Mobil #1 base stock (MCP 151) and normal hexadecane. The influence of temperature on activity (carbon monoxide conversion), product distribution (C_2-C_4 hydrocarbon and carbon dioxide yields) and selectivity (olefin/paraffin ratio for C_2, C_3, and C_4 hydrocarbons) was studied at a fixed reactor pressure (2760 KPa), space velocity (1 $cm^3g^{-1}s^{-1}$) and hydrogen to carbon monoxide ratio (2/1). The results from these experiments for the diluted bed reactor and the diluted bed pseudo slurry reactor are summarized in Tables 5 and 6, respectively.

The effect of the reaction temperature on carbon monoxide conversion is presented in Figure 21. As the reaction temperature increased, the conversion of carbon monoxide increased for both the diluted bed and the diluted bed, pseudo slurry reactors. If heat transport limitations are to be avoided in the fixed bed catalytic systems it is generally accepted that the conversion of reactants must be kept below ten percent. Thus with the diluted bed reactor, the upper operating limit for temperature is 495 K at the process operating conditions previously stated. The circulation of the heat transfer liquids through the catalyst bed reduced the conversion level by better than 50% at all temperatures. The nature of the heat transfer medium did have an influence on the conversion of carbon monoxide at reaction temperatures above 500 K, that is, at a fixed temperature, the conversion was higher when n-hexadecane was used as the heat transfer liquid. The yields of C_2-C_4 hydrocarbons and carbon dioxide as a function of the reaction temperature are plotted in Figures 22 and 23, respectively. The diluted bed reactor produced a higher yield of C_2-C_4 hydrocarbons and a lower yield of carbon dioxide

Table 5

Effect of Temperature on Activity and Selectivity of Carbon Monoxide Hydrogenation in the Diluted Bed Reactor.

Pressure = 2760 KPa; H_2/CO = 2/1 and Space Velocity = 1 $cm^3 g^{-1} s^{-1}$.

Reaction Temp. K	CO Conversion %	PRODUCT SELECTIVITY (%)								OLEFIN/PARAFFIN RATIO			
		C_1	C_2	C_3	C_4	C_2-C_4	C_5^+	CO_2	ROH	C_2	C_3	C_4	C_2-C_4
473	2.66	18.1	16.3	20.4	15.4	52.2	19.4	5.2	5.1	2.7	2.4	1.9	2.3
478	3.26	17.7	16.0	20.2	15.4	51.7	20.2	5.6	5.0	2.6	2.5	1.9	2.3
483	4.49	17.4	15.3	20.0	15.5	50.9	21.3	6.4	4.2	2.4	2.6	2.0	2.4
488	5.31	16.0	14.4	19.2	16.0	49.6	23.0	6.6	4.9	2.4	2.7	2.3	2.5
493	7.06	17.3	14.9	20.1	16.2	51.2	19.7	8.0	3.8	2.1	2.8	2.2	2.4
498	8.45	16.6	14.3	19.4	15.8	49.6	20.3	9.0	4.5	2.0	2.8	2.2	2.4
503	10.38	16.0	14.1	19.3	15.6	49.0	21.8	10.1	3.1	2.0	2.9	2.3	2.4
508	11.74	15.6	13.6	18.9	15.4	47.9	21.8	11.5	3.0	1.9	3.0	2.3	2.4
513	14.01	15.2	13.3	18.8	15.6	47.9	20.8	12.7	3.2	2.0	3.2	2.5	2.6
523	20.29	13.3	12.1	17.1	15.0	44.2	22.3	16.9	3.2	2.2	3.5	2.7	2.8

Table 6

Effect of Temperature on Activity and Selectivity of Carbon Monoxide Hydrogenation in the Diluted Bed, Pseudo Slurry Reactor.

Pressure = 2760 KPa; H_2/CO = 2/1; Space Velocity = 1 $cm^3 g^{-1} s^{-1}$; and Heat Transfer Liquid Rate = 1 $cm^3 s^{-1}$.

Heat Transfer Medium	Reaction Temp. K	CO Conversion %	PRODUCT SELECTIVITY (%)								OLEFIN/PARAFFIN RATIO			
			C_1	C_2	C_3	C_4	C_2-C_4	C_5^+	CO_2	ROH	C_2	C_3	C_4	C_2-C_4
Mobil #1 Base Stock	493	3.14	10.5	13.3	17.1	12.6	43.0	16.9	26.0	3.6	2.1	2.3	1.7	2.0
	503	4.21	10.7	12.1	16.3	11.5	40.9	16.3	28.9	3.2	2.0	2.7	1.8	2.2
MCP 151	513	5.13	11.1	11.1	14.0	10.2	35.2	14.2	37.5	2.0	2.1	3.3	2.1	2.5
	523	6.10	11.3	10.3	12.6	8.8	31.7	14.0	41.4	1.7	1.9	4.2	2.8	2.8
n-Hexadecane	493	3.56	13.8	14.8	17.6	13.2	45.6	18.7	16.5	5.4	3.2	3.2	2.4	2.9
	503	5.11	12.1	13.8	17.3	13.3	44.4	17.4	20.2	6.0	3.6	3.6	2.5	3.2
	513	6.96	11.4	12.6	15.8	12.0	40.5	14.9	26.9	2.6	3.7	4.1	2.9	3.6
	523	9.78	11.2	11.2	14.5	10.8	37.1	16.1	33.9	1.7	3.7	4.7	3.3	3.9

Figure 21

Effect of Temperature on Carbon Monoxide Conversion

Diluted Bed and Diluted Bed, Pseudo Slurry Reactors

Heat Transfer Liquids: n-Hexadacane or Mobil #1 MCP 151

Pressure = 2760 KPa; H_2/CO = 2/1;

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

and Heat Transfer Liquid Feed Rate = 0.103 $cm^3 s^{-1}$.

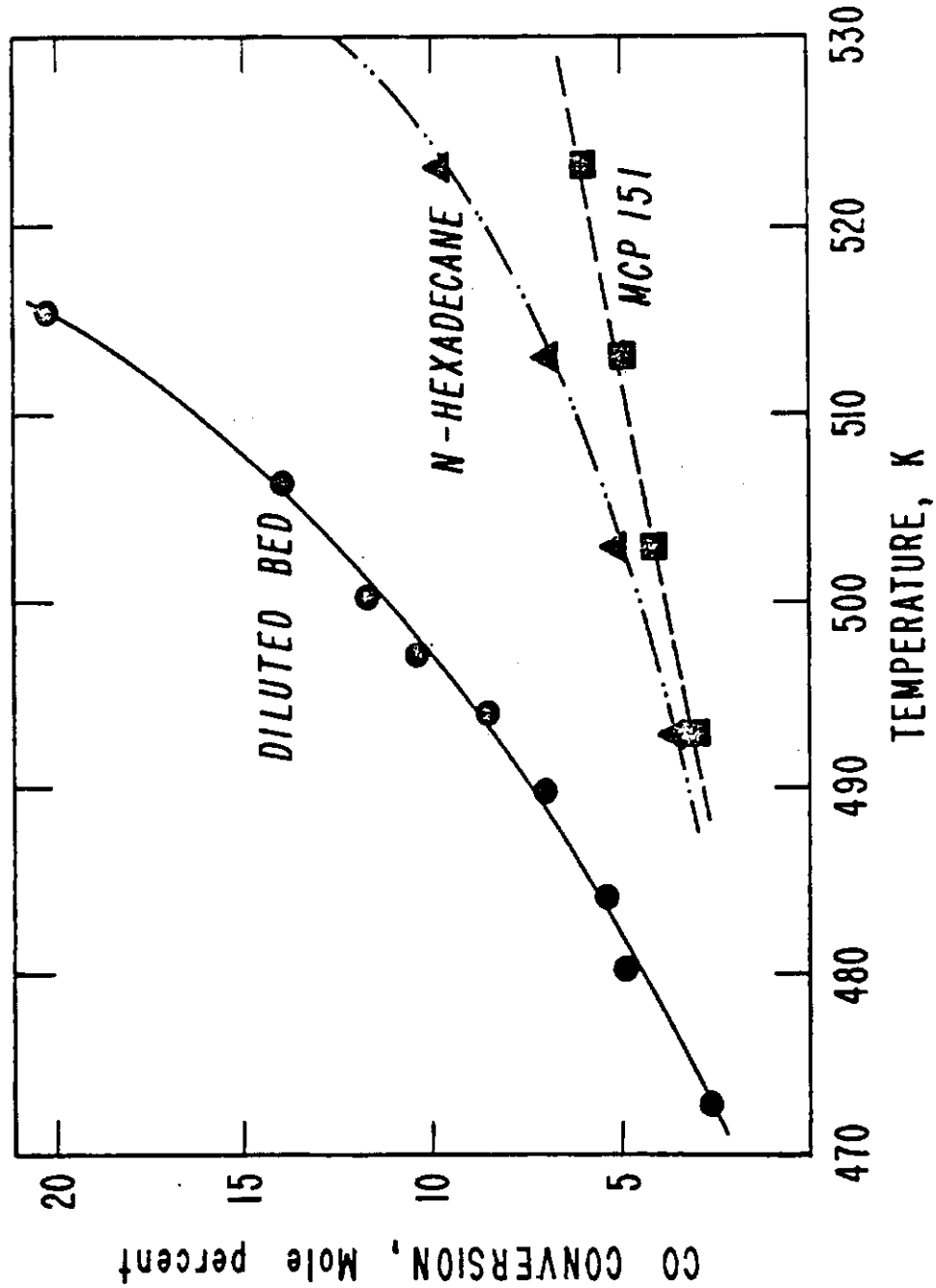

DILUTED BED
N-HEXADECANE
MCP 151
CO CONVERSION, Mole percent
TEMPERATURE, K
20
15
10
5
470
480
490
500
510
520
530

Figure 22

Effect of Temperature on C_2-C_4 Hydrocarbon Yield

Diluted Bed and Diluted Bed, Pseudo Slurry Reactors

Heat Transfer Liquids: n-Hexadecane or MCP 1:1

Pressure = 2760 KPa; H_2/CO = 2/1;

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

Heat Transfer Liquid Flow Rate = 0.103 $cm^3 s^{-1}$.

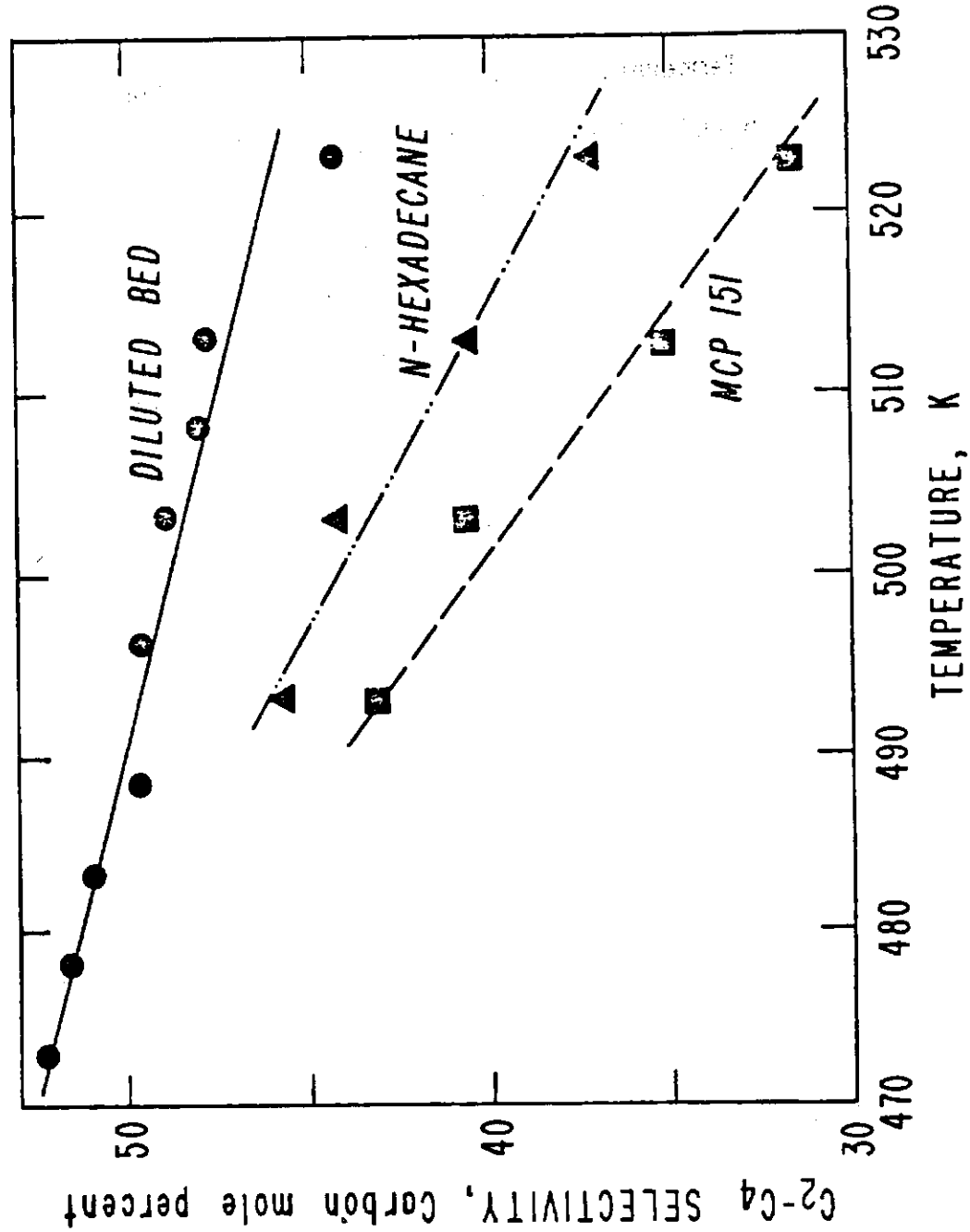

DILUTED BED
N-HEXADECANE
MCP 151
C2-C4 SELECTIVITY, Carbon mole percent
50
40
30
470
480
490
500
510
520
530
TEMPERATURE, K

Figure 23

Effect of Temperature on Carbon Dioxide Yield

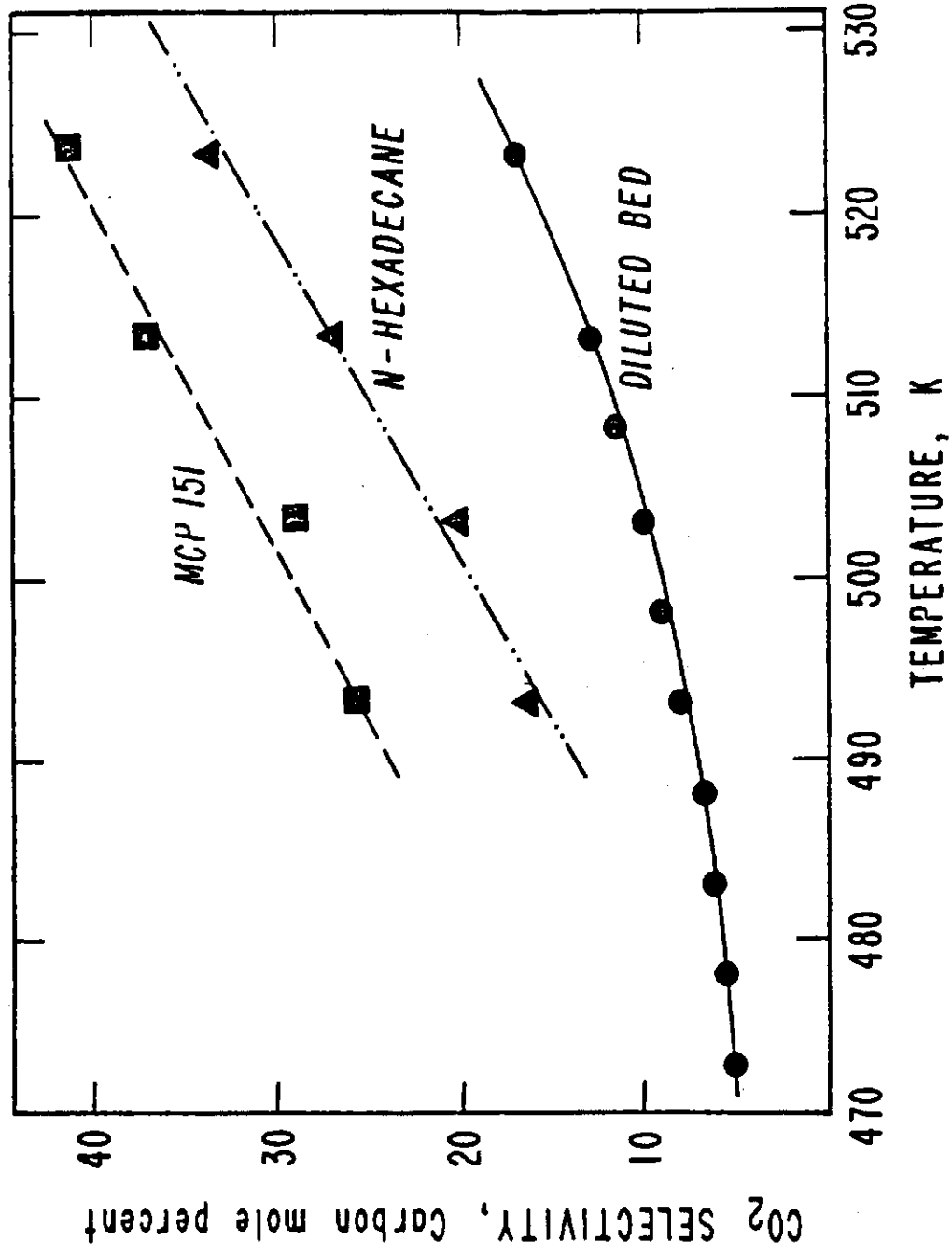
Diluted Bed and Diluted Bed, Pseudo Slurry Reactors

Heat Transfer Liquids: n-Hexadecane or MCP 151

Pressure = 2760 KPa; H_2/CO = 2/1;

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

Heat Transfer Liquid Flow Rate = 0.103 $cm^3 s^{-1}$.


MCP 151
N-HEXADECANE
DILUTED BED
CO2 SELECTIVITY, carbon mole percent
TEMPERATURE, K
40
30
20
10
470
480
490
500
510
520
530

than the diluted bed, pseudo slurry reactor at all temperatures. The yield of C_2-C_4 hydrocarbons was greater and the yield of carbon dioxide was lower when n-hexadecane rather than MCP 151 was used as the heat transfer liquid for the pseudo slurry reactor experiments.

The olefin selectivity for ethane, propane, butane, and total C_2-C_4 hydrocarbons is presented in Figures 24 through 27. At the reaction conditions used in this test the catalyst was more selective for olefins when n-hexadecane was used as the heat transfer medium in the pseudo slurry reactor. The difference in selectivity was most pronounced for ethane and became less significant as the molecular weight of the product increased.

In general, at fixed pressure, space velocity and hydrogen to carbon monoxide ratio, the n-hexadecane appeared to be superior to the MCP-151 as a heat transfer medium in the pseudo slurry reactor. This conclusion was based primarily on the olefin selectivity advantage and on the fact that it more nearly approximates the structure of the recycle liquid which would be used as the heat transfer liquid in a large scale operation. Thus n-hexadecane was chosen as the heat transfer medium for the process variable study in the diluted bed, pseudo slurry reactor.

4.4 Test of the Schulz-Flory Distribution Law

The Schulz-Flory distribution law and its application to the hydrogenation of carbon monoxide has been discussed in Chapter 2. The Schulz-Flory distribution law is given by

$$\log_{10}(m_p/p) = p \log_{10}\alpha + \log_{10}(\ln_e^2\alpha)$$

Figure 24

Effect of Temperature on C_2 Hydrocarbon Olefin/Paraffin Ratio

Diluted Bed and Diluted Bed, Pseudo Slurry Reactors

Heat Transfer Liquids: n-Hexadecane or MCP 151

Pressure = 2760 KPa; H_2/CO = 2/1;

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

Heat Transfer Liquid Flow Rate = 0.103 $cm^3 s^{-1}$.

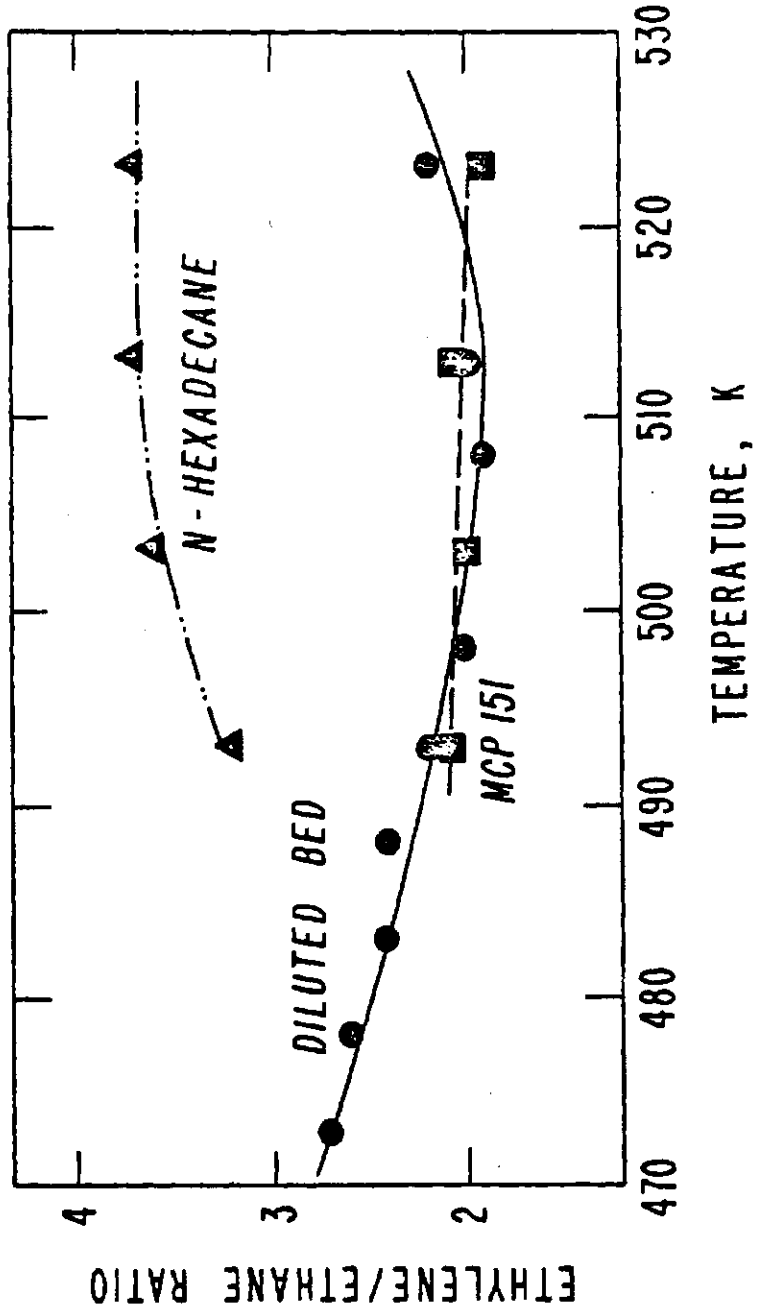

ETHYLENE/ETHANE RATIO
4
3
2
TEMPERATURE, K
470
480
490
500
510
520
530
N-HEXADECANE
DILUTED BED
MCP 151

Figure 25

Effect of Temperature on C_3 Hydrocarbon Olefin/Paraffin Ratio

Diluted Bed and Diluted Bed, Pseudo Slurry Reactors

Heat Transfer Liquids: n-Hexadecane or MCP 151

Pressure = 2760 KPa; H_2/CO = 2/1;

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

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

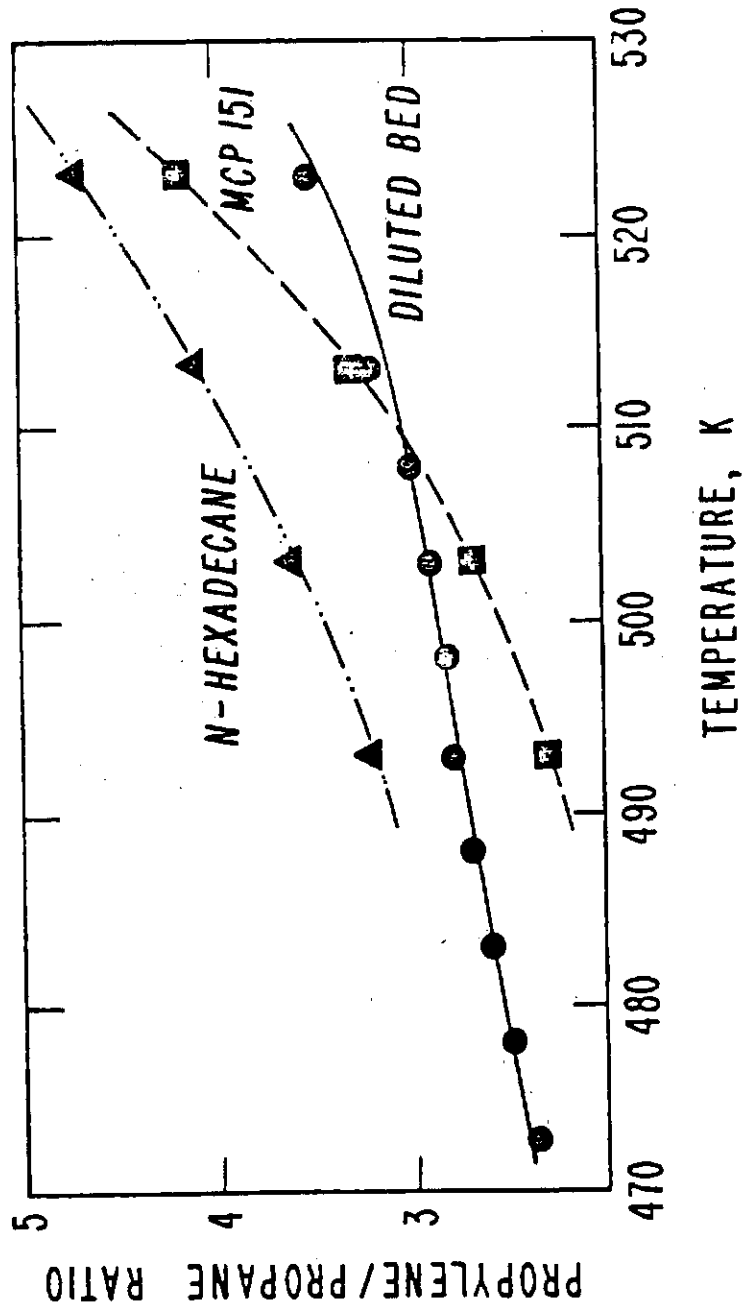

PROPYLENE/PROPANE RATIO
5
4
3
470
480
490
500
510
520
530
TEMPERATURE, K
N-HEXADECANE
MCP 151
DILUTED BED

Figure 26

Effect of Temperature on C_4 Hydrocarbon Olefin/Paraffin Ratio

Diluted Bed and Diluted Bed, Pseudo Slurry Reactors

Heat Transfer Liquids: n-Hexadecane or MCP 151

Pressure = 2760 KPa; H_2/CO = 2/1;

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

Heat Transfer Liquid Flow Rate = 0.103 $cm^3 s^{-1}$.

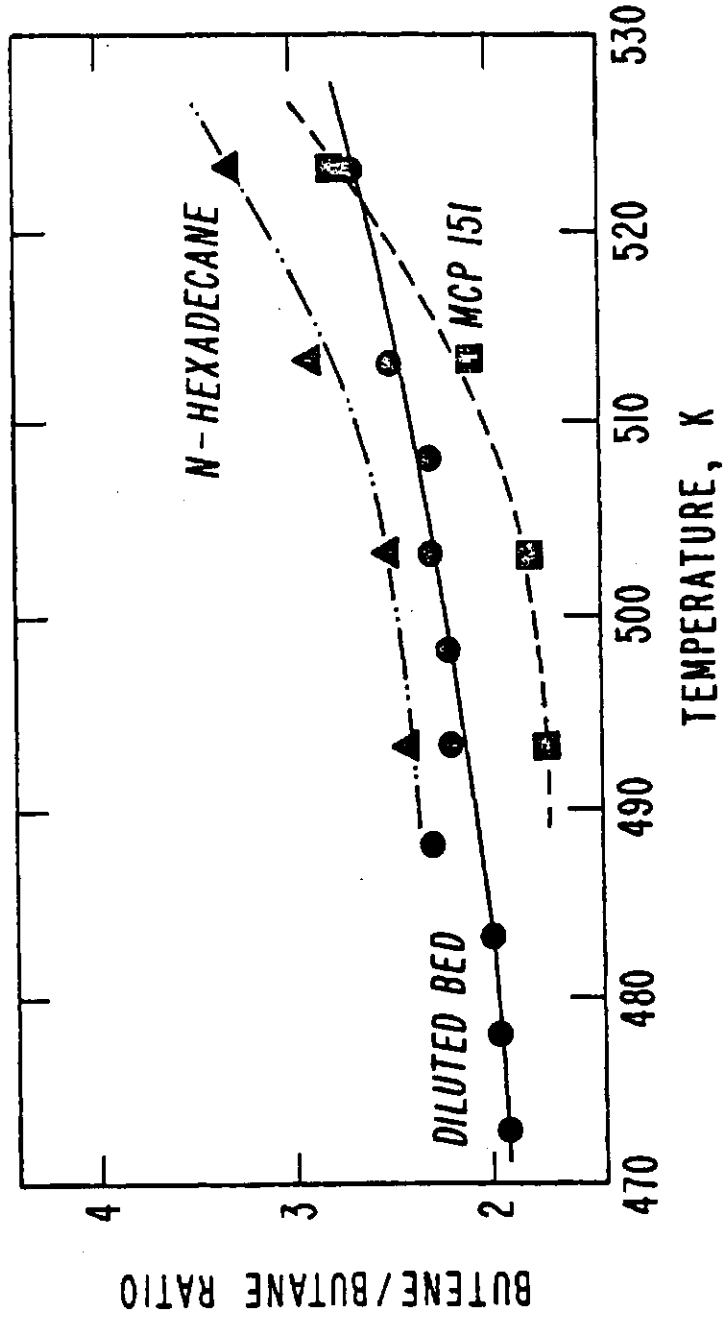

N-HEXADECANE
MCP 151
DILUTED BED
BUTENE/BUTANE RATIO
TEMPERATURE, K
4
3
2
470
480
490
500
510
520
530

Figure 27

Effect of Temperature on C_2-C_4 Hydrocarbon Olefin/Paraffin Ratio

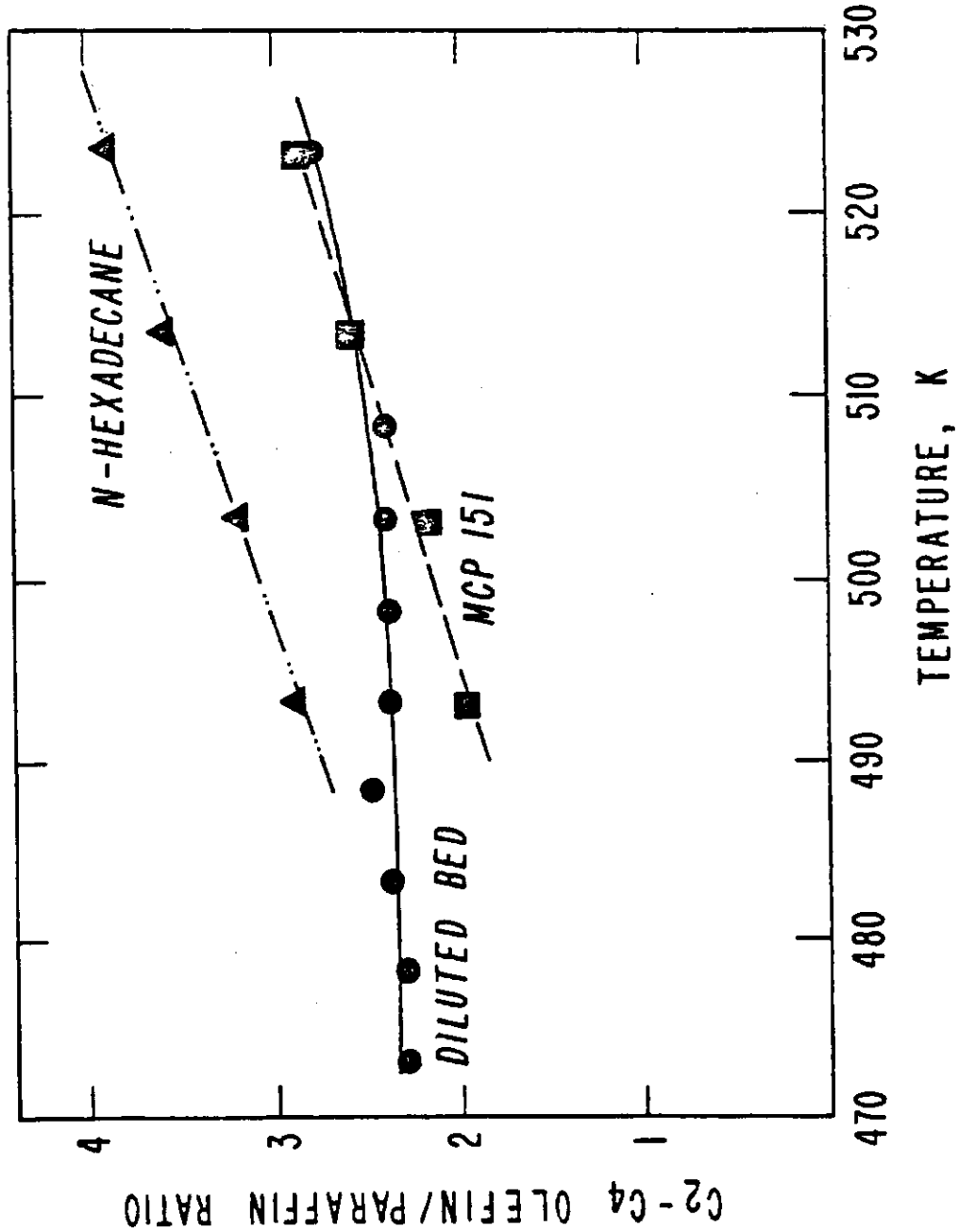
Diluted Bed Reactor and Diluted Bed, Pseudo Slurry Reactors

Heat Transfer Liquids: n-Hexadecane or MCP 151

Pressure = 2760 KPa; H_2/CO = 2/1;

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

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


N-HEXADECANE
MCP 151
DILUTED BED
C2 - C4 OLEFIN/PARAFFIN RATIO
TEMPERATURE, K
4
3
2
1
470
480
490
500
510
520
530

where

m_p is the weight fraction of oligomers for a certain degree of polymerization p;

p is the number of carbons in the chain; and

α is the chain growth probability factor.

The chain growth probability factor may be determined by plotting $\log_{10}(m_p/p)$ versus p and calculating α from the slope and intercept of the straight line.

The series of experiments run to test the Schulz-Flory distribution law each lasted for a period of time in excess of eight hours in order to insure that an adequate amount of liquid hydrocarbon product could be obtained for analysis. The gas samples taken at the reactor outlet during each experiment and the collected liquid product were analyzed chromatographically. The product distribution was determined by combining the gas and liquid product analyses. A sample calculation of the complete product distribution is presented in Appendix F. The $\log_{10}(m_p/p)$ versus p plots for two different reaction temperatures, 518 K and 533 K, are presented in Figures 28 and 29. A change in slope was observed at C_{15} for both reaction temperatures. The values of $\log_{10}(m_p/p)$ for hydrocarbons with a carbon number from six to nine were lower than expected. This is most likely due to an inefficient sampling technique which results in a loss of more volatile C_6-C_9 hydrocarbons when preparing to inject the liquid into the chromatograph. The chain growth probability factors, α, calculated from the slopes and intercepts in Figures 28 and 29 are presented in Tables 7 and 8. The calculated chain growth probability factor at

Figure 28

Schulz-Flory Distribution Law

Log (m_p/p) versus p;

Diluted Bed Reactor

Manganese/Iron Atomic Ratio = 2.4/100;

Temperature = 518 K; Pressure = 3450 KPa;

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