

5.2.1.4.3 Establishment of the Effect of Operational Conditions with Tests at $H_2:CO$ Feed Ratio = 2, 208-250°C, 35-103 atm

Catalyst 4966-96-1 with mostly 3-7 nm ruthenium particles was tested in Runs 23, 24 and 33 with feeds having $H_2:CO$ ratios in the range of 1.9 to 2.0, at various temperatures, pressures and space velocities to determine the effect of operational conditions on catalytic performance.

In Run 23 the catalyst was evaluated at the following set of conditions:

1. 208°C, 35 atm, 500 GHSV, 0-6 hours
2. 208°C, 69 atm, 500 GHSV, 10-16 hours
3. 225°C, 69 atm, 500 GHSV, 19-25 hours
4. 250°C, 69 atm, 500 GHSV, 28-33 hours
5. 250°C, 103 atm, 500 GHSV, 36-48 hours
6. 250°C, 35 atm, 500 GHSV, 52-59 hours
7. 250°C, 35 atm, 250 GHSV, 59-65 hours
8. 250°C, 35 atm, 180 GHSV, 65-69 hours
9. 208°C, 35 atm, 180 GHSV, 73-76 hours

The results obtained in Run 23 are summarized in Figures 5-165 through 5-168. The CO conversions were typically very low, <15%, and continuously declined with time under all set of conditions studied. The light hydrocarbon (C_1, C_2) selectivities increased with pressure and temperature.

Figure 5-165. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles; Conversions in Run 23 Under Various Operating Conditions

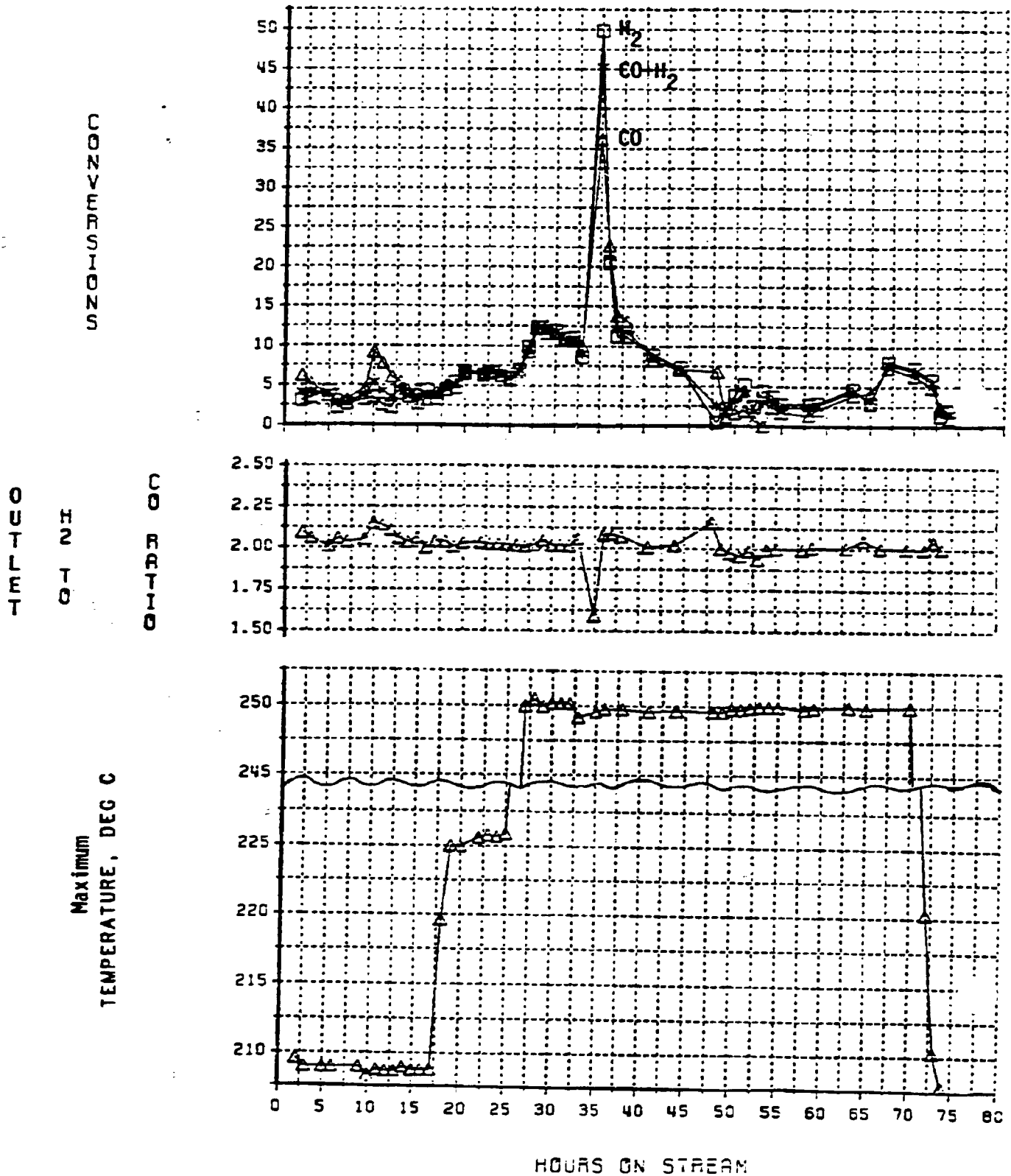


Figure 5-166. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles: Water Gas Shift Activity in Run 23 Under Various Operating Conditions

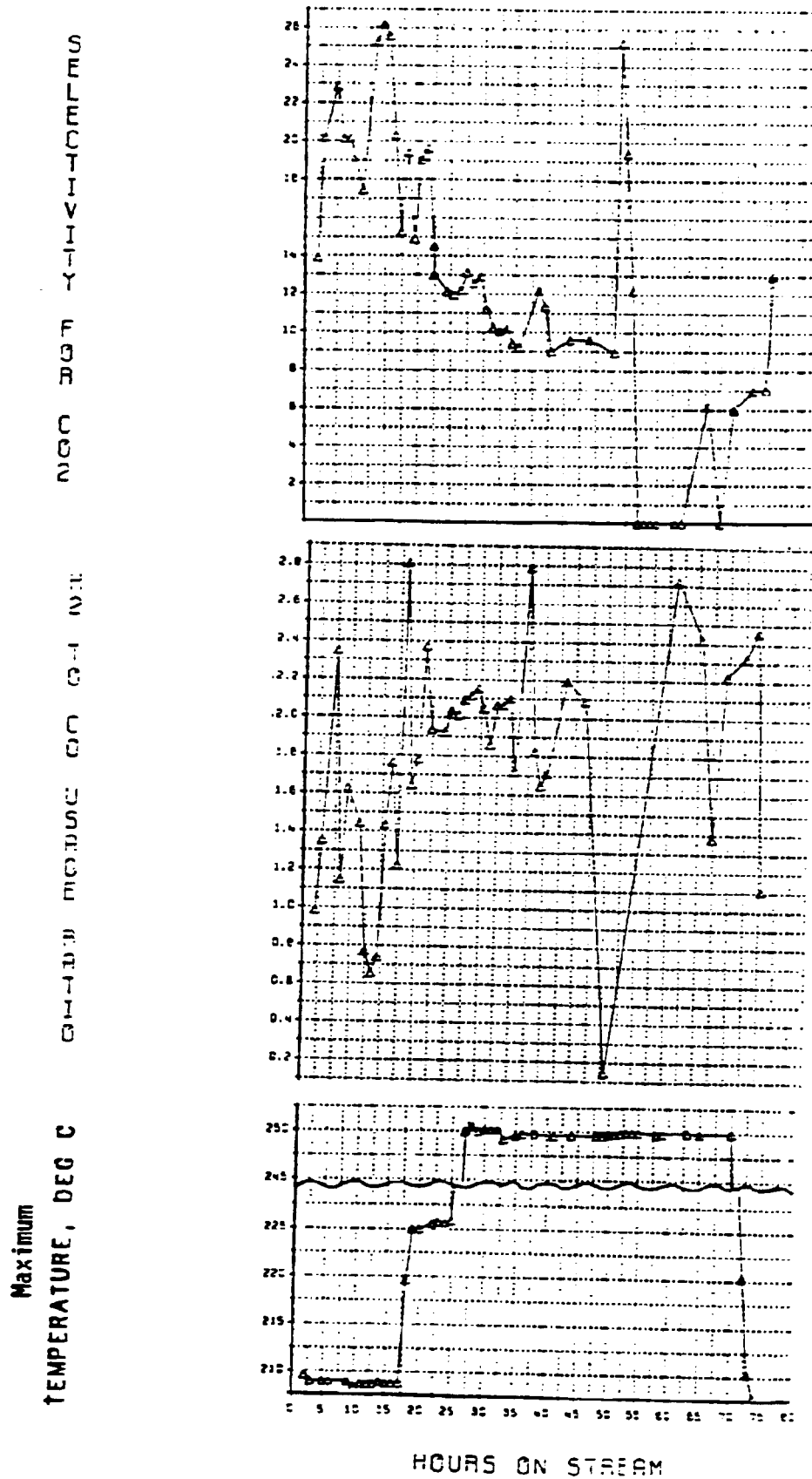


Figure 5-167. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles: C_1 and C_2 Selectivities in Run 23 Under Various Operating Conditions

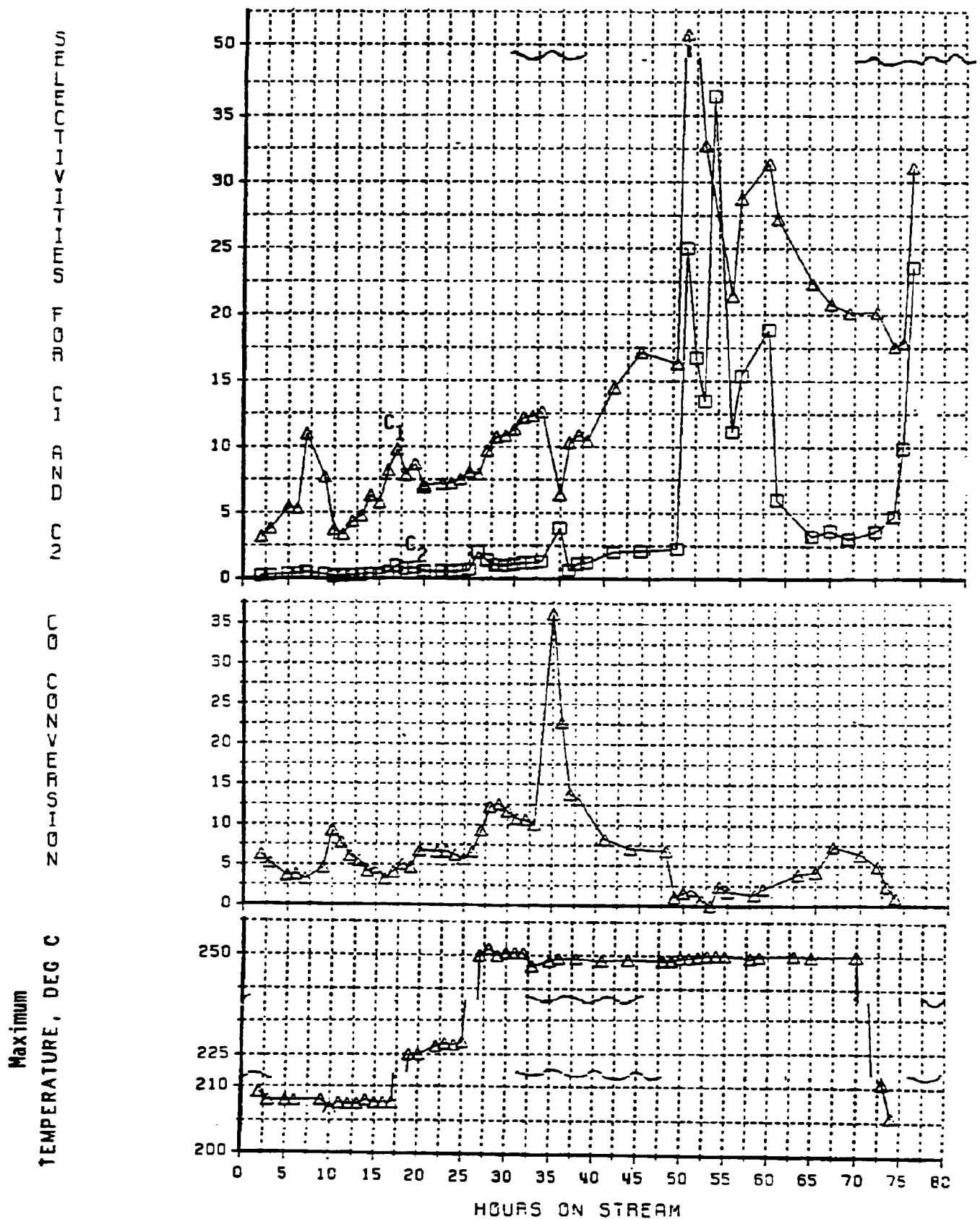
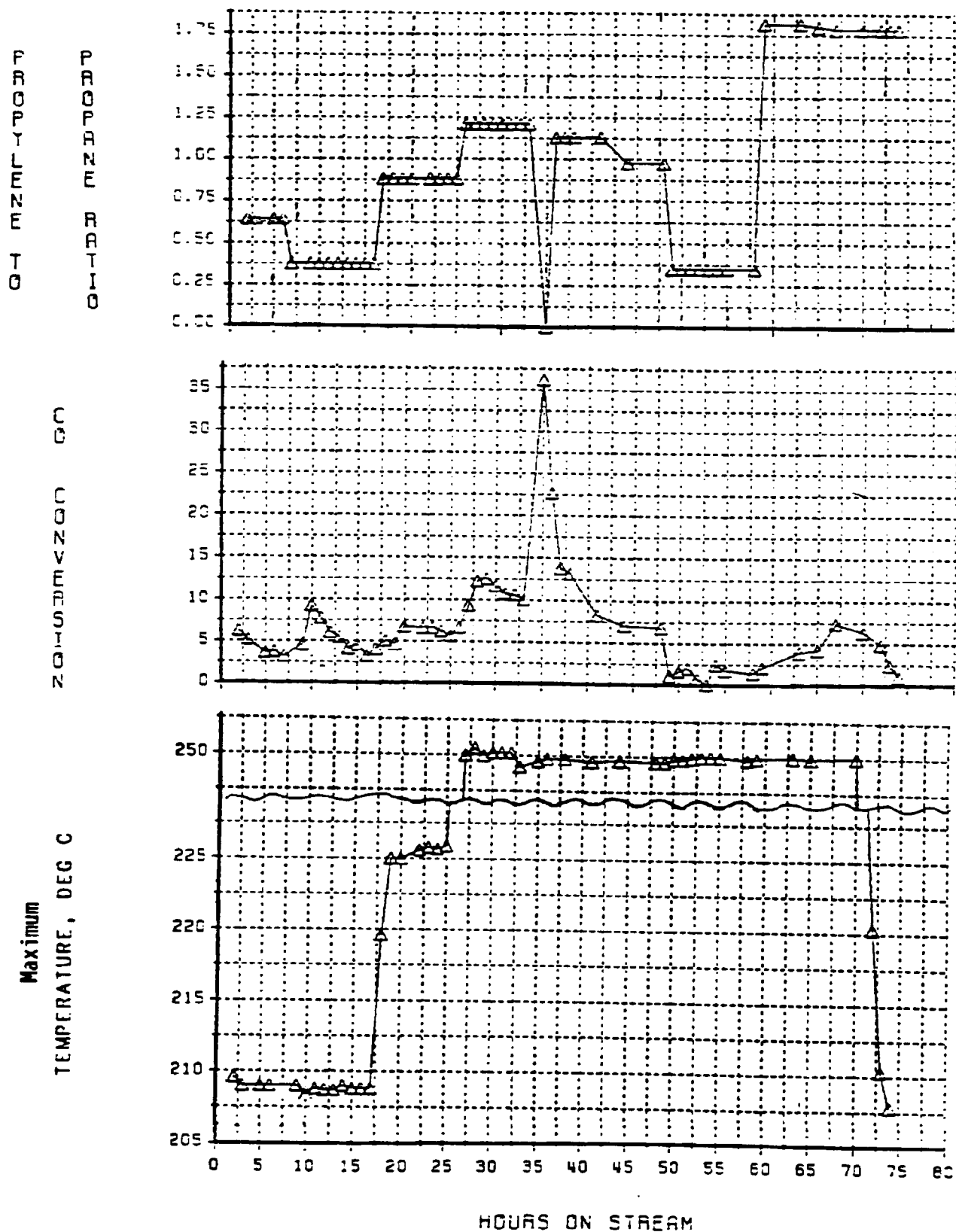


Figure 5-168. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles;
Propylene:Propane Ratios in Run 23 Under Various Operating
Conditions



In Run 24, lower space velocities were used in order to achieve higher conversions. The following set of conditions were used:

1. 208°C, 35 atm, 63 GHSV, 0-20 hours
2. 208°C, 35 atm, 125 GHSV, 20-36 hours
3. 208°C, 35 atm, 250 GHSV, 36-49 hours
4. 208°C, 35 atm, 63 GHSV, 49-59 hours
5. 225°C, 35 atm, 63 GHSV, 59-74 hours
6. 225°C, 52 atm, 63 GHSV, 74-86 hours
7. 225°C, 52 atm, 125 GHSV, 86-98 hours
8. 225°C, 35 atm, 125 GHSV, 98-120 hours
9. 208°C, 35 atm, 125 GHSV, 120-135 hours

The results obtained in Run 24 are summarized in Figures 5-169 through 5-175. After 49 hours on stream the catalyst was brought back, for 10 hours, to the initial operating conditions that prevailed between 0 and 20 hours. It was then found that the $\text{CO}+\text{H}_2$ conversion was lower relative to initial conversion; -53% vs. 64%. Also, between 120-135 hours the conditions were the same as those between 20 to 36 hours, while the $\text{CO}+\text{H}_2$ conversion was only 44% of the earlier value. In Run 24 the use of lower space velocities relative to Run 23 allowed the catalytic performance to be studied over a wide range of conversion levels from 6% to 80%.

In Run 24 the selectivity of CO to CO_2 was typically less than 3%, while the $\text{H}_2:\text{CO}$ usage ratio typically varied between 2.0 and 2.2, (Figure 5-169). These results indicate that there was essentially no water gas shift activity. Since the $\text{H}_2:\text{CO}$ usage ratio was essentially equal to the feed $\text{H}_2:\text{CO}$ ratio, the $\text{H}_2:\text{CO}$ ratio at the catalyst outlet was also equal to 2.

Figure 5-169. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles; Conversions in Run 24 Under Various Operating Conditions

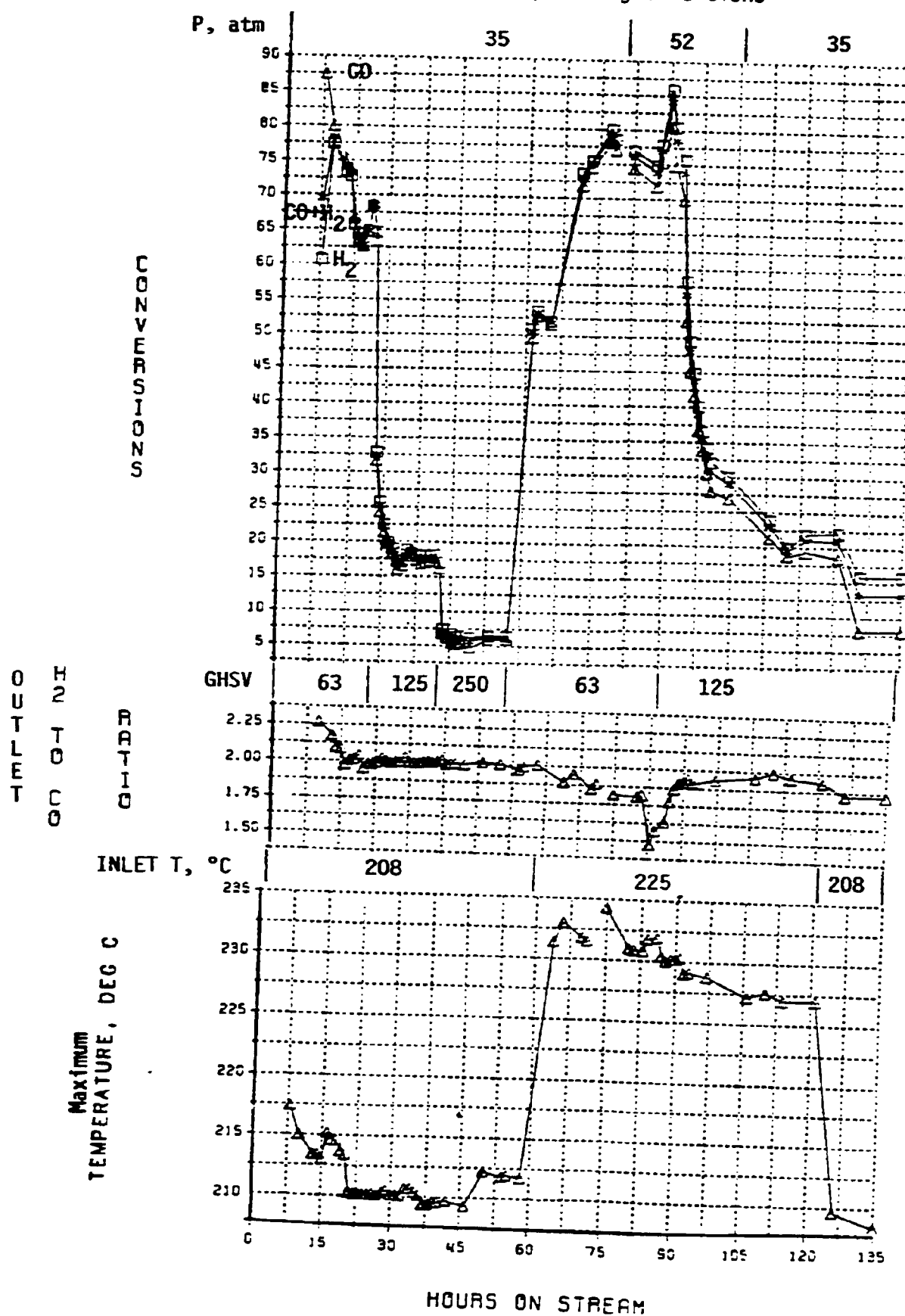


Figure 5-170. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles; Water Gas Shift Activity in Run 24 Under Various Operating Conditions

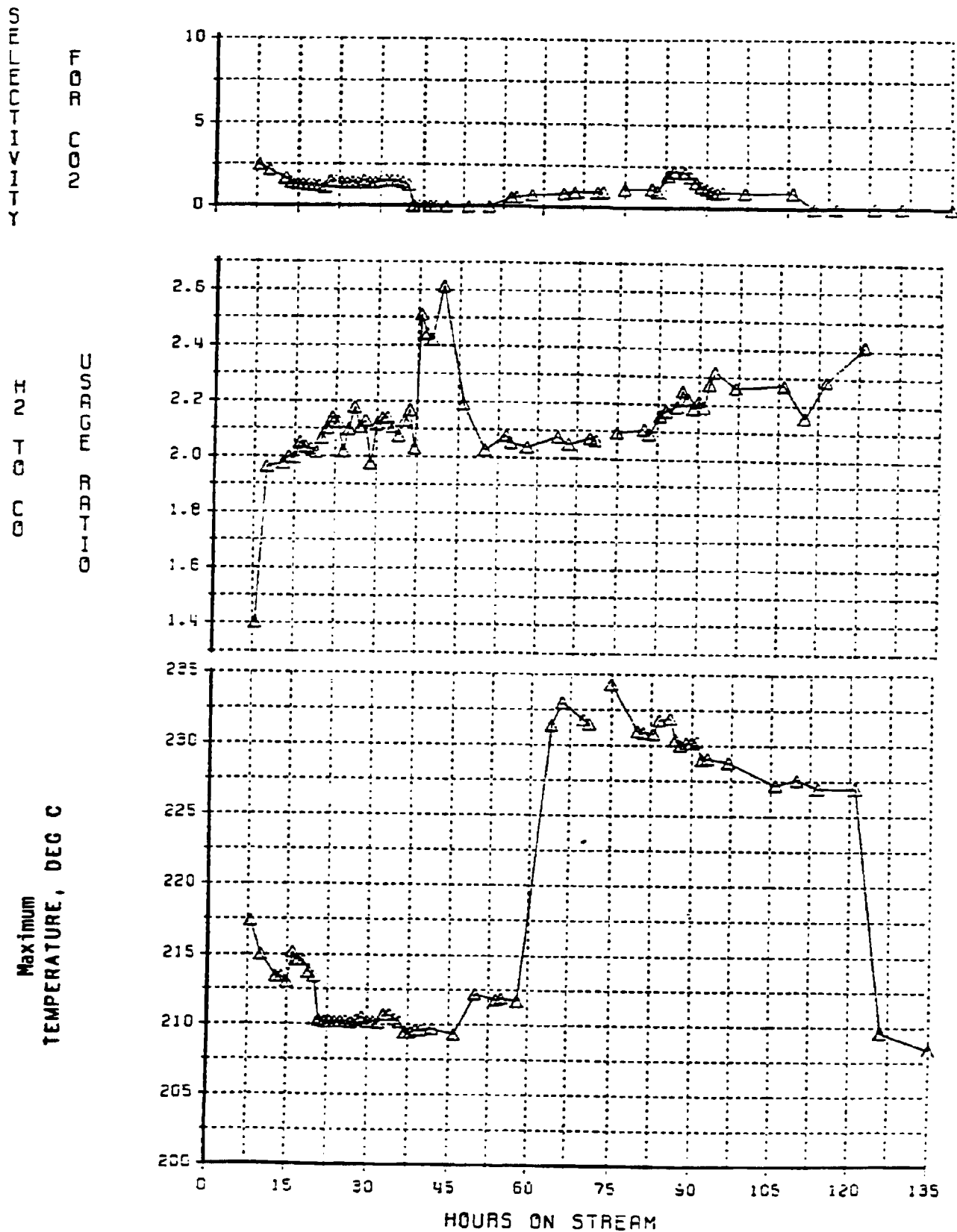


Figure 5-171. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles; C_1 and C_2 Selectivities in Run 24 Under Various Operating Conditions

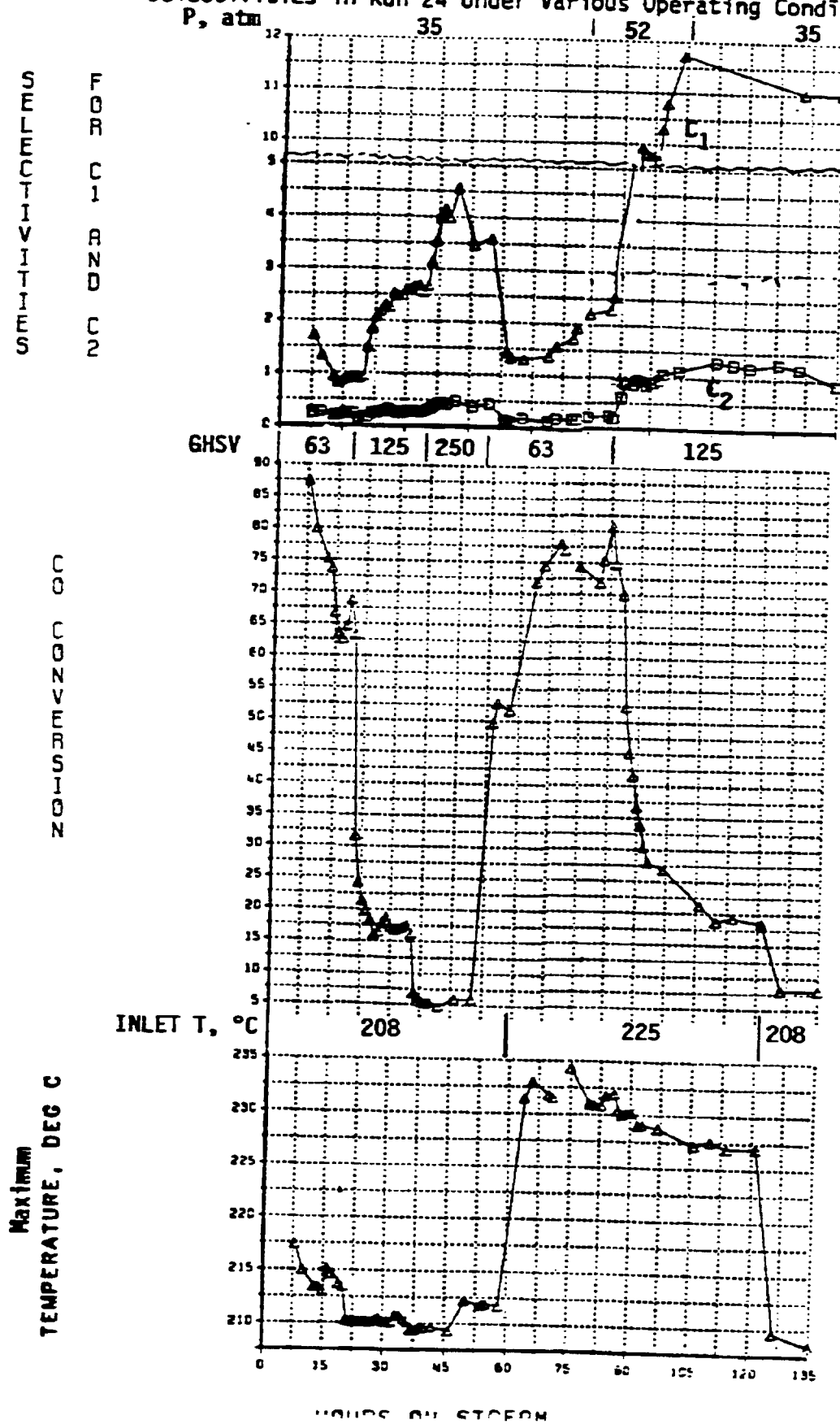


Figure 5-172. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles; C_3 and C_4 Selectivities in Run 24 Under Various Operating Conditions

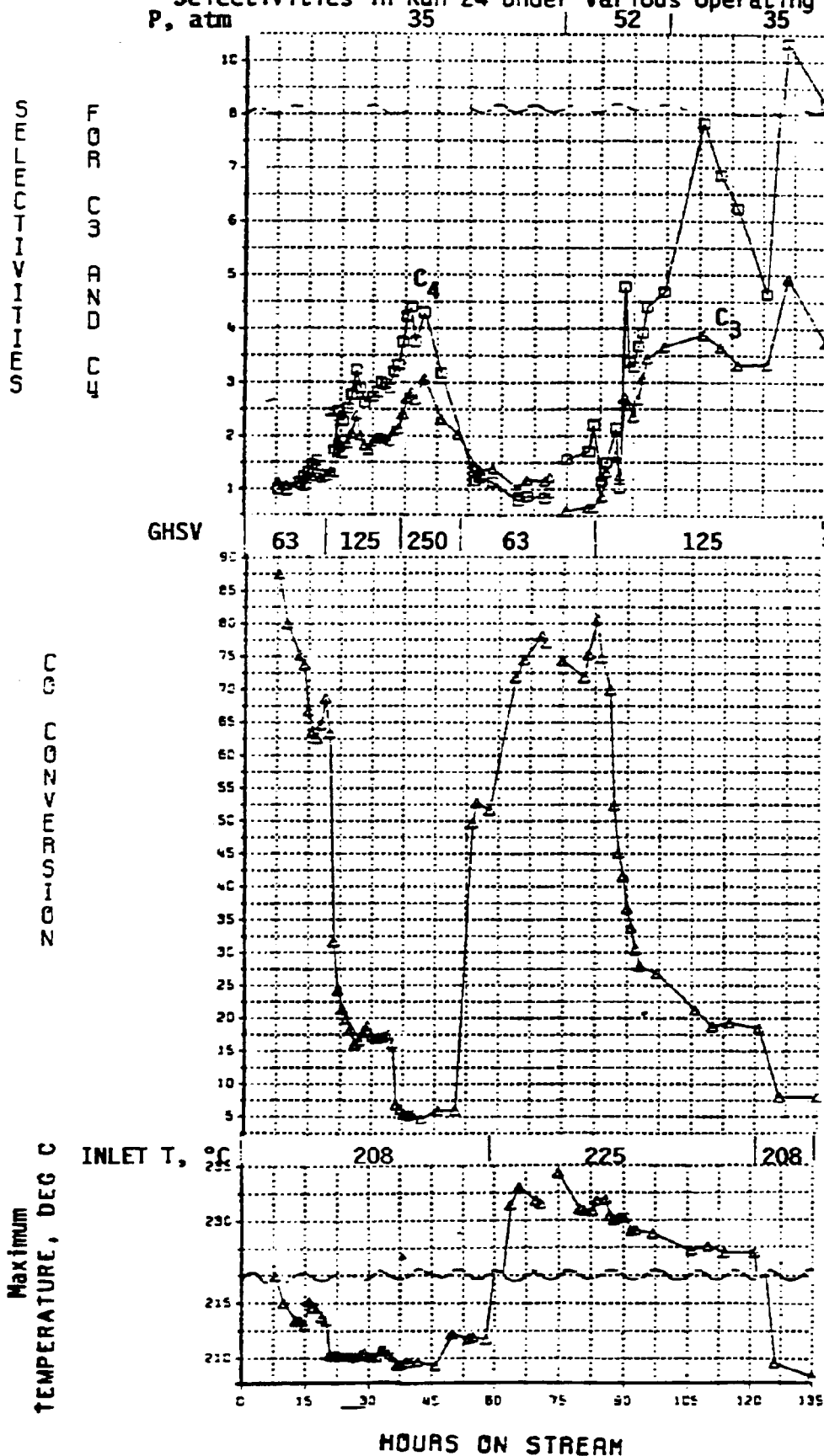


Figure 5-173. Catalyst 4966-96-1 with 3-7 nm Ruthenium Particles: Propylene: Propane Ratios in Run 24 Under Various Operating Conditions

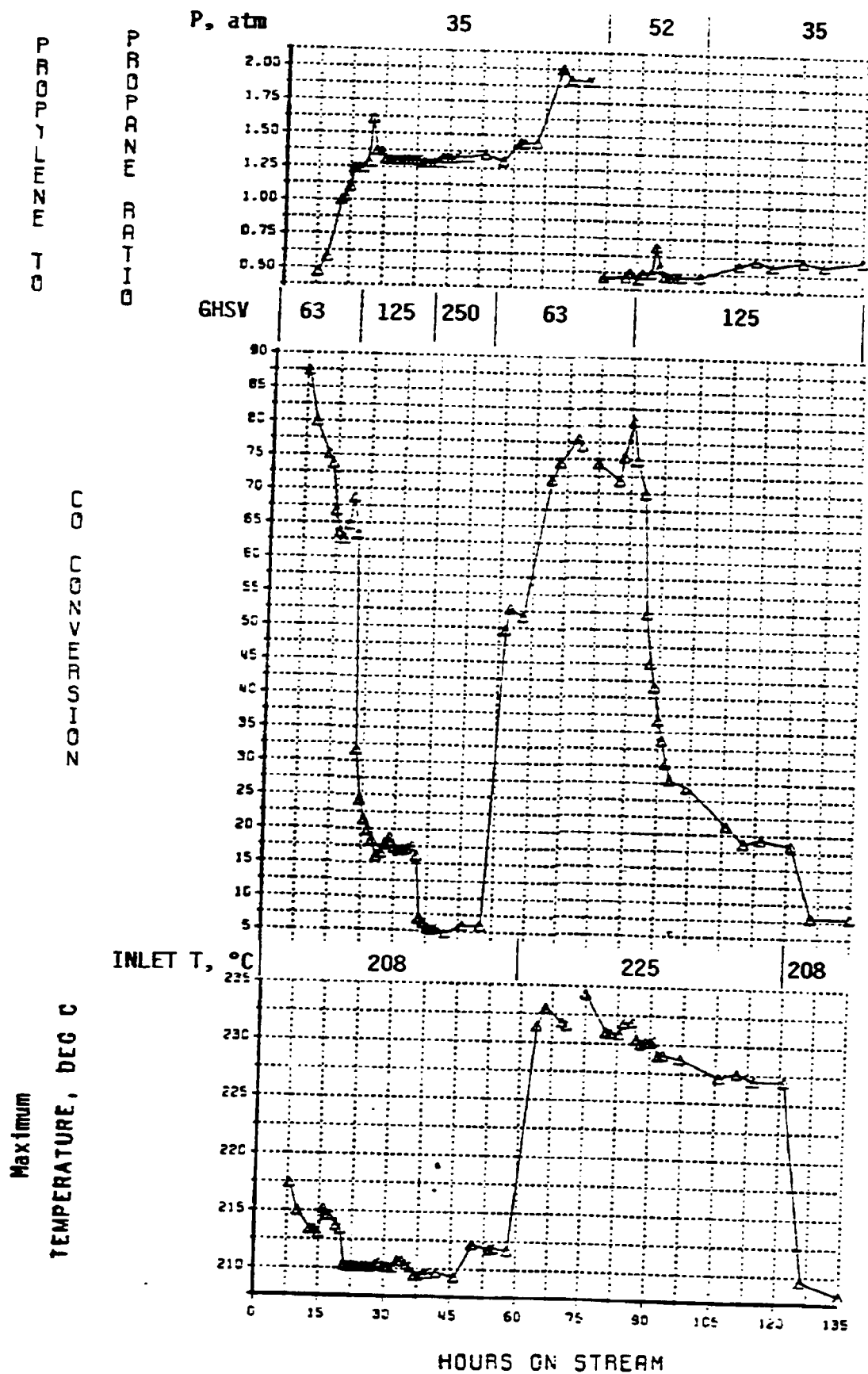


Figure 5-174. Effect of Conversion on Light Hydrocarbon Selectivities in Run 24 with Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles ($H_2:CO$ Feed Ratio = 2.0, 208°C at Inlet, 35 atm)

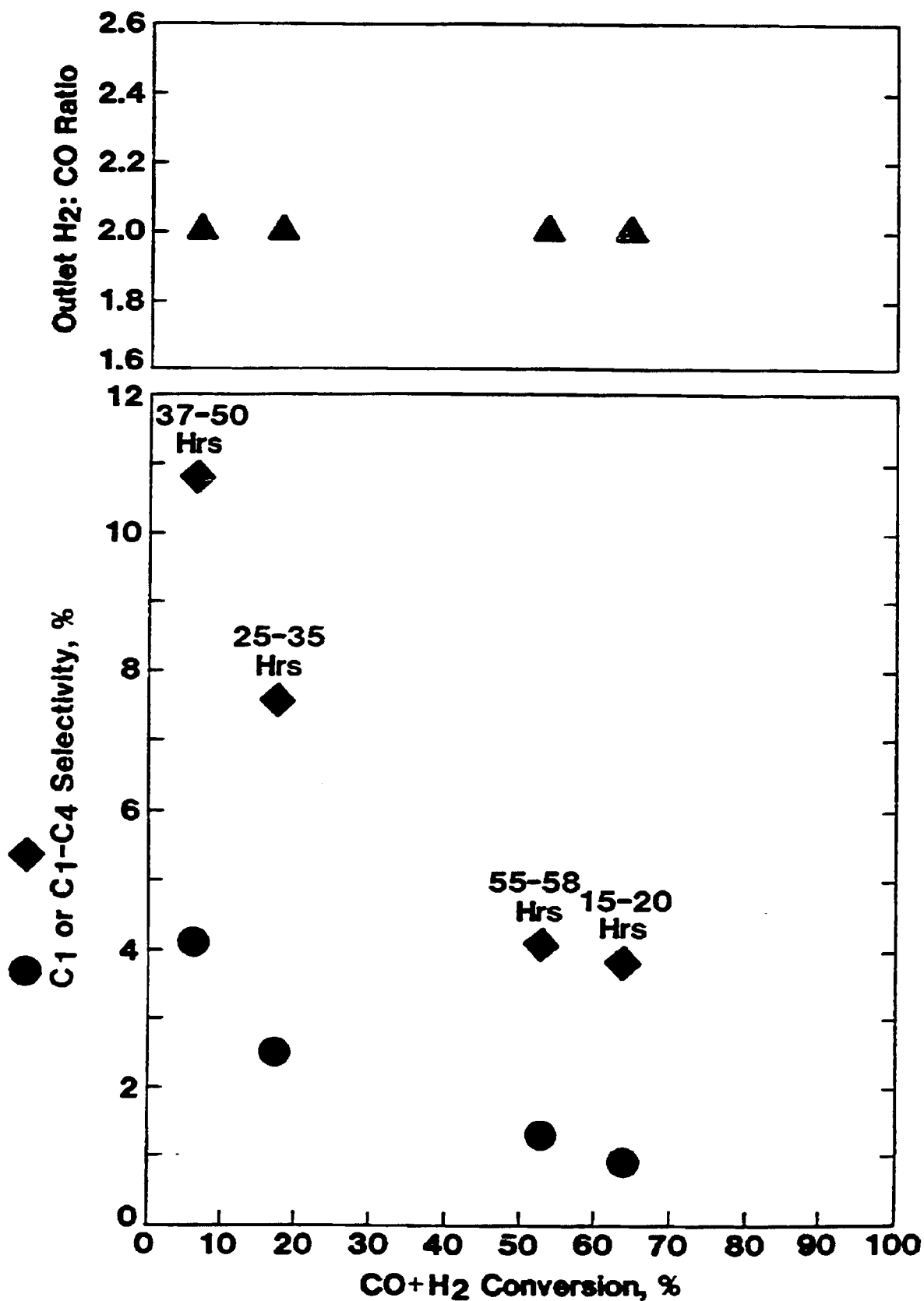


Figure 5-175. Effect of Conversion on Light Hydrocarbon Distribution in Run 24 with Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles ($H_2:CO$ Feed Ratio = 2.0, 208°C at Inlet, 35 atm)

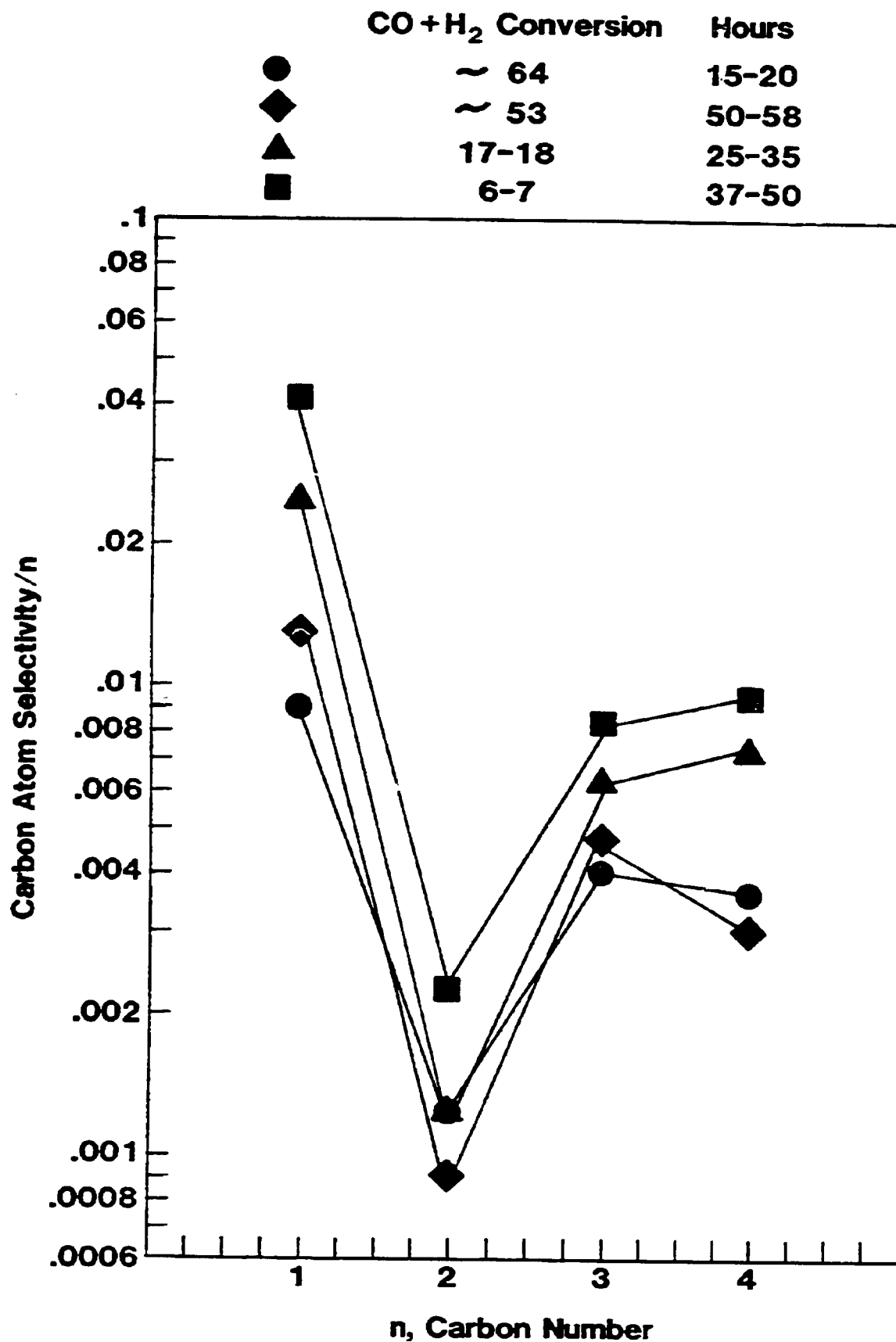
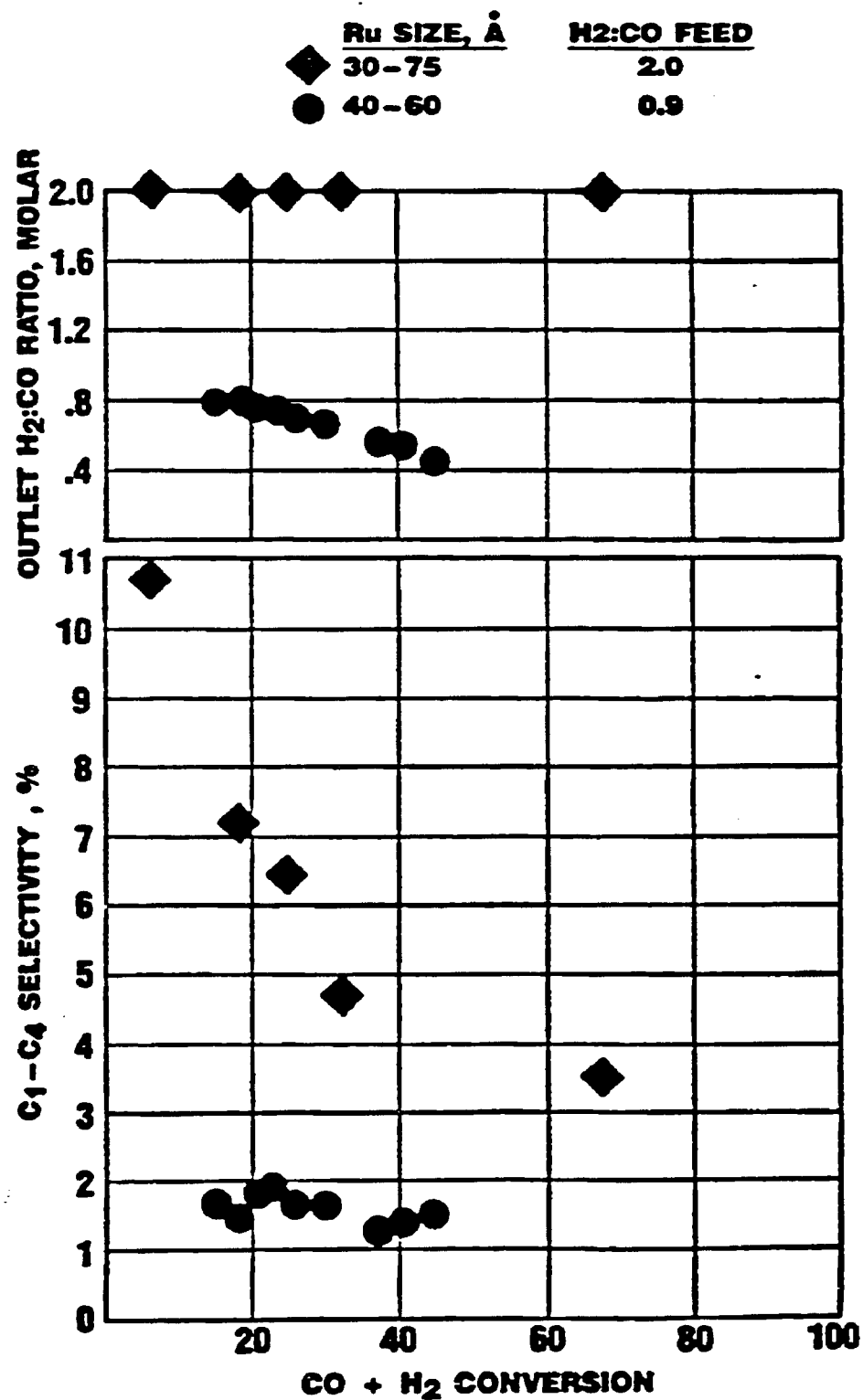


Figure 5-176

EFFECT OF CONVERSION ON LIGHT ENDS PRODUCTION

1% Ru ON Al_2O_3 , 208°C, 34 ATM



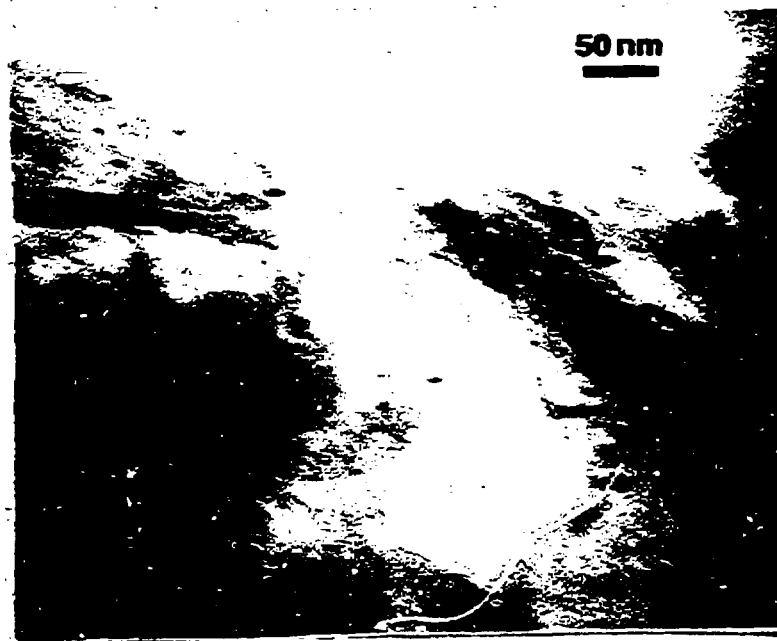


Figure 5-177. STEM Micrograph of Catalyst 4966-96-1 After Use in Run 24

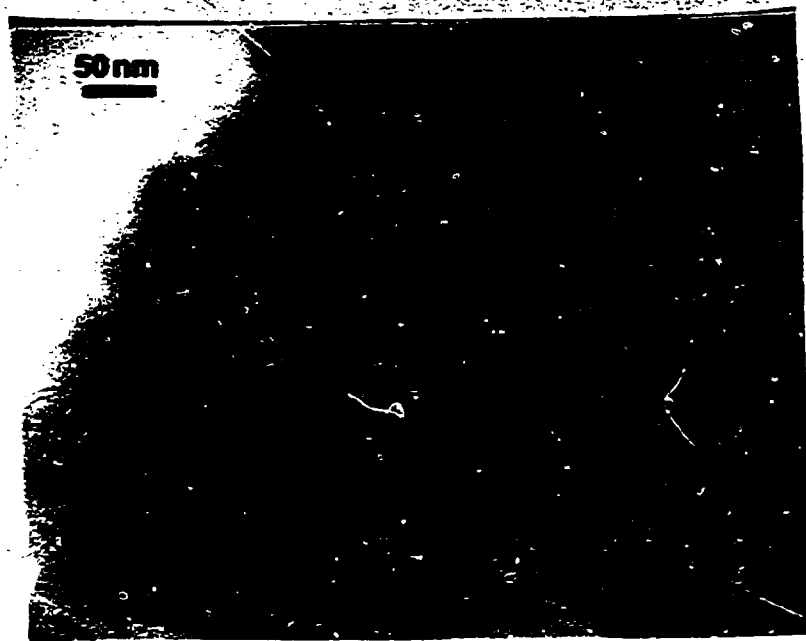


Figure 5-178. STEM Micrograph of Catalyst 4966-96-1 After Use in Run 24

In Run 33 Catalyst 4966-96-1 was tested at 225°C and 35 atm with a 1.9 H₂:CO feed ratio gas at various gas hourly space velocities (Figures 5-179 through 5-185).

1. 140 GHSV, 1-6 hours
2. 270 GHSV, 6-18 hours
3. 390 GHSV, 18-23 hours
4. 510 GHSV, 23-28 hours
5. 140 GHSV, 28-40 hours
6. 70 GHSV, 40-47 hours

In Run 33 at 225°C inlet temperature, the catalyst's water gas shift activity declined more rapidly than in Run 24 at 208°C inlet temperature.

The catalyst's hydrocarbon synthesis activity also declined during the test, as it is obvious from comparisons of CO+H₂ conversions at 140 gas hourly space velocity at 1-6 hours and 28-40 hours.

The H₂:CO usage ratio was slightly higher than the H₂:CO feed ratio and therefore the H₂:CO ratio at the catalyst outlet decreased with increase in the conversion level. Because of the higher temperature used, the light hydrocarbon selectivities were higher in Run 33 relative to Run 24, although the average H₂:CO ratios were slightly lower (Figure 5-184). It is important to note that at the high temperature, most of the excess light hydrocarbon selectivity (C₁-C₄) was caused by an increase in selectivity to methane (Figure 5-184).

The light hydrocarbon selectivities obtained in Run 33 were significantly lower than the selectivities reported for the Sasol Arge process which runs at approximately the same temperature and H₂:CO ratio.

After 36 hours on stream, the catalyst rapidly deactivated, accompanied by a rapid increase in selectivity to light hydrocarbons, particularly to methane.

Figure 5-179. Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles: Conversions in Run 33 ($H_2:CO$ Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

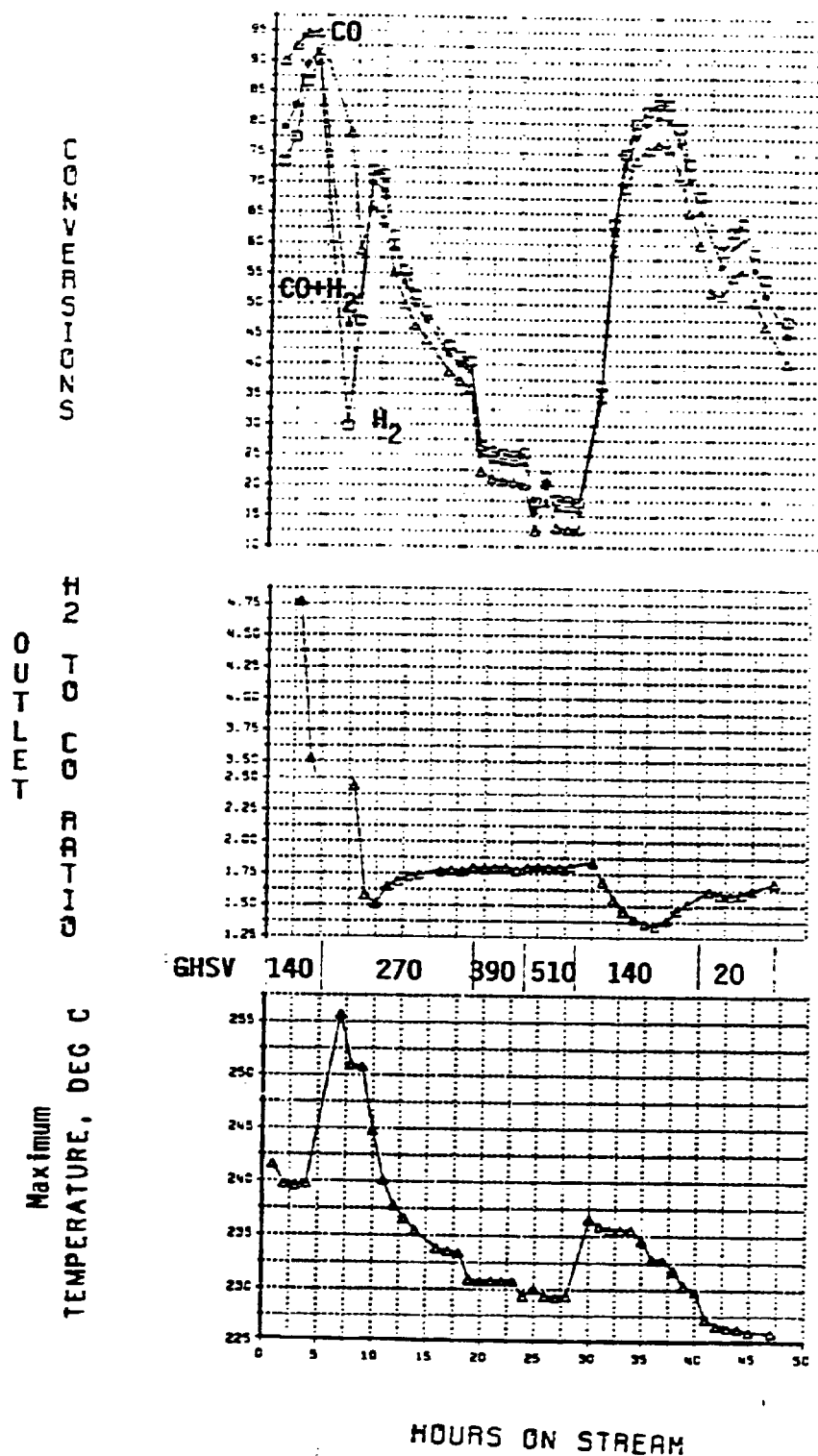
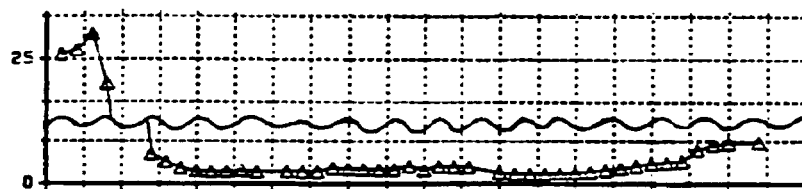


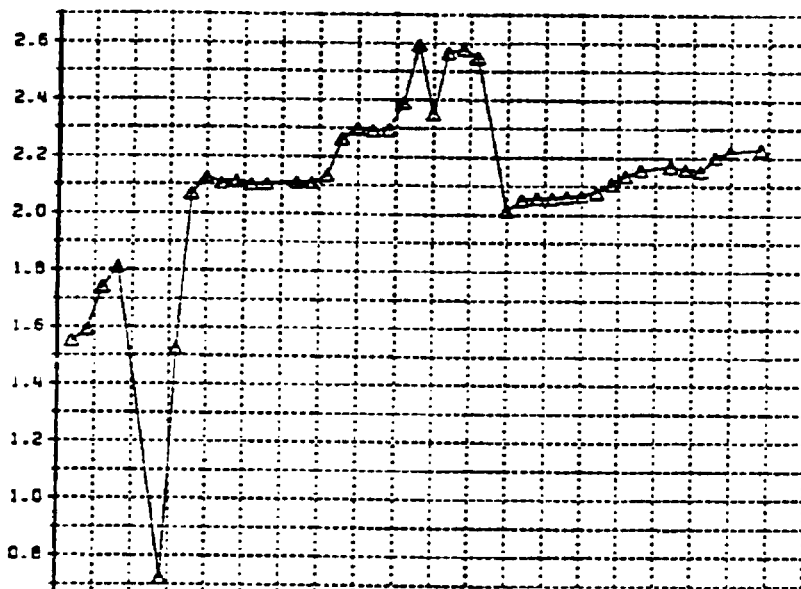
Figure 5-180. Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles: Water Gas Shift Activity in Run 33 ($H_2:CO$ Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

SELE
CTIVITY

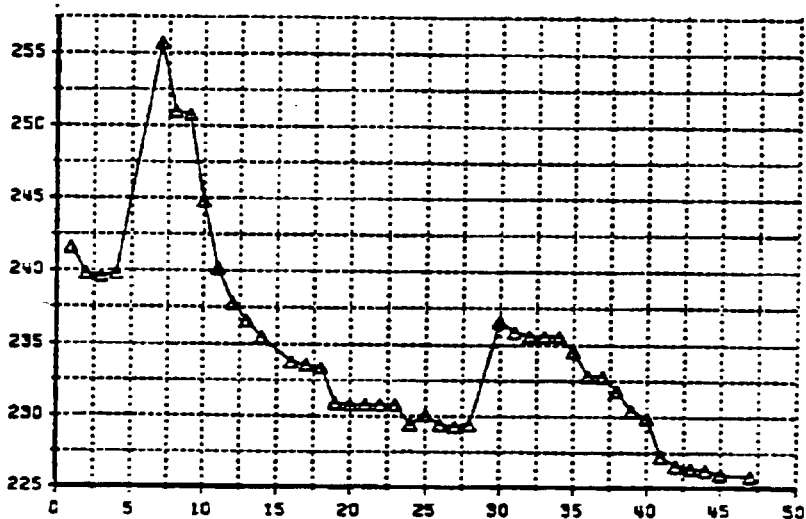
FOR
CO₂



H₂ TO
CO
RATIO



Maximum
TEMPERATURE, DEG C



HOURS ON STREAM

Figure 5-181. Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles; C₁ and C₂ Selectivities in Run 33 (H₂:CO Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

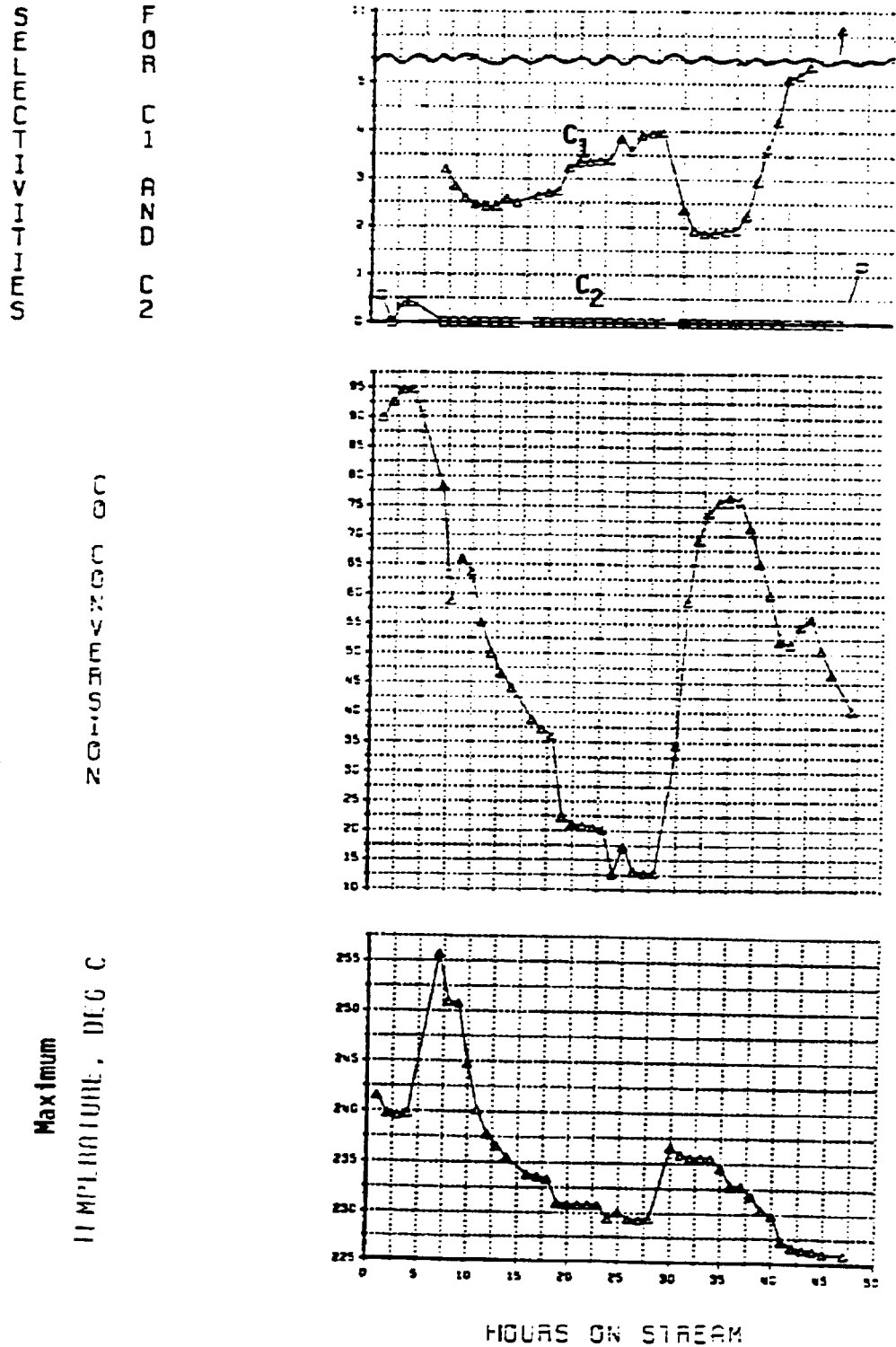
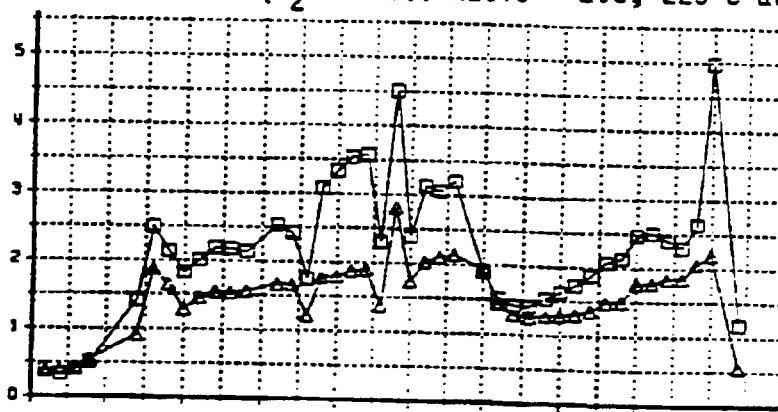


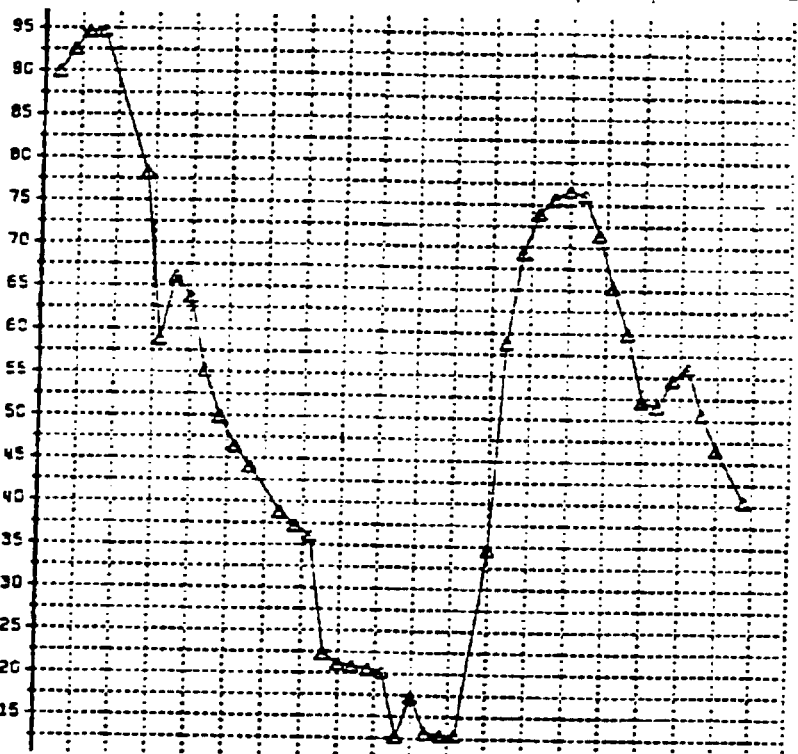
Figure 5-182. Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles: C_3 and C_4 Selectivities in Run 33 ($H_2:CO$ Feed Ratio = 2.0, $225^\circ C$ at Inlet, 34 atm)

SELECTIVITIES

FOR
 C_3
AND
 C_4

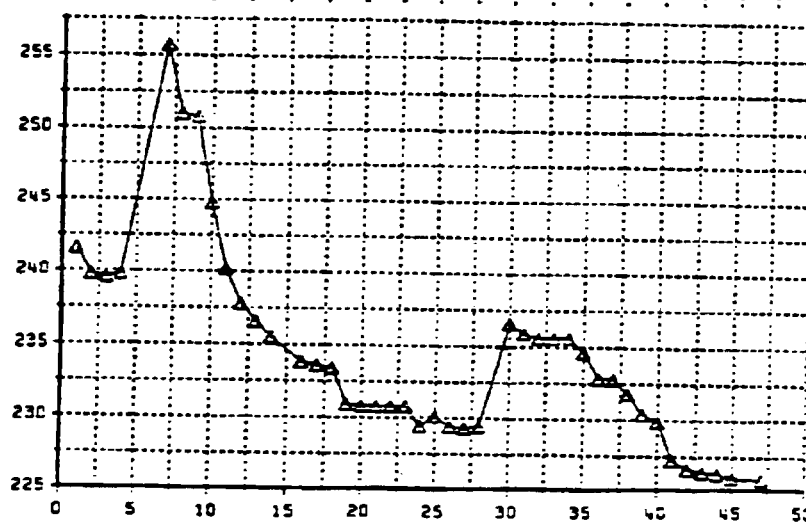


TEMPERATURE, DEG C



Maximum

TEMPERATURE, DEG C



HOURS ON STREAM

Figure 5-183. Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles: Propylene: Propane Ratios in Run 33 ($H_2:CO$ Feed Ratio = 2.0, 225°C at Inlet, 34 atm)

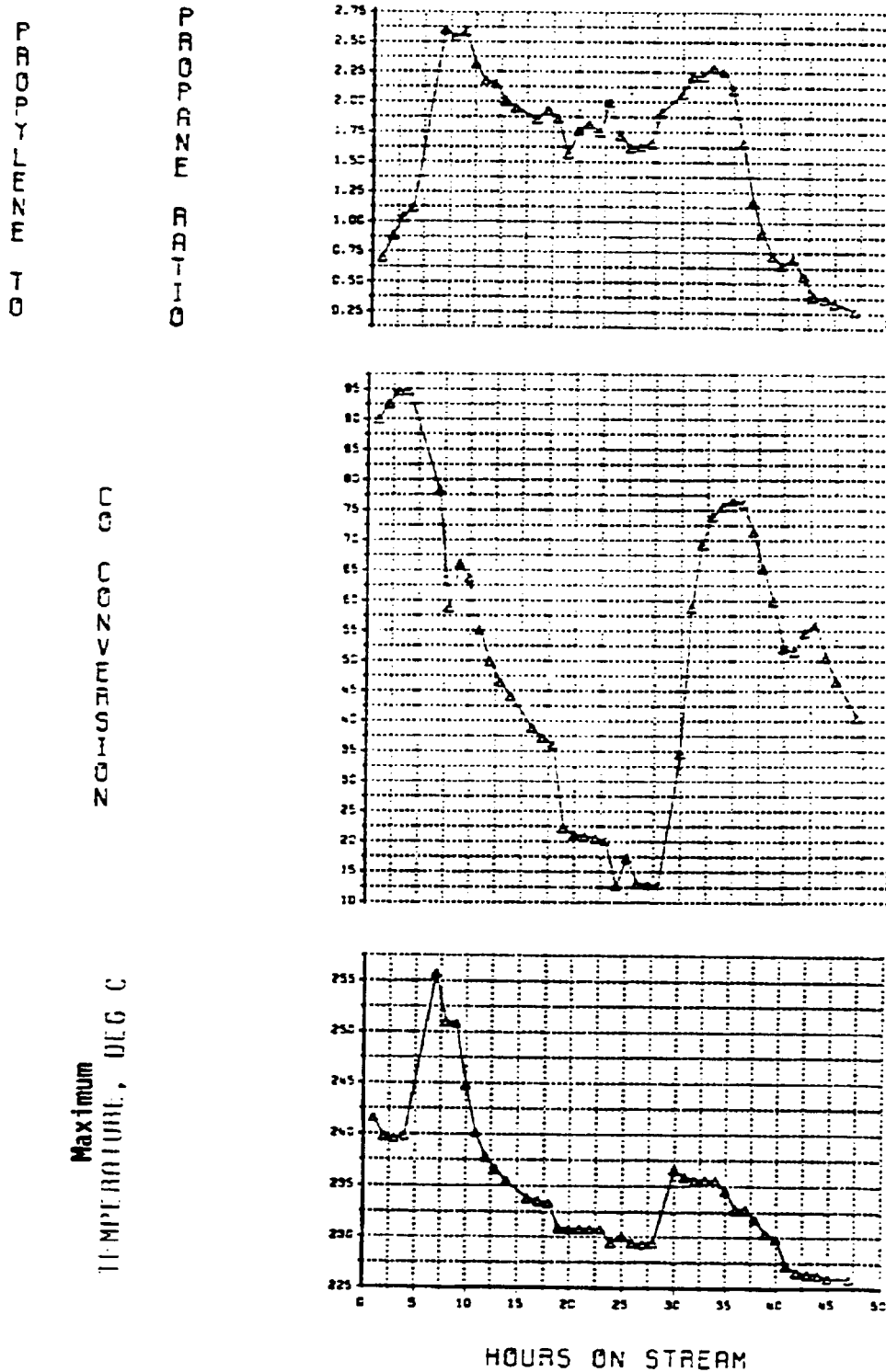


Figure 5-184. Effect of Conversion and Temperature on Light Hydrocarbon Selectivities with Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles at 35 atm

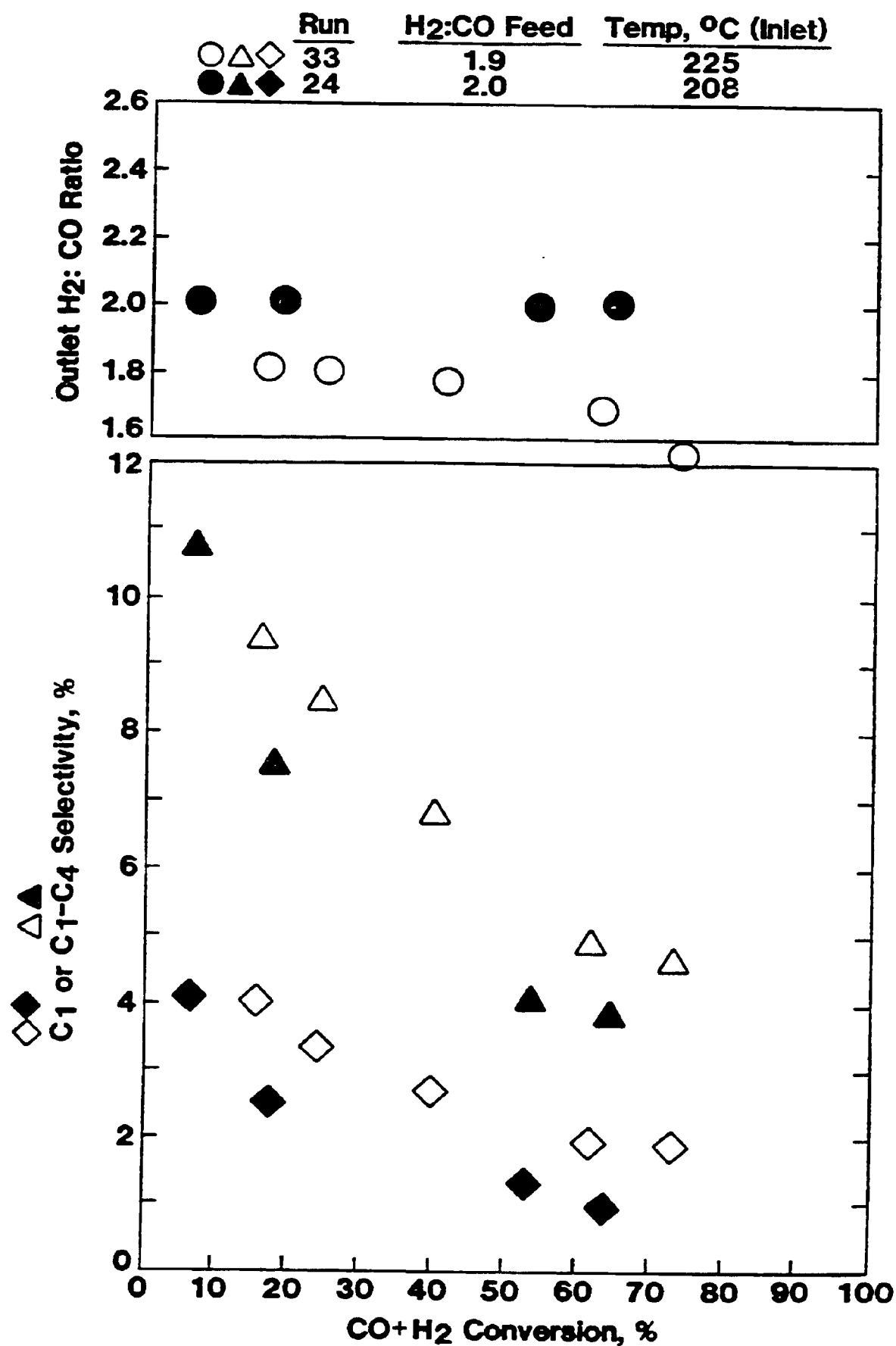


Figure 5-185. Effect of Conversion Level on Light Hydrocarbon Distribution in Run 33 with Catalyst 4966-96-1 Having 3-7 nm Ruthenium Particles ($H_2:CO$ Feed Ratio = 1.9, $225^\circ C$ at Inlet, 35 atm)

