July, 1, 1983

TITLE: Fischer-Tropsch Synthesis in Slurry Reactor Systems

PI: Charles N. Satterfield

INSTITUTION: Massachusetts Institute of Technology
Cambridge, MA 02139
(617)253-4584

CONTRACT NO.: DE-FG22-81PC 40771

PERIOD OF PERFORMANCE: June 1, 1982 to June 30, 1983

I. ABSTRACT

OBJECTIVE: To establish a quantitative understanding of the mass transfer-related factors that determine selectivity and reaction rate in a slurry reactor. By use of a mechanically-stirred autoclave that can be operated as a isothermal CSTR, to reliably compare and contrast the performance of specified catalysts.

WORK DONE AND CONCLUSIONS: New data and reexamination of several previous studies in either vapor-phase or liquid-phase reactors with iron catalysts show a Flory carbon number distribution that exhibits a marked break at about C_{10}. At higher carbon numbers hydrocarbons are produced with a much higher probability of chain growth (α) than for lower carbon numbers. Total product distribution based on light product analysis may therefore be in substantial error. Results are interpreted in terms of a two-site catalyst structure.

On a reduced fused magnetite catalyst the inhibiting effects of CO and H_2O were determined quantitatively and led to the following rate expression: $-R_{H_2O} = ab' P_{CO}P_{H_2}{}^2/(P_{H_2O} + b' P_{CO}P_{H_2})$. In most previous kinetic studies the partial pressure of hydrogen did not vary significantly with conversion so the hydrogen functionality was not clearly established. In our model, b' is a function of temperature only, but the above expression reduces to the form proposed by Anderson (1956) if b in his expression is inversely proportional to P_{H_2}.

With a precipitated Mn/Fe catalyst, the olefin/paraffin ratio of the products at all carbon numbers was less than that with a reduced fused magnetite catalyst containing 0.4 to 0.8 wt% K_2O and the β-olefin/α-olefin ratio was much greater. Secondary hydrogenation and olefin isomerization reactions appear to be much more significant with the Mn/Fe catalyst. With both catalysts the Flory distribution was followed but in each case two values of the chain growth probability, α, were found, with a sharp increase above about C_{11}. Values of α based on the C_1-C_{10} products were less for the Mn/Fe catalyst than for the fused magnetite catalyst, attributed to the absence of potassium in the Mn/Fe catalyst. The activity of the present Mn/Fe catalyst was moderately less than that reported for a similar catalyst studied elsewhere in a bubble column.

With a precipitated iron-copper catalyst, the carbon number distribution of products was very similar to that observed with a reduced fused magnetite catalyst. The chain growth probability, α, had two values, 0.68 and 0.86, breaking at about C_8. Compared to results in a fixed bed with the same precipitated catalyst, methane formation was less and the olefin/paraffin ratio of products was slightly greater in the slurry reactor.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM: A liquid-phase Fischer-Tropsch process is a promising route for conversion of carbonaceous sources such as coal to liquid transportation fuels. However, in order to achieve maximum selectivity and activity, there must be an adequate understanding of the effect of mass transfer on the nature and distribution of products. Further, the stirred autoclave system developed provides a unique method of comparing catalysts under isothermal intrinsic kinetic conditions.

PLANS FOR THE COMING YEAR: The effect of the nature of the liquid on rate and selectivity of a slurry reactor will be studied. The effect of solids loading, particle size and other variables on gas-liquid transfer will be determined.

II. HIGHLIGHT ACCOMPLISHMENTS

The occurrence of two values of the chain growth probability (α) breaking at about C_{10}, is characteristic of a variety of iron-based catalysts. In a representative case, the amount of Diesel and jet fuel actually synthesized is about double what would be predicted from the light product analysis if a single value of α indeed applied. A precipitated Mn/Fe catalyst, reported to produce highly olefinic products, actually formed products in a stirred autoclave of lower olefin/paraffin ratio than a reduced fused magnetite catalyst.

III. ARTICLES AND PRESENTATIONS

C.N. Satterfield and G.A. Huff, Jr., "Usefulness of a Slurry-Type Fischer-Tropsch Reactor for Processing Synthesis Gas of Low Hydrogen-Carbon Monoxide Ratios," Can. J. Chem. Eng., 60, 159 (1982).

C.N. Satterfield and G.A. Huff, Jr., "Carbon Number Distribution of Fischer-Tropsch Products Formed on an Iron Catalyst in a Slurry Reactor," J. Catalysis, 73, 187 (1982).

G.A. Huff, Jr., and C.N. Satterfield, "A Stirred Autoclave Apparatus for Study of the Fischer-Tropsch Synthesis in a Slurry Bed. I. Reactor and Trapping Procedures." Ind. Eng. Chem., Fundam., 21, 479 (1982).

G.A. Huff, Jr., and C.N. Satterfield, "A Stirred Autoclave Apparatus for Study of the Fischer-Tropsch Synthesis in a Slurry Bed. II. Analysis of Products." Ind. Eng. Chem., Fundam., 22, 258 (1983).

C.N. Satterfield and G.A. Huff, Jr., "Mass Transfer and Product Selectivity in a Mechanically-Stirred Fischer-Tropsch Slurry Reactor", Seventh International Symposium on Chemical Reaction Engineering, A.C.S. Symposium Series, No. 196, 225, 1982.

C.N. Satterfield, G.A. Huff, Jr., and R. Summerhayes, "Olefin Addition in Fischer-Tropsch Synthesis on an Iron Catalyst", J. Catalysis, 80, 486 (1983).

C.N. Satterfield and G.A. Huff, Jr., "Reply to Letters of Bukur and Gupte and of van Vuuren concerning mass transfer limitations in Fischer-Tropsch slurry reactors", Chem. Eng. Sci., in press.

C.N. Satterfield and H.G. Stenger, "Fischer-Tropsch Synthesis on a Precipitated Mn/Fe Catalyst in a Well-Mixed Slurry Reactor", Ind. Eng. Chem. Process Design Develop., in press, March, 1983.

G.A. Huff, Jr., and C.N. Satterfield, "Evidence for Multiple Chain Growth Probabilities on Iron Catalysts in the Fischer-Tropsch Synthesis", J. Catal., submitted, March 15, 1983.

C.N. Satterfield and H.G. Stenger, "Fischer-Tropsch Synthesis in a Slurry Reactor: Precipitated Iron-copper Catalyst", Ind. Eng. Chem. Process Design Develop., submitted.

Sixth International Symposium on Chemical Reaction Engineering, Nice France, March, 1980.
Royal Dutch Shell, Amsterdam, Holland, June, 1980.
Annual A.I.Ch.E. meeting, Chicago, November, 1980.
Philadelphia Catalysis Club, April, 1981.
Mobil Oil Co., Paulsboro, New Jersey, May, 1981.
Montedison, Milan, Italy, June, 1981.
Engler-Bunte Institute, Karlsruhe, West Germany, June, 1981.
Chevron Research Co., Richmond, California, October, 1981.
Annual A.I.Ch.E. meeting, New Orleans, November, 1981.
Seventh International Symposium on Chemical Reaction Engineering, Boston, October, 1982.
Annual A.I.Ch.E. meeting, Los Angeles, November, 1982.
(Keynote Speaker) Symposium on Production of Energy Carriers and Chemicals, Dutch Organization of Pure Scientific Research, Utrecht, May, 1983.
ANIC-Enichimica, Milan, June, 1983.

Fischer-Tropsch Synthesis in
Slurry Reactor Systems
DE-FG22-81PC40771

Massachusetts Institute of Technology
C.N. Satterfield

List of figures

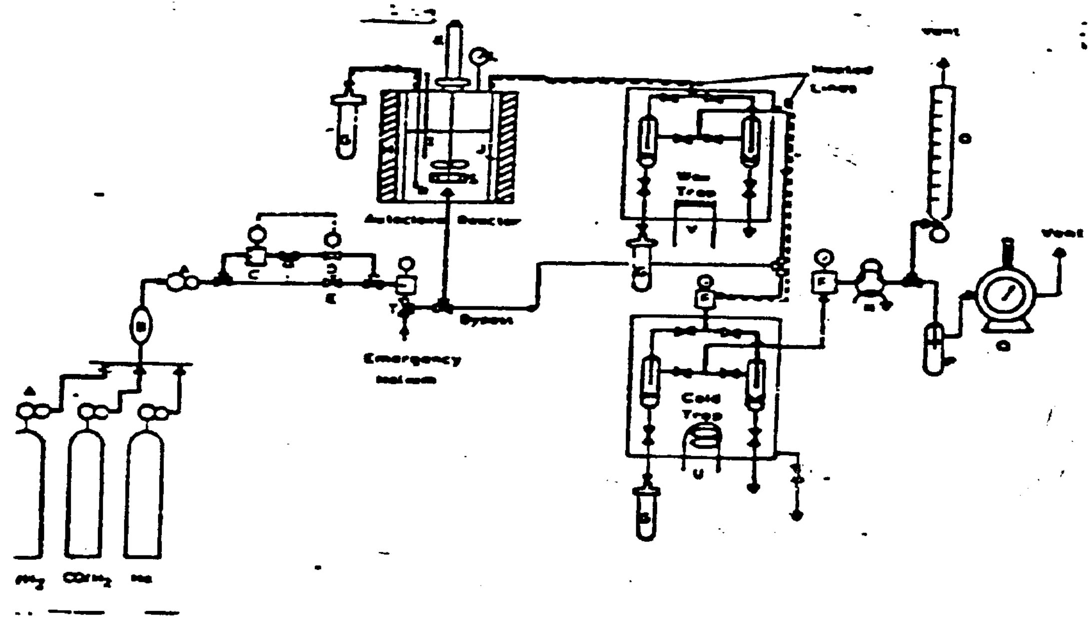

Autoclave Reactor
Heated Lines
Vent
Wax Trap
V
Cold Trap
U
Vent
Bypass
Emergency Release
A
B
C
D
E
T
K
O
Q
N2
CO/H2
H2

FIGURE 1

GENERAL CHARACTERISTICS OF RATE OF REACTION

1. ABOUT PROPORTIONAL TO P_{H_2}
2. INDEPENDENT OF P_{CO} OR SLIGHTLY INHIBITED BY CO
3. INHIBITED BY H_2O
4. ACTIVATION ENERGY OF ABOUT 20 TO 25 KCAL/MOLE (84 TO 105 KJ/MOLE)

FIGURE 2

EXPERIMENTAL CONDITIONS

232 TO 263°C

445 TO 1480 KPA (4.45 TO 14.8 ATM)

$\left(\frac{H_2}{CO}\right)_{FEED}$ = 0.55 TO 1.81

H_2 CONVERSIONS 17 TO 68%

CO CONVERSIONS 16 TO 98%

FIGURE 3

ANDERSON:

$$-R = \frac{A\, P_{CO}\, P_{H_2}}{P_{CO} + B\, P_{H_2O}} \qquad (1)$$

PRESENT STUDY:

$$-R = \frac{A\, B'\, P_{CO}\, P_{H_2}^{\,2}}{P_{H_2O} + B'\, P_{CO} P_{H_2}} \qquad (2)$$

EQ. (2) REDUCES TO FORM OF EQ. (1) IF $B \propto \dfrac{1}{P_{H_2}}$

FIGURE 4

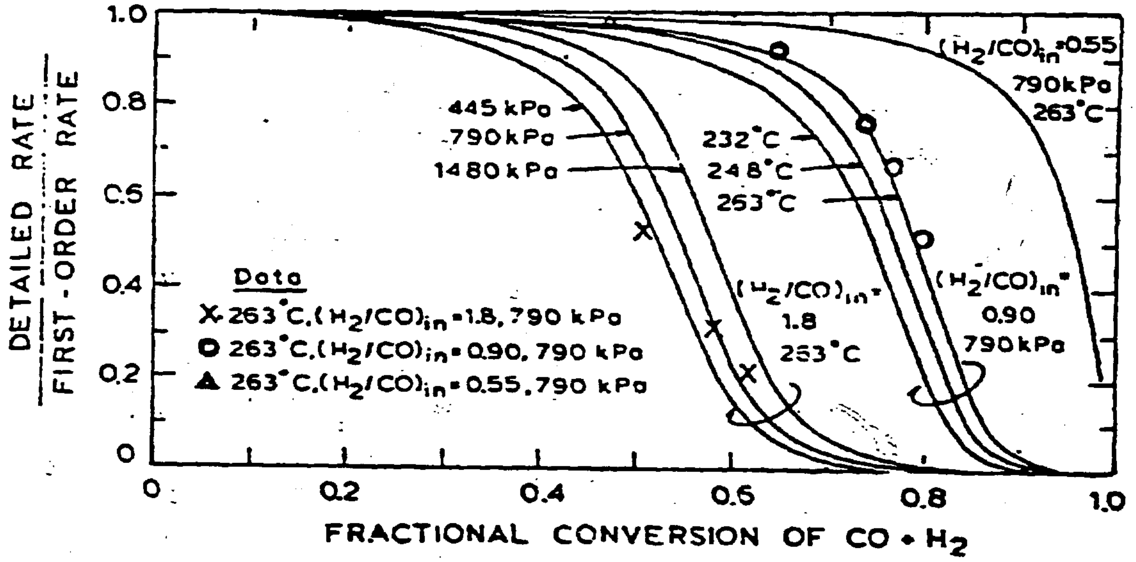
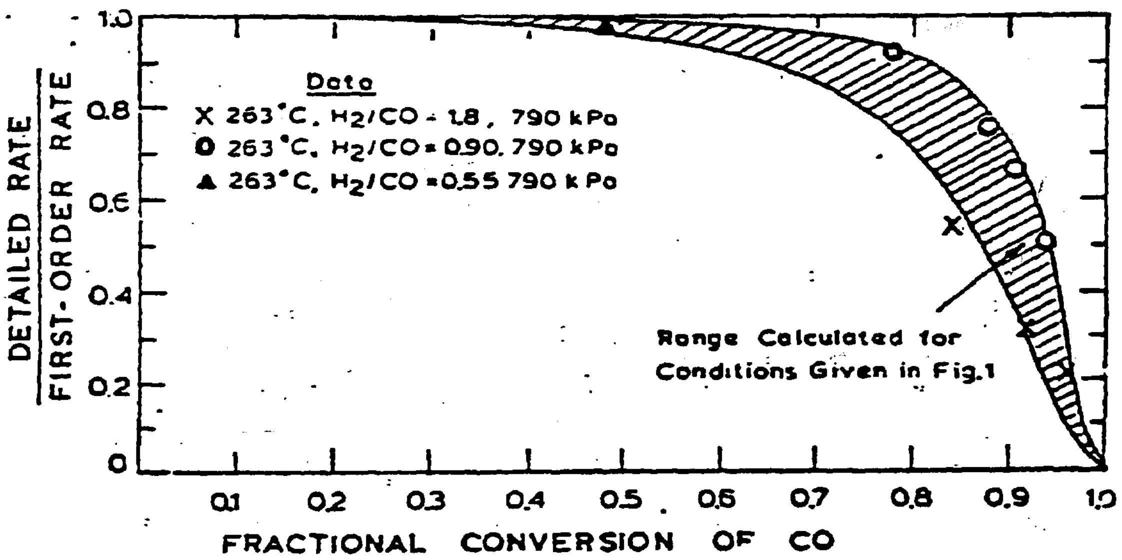

DETAILED RATE
FIRST - ORDER RATE
1.0
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1.0
FRACTIONAL CONVERSION OF CO + H2
445 kPa
790 kPa
1480 kPa
232°C
248°C
263°C
(H2/CO)in=0.55
790 kPa
263°C
(H2/CO)in=
1.8
263°C
(H2/CO)in=
0.90
790 kPa
Data
X 263°C,(H2/CO)in=1.8, 790 kPa
O 263°C,(H2/CO)in=0.90, 790 kPa
▲ 263°C,(H2/CO)in=0.55, 790 kPa

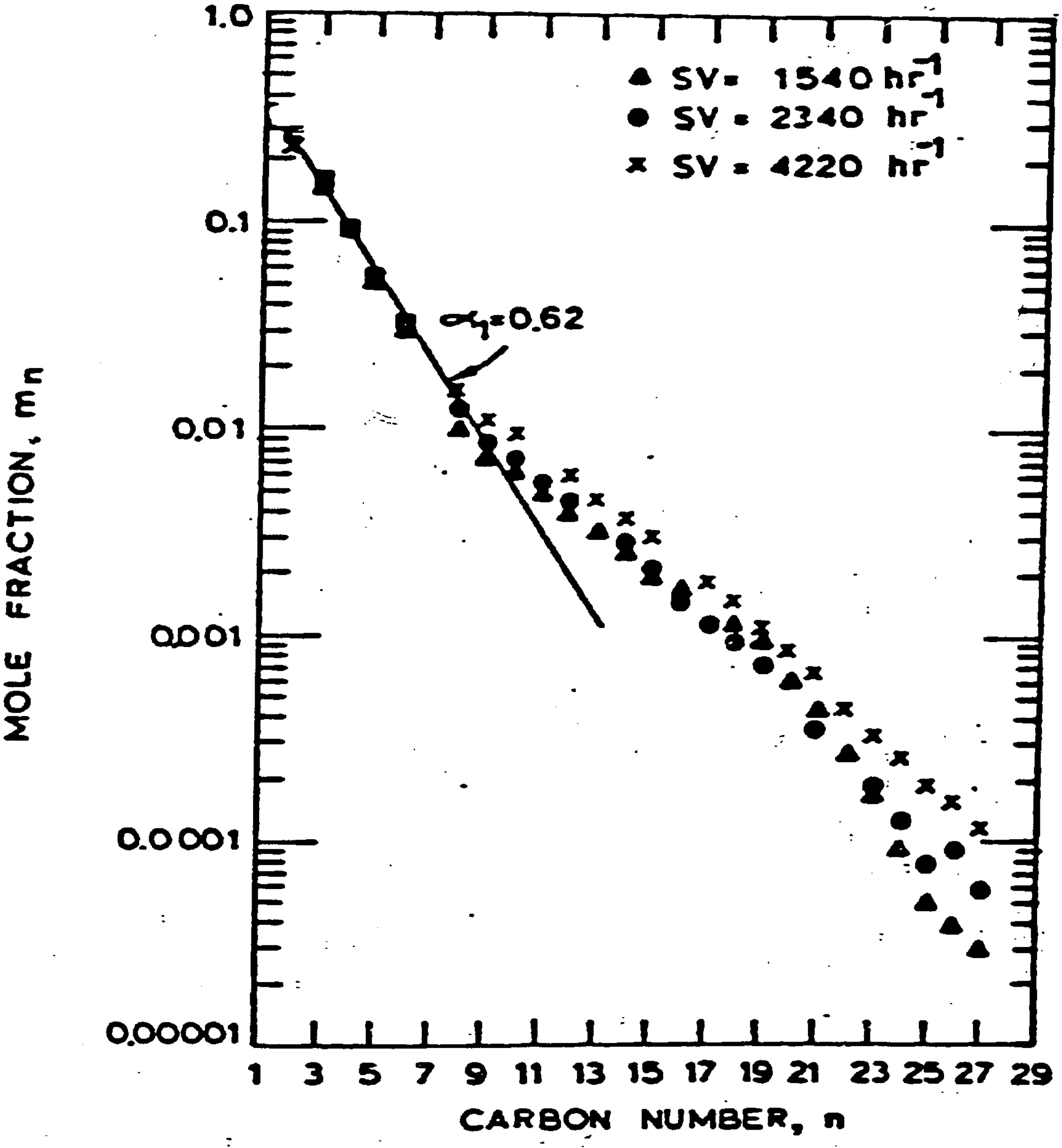
FIGURE 5



DETAILED RATE / FIRST-ORDER RATE
1.0
0.8
0.6
0.4
0.2
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
FRACTIONAL CONVERSION OF CO
Data
X 263°C, H2/CO = 1.8, 790 kPa
O 263°C, H2/CO = 0.90, 790 kPa
▲ 263°C, H2/CO = 0.55 790 kPa
Range Calculated for Conditions Given in Fig.1

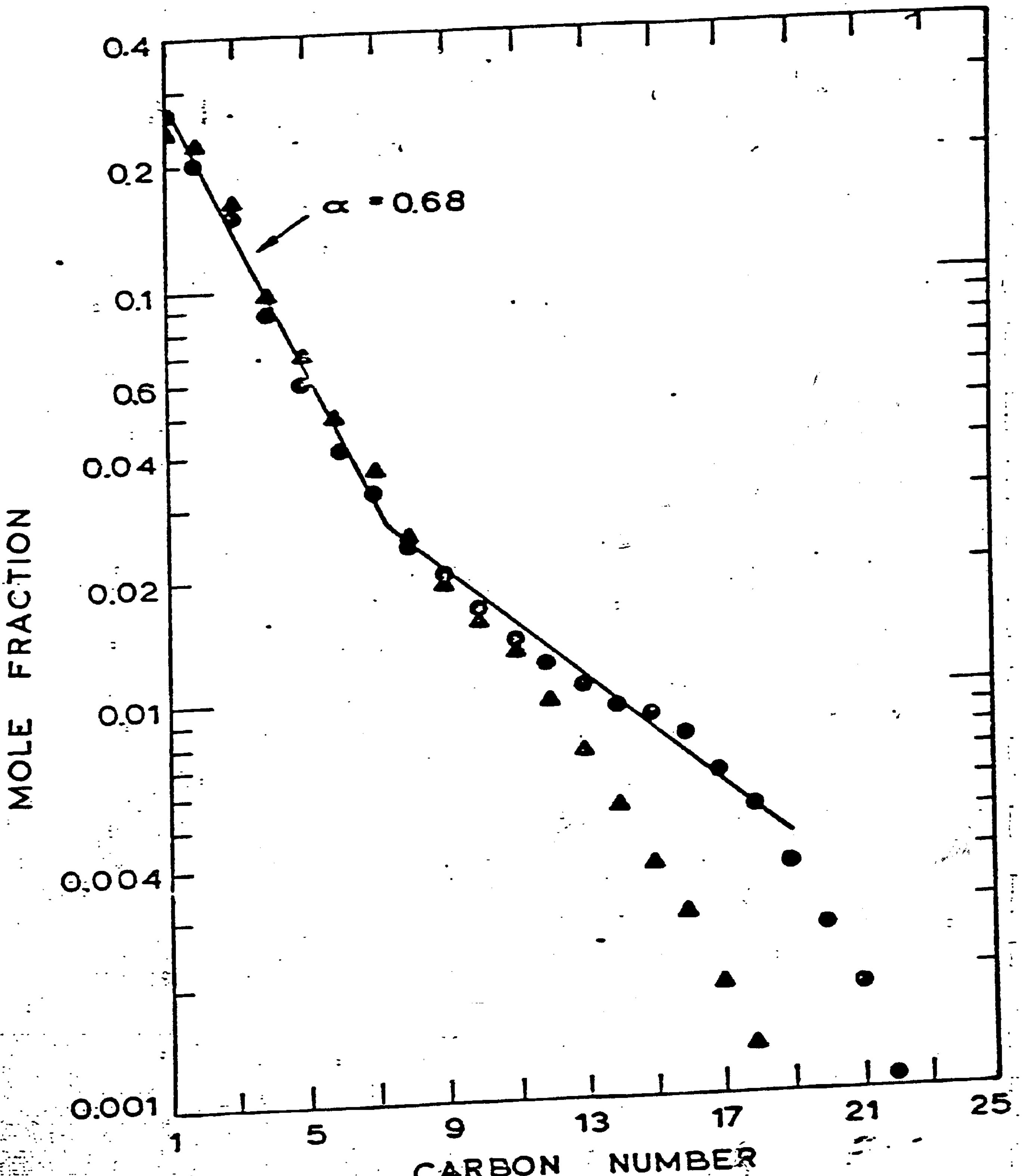
FIGURE 6

FIGURE 7



▲ SV = 1540 hr^{-1}
● SV = 2340 hr^{-1}
x SV = 4220 hr^{-1}
α_1 = 0.62
MOLE FRACTION, m_n
1.0
0.1
0.01
0.001
0.0001
0.00001
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29
CARBON NUMBER, n

FIGURE 8



0.4
0.2
0.1
0.6
0.04
0.02
0.01
0.004
0.001
MOLE FRACTION
α = 0.68
1
5
9
13
17
21
25
CARBON NUMBER

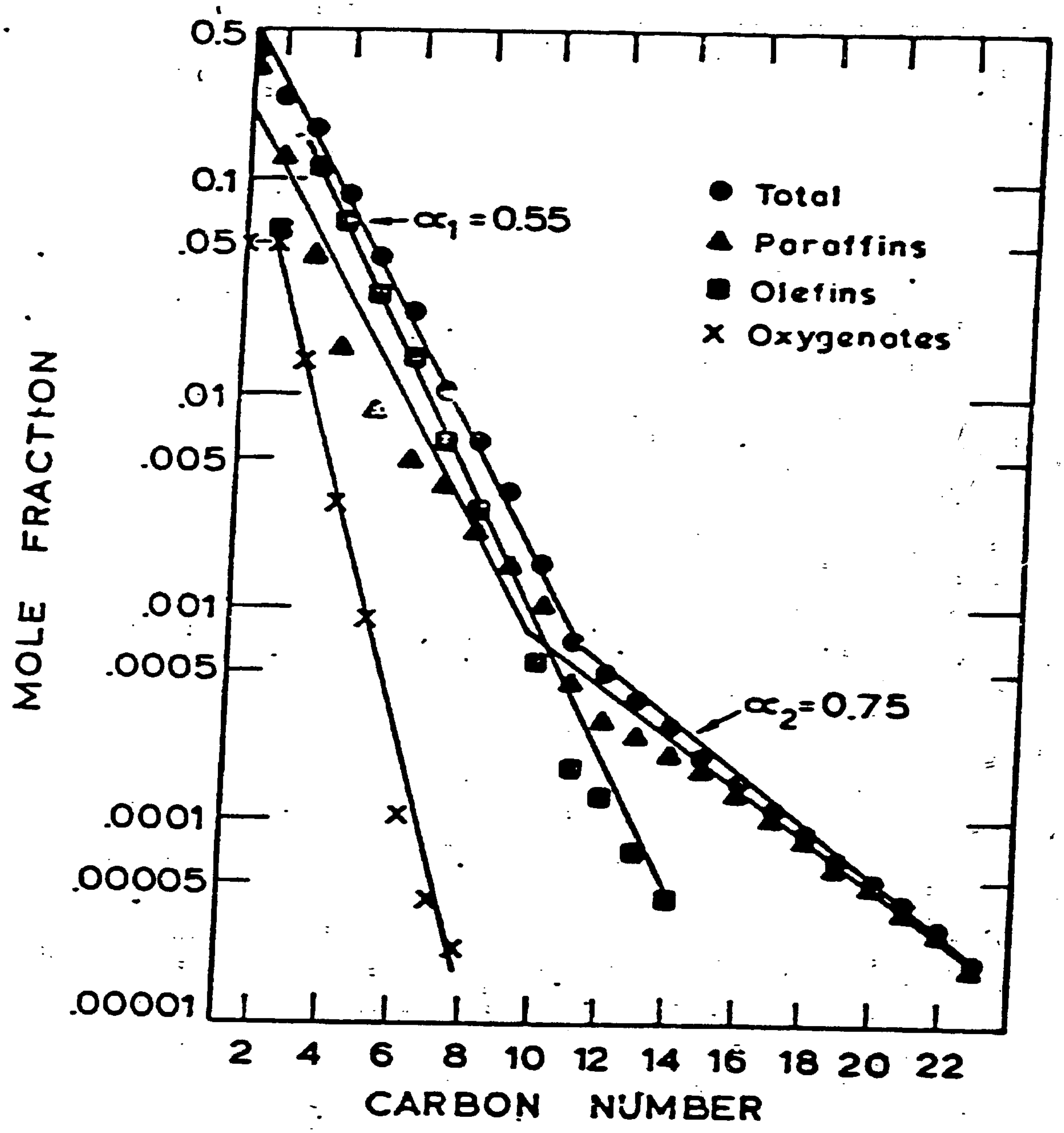
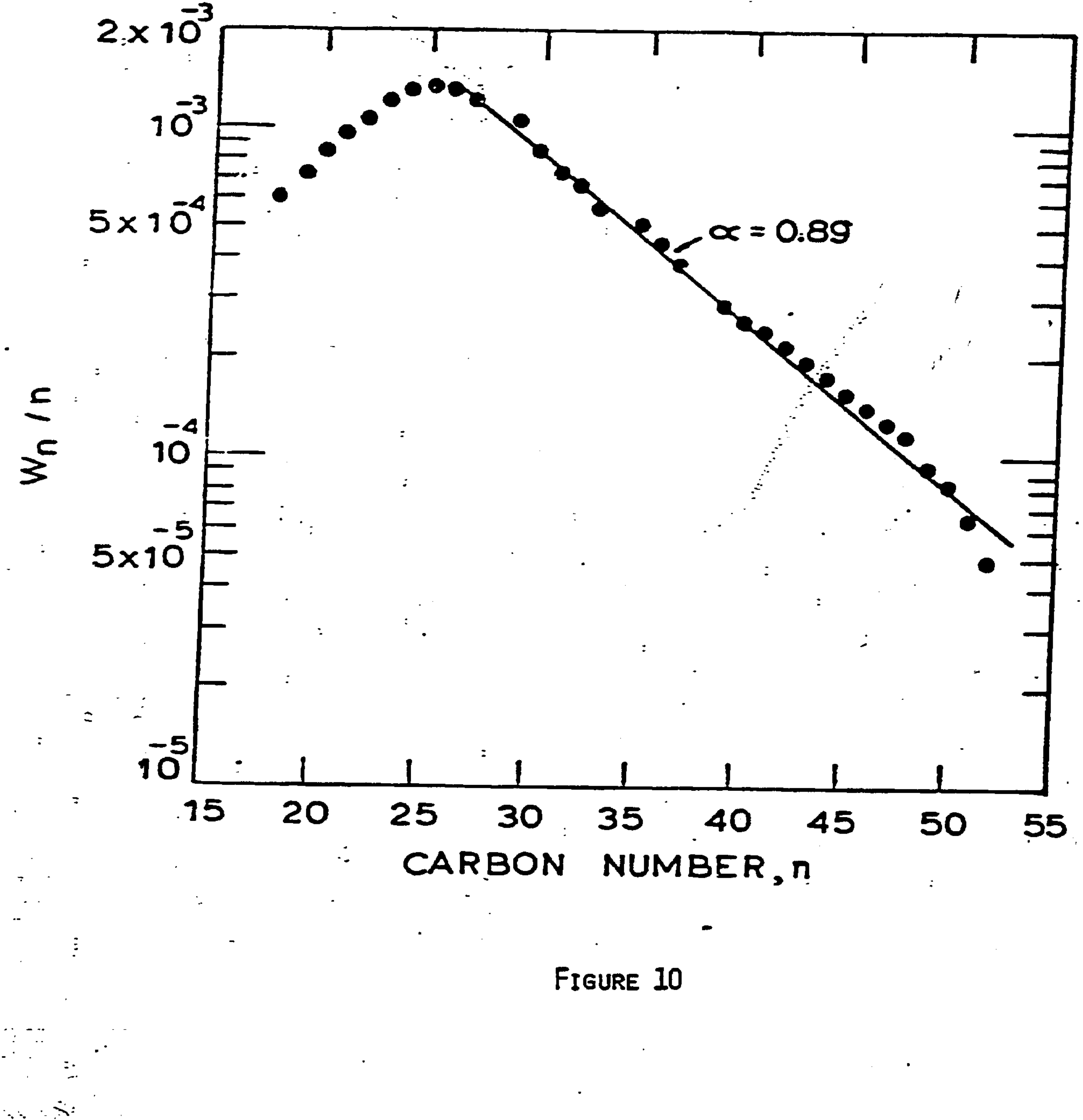

0.5
0.1
.05
.01
.005
.001
.0005
.0001
.00005
.00001
MOLE FRACTION
2
4
6
8
10
12
14
16
18
20
22
CARBON NUMBER
● Total
▲ Paraffins
■ Olefins
X Oxygenates
$\alpha_1 = 0.55$
$\alpha_2 = 0.75$

FIGURE 9



2×10^{-3}
10^{-3}
5×10^{-4}
10^{-4}
5×10^{-5}
10^{-5}
W_n / n
$\alpha = 0.89$
15
20
25
30
35
40
45
50
55
CARBON NUMBER, n

FIGURE 10

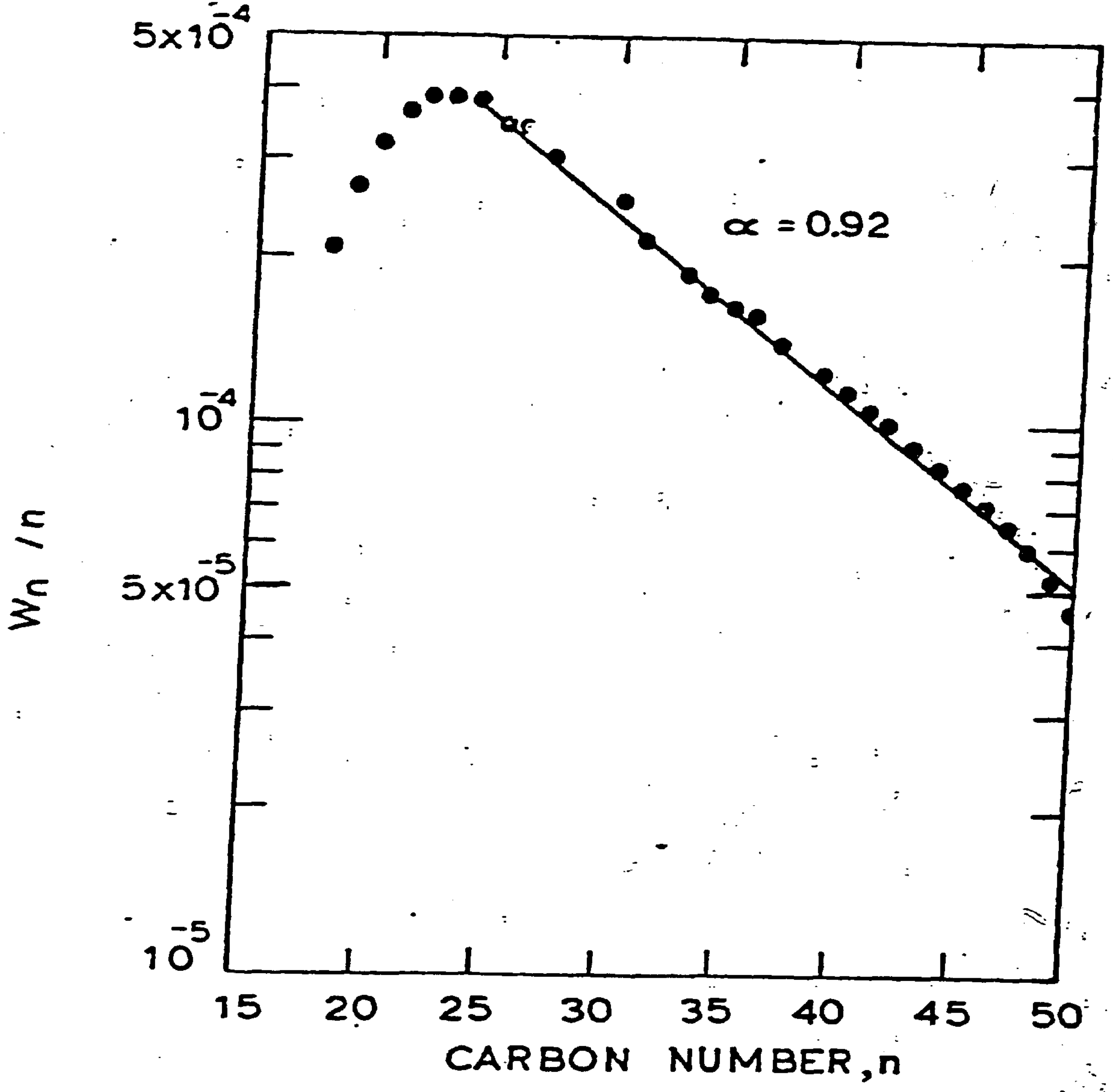

5x10^-4
10^-4
5x10^-5
10^-5
W_n / n
α = 0.92
15
20
25
30
35
40
45
50
CARBON NUMBER, n

FIGURE 11

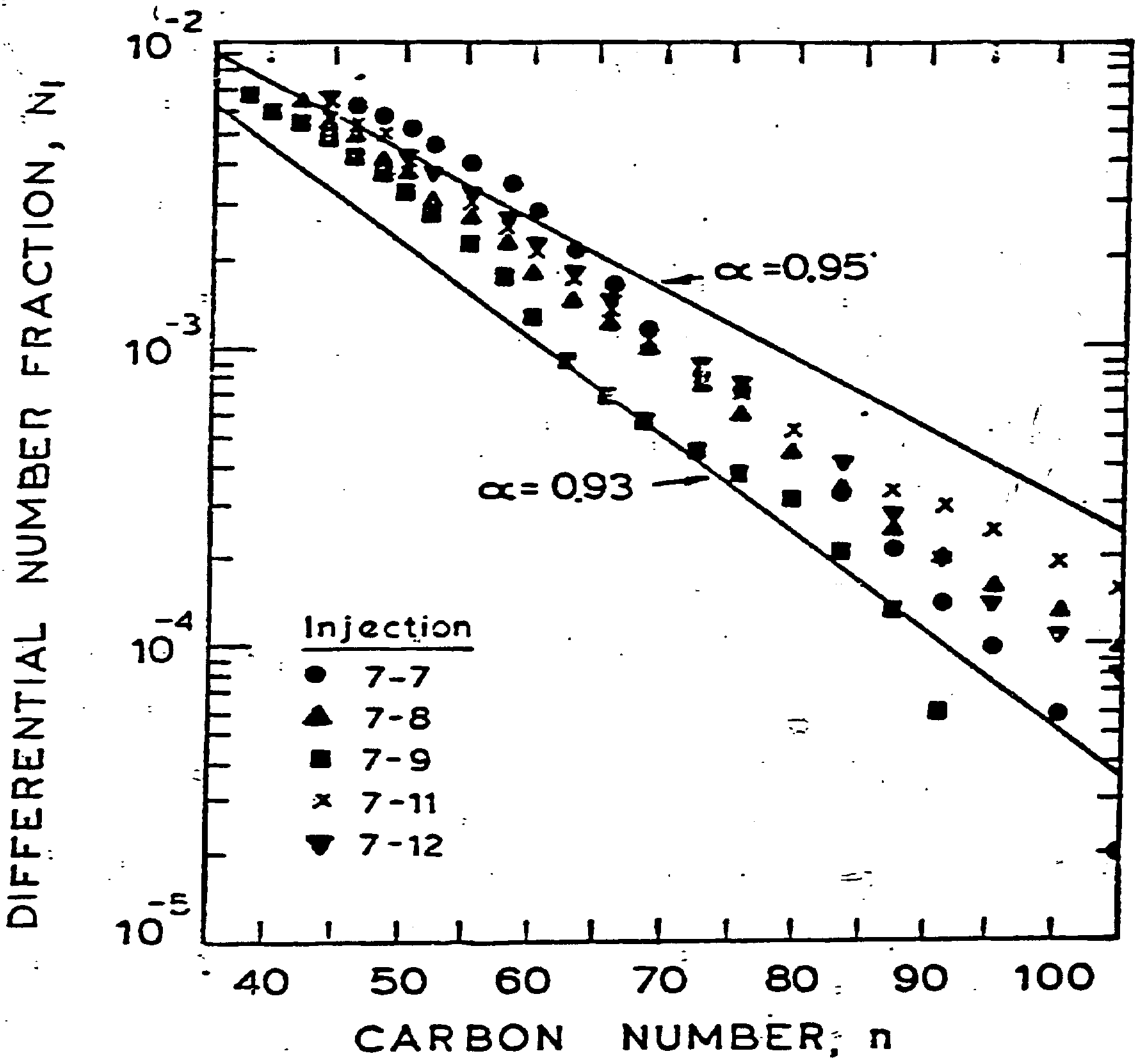
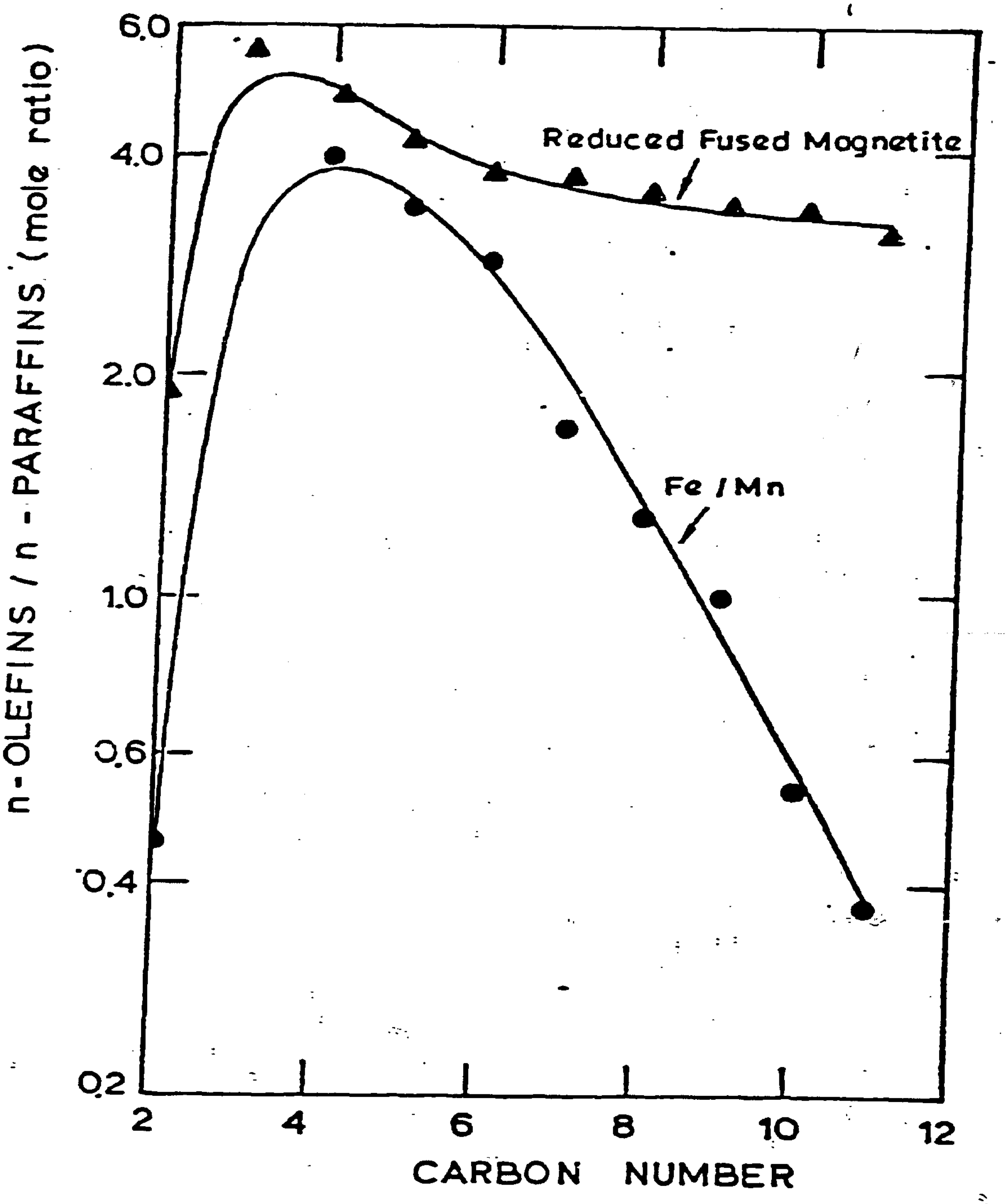
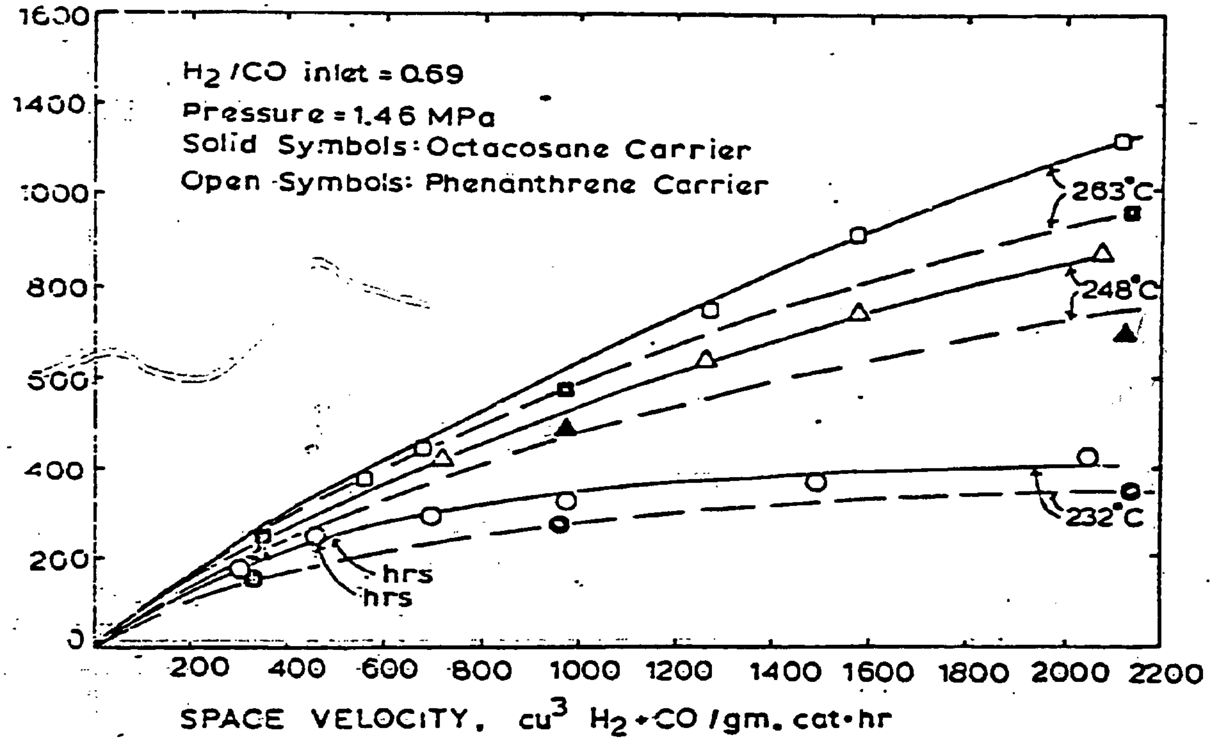

10^{-2}
10^{-3}
10^{-4}
10^{-5}
DIFFERENTIAL NUMBER FRACTION, N_i
40
50
60
70
80
90
100
CARBON NUMBER, n
$\alpha = 0.95$
$\alpha = 0.93$
Injection
● 7-7
▲ 7-8
■ 7-9
× 7-11
▼ 7-12

FIGURE 12



6.0
4.0
2.0
1.0
0.6
0.4
0.2
2
4
6
8
10
12
n-OLEFINS / n - PARAFFINS (mole ratio)
CARBON NUMBER
Reduced Fused Magnetite
Fe / Mn

FIGURE 13



1600
1400
1000
800
600
400
200
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
H_2/CO inlet = 0.69
Pressure = 1.46 MPa
Solid Symbols: Octacosane Carrier
Open Symbols: Phenanthrene Carrier
263°C
248°C
232°C
hrs
hrs
SPACE VELOCITY, cu^3 H_2+CO/gm. cat·hr

FIGURE 14

FIGURE 15

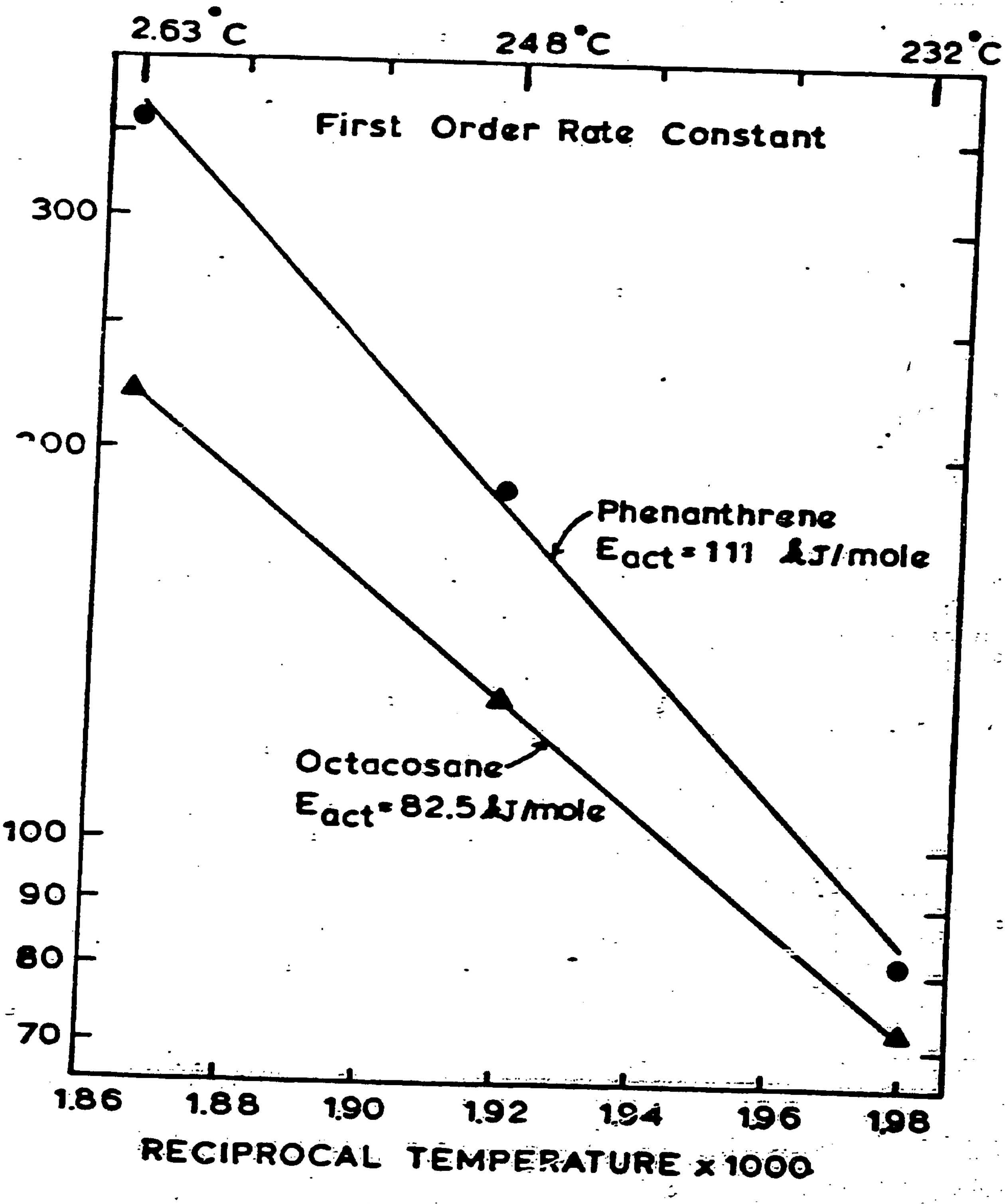
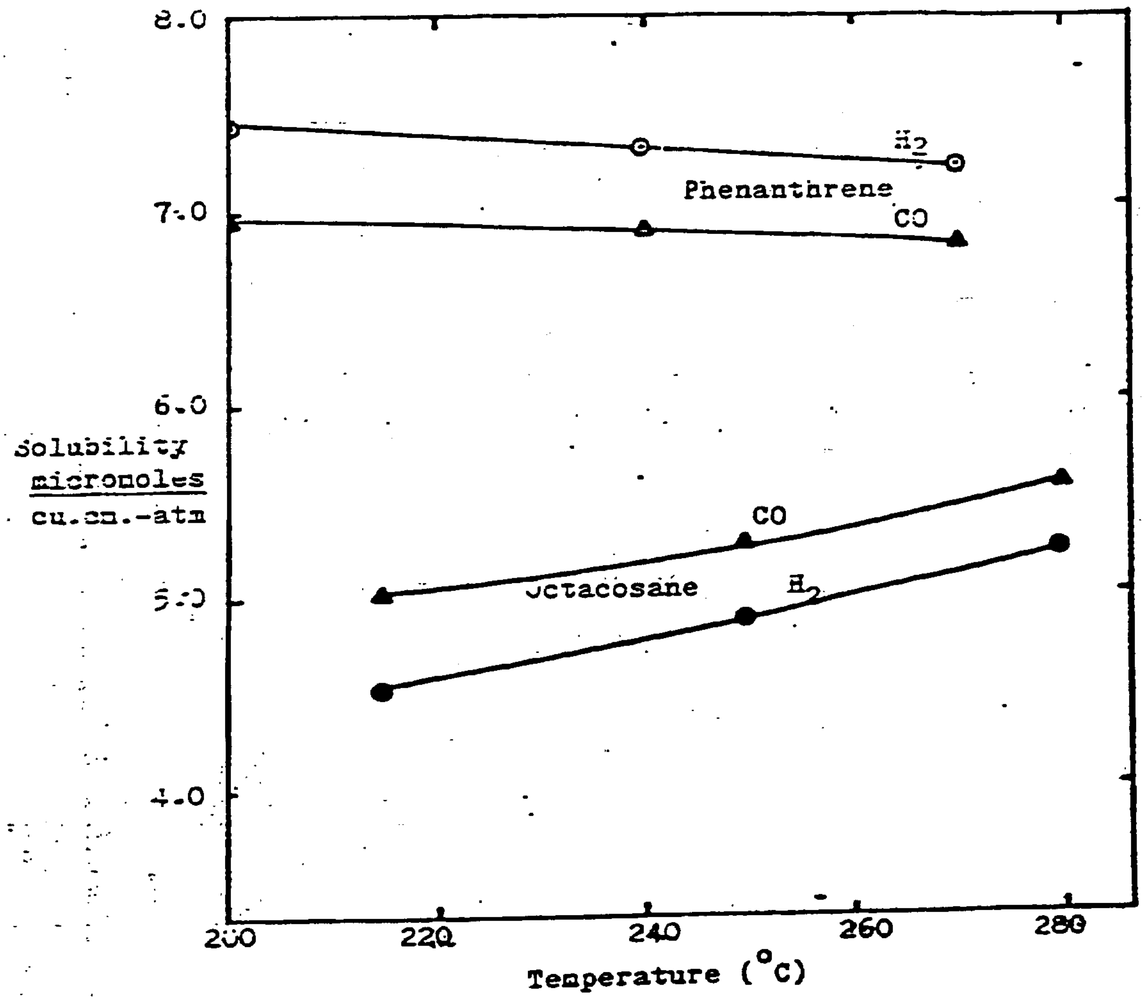
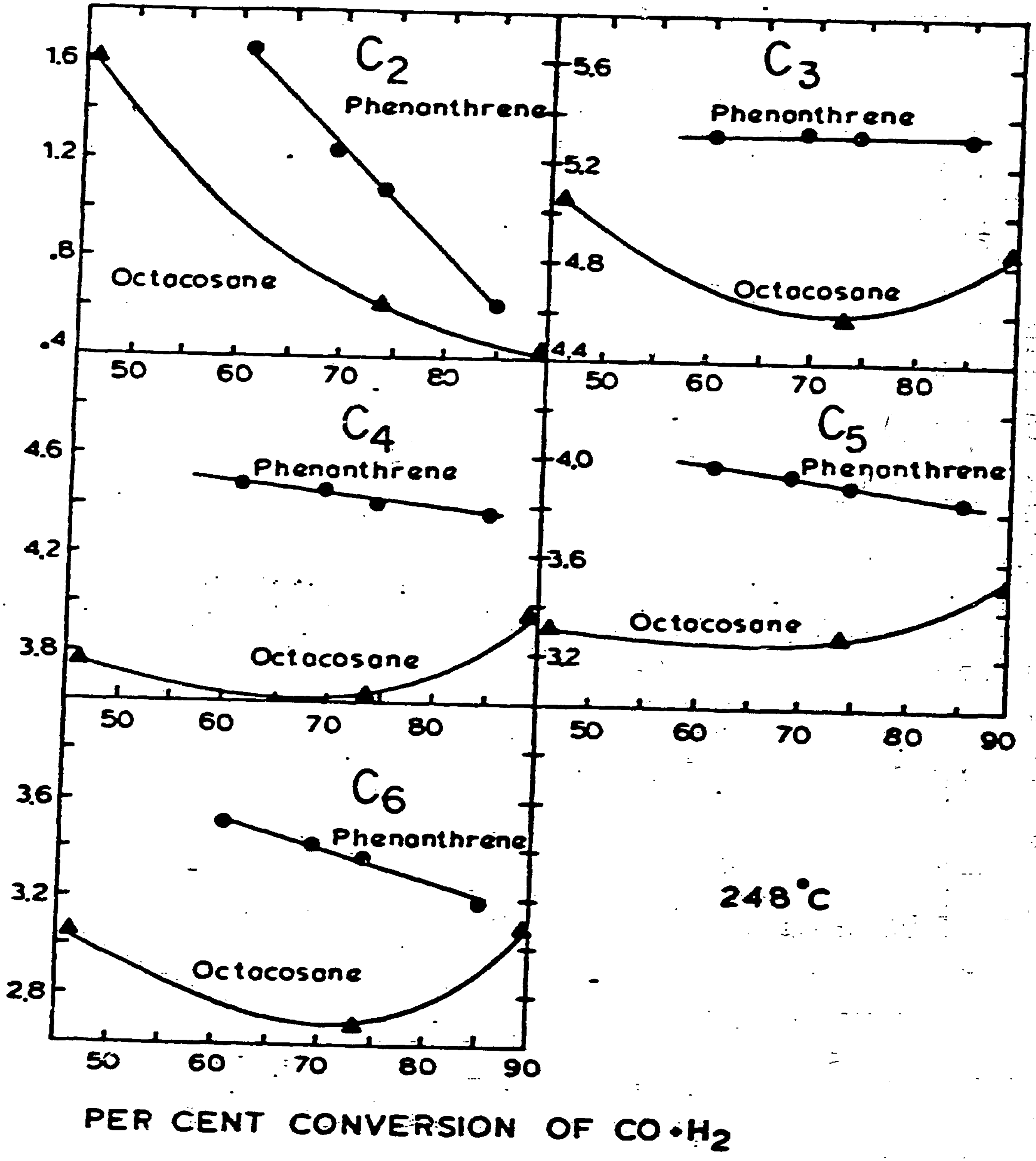

2.63°C
248°C
232°C
First Order Rate Constant
300
200
100
90
80
70
Phenanthrene
E_{act} = 111 kJ/mole
Octacosane
E_{act} = 82.5 kJ/mole
1.86
1.88
1.90
1.92
1.94
1.96
1.98
RECIPROCAL TEMPERATURE x 1000

FIGURE 16

SOLUBILITIES OF H_2 and CO
IN THE LIQUID CARRIERS





C2
Phenanthrene
Octacosane
1.6
1.2
.8
.4
C3
Phenanthrene
Octacosane
5.6
5.2
4.8
4.4
C4
Phenanthrene
Octacosane
4.6
4.2
3.8
C5
Phenanthrene
Octacosane
4.0
3.6
3.2
C6
Phenanthrene
Octacosane
3.6
3.2
2.8
50
60
70
80
90
248°C
PER CENT CONVERSION OF CO + H2

FIGURE 17

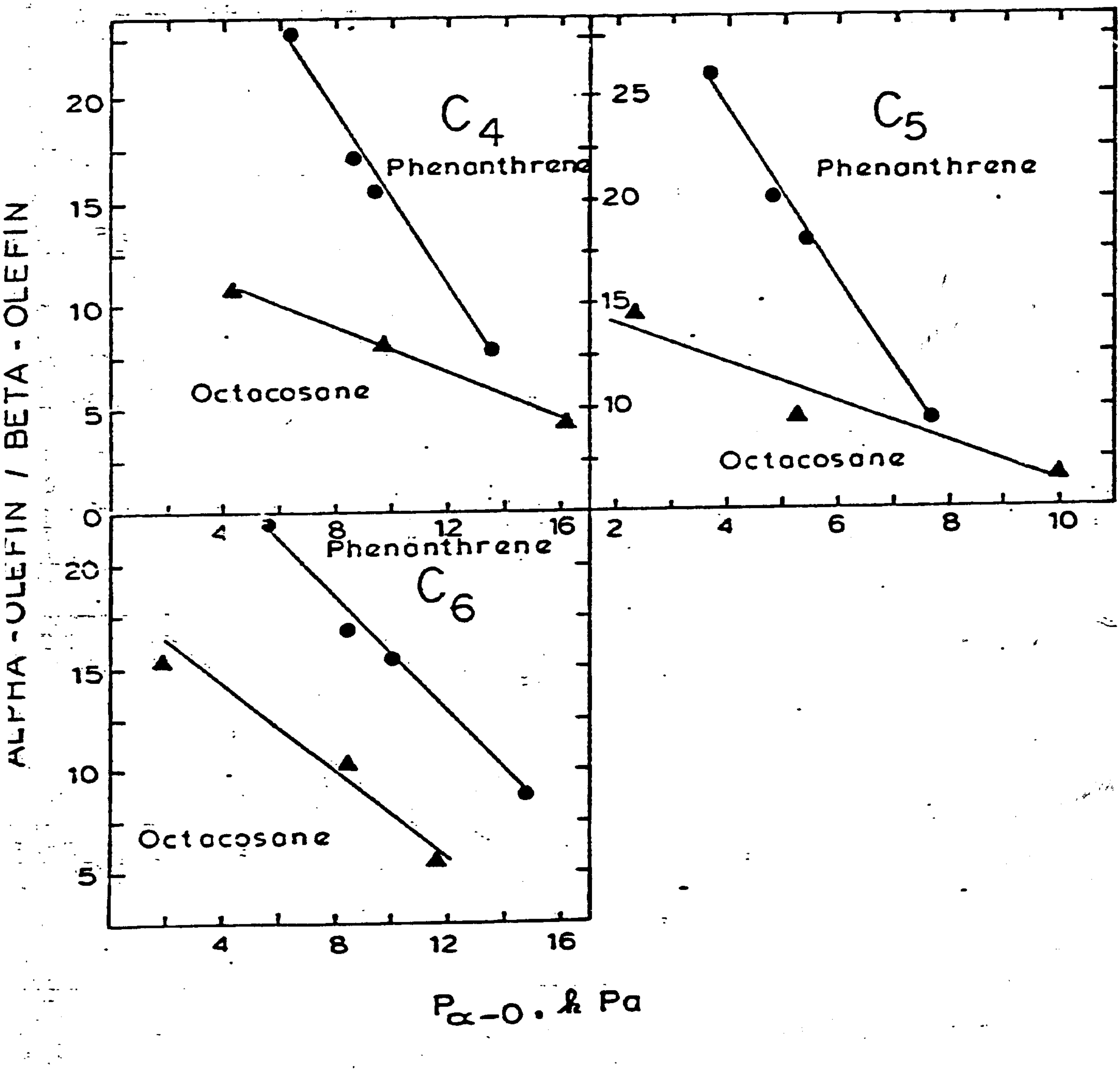

ALPHA - OLEFIN / BETA - OLEFIN
C4
Phenanthrene
Octacosane
C5
Phenanthrene
Octacosane
C6
Phenanthrene
Octacosane
0
5
10
15
20
25
4
8
12
16
2
6
10
$P_{\alpha-O}$, k Pa

FIGURE 18

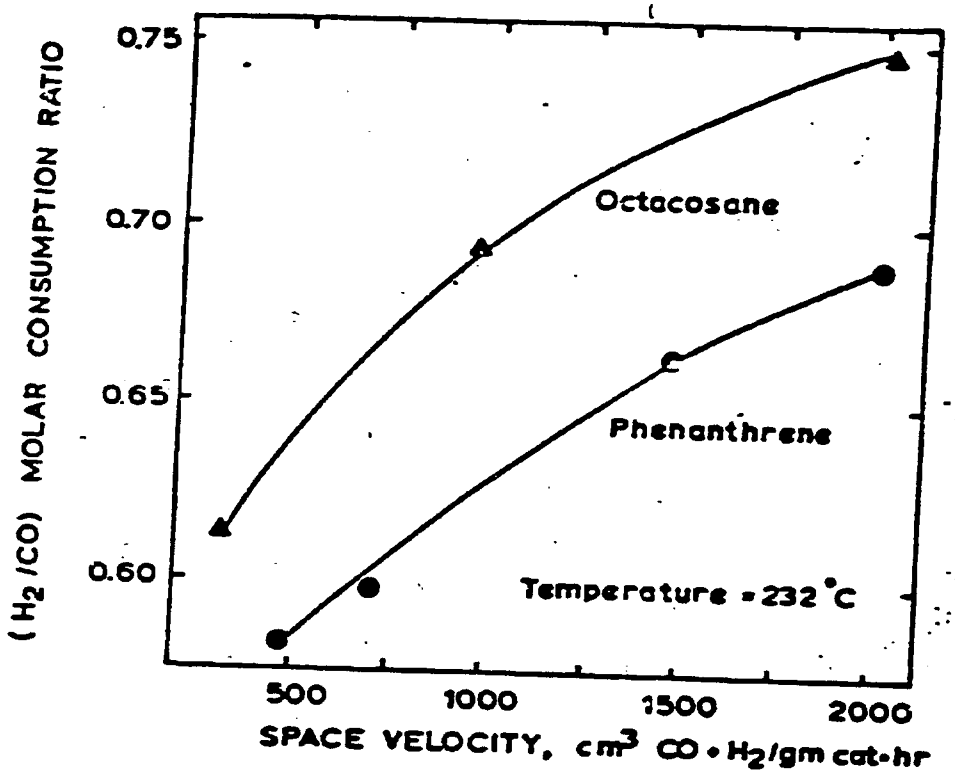

0.75
0.70
0.65
0.60
(H₂/CO) MOLAR CONSUMPTION RATIO
Octacosane
Phenanthrene
Temperature = 232 °C
500
1000
1500
2000
SPACE VELOCITY, cm³ CO + H₂/gm cat-hr

FIGURE 19