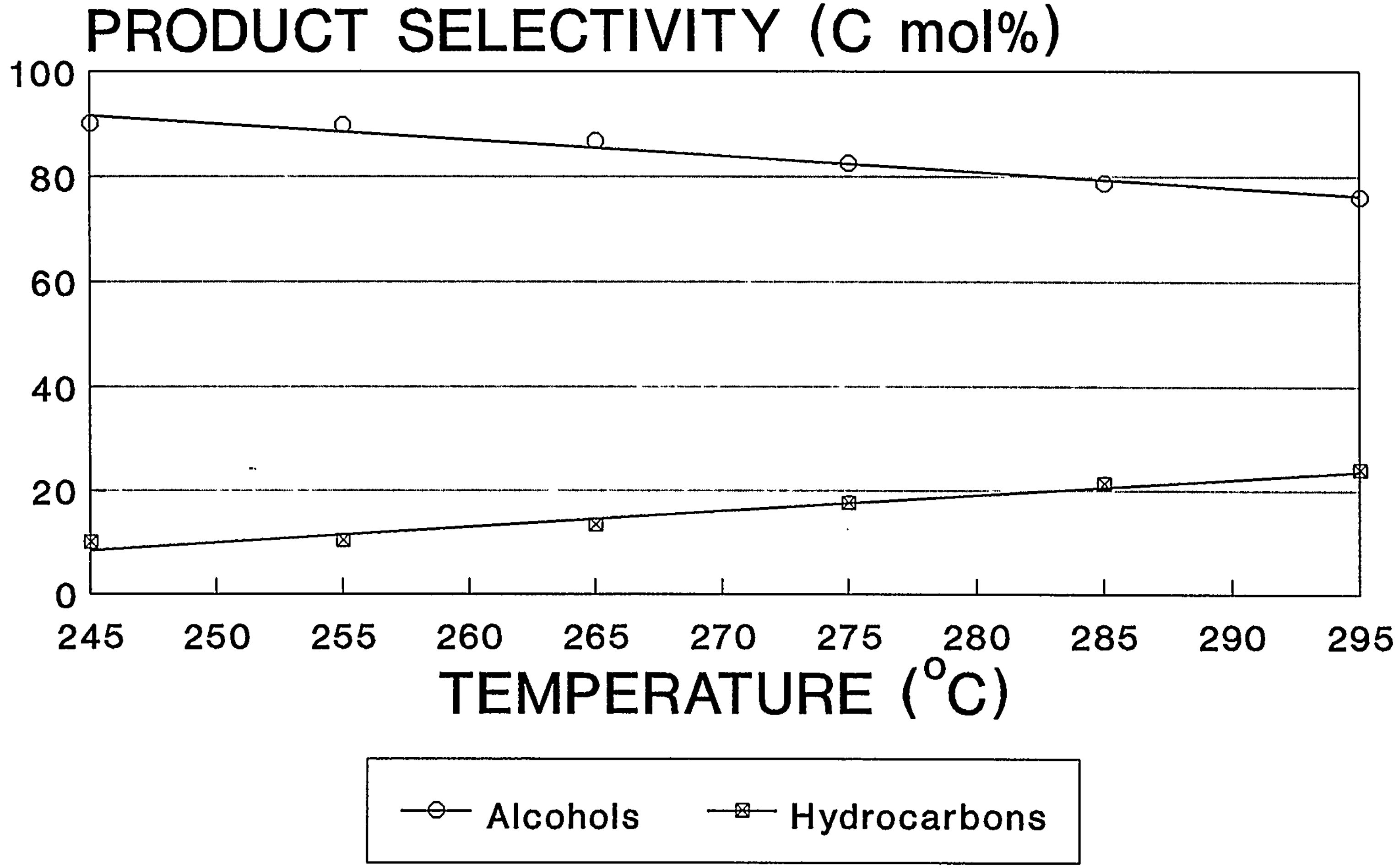


FIGURE 41. Hydrocarbon/Alcohol Molar Ratio Over Cs/MoS_2

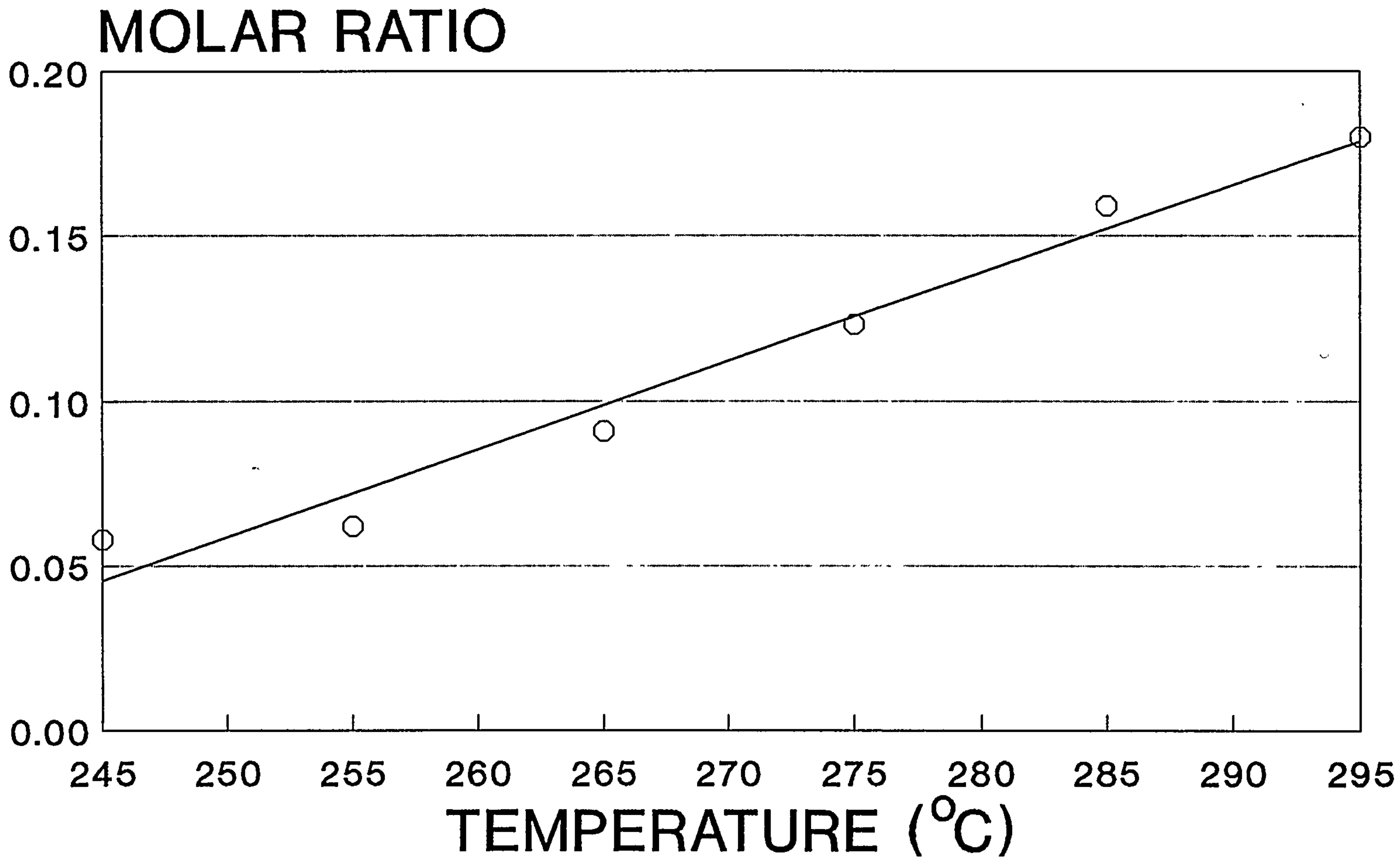


FIGURE 42. Methanol/C_2^+ Oxygenated Products Molar Ratio

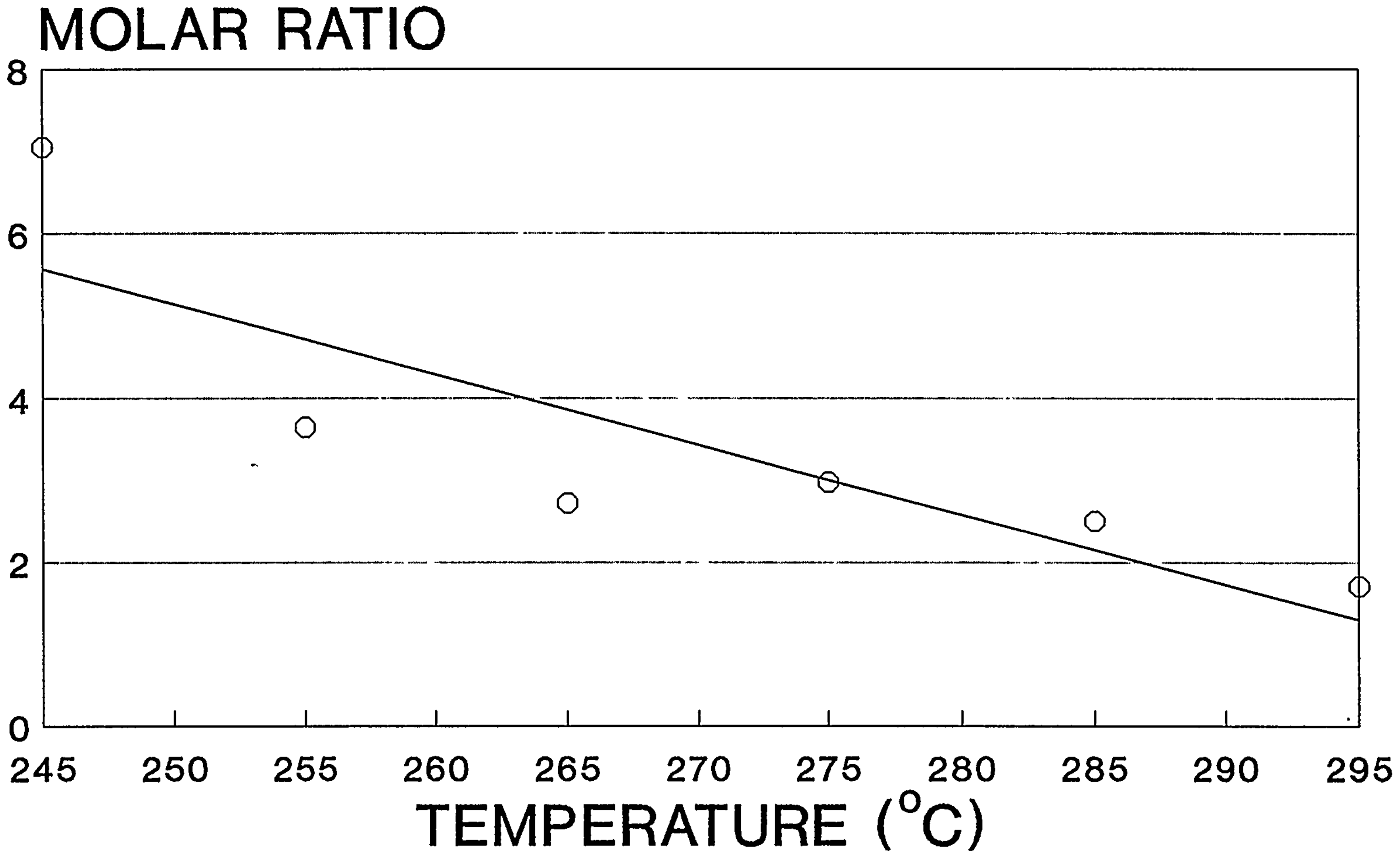


FIGURE 43. Space Time Yield of Products Over Cs/MoS_2 with H_2/CO = 1 vs Temperature at 8.1 MPa