

Report 12

**CATALYST AND REACTOR DEVELOPMENT FOR A SLURRY  
PHASE FISCHER-TROPSCH PROCESS**

P. Dyer  
Air Products and Chemicals, Inc.



CATALYST AND REACTOR DEVELOPMENT  
FOR A SLURRY PHASE FISCHER-TROPSCH PROCESS  
DOE CONTRACT DE-AC22-80PC30021

BY

JEFFREY V. BAUER, BARRY W. BRIAN, PAUL N. DYER, RONALD PIERANTOZZI  
CORPORATE RESEARCH AND DEVELOPMENT DEPARTMENT  
AIR PRODUCTS AND CHEMICALS, INC.

P. O. BOX 538  
ALLENTOWN, PA 18105

PRESENTED BY  
DR. PAUL N. DYER

INTRODUCTION

This paper describes work that is being undertaken as part of a three year contract, which began in October 1980, between the United States Department of Energy and Air Products and Chemicals, Inc<sup>1</sup>. The objective of the contract is stated concisely by the following extract: "To evaluate catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels via a single stage liquid phase process".

Current activities are divided into two major areas, as illustrated in Figure 1. These are:

- 1) Slurry catalyst development using stirred test reactors to optimize selectivity and activity. The aim is to maximize the space time yield of hydrocarbons in the transportation fuels range, and to overcome the limitations of the standard Schulz-Flory distribution on product yield. Diesel fuel is the primary objective because of the suitability of the Fischer-Tropsch product, with its high n-alkane content, for this type of fuel with minimal or no further refining.
- 2) Slurry reactor modelling using cold flow techniques to study the hydrodynamics of three phase, bubble column reactors and obtain scale-up

correlations. Apart from its excellent temperature control and the ability to operate at high conversions with direct utilization of CO rich syngas, the slurry reactor system also enables continuous operation of the Fischer-Tropsch synthesis with maximum product in the diesel fuel range, without the plugging or pressure drop problems experienced with other types of reactors.

In an optional final stage of the contract, the results from these two major program areas will be combined to produce a design for a pilot plant, single stage, slurry phase Fischer-Tropsch process.

#### SLURRY CATALYST DEVELOPMENT

##### a) Status

The current status of the slurry catalyst testing program is shown in Table 1. Three slurry reactor systems have been constructed and successfully operated continuously for a minimum period of 21 days. Carbon and hydrogen material balances to within 1-3% are routinely obtained by a total analysis of the product stream for hydrocarbons from C<sub>1</sub>-C<sub>40</sub>, CO<sub>2</sub>, H<sub>2</sub>O, oxygenates and unreacted syngas, and by the inclusion of any products that may accumulate within the reactor. Details of the analytical and computerized data handling systems have been published <sup>2</sup>.

Under the contract schedule, 20 "modified conventional" Fischer-Tropsch catalysts will be tested in the slurry phase for up to 21 days each. Four of these have been carried out so far along with two tests using a sintered Fe<sub>2</sub>O<sub>3</sub> catalyst.

An additional modification was obtained during the year for parametric gas phase screening in order to optimize the preparation of this type of catalyst prior to slurry phase testing. The parameters studied include loading, calcination and activation procedures, all of which influence catalyst selectivity and activity.

Novel supported metal cluster catalysts have also been synthesized, and 46 out of the 50 scheduled in the program have been screened in the gas phase.

Twelve slurry tests of this type of catalyst have also been carried out. From the total of slurry phase tests, up to four catalysts will be chosen for further long term testing.

Figure-2 illustrates diagrammatically the continuous stirred reactors used for the slurry phase tests. The level of slurry is continuously monitored by a differential pressure gauge, and any buildup can be detected of higher molecular weight products that are not removed from the reactor with the exit gas flow. When this occurs, hydrocarbon product is removed from the reactor via a filtered side stream and subjected to analysis. By monitoring the rate of buildup of slurry, and determining the amount of slurry oil withdrawn to maintain a constant level at a particular set of process conditions, the higher molecular weight hydrocarbons can be quantitatively included in the material balance.

The results presented in this paper are all obtained during a 21 day continuous test period, and therefore are not transient initial phenomena. After a change in process parameters, the reactor system is allowed to equilibrate for 14-16 hours before obtaining carbon and hydrogen material balances over an additional 8 hour period.

b) Baseline Slurry Tests - Sintered Fe<sub>2</sub>O<sub>3</sub>

Initial slurry phase tests were made using an ammonia synthesis catalyst, sintered Fe<sub>2</sub>O<sub>3</sub> promoted with 2% Al<sub>2</sub>O<sub>3</sub>, 0.5% K<sub>2</sub>O and 0.7% CaO, reduced in H<sub>2</sub> before being slurried in oil. The range of conditions used in these baseline tests is listed in Table 2.

The tests fulfilled three functions:

- (1) to establish a baseline catalyst activity,
- (2) to thoroughly test the analytical and data handling systems, and
- (3) to determine the mass transfer limitations of the stirred three phase reactors.

The third function is very important in any experimental slurry catalyst testing system, because the effects of gas to liquid diffusional limitations must

be avoided or subtracted from the observed results to obtain meaningful and reproducible kinetic parameters.

The results of the baseline tests can be summarized as follows: Firstly, hydrocarbon products closely approximating a straight-line Schulz-Flory distribution were obtained with all but very CO rich syngas, i.e. for CO/H<sub>2</sub> < 2.8. A typical hydrocarbon distribution obtained with CO/H<sub>2</sub> = 0.5 is shown in Figure 3, and the resulting statistical plot closely approximates a straight-line, standard Schulz-Flory distribution with  $\alpha = 0.78$ , Figure 4. When the CO/H<sub>2</sub> ratio was increased to 1.4 under similar operating conditions, the yield of methane was significantly reduced to 6.8 wt%, while the amount of C<sub>20+</sub> products increased, as illustrated in Figure 5. However, a statistical plot of the hydrocarbon distribution still closely approximated a standard Schulz-Flory distribution up to C<sub>22</sub>, with again  $\alpha = 0.78$ , Figure 7.

When the CO/H<sub>2</sub> ratio was increased to 2.8 at the same temperature and pressure, however, the conversion decreased to 28%. The hydrocarbon product showed a lower methane yield of 4.7 wt% and a significant increase in C<sub>10+</sub> and higher molecular weight material, resulting in a Schulz-Flory distribution with a distinct break at C<sub>10</sub>, and a value of  $\alpha = 0.93$  in the C<sub>10+</sub> region, Figure 6 and 7. Therefore the baseline, sintered Fe<sub>2</sub>O<sub>3</sub> catalyst operated in the slurry phase can give a hydrocarbon product that is characterized on a Schulz-Flory distribution plot, either by a single or a dual value of  $\alpha$ , depending on the operating conditions. This type of effect may be due to re-incorporation of less volatile olefins induced by the liquid phase surrounding the catalyst, or be the result of a multi-site catalyst. However, not enough information is presently available to distinguish between these and other possibilities.

During the baseline tests, the space velocity and stir speed were varied as a function of temperature. With CO/H<sub>2</sub> > 1 and T  $\geq$  280°C, evidence was obtained of a significant mass transfer limitation of the observed overall conversion. A model of the stirred reactor system utilizing the baseline results is currently being derived to incorporate this. Initial results indicate that the mass transfer limitations in the slurry reactor system are comparable to

to those predicted by standard two-phase stirred reactor correlations. Utilizing the model it has been possible to deconvolute the mass transfer and kinetic resistances, and obtain activation energies and kinetic parameters. The kinetic activation energy was determined to be 108.4 kJ/mol, in good agreement with the value obtained by W. D. Deckwer in his analysis of the published results from bubble column-slurry reactors<sup>3</sup>. The rate constant is also in agreement with that derived by Deckwer from Schlesinger's data<sup>4</sup>.

c) Modified Conventional Catalysts

Several slurry tests have produced evidence that the limitations on Fischer-Tropsch product selectivity imposed by the Schulz-Flory distribution can be overcome, and these represent stages in the development of a selective diesel fuel catalyst. The results obtained from one test of catalyst A, using 1:1 CO/H<sub>2</sub> syngas, are illustrated in Figure 8, which indicates a buildup of product around the C<sub>10</sub> region. This is also illustrated in the hydrocarbon Schulz-Flory distribution, Figure 9, which further shows how the product selectivity is a function of operating conditions such as temperature and space velocity. The positive gradient observed in Figure 9 is impossible for a standard Schulz-Flory distribution, since  $\log \alpha \leq 0$ . In terms of hydrocarbon fractions, the product contained 30.4 wt% C<sub>1</sub>-C<sub>4</sub>, 41.3 wt% C<sub>5</sub>-C<sub>11</sub>, and 50.8 wt% C<sub>9</sub>-C<sub>22</sub>. For the same yield of methane (9.5 wt%), a standard Schulz-Flory distribution would produce 47.3, 44.2 and 20.0 wt% respectively.

A very selective product distribution was obtained from a slurry test of another catalyst, B, and is illustrated in Figure 10. The distribution was essentially bi-modal with 25 wt% CH<sub>4</sub>, and 64 wt% C<sub>10</sub>-C<sub>25</sub>, but the catalyst was relatively inactive, and conversions were low.

Results such as this indicate that product selectivity can be enhanced in the diesel fuel range, and work is continuing towards controlling selectivity while increasing catalyst activity.

d) Supported Metal Cluster Catalysts

The extensive gas phase screening of supported metal cluster catalysts for Fischer-Tropsch synthesis carried out under the contract, has produced many examples of modification of the type of product by support metal interactions. It has also been possible to carry over these effects into slurry phase operation and obtain high activity. Two examples of slurry phase tests of this type of catalyst are illustrated in Figures 11 and 12. With catalyst C, it was possible to produce a non-Schulz-Flory product distribution with a molecular weight cutoff at around C<sub>28</sub> by variation of operating parameters such as CO/H<sub>2</sub> ratio and pressure. Catalyst D produced a similar product cutoff, but maintained 40-50 wt% 1-alkene in the hydrocarbon product, irrespective of the process conditions that were used.

SLURRY REACTOR MODELLING

a) Status

Table 3 shows the current status of this portion of the contract. Two cold flow models have been utilized; a 5' x 5" Plexiglas<sup>®</sup> column and a 15' x 32" glass column. The range of dependent and independent variables studied in the 5" column was described previously<sup>5</sup>, and the study is nearly finished with gas holdup and solids dispersion measurements complete.

Another modification to the contract was obtained during the year to measure directly gas bubble diameters in three phase systems using a hot wire anemometer probe. This study will provide information about the influence of three phase operation on gas/liquid interfacial area, which is expected to be a critical factor in optimizing space time yield and conversion.

b) Gas Holdup

Two of the correlations derived from gas holdup studies in the 5" column are listed in Table 4 for the isoparaffin/silica and isoparaffin/iron oxide systems. The ranges of particle size utilized were 1-5  $\mu\text{m}$ , 45-53  $\mu\text{m}$  and 90-106  $\mu\text{m}$ , while the superficial gas and liquid velocities were varied from

0.05-0.5 ft/sec and 0-0.1 ft/sec respectively. The correlations show that gas holdup is a function of superficial gas velocity, but essentially independent of net slurry velocity. Gas holdup does, however, depend on solid particle size and slurry loading.

Gas holdup as a function of superficial gas velocity is illustrated in Figure 13 for a 1-5  $\mu\text{m}$  silica/isoparaffin slurry, together with standard literature correlations for comparison <sup>6-8</sup>. As the loading of the slurry was increased, gas holdup at a particular superficial gas velocity decreased.

c) Solids Dispersion

General results and conclusions from the measurements of solids dispersion in the 5" column are listed in Table 5. Non-uniform dispersions of solid in the column were commonly observed for particles > 50  $\mu\text{m}$ . The degree of suspension of particles was more dependent on superficial liquid velocity than on superficial gas velocity, as might be expected from the higher kinetic energy of the denser phase. However, an anomalous result was observed with hydrocarbon slurries of 100  $\mu\text{m}$  particles, where the dispersion of iron oxide was found to be more uniform than the less dense silica.

The non-uniformity of the dispersion of 100  $\mu\text{m}$  silica/isoparaffin at zero superficial liquid velocity is illustrated in Figure 14, where solid weight fraction is plotted as a function of column height. A comparison of the nominal slurry loading with the weight fraction determined at various positions in the column indicates that much of the solid was undispersed 3" above the distributor plate at low gas velocities. Silica is much more easily dispersed in water than in isoparaffin, and requires a longer time to settle in water after agitation is stopped. This illustrates the importance in cold flow modelling of using materials that resemble the real reactor not only in physical properties such as density, velocity, surface tension etc, but also in chemical type because of solid/liquid interaction effects.

d) 12" x 15' Column

The 12" column (figure 15) has been constructed and is currently in a shakedown phase. The column is made of 5' x 12" glass process pipe sections, and is situated in a continuously ventilated Plexiglas<sup>®</sup> hood to prevent



potential hazards due to use of hydrocarbon based slurries. Access and sampling points are available between the flanges of the process pipe as illustrated.

The range of dependent and independent variables to be measured in the 12" cold flow model are listed in Table 6. In addition to those studied in the 5" column, the dependent variables include bubble diameter and heat transfer coefficients. As already mentioned bubble diameter will be measured directly. Variations in the perforated distributor plate hole size will be made as shown in Table 6, and heat transfer coefficients will be measured in the three phase slurry with two types of heat transfer internals; seven symmetrically arranged, plain and finned vertical tubes. The finned tube configuration may help to stabilize bubble dispersion, facilitating reactor scaleup.

## CONCLUSIONS

- a) Baseline slurry phase tests utilizing an ammonia synthesis catalyst have verified the slurry reactor design and operation, indicated standard Schulz-Flory hydrocarbon product distributions for  $\text{CO}/\text{H}_2 \leq 1.4$ , and served as the basis for a preliminary reactor model. Significant mass transfer limitation of conversion was observed at  $T \geq 280^\circ\text{C}$ .
- b) Slurry phase tests of "modified conventional" Fischer-Tropsch catalysts have shown that it is possible to overcome the limitations on the yield of fuel product fractions, previously thought to be imposed by the standard Schulz-Flory distribution. Work is in progress to maximize the activity of selective catalysts for the production of diesel fuel range hydrocarbons.
- c) Gas phase screening tests of supported metal cluster catalysts have shown that metal-support interactions can alter the product type. Slurry phase tests of selected, supported metal cluster catalysts have indicated the maintenance of activity, and confirmed the variation of product selectivity.

The potential exists therefore to design catalysts incorporating both product type and carbon number selectivity.

- d) Cold flow modelling studies have indicated a decrease in gas holdup with decreasing particle size and increasing slurry solids loading, and non-uniform solids dispersions for particle size  $\geq 50 \mu\text{m}$ , under conditions that would be utilized with internal heat transfer.
- e) The slurry phase Fischer-Tropsch reactor is ideally suited for producing enhanced yields of material in the  $C_{10}$ - $C_{20}$  range without encountering conditions, such as plugging due to wax buildup, that would inhibit the use of a fixed bed or gas entrained solid reactor. High product yields in this range can be successfully accommodated without any interruption in operation and with the use of CO rich syngas. Any higher molecular weight product buildup that does occur can be controlled by the withdrawal of a small side stream directly from the reactor.

#### REFERENCES

1. P. N. Dyer, R. Pierantozzi, B. W. Brian and J. V. Bauer, Quarterly Technical Progress Reports 1-7, US DOE PC/30021, 1980-82.
2. J. V. Bauer and P. N. Dyer, Chemical Engineering Progress, 1982, 78 (9), 51.
3. W. D. Deckwer, Y. Serpeman, M. Ralek and B. Schmidt, Chem. Eng. Sci., 1981, 36, 765.
4. M. Schlesinger, H. Benson, E. Murphy and H. Storch, Ind. Eng. Chem., 1954, 46, 1322.
5. P. N. Dyer, R. Pierantozzi, B. W. Brian, J. V. Bauer, Proceedings of the DOE Contractor's Conference on Indirect Liquefaction, Pittsburgh, PA, May 1981.
6. Akita, K. and F. Yoshida, Ind. Eng. Chem. Proc. Des. Dev., 1973, 12, 76.
7. Hikita, H., and Kikukawa, Chem. Eng. J., 1973, 81, 74.
8. Pilhofer, T. H., Bach, H. F., and Mangartz, K. H., ACS Symp. Ser., 1978, 65, 372.

TABLE 1

## SLURRY CATALYST TESTING — STATUS

- SLURRY REACTOR SYSTEMS
  - 3 OPERATIONAL
  - 21 DAY CONTINUOUS OPERATION
  - C, H MATERIAL BALANCES
- CONVENTIONAL CATALYSTS
  - 2 BASELINE/MASS TRANSFER TESTS
  - 4 SLURRY TESTS
  - CONTRACT MODIFICATION FOR PARAMETRIC GAS PHASE SCREENING
- SUPPORTED CLUSTER CATALYSTS
  - 46 GAS PHASE SCREENING TESTS
  - 12 SLURRY TESTS

TABLE 2

# SLURRY TEST — BASELINE $\text{Fe}_2\text{O}_3$

• CONDITIONS

CO/ $\text{H}_2$  RATIO

: 0.5, 1.4, 2.8

T°C

: 220 - 300

P PSIG

: 450

GHSV  $\text{h}^{-1}$

: 145 - 300

STIR SPEED RPM

: 800 - 1600

SLURRY WT%

: 14.7, 19.3

• RESULTS

— STANDARD SF DISTRIBUTION EXCEPT FOR  
CO/ $\text{H}_2$  = 2.8

— LOW  $\text{CH}_4$  AT CO/ $\text{H}_2 \geq 1$

— ACTIVITY  $\sim 27$  MOL SYNGAS/KG CAT./H

—  $\text{H}_2$  MASS TRANSFER LIMITATIONS FOR  $T \geq 280^\circ\text{C}$ ,  
CO/ $\text{H}_2 \geq 1$

— EQUAL FEED AND USAGE RATIOS AT  $280^\circ\text{C}$  FOR  
CO/ $\text{H}_2 = 1.4$

## SLURRY REACTOR MODELLING STATUS

- 5" COLUMN
  - GAS HOLDUP AND SOLID DISPERSION: COMPLETE
  - LIQUID DISPERSION AND MASS TRANSFER: NEAR COMPLETION
- 12" COLUMN
  - CONSTRUCTED AND IN SHAKEDOWN PHASE
  - CONTRACT MODIFICATION FOR BUBBLE DIAMETER MEASUREMENT IN THREE PHASE SLURRY

TABLE 4

## GAS HOLDUP CORRELATIONS

### ISOPARAFFIN — SILICA SYSTEM

$R^2 = 0.94$

$$E_G / (1 - E_G)^4 = 1.70 V_G^{1.01} D_P^{0.12} / W_S^{0.27} \rho_{SL}^{0.28}$$

### ISOPARAFFIN — IRON OXIDE SYSTEM

$R^2 = 0.85$

$$E_G / (1 - E_G)^4 = 1.09 V_G^{0.98} D_P^{0.076}$$

WHERE,

$E_G$  = GAS HOLDUP,

$D_P$  = PARTICLE DIAMETER,

$V_G$  = GAS VELOCITY,

$\rho_{SL}$  =  $W_S(\rho_S - \rho_L) + \rho_L$ , SLURRY DENSITY,

$W_S$  = SOLIDS WEIGHT FRACTION IN  
SLURRY

VOL%

$\mu\text{M}$

FT/SEC

LBM/FT

TABLE 5

## SOLID DISPERSION

### • RESULTS

- NON-UNIFORM DISPERSION FOR  $>50 \mu\text{M}$  SIZE
- SUSPENSION MORE DEPENDENT ON  $V_L$  THAN  $V_G$
- $100 \mu\text{M Fe}_3\text{O}_4$  ( $\rho = 5.2$ ) MORE UNIFORM THAN  $\text{SiO}_2$  ( $\rho = 2.6$ )

### • CONCLUSIONS

- $\leq 50 \mu\text{M}$  SIZE FOR  $V_L = 0$  (INTERNAL HEAT TRANSFER)
- $100 \mu\text{M}$  SUSPENSION AT  $0.05 \leq V_L \leq 0.1$  DEPENDS ON SOLID/LIQUID INTERACTION

TABLE 6

# SLURRY REACTOR MODELLING 12" COLUMN

• DEPENDENT VARIABLES

GAS HOLD-UP  
SOLIDS DISPERSION  
BUBBLE DIAMETER

MASS TRANSFER  
LIQUID DISPERSION  
HEAT TRANSFER

• INDEPENDENT VARIABLES

SLURRY MEDIUM  
SUPERFICIAL GAS VELOCITY  
SUPERFICIAL LIQUID VELOCITY  
SOLID  
SOLID SIZE  
SOLID CONCENTRATION  
HEAT TRANSFER INTERNAL TUBES  
DISTRIBUTOR HOLE SIZE

: PARAFFIN, WATER  
: 0.05 — 0.5 FT/SEC  
: 0 — 0.015 FT/SEC  
: SILICA, IRON OXIDE  
: 1-5  $\mu$ M, 45-53  $\mu$ M, 90-106  $\mu$ M  
: 0 — 30 WT%  
: NONE, PLAIN, FINNED  
: 0.035, 0.125, 0.5 INCH



FIGURE 1

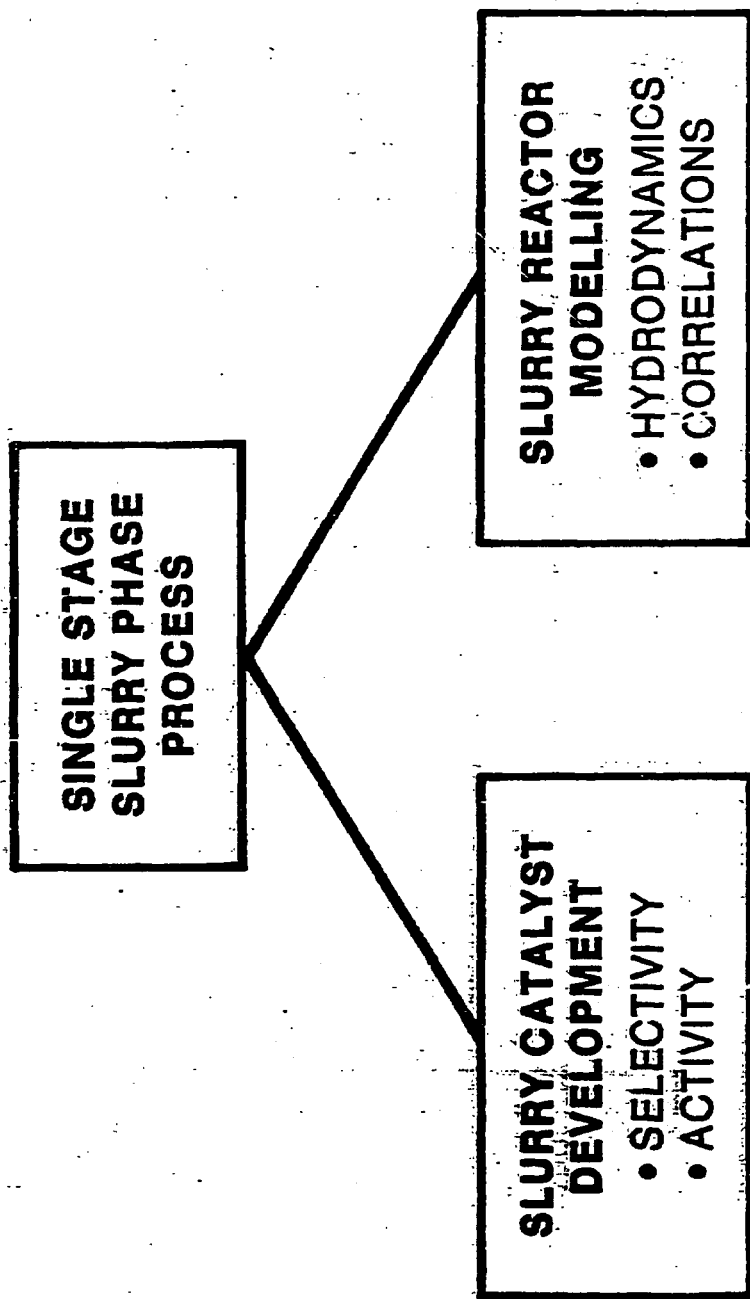


FIGURE 2

# FISCHER-TROPSCH SLURRY REACTOR

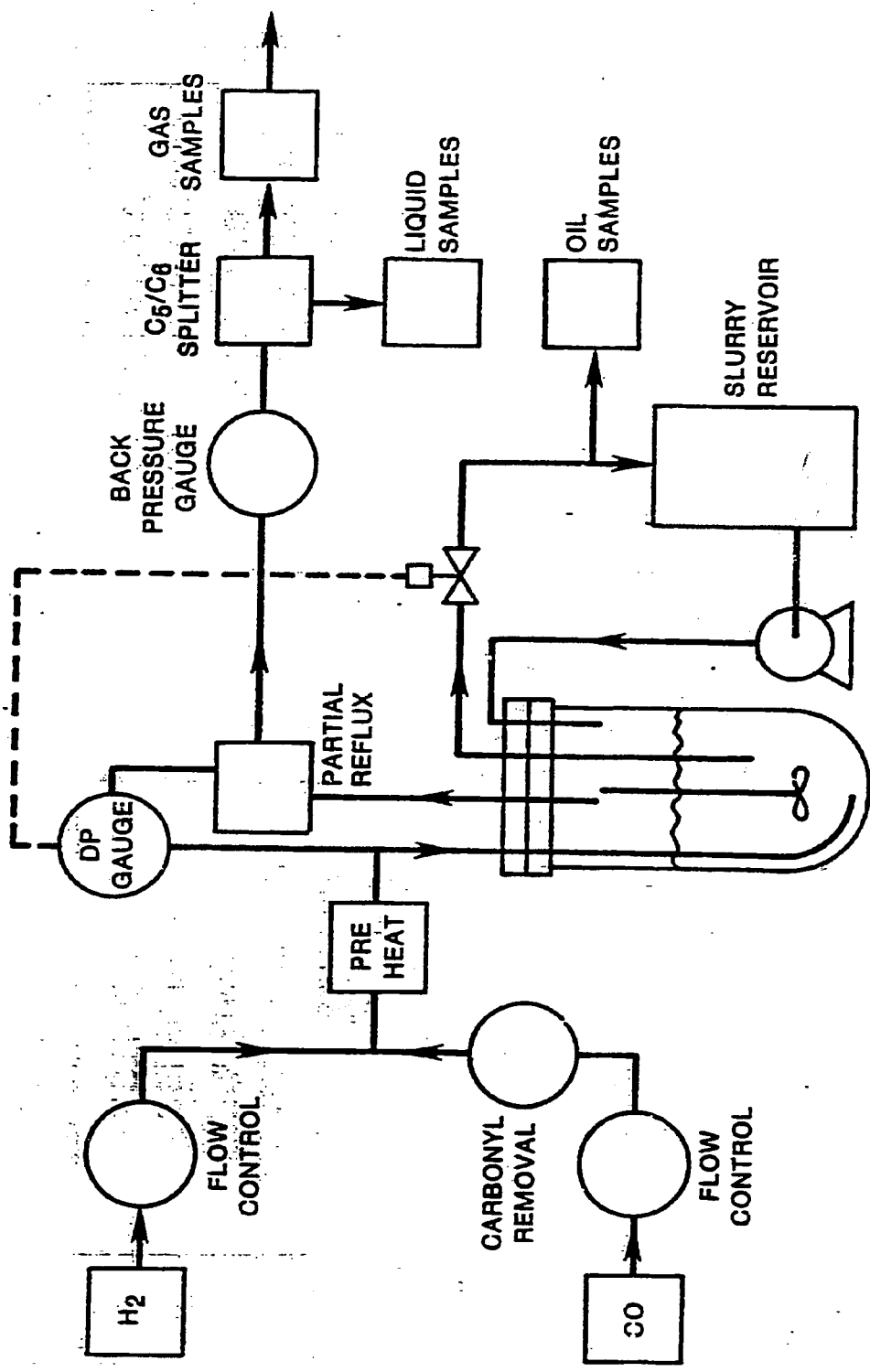


FIGURE 3

# HYDROCARBON WEIGHT DISTRIBUTION $Fe_2O_3$

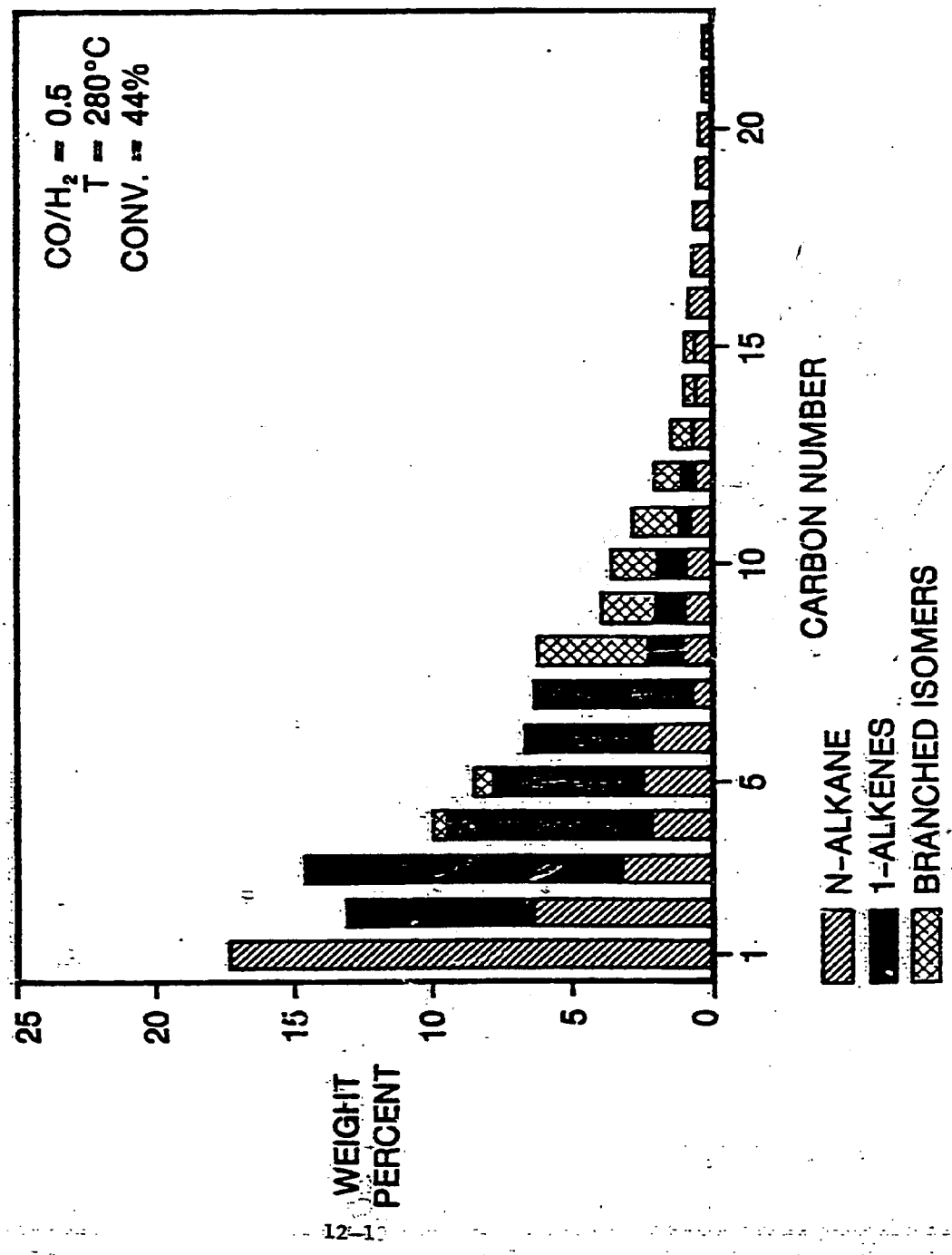


FIGURE 4

# HYDROCARBON SCHULZ-FLORY DISTRIBUTION

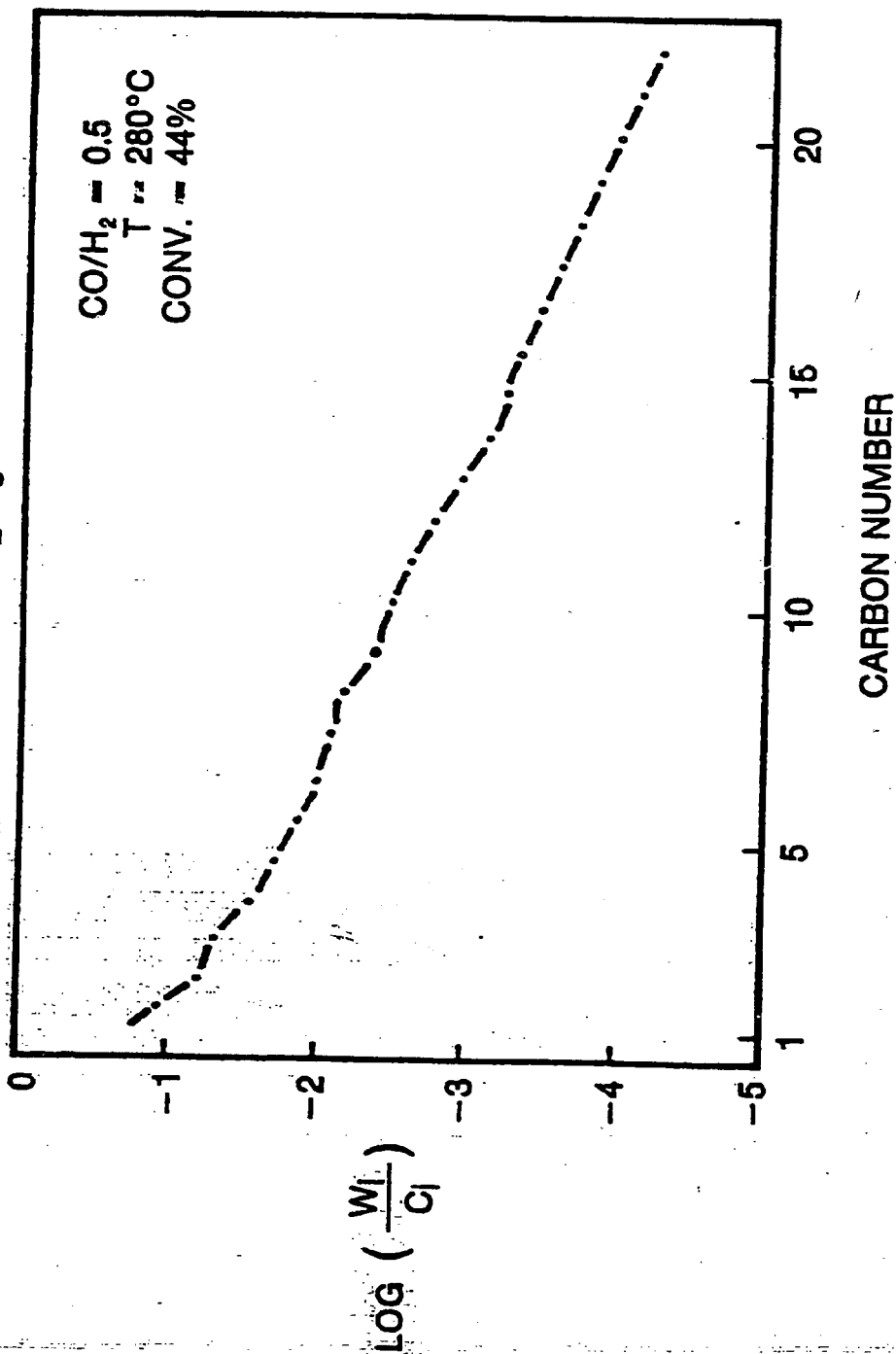
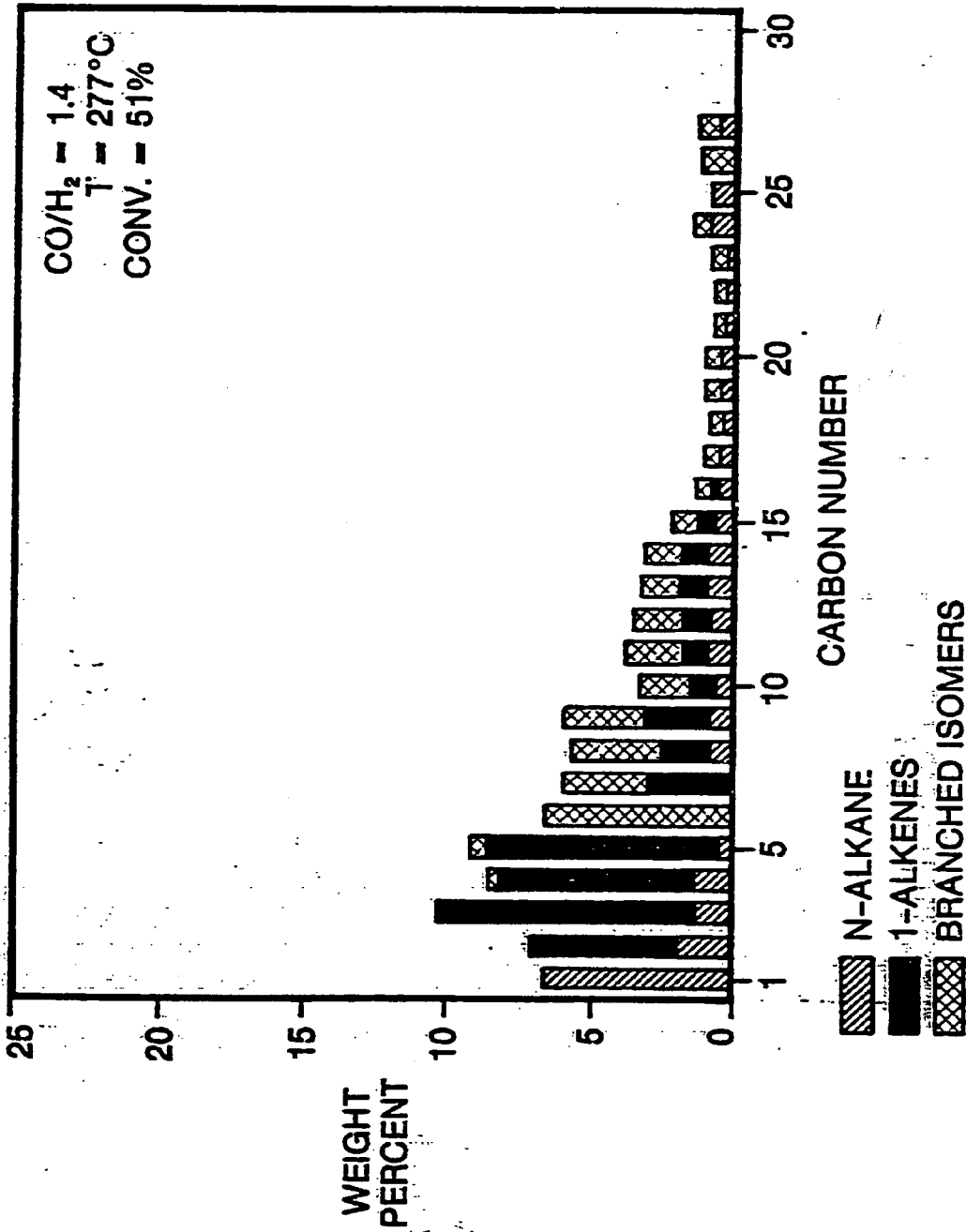


FIGURE 5

# HYDROCARBON WEIGHT DISTRIBUTION $\text{Fe}_2\text{O}_3$



**FIGURE 6**  
**HYDROCARBON WEIGHT DISTRIBUTION**  
**Fe<sub>2</sub>O<sub>3</sub>**

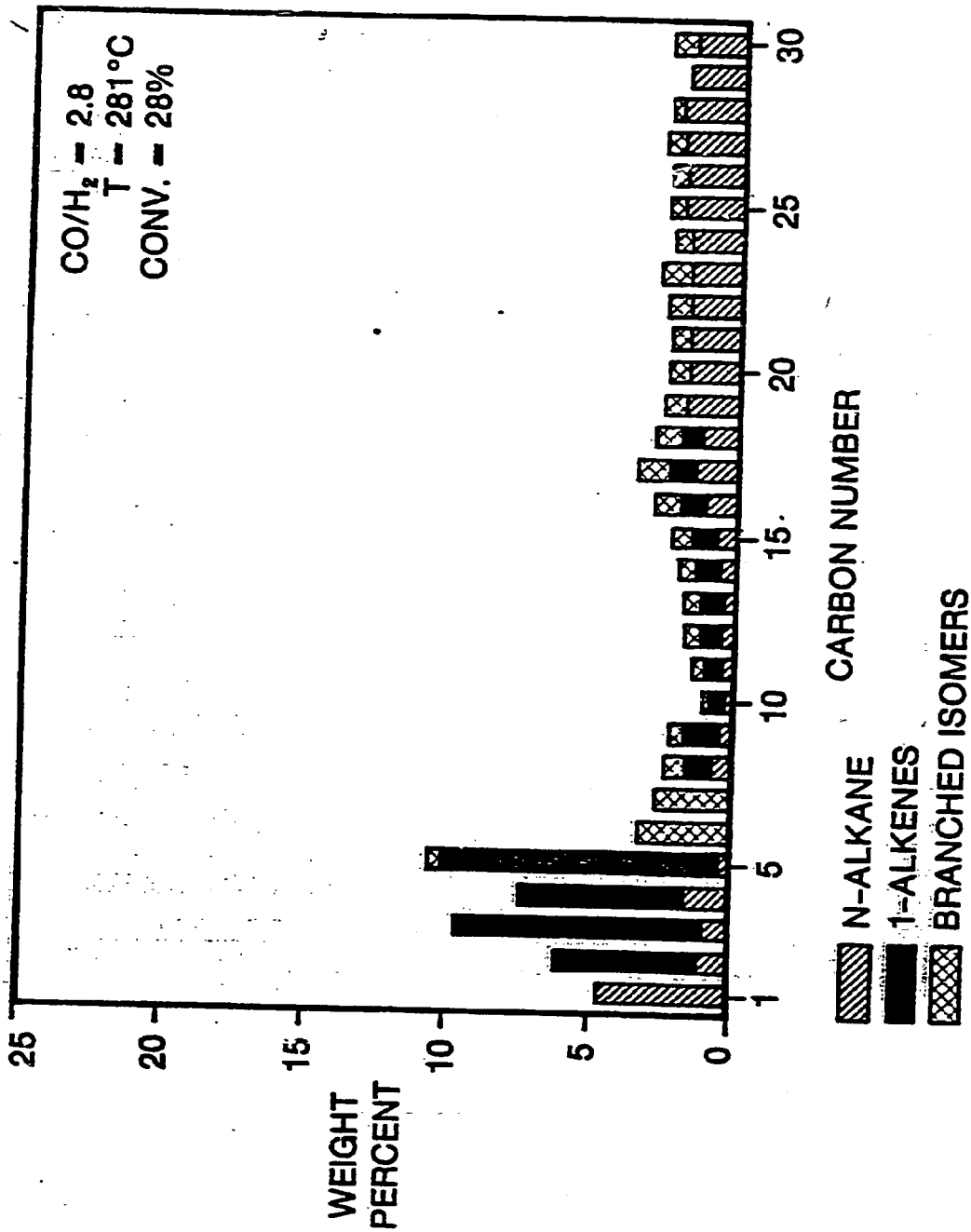


FIGURE 7  
HYDROCARBON SCHULZ-FLORY  
DISTRIBUTION  
 $\text{Fe}_2\text{O}_3$

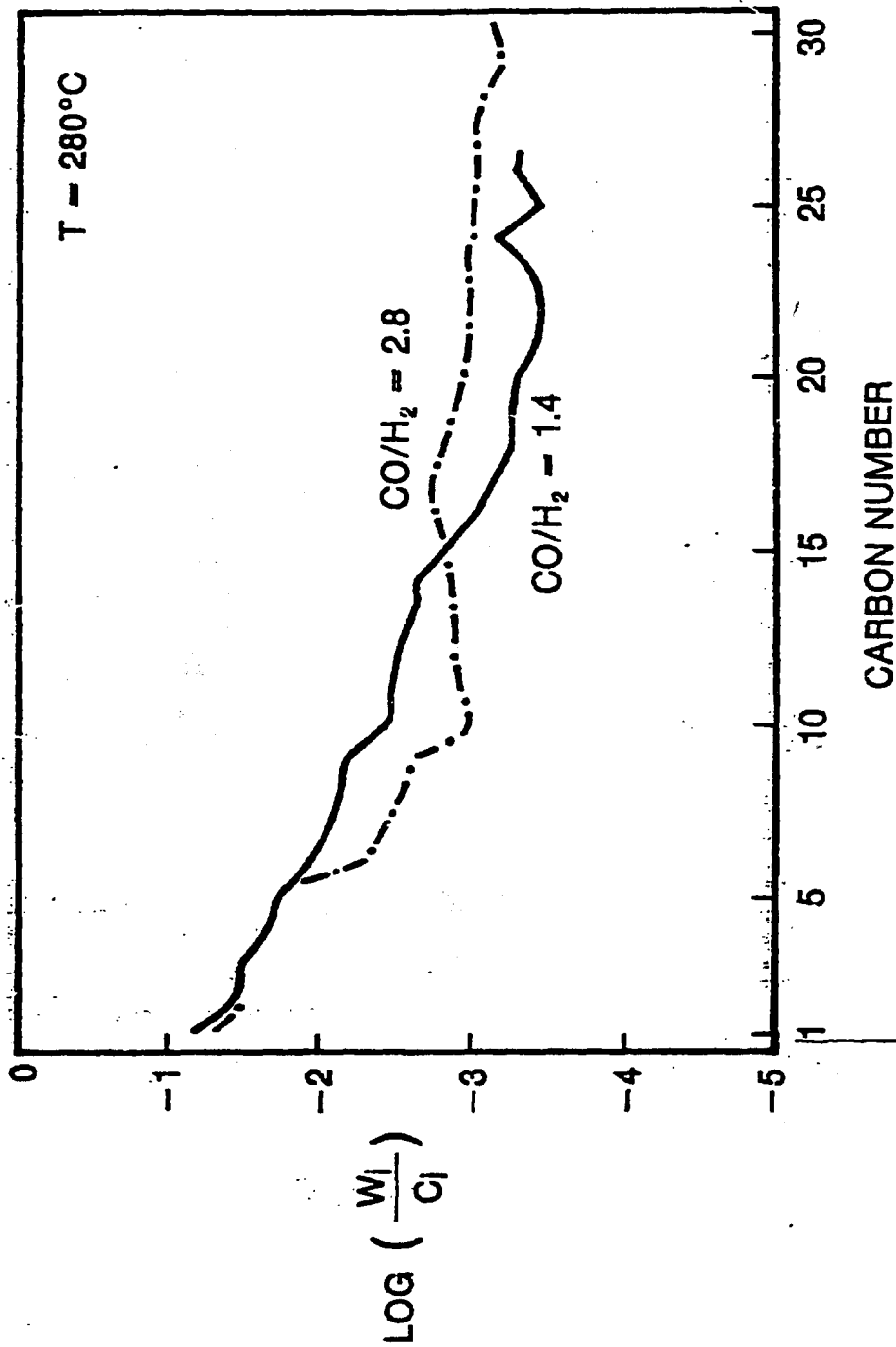


FIGURE 8

# HYDROCARBON WEIGHT DISTRIBUTION CATALYST A

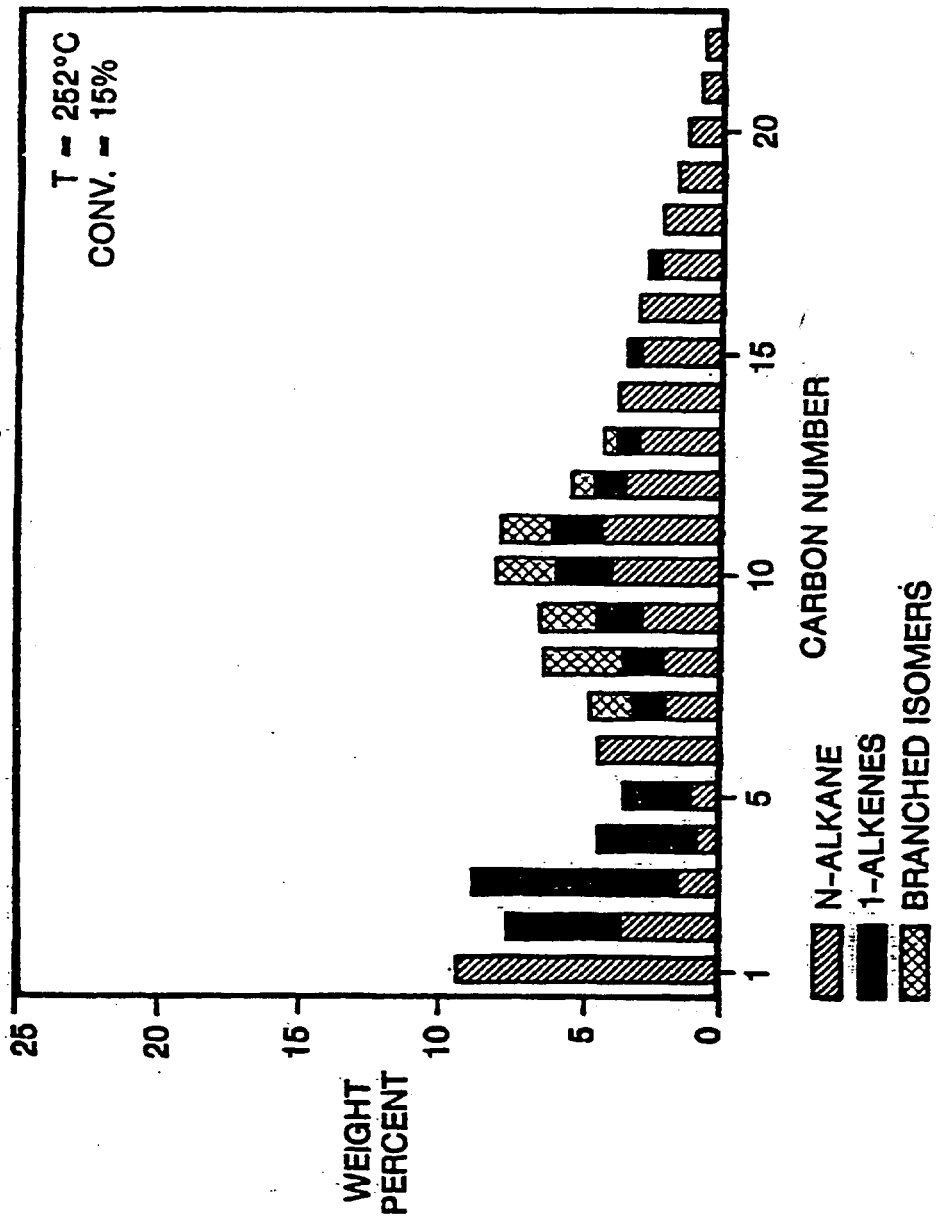




FIGURE 9  
**HYDROCARBON SCHULZ-FLORY  
DISTRIBUTION  
CATALYST A**

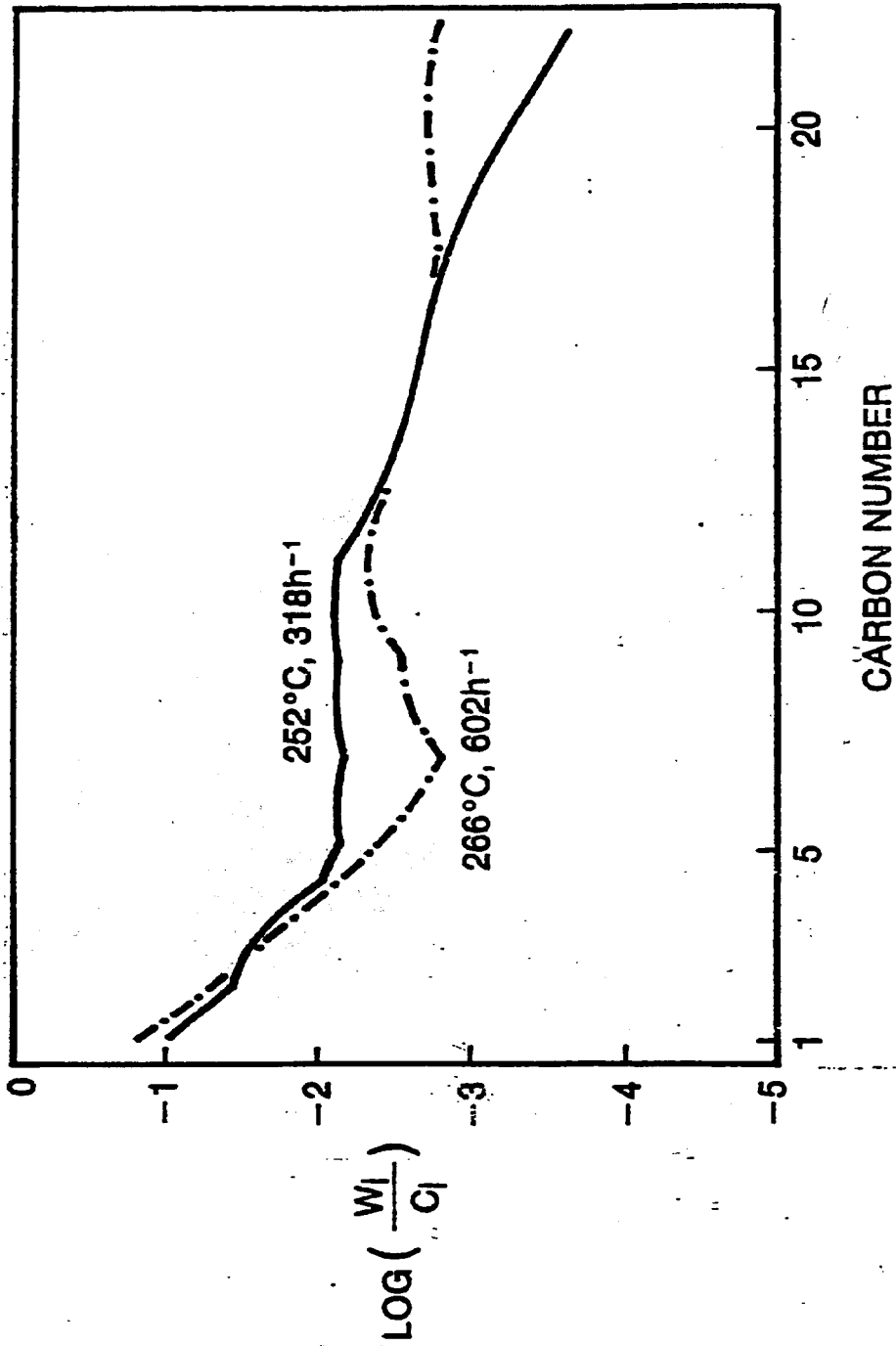


FIGURE 10

# HYDROCARBON WEIGHT DISTRIBUTION CATALYST B

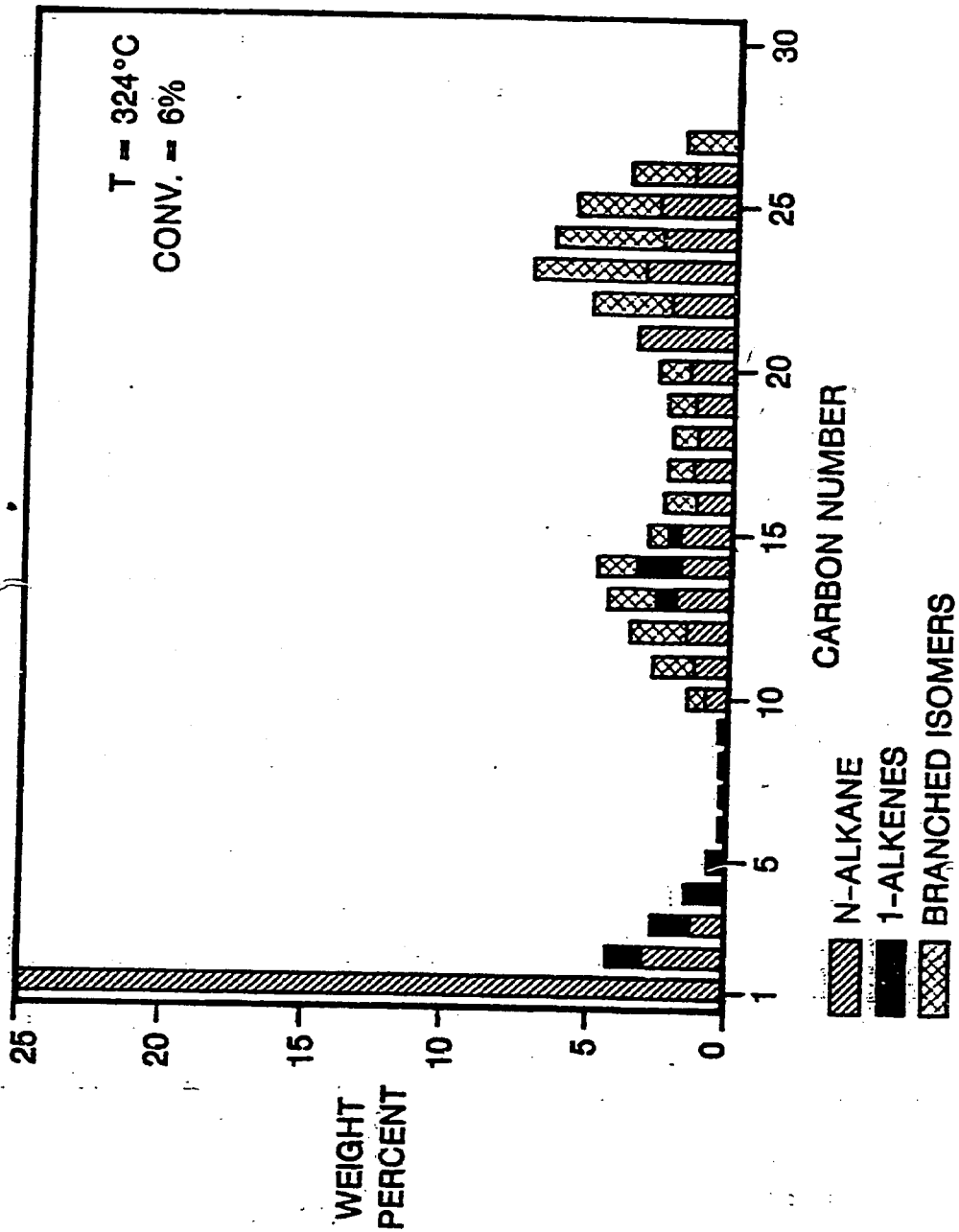


FIGURE 11

# HYDROCARBON WEIGHT DISTRIBUTION CATALYST C

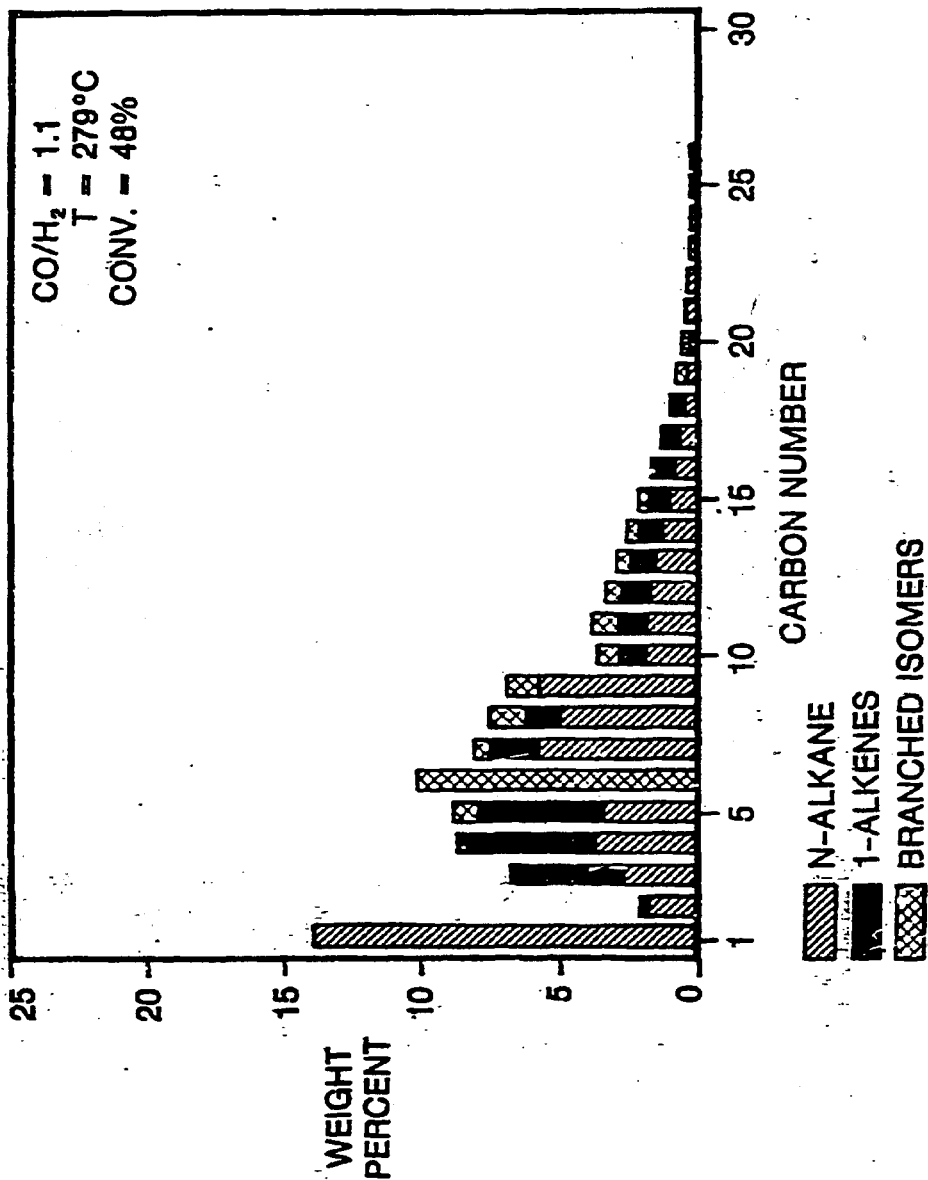


FIGURE 12

# HYDROCARBON WEIGHT DISTRIBUTION CATALYST D

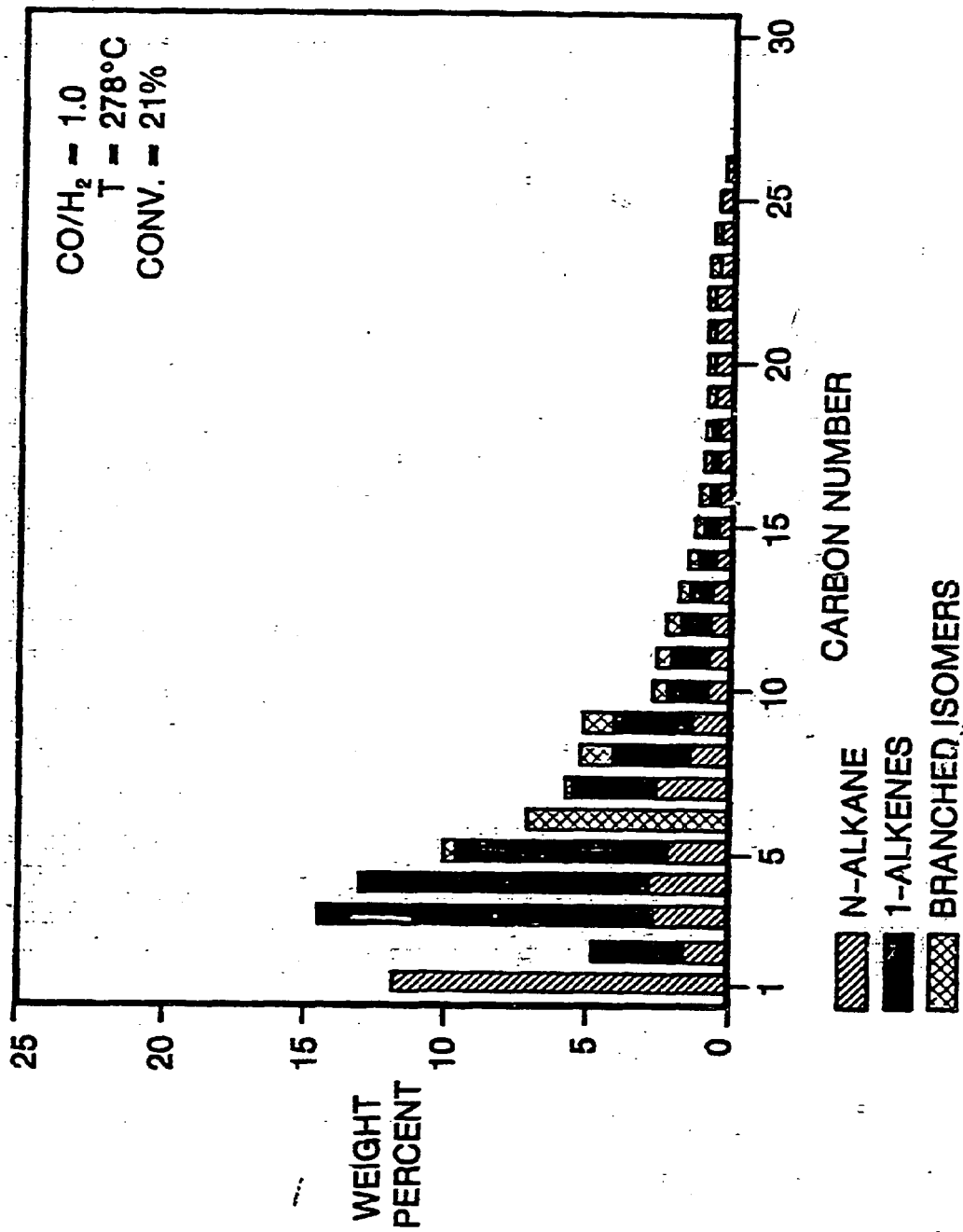


FIGURE 13

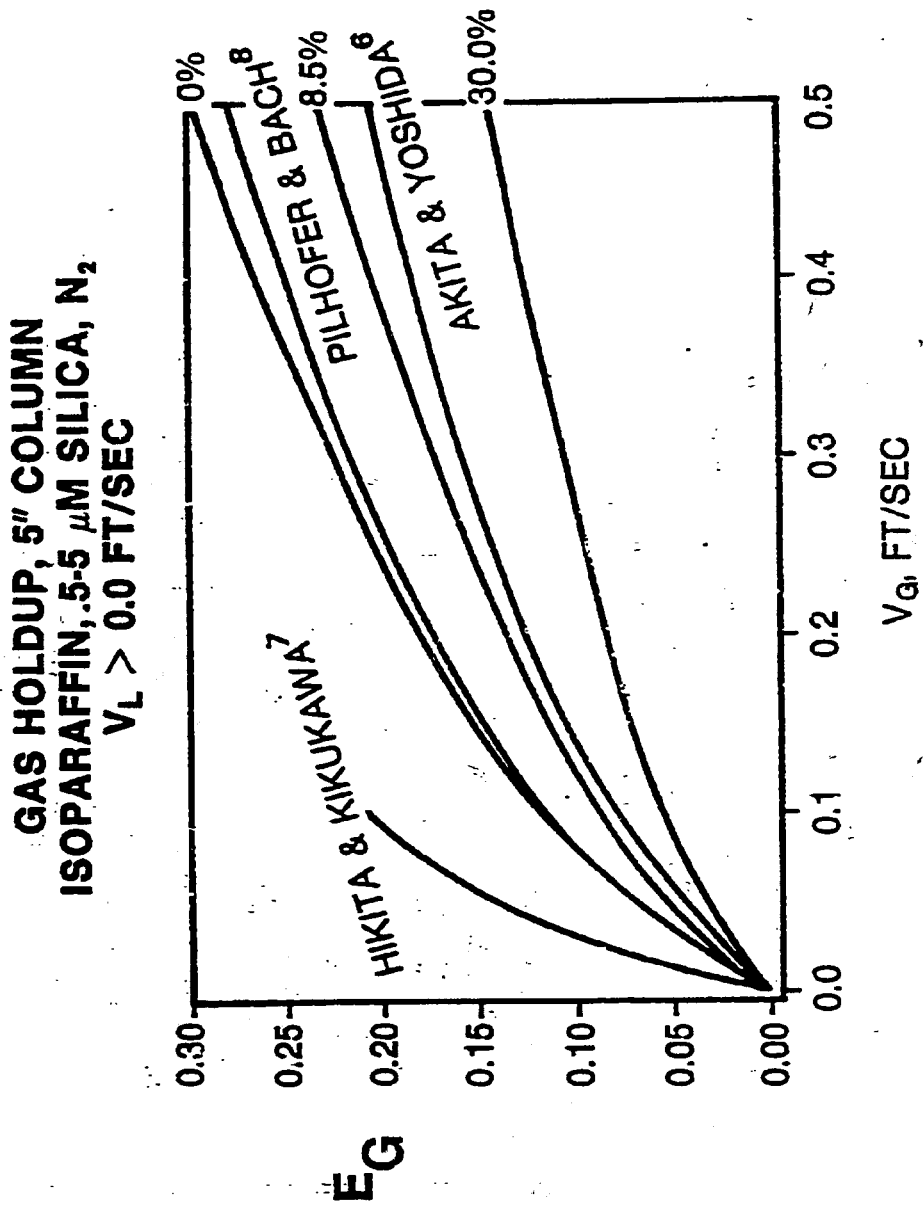
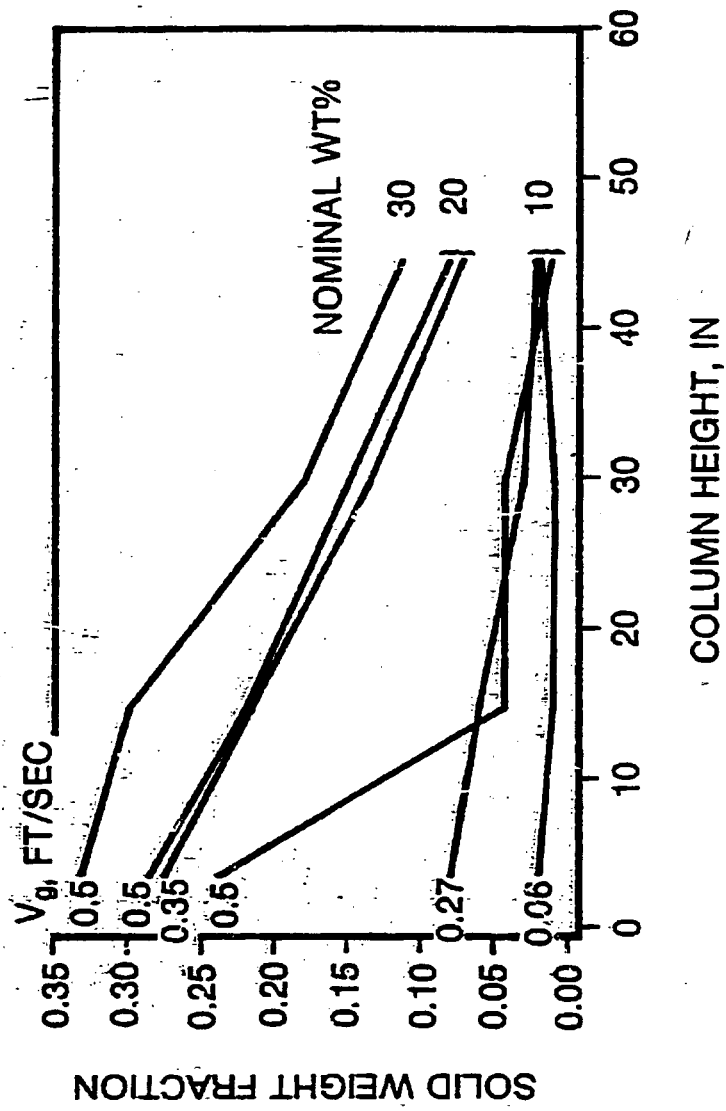


FIGURE 14

**SOLID CONCENTRATION PROFILES, 5" COLUMN  
ISOPARAFFIN, 98-115  $\mu$ M SILICA, N<sub>2</sub>  
V<sub>L</sub> = 0.0 FT/SEC**



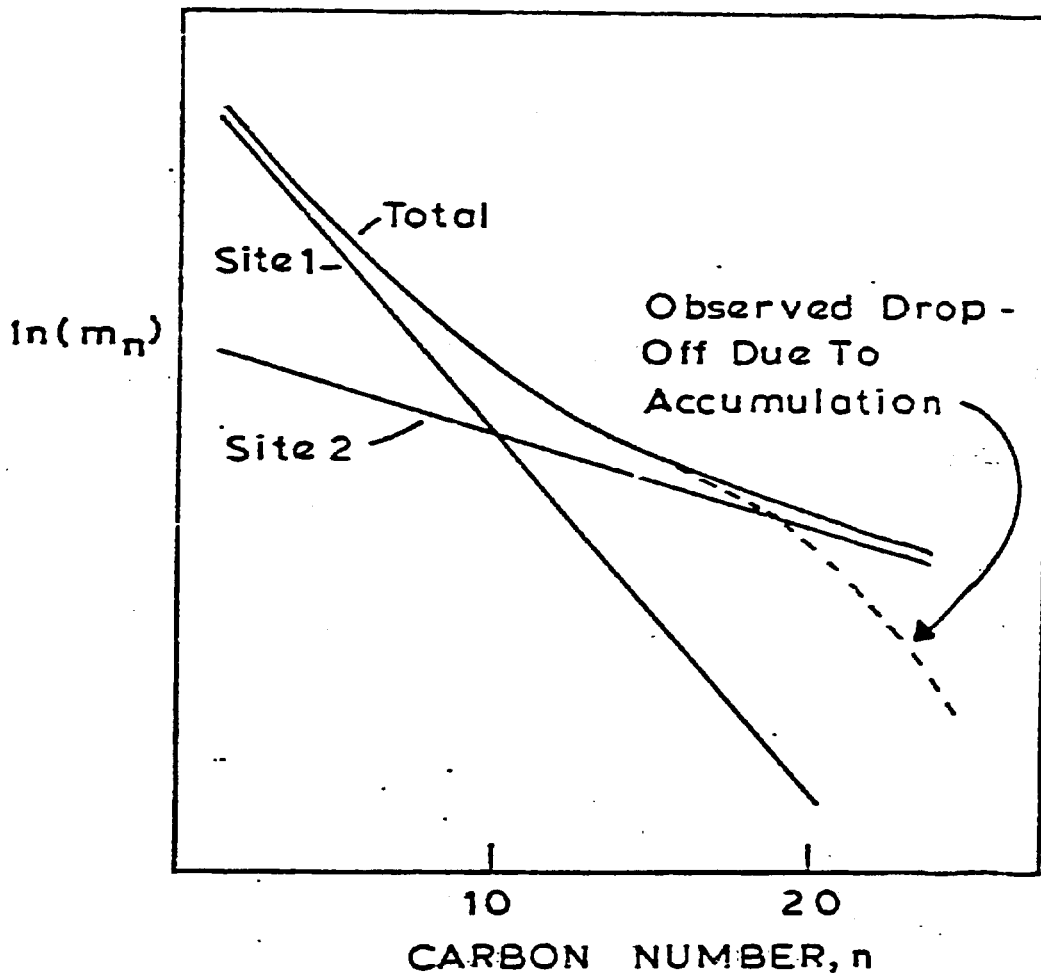


FIGURE 15

### 12" x 15' COLUMN

