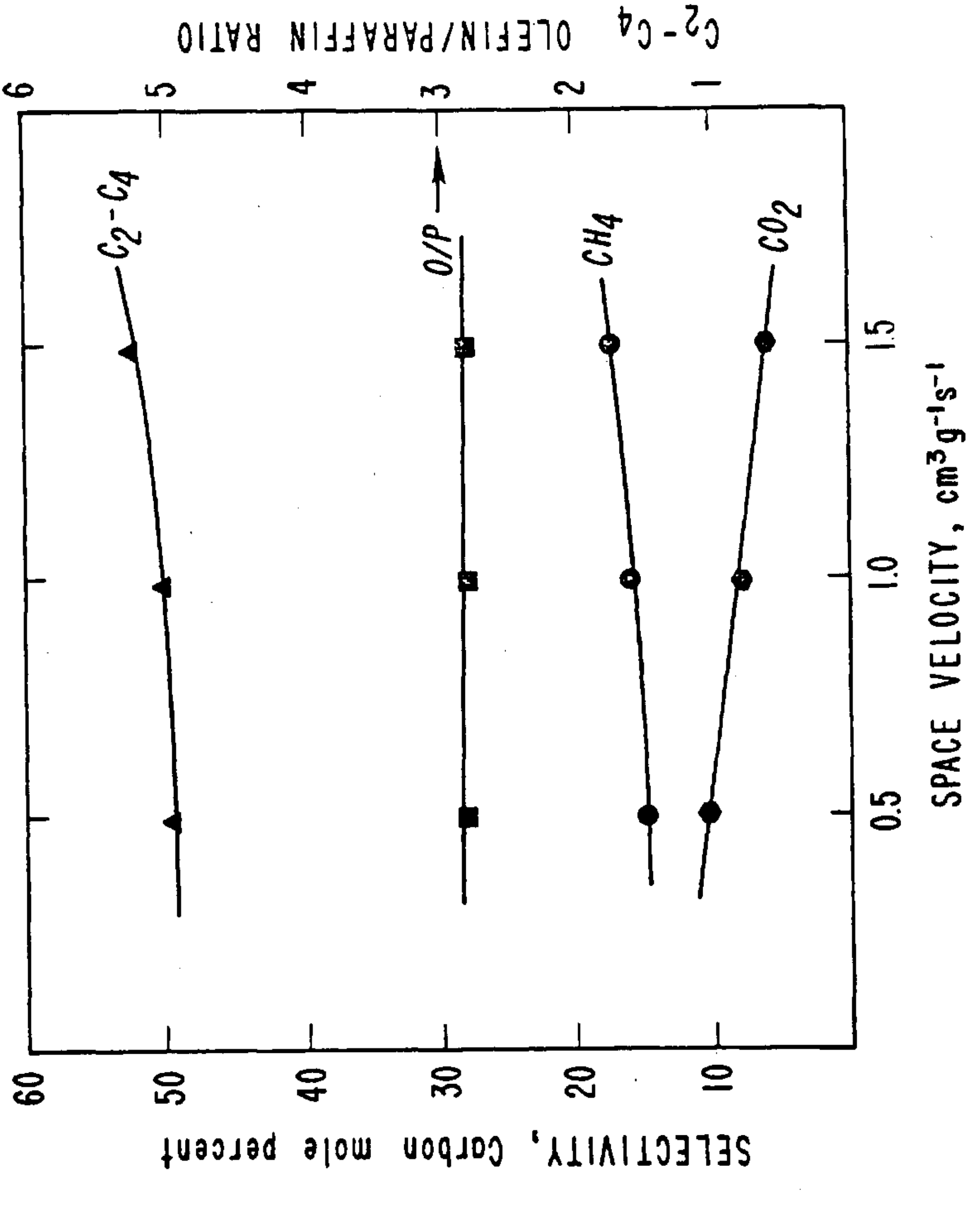

SELECTIVITY, Carbon mole percent
60
50
40
30
20
10
SPACE VELOCITY, cm^{3}g^{-1}s^{-1}
0.5
1.0
1.5
C_2 - C_4 OLEFIN/PARAFFIN RATIO
1
2
3
4
5
6
C_2-C_4
O/P
CH_4
CO_2

Figure 38

Effect of Space Velocity on Yield and Selectivity

Diluted Bed Reactor

Temperature = 483 K; Pressure = 2760 KPa;

$H_2/CO = 2/1$.

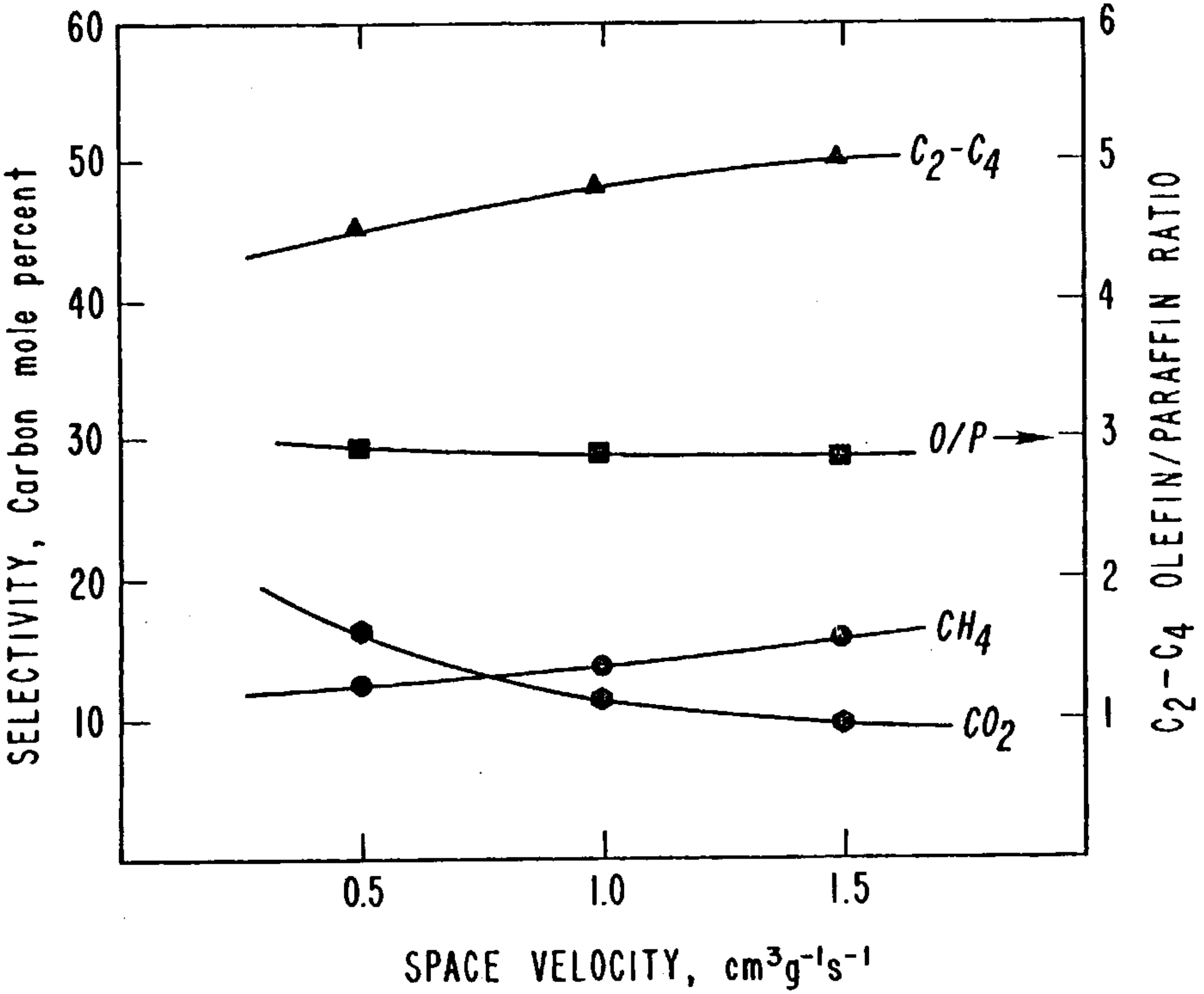

60
50
40
30
20
10
SELECTIVITY, Carbon mole percent
6
5
4
3
2
1
C_2-C_4 OLEFIN/PARAFFIN RATIO
C_2-C_4
O/P →
CH_4
CO_2
0.5
1.0
1.5
SPACE VELOCITY, $cm^3g^{-1}s^{-1}$

Figure 39

Effect of Space Velocity on Yield and Selectivity

Diluted Bed Reactor

Temperature = 463 K; Pressure = 3450 KPa;

$H_2/CO = 2/1$.

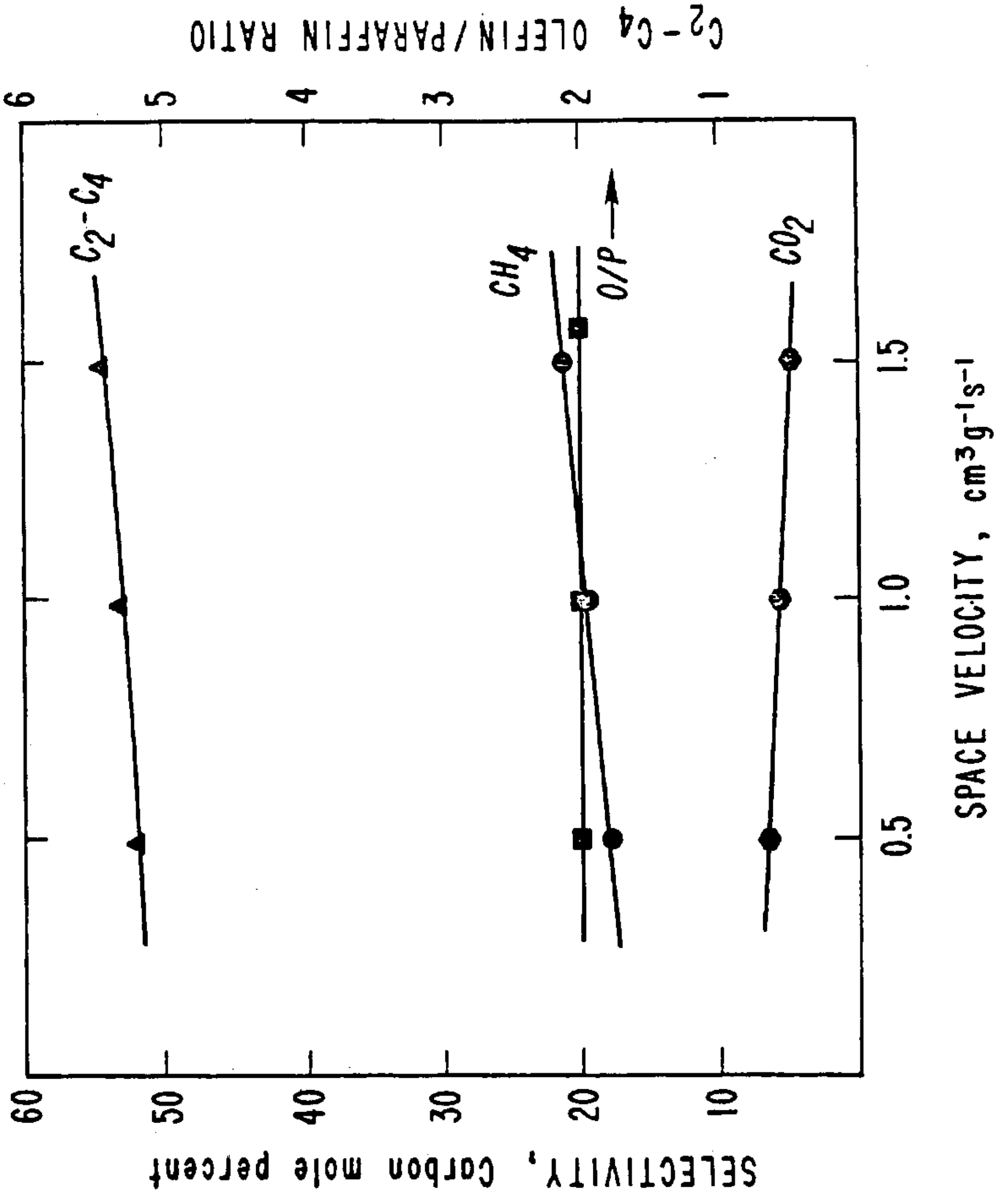

SELECTIVITY, carbon mole percent
60
50
40
30
20
10
C_2-C_4 OLEFIN/PARAFFIN RATIO
6
5
4
3
2
1
SPACE VELOCITY, $cm^3g^{-1}s^{-1}$
0.5
1.0
1.5
C_2-C_4
CH_4
O/P →
CO_2

Figure 40

Effect of H_2/CO Ratio on Yield and Selectivity

Diluted Bed Reactor

Temperature = 473 K; Pressure = 2070 KPa;

Space Velocity = 0.5 $cm^3g^{-1}s^{-1}$.

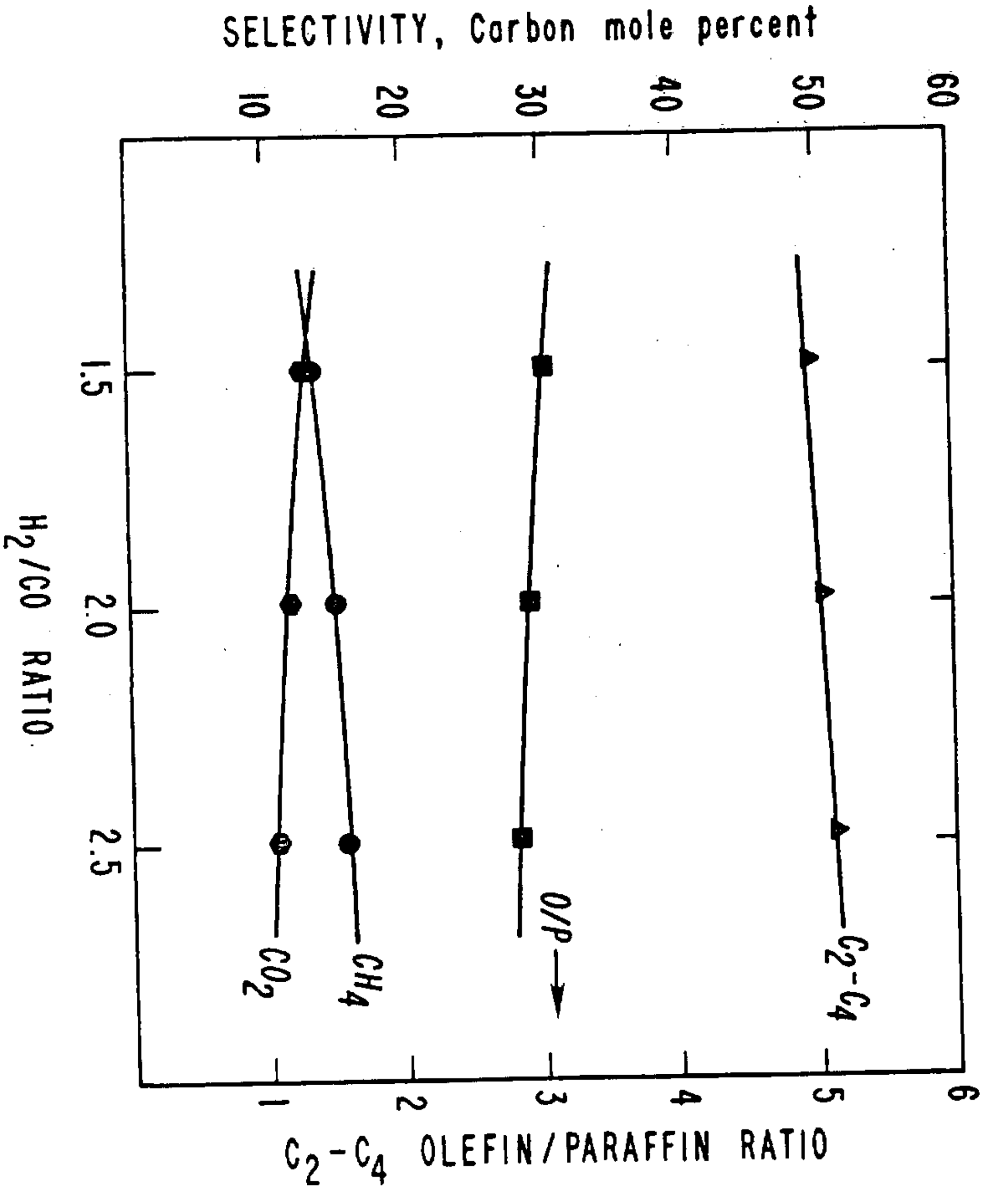

SELECTIVITY, Carbon mole percent
10
20
30
40
50
60
1.5
2.0
2.5
H_2/CO RATIO
C_2-C_4
O/P →
CH_4
CO_2
1
2
3
4
5
6
C_2-C_4 OLEFIN/PARAFFIN RATIO

Figure 41

Effect of H_2/CO Ratio on Yield and Selectivity

Diluted Bed Reactor

Temperature = 483 K; Pressure = 3450 KPa;

Space Velocity = 1 $cm^3g^{-1}s^{-1}$.

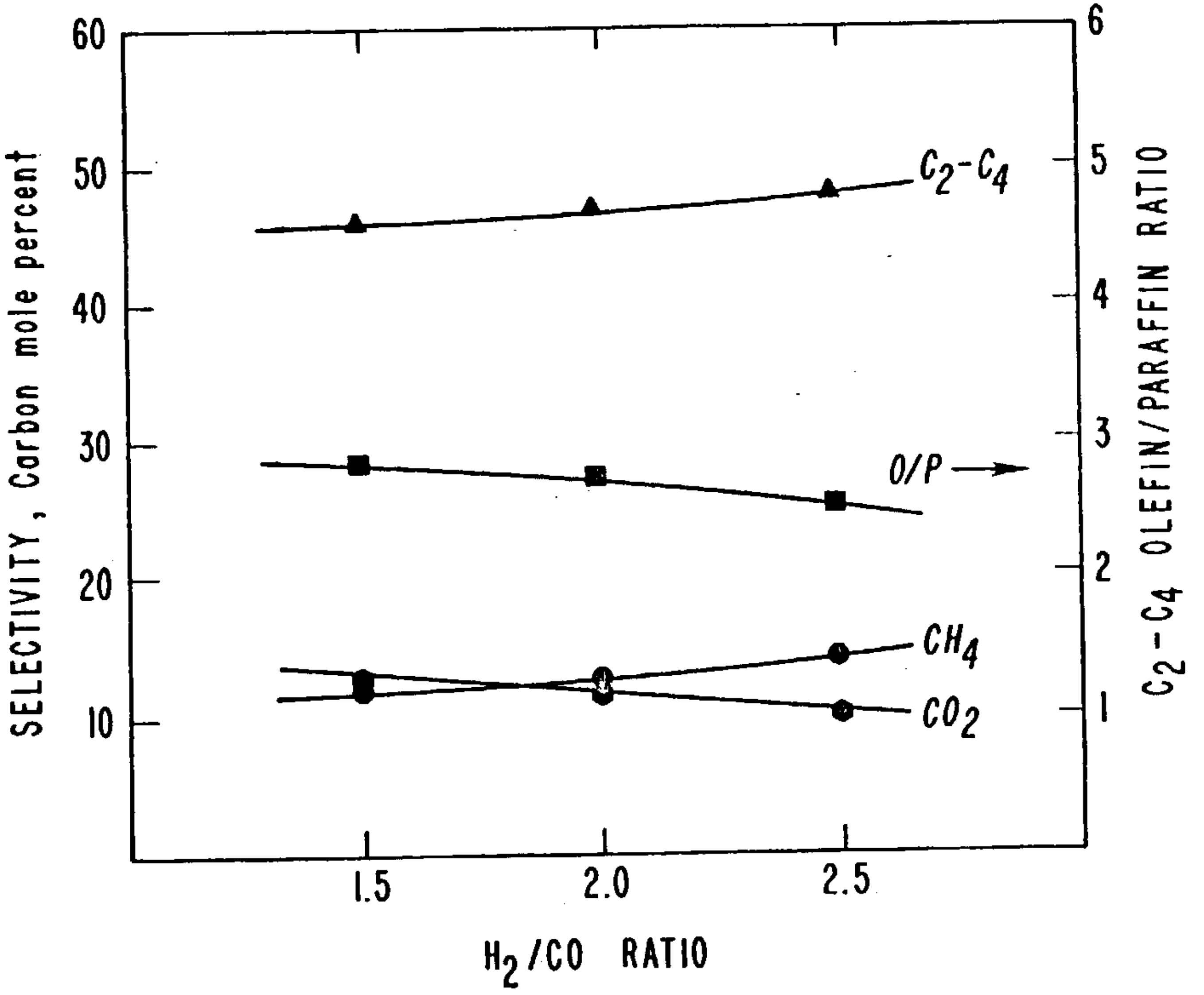
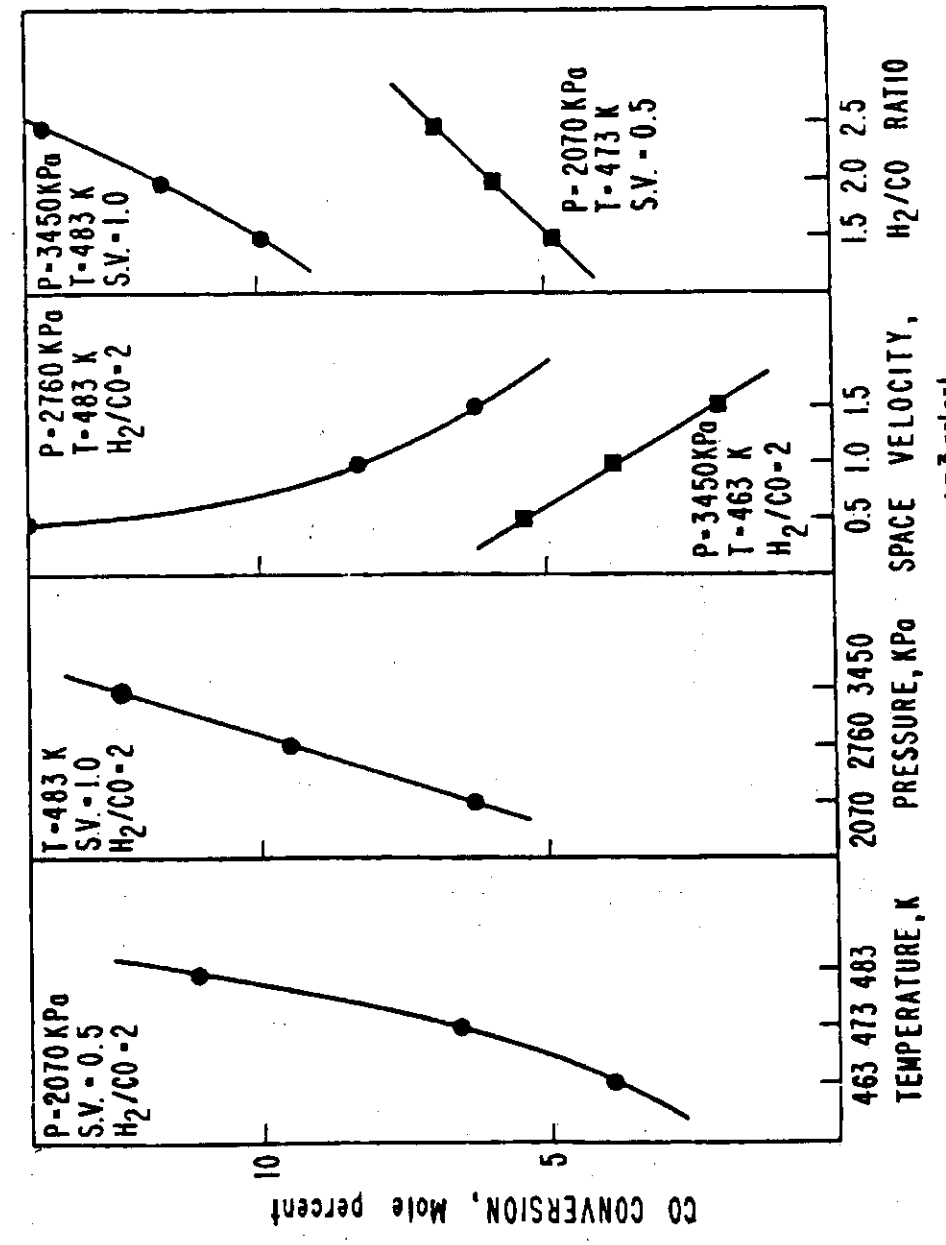

60
50
40
30
20
10
SELECTIVITY, Carbon mole percent
6
5
4
3
2
1
C_2-C_4 OLEFIN/PARAFFIN RATIO
C_2-C_4
O/P →
CH_4
CO_2
1.5
2.0
2.5
H_2/CO RATIO

Figure 42

Effect of Process Variables on Carbon Monoxide Conversion

Diluted Bed Reactor


CO CONVERSION, Mole percent
10
5
P-2070 KPa
S.V.-0.5
H_2/CO-2
463 473 483
TEMPERATURE, K
T-483 K
S.V.-1.0
H_2/CO-2
2070 2760 3450
PRESSURE, KPa
P-2760 KPa
T-483 K
H_2/CO-2
P-3450 KPa
T-463 K
H_2/CO-2
0.5 1.0 1.5
SPACE VELOCITY,
$cm^3g^{-1}s^{-1}$
P-3450 KPa
T-483 K
S.V.-1.0
P-2070 KPa
T-473 K
S.V.-0.5
1.5 2.0 2.5
H_2/CO RATIO

increased, in the range of temperatures investigated, the methane and C_2-C_4 hydrocarbon yields decreased and the carbon dioxide yield increased. The olefin selectivity is presented in Figures 30 and 31. The olefin/paraffin ratio of the C_3 and C_4 hydrocarbons increased as the reaction temperature increased; however, the olefin/paraffin ratio for the C_2 hydrocarbons passed through a minimum at 508 K and then increased as the reaction temperature increased. The olefin/paraffin ratio of the total C_2-C_4 hydrocarbon fraction increased slightly with temperatures up to 520 K. The temperature effect on the yields and selectivity for carbon monoxide hydrogenation in the diluted bed reactor were also investigated at other reaction conditions (Figure 32 through 34). The same product selectivity trends with reaction temperature were observed at different space velocities, pressures and hydrogen to carbon monoxide ratios as were observed at the standard conditions: reactor pressure = 2760 KPa., space velocity = 1 $cm^3g^{-1}s^{-1}$, and hydrogen to carbon monoxide ratio = 2/1. As expected, higher reaction temperature caused higher carbon monoxide conversion in the diluted bed reactor.

The effect of total reactor pressure on the product distribution and selectivity in the diluted bed reactor is presented in Figures 35 and 36 . The hydrogen to carbon monoxide ratio of the reactant feed stream was 2/1 in the pressure effect experiments thus the observations are limited to that specific reaction condition. Furthermore, the range of reactor pressures investigated was not sufficiently large to cause significant changes in product distribution and olefin selectivity in the range of space velocities and reaction temperatures studied. The following trends were nonetheless observed: the methane and carbon dioxide yields decreased slightly as the reactor pressure increased; the total C_2-C_4 hydrocarbon yield increased slightly as the reactor pressure increased and the C_2-C_4 olefin selectivity decreased as the reactor pressure increased.

The effects of space velocity on the product distribution and selectivity in the diluted bed reactor are presented in Figure 37 through Figure 39. The methane and C_2-C_4 hydrocarbon yields increased and the carbon dioxide yield decreased as the space velocity increased from 0.5 to 1.5 $cm^3g^{-1}s^{-1}$. The olefin to paraffin ratio of the C_2-C_4 hydrocarbon fraction was independent of the space velocity in the range of temperatures and pressures studied.

Figure 40 and Figure 41 show the effect of the hydrogen to carbon monoxide ratio on the product distrubution and selectivity. It was observed that as the hydrogen to carbon monoxide ratio increased from 1.5 to 2.5, the methane and C_2-C_4 hydrocarbon yields increased while the carbon dioxide yield and the olefin to paraffin ratio of the C_2-C_4 hydrocarbon fraction decreased. Detailed analysis of the data indicated that the olefin to paraffin ratio of C_2, C_3, and C_4 hydrocarbons increased as the hydrogen to carbon monoxide ratio of the reactant gas decreased.

The effect of the process variables on carbon monoxide conversion in the diluted bed reactor is summarized in Figure 42. The temperature effect on carbon monoxide conversion was also presented in Figure 26. Higher carbon monoxide conversion was achieved at higher reaction temperatures, higher total pressures, higher reactant gas hydrogen to carbon monoxide ratios and lower reactant gas space velocities. Data used in all figures in this section are listed in Tables G-1 through G-10 in Appendix G.

4.6 Process Variables Studies in the Diluted Bed, Pseudo Slurry Reactor

The preliminary studies indicated that the temperature distribution in the diluted bed, pseudo slurry reactor was quite flat in the standard range reaction conditions used in this investigation. In this investigation, effects of process variables such as temperature, pressure, reactant gas hydrogen to carbon monoxide ratio, and space velocity on activity and selectivity on #913 iron/manganese catalyst in the diluted bed, pseudo slurry reactor witn n-hexadecane as heat transfer liquid were studied. The circulation rate of the n-hexadecane was maintained constant throughout the study, that is, 0.103 cm^3s^{-1}. Catalyst pretreatment and stabilization procedures were the same as described before.

The effect of the reaction temperature on carbon monoxide conversion in the diluted bed, pseudo slurry reactor at different reactor pressures is presented in Figure 43. Carbon monoxide conversion increased with increasing reaction temperature at constant reactor pressure and with increasing reactor pressure at constant reaction temperature. The effect of temperature on carbon dioxide and C_2-C_4 hydrocarbon yields at different reactor pressures is presented in Figure 44 and Figure 45. The yield of carbon dioxide increased with increasing reaction temperature at constant pressure and it decreased with increasing reactor pressure at constant temperatures. The same trend was observed in the absence of the heat transfer liquid. The C_2-C_4 hydrocarbon yield decreased with

Figure 43

Effect of Temperature on Carbon Monoxide Conversion

Diluted Bed, Pseudo Slurry Reactor

Pressure = 1400-4400 KPa; $H_2/CO = 2/1$;

Space Velocity = 1 $cm^3g^{-1}s^{-1}$;

Heat Transfer Liquid Flow Rate (n-C16) = 0.103 cm^3s^{-1}.

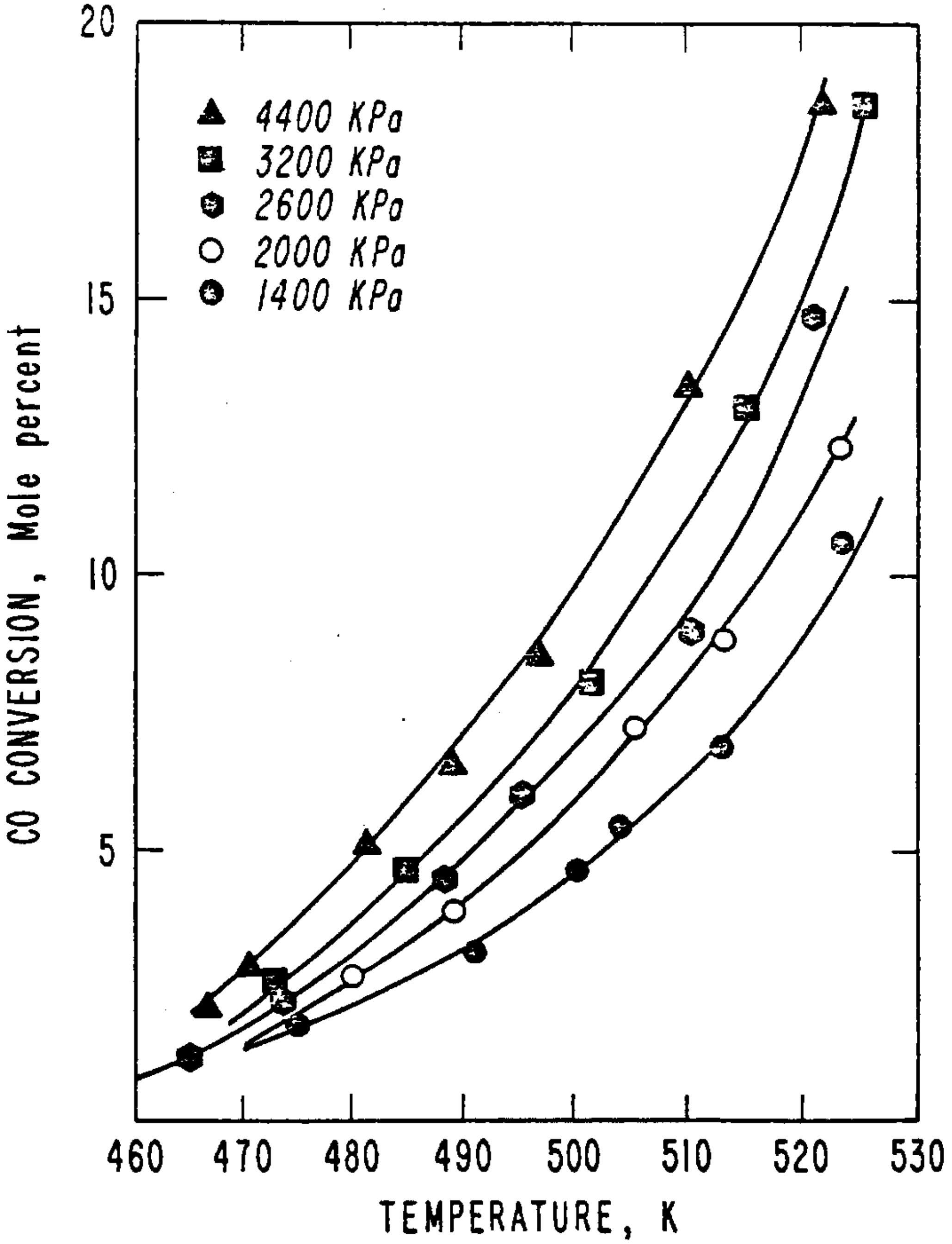

▲ 4400 KPa
■ 3200 KPa
⬢ 2600 KPa
○ 2000 KPa
● 1400 KPa
CO CONVERSION, Mole percent
20
15
10
5
460
470
480
490
500
510
520
530
TEMPERATURE, K

Figure 44

Effect of Temperature on Carbon Dioxide Yield

Diluted Bed, Pseudo Slurry Reactor

Pressure = 1400, 2600 and 4400 KPa;

H_2/CO = 2/1; Space Velocity = 1 $cm^3g^{-1}s^{-1}$;

Heat Transfer Liquid Flow Rate (n-C16) = 0.103 cm^3s^{-1}.

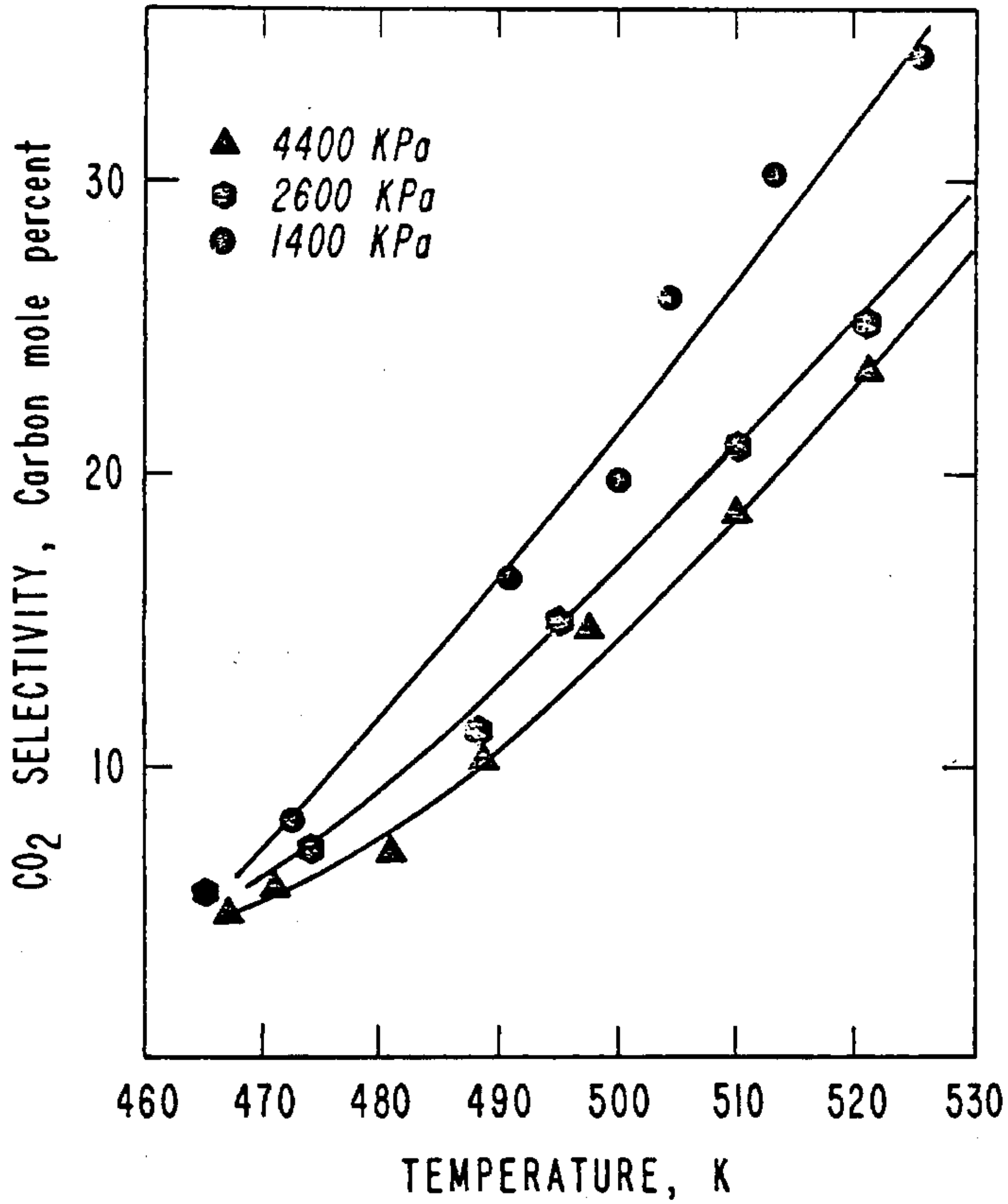
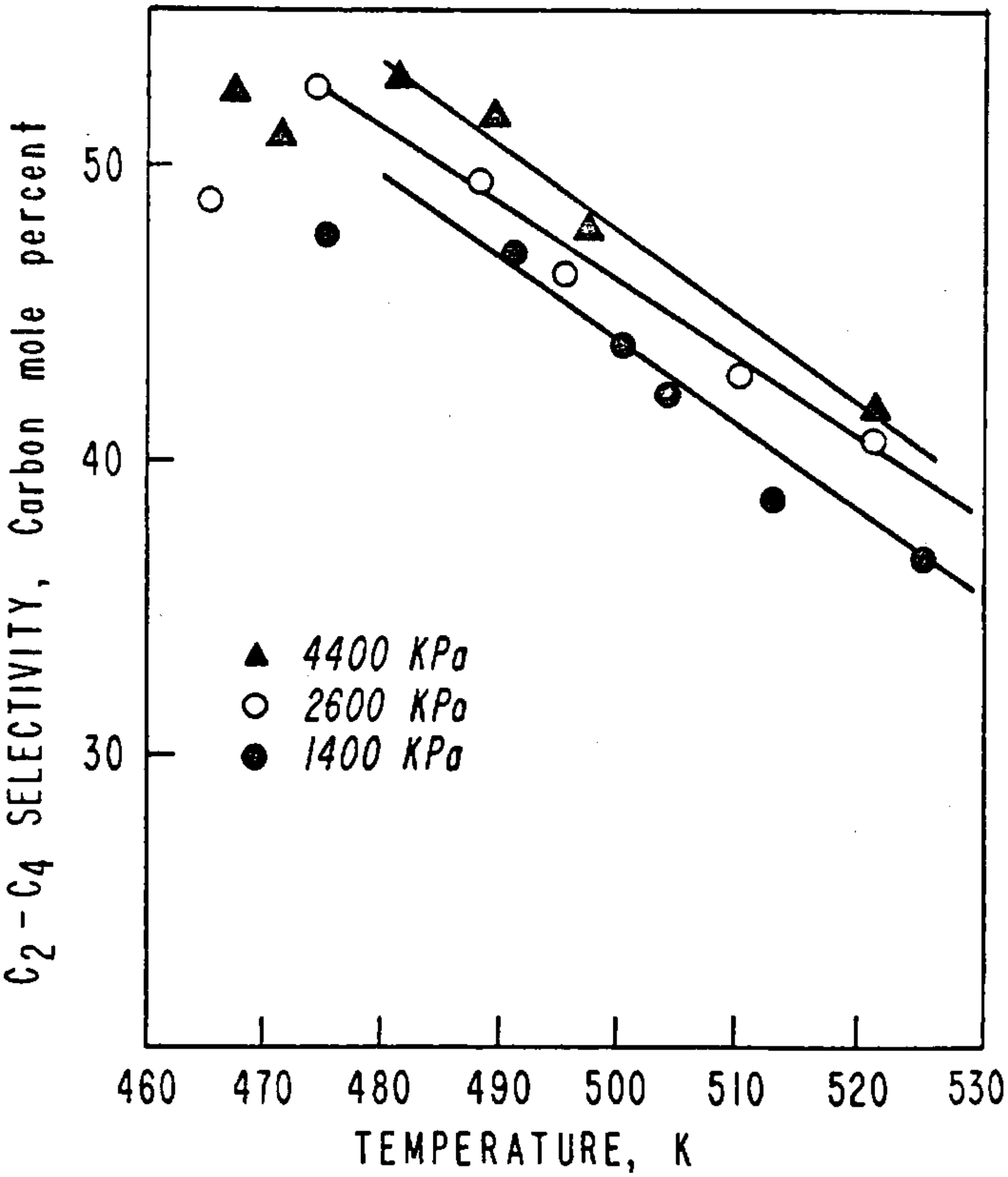

▲ 4400 KPa
● 2600 KPa
● 1400 KPa
CO_2 SELECTIVITY, Carbon mole percent
10
20
30
460
470
480
490
500
510
520
530
TEMPERATURE, K

Figure 45

Effect of Temperature on C_2-C_4 Hydrocarbon Yield
Diluted Bed, Pseudo Slurry Reactor
Pressure = 1400, 2600 and 4400 KPa;
$H_2/CO = 2/1$; Space Velocity = 1 $cm^3g^{-1}s^{-1}$;
Heat Transfer Liquid Flow Rate (n-C16) = 0.103 cm^3s^{-1}.


C_2 - C_4 SELECTIVITY, Carbon mole percent
50
40
30
▲ 4400 KPa
○ 2600 KPa
● 1400 KPa
460
470
480
490
500
510
520
530
TEMPERATURE, K