Catalyst and Reactor Development for a Liquid Phase Fischer-Tropsch Process

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Indirect Liquefaction Catalyst Development

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1.0 Introduction

1.1 Objectives

Previous studies have pointed out the advantages in thermal efficiency and economics that may be gained by coupling advanced gasifiers, which produce little or no methane and a CO rich syngas, with a slurry phase Fischer-Tropsch (FT) unit such as the one operated by Kolbel at Rheinpreussen (1). The particular advantages of the Kolbel slurry phase FT process are:

- its ability to accept CO rich syngas without external shift,
- high selectivity to liquid fuels, in Kolbel's case gasoline range hydrocarbons, with correspondingly low yields of CH_4 and C_2,
- high single pass conversion, reducing the need for syngas recycle, and
- increased thermal efficiency in removing and recovering the exothermic heat of reaction.

In 1980, Air Products, under contract to the DOE, began an experimental program to investigate the slurry phase FT process. The overall objective was:

- to evaluate catalysts and a slurry reactor system for the selective conversion of syngas into transportation fuels via a single stage, liquid phase process.

Objectives by task were:

- slurry catalyst development - evaluate and test catalysts for their potential to convert syngas to gasoline, diesel fuel, or a mix of transportation fuels, quantifying catalyst activity, selectivity, stability and aging.

- slurry reactor design - evaluate, using cold flow reactor simulators, the flow characteristics and behavior of slurry reactors for the production of hydrocarbons from synthesis gas.

- develop a preliminary design for a bench scale slurry phase FT reactor.

1.2 Baseline Slurry Process

A large amount of R&D work has previously been carried out in the FT process. Early work in fixed bed reactors was reviewed by Storch, Golumbic and Anderson (2), with more recent work on FT synthesis in the slurry phase reviewed by Kolbel and Ralek (3), Poutsma (4), Deckwer (5), and Satterfield and Huff (6). One conclusion from this previous work is that hydrocarbon product selectivities follow a Schulz-Flory distribution, characterized by a chain growth probability factor α. This unselective type of polymerization process is represented by a straight line on a plot of log (W_i/C_i) against C_i, and has significant implications for the maximum yield of transportation fuel product fractions. This is illustrated in Figure 1, and the maximum amounts of gasoline range and diesel range hydrocarbons, 47.6 wt% C_5-C_{11} and 54.1 wt% C_9-C_{25}, are listed in Table 1.

The previous work indicates that FT products adhere to this type of distribution, irrespective of catalyst type. In particular, Satterfield, et al (6) concluded the SF distribution held generally for Fe based catalysts, with values of α ranging from .55 to .94.

Coprecipitated Fe/Cu/K was used as a catalyst by Kolbel and Ralek in the 1.6 meter id x 8.6 meter high pilot plant, three phase bubble column reactor at Rheinpreussen (3), and possibly also in bench scale column experiments (8).

Published data for Kolbel's slurry operations are listed in Table 2, together with typical product distributions obtained from commercial FT units at Sasol.

The Rheinpreussen operation was able to operate with CO rich syngas (CO/H_2 = 1.5), at a high conversion of 89% with no recycle. The contrast is evident in Table 2 between this and the Arge and Synthol reactors at Sasol, which operate with H_2 rich syngas, produced by the dry-ash Lurgi gasifiers, at recycle ratios of 2-2.5.

The space time yield of the Rheinpreussen slurry reactor was lower than that of the gas entrained solid reactor at Sasol, and closer to the lower range of the Arge fixed bed. However, as a Mitre report showed, this was offset by the higher yield of liquid products and avoidence of external shift, leading to an improvement in overall operating efficiency (1).

The operation at Rheinpreussen was geared to maximize the yield of gasoline. Some doubt exists about the overall product analysis, however, since the data reported in Table 2 was stated to be a "sample from large storage tanks which contained the products from one of the longer operating periods" (2). It may not, therefore, fully represent the percentage of light products obtained from the plant, which were removed by oil scrubbing and activated carbon adsorption. With this in mind, a comparison of the product fractions in Tables 1 and 2 indicates that previous slurry phase operations, together with the Sasol reactors, gave products which were again unselective and of the SF limited type.

The Rheinpreussen bubble column was operated at moderate superficial gas velocity rates (0.31 ft/sec), with 89% overall syngas conversion. The rate of deactivation of the catalyst was such that regeneration was necessary after about 666 hours of operation (2). In terms of product selectivity, activity and conversion, and because of the size of the bubble column, Kolbel's operation at Rheinpreussen has generally been accepted as the benchmark for further development of slurry phase FT technology.

2.0 Development of Slurry Catalysts, Selective for Diesel Fuel

2.1 R & D Approach

The strategy utilized to develop selective slurry FT catalysts was:

- Identify potential metal cluster or modified conventional catalysts, from the existing literature and in-house knowledge.
- Optimize activity and selectivity of modified conventional catalysts through a sequence of alternative preparation and activation procedures, using a gas phase fixed bed reactor.
- Screen supported metal cluster catalysts with a fixed bed reactor, using a range of CO/H_2 ratios and other process conditions.
- Use a sintered Fe_2O_3 ammonia synthesis catalyst to determine regimes of operation in the lab CSTR, in which diffusion from the gas to liquid phase was not a rate limiting factor in the overall conversion.
- Test in the slurry phase, for continuous periods up to 21 days, optimized modified conventional catalysts and selected metal cluster catalysts, to determine activity and product selectivity for transportation fuels. Process conditions included syngas ratios from 2:1 to 1:2, concentrating on CO rich mixtures.
- Select a few catalysts showing potential for high conversions to diesel fuel, and test in the slurry phase for extended periods under constant conditions, to determine variations of selectivity and deactivation rates.

- Use a backmixed, stirred reactor model to determine kinetic parameters from slurry tests carried out under non-mass transfer limited conditions, to enable accurate comparison of relative rates.

- Utilize kinetic parameters in a computer model of bubble column operation to predict the conversion and space time yield that would be obtained under a bench-scale bubble column or Rheinpreussen conditions.

Air Products has currently found three promising catalysts for fuel selectivity: a precipitated catalyst, A, and two supported metal cluster catalysts, B and C.

Figure 2 illustrates graphically the product selectivities obtained with these three catalysts, compared with the operation at Rheinpreussen.

The limitations of the Schulz-Flory distribution have been overcome by a combination of catalyst design and operation in the slurry phase under the correct process conditions.

2.2 Experimental

(a) Stirred Slurry Reactors

The continuous, stirred, slurry phase reactor used for the Fischer-Tropsch synthesis is based on either a 300 mL or a 1 liter Autoclave Engineers unit, and is illustrated diagramatically in Figure 3. Inlet CO and H_2 streams are passed through separate oxygen removal and drying stages, and for the CO stream, an additional iron carbonyl removal stage using a heated alumina trap, before being mixed and preheated. Using mass flow controllers, any desired ratio of CO/H_2 can be input to the stirred reactor system. The reactor is fully baffled, and the gas inlet point is directly beneath the six, flat-bladed impeller to maximize gas shear. The reactor operates in a temperature range of 220-330°C, pressures of 1.1 to 3.5 MPa, and space velocities up to a GHSV of 1000 h^{-1}. Products, together with unreacted syngas, are taken overhead through a heated partial reflux condenser, maintained at a top temperature of about 200°C to return vaporized slurry oil to the reactor.

The level of slurry in the reactor is continuously monitored by determining the differential pressure between the gas inlet and outlet streams, so that any buildup of higher molecular weight products that are not removed from the reactor with the exit gas flow can be detected. When this occurs, hydrocarbon product can be removed from the reactor directly via a heated sidestream, filtered through a 5 μm stainless steel sinter, and subjected to analysis. Automatic slurry level control is possible via feedback from the dp gauge, and a pump enables fresh or regenerated slurry catalyst to be recycled back into the reactor. By determining the amount of slurry oil withdrawn to maintain a constant level at a particular set of process conditions, the higher molecular weight hydrocarbons that do not distill with the gas phase product can be quantitatively included in the material balance of the system. This procedure is essential to obtain an overall product selectivity.

The product stream from the partial reflux condenser is led via a heated line to a pressure reduction stage, and thence to a C_5/C_6 splitting column, to produce a condensed liquid phase and a gaseous phase. The gaseous stream consists of unreacted CO/H_2, CO_2 and products with carbon numbers from C_1-C_5. The condensed liquid product consists of hydrocarbons with carbon numbers C_6 and above and an aqueous phase containing dissolved oxygenates. This method of product collection avoids the use of high pressure traps, is more suited to continuous operation, and, by reducing the number of product fractions, is more accurate in obtaining material balances.

The whole system is designed to run continuously and automatically when unattended, with automatic sampling of the split gas phase stream and collection of liquid samples. The results presented in this paper are all obtained during 21 day or longer continuous test periods, to avoid transient or initial phenomena. After any change in process parameters, the reactor system is allowed to equilibrate for 14 to 16 hours before obtaining carbon and hydrogen material balances over an additional 8 hour period.

Because of the complexity of the Fischer-Tropsch product, equilibration of the reactor and the product collection systems, and a flexible quantitative analysis scheme incorporating all products including waxes, are required to produce good carbon and hydrogen material balances and prevent misleading results. This procedure routinely produces material balances for C and H of 99 ±1 to 3%.

(b) Analytical and Data Handling System

Details of the analytical and computerized data handling system have been published (10). The scheme is illustrated diagramatically in Figure 4, and consists of five separate gas chromatographs linked, via a Sigma 10 computing integrator, to a Tektronix 4052 microcomputer equipped with a 1.8 Mbyte disk system.

Unreacted syngas, CO_2, and C_1 to C_5 isomers are analyzed by a Carle 397B process gas chromatograph, while low concentrations of C_6+ in the gas phase product, due to inefficiencies in the C_5/C_6 splitting column, are analyzed by a Carle 111 g.c. with a Porapak QS column. After separation and weighing of the condensed liquid phases, aqueous phase samples are analyzed for C_1-C_6 alcohols, aldehydes, ketones and acids using a 3 mm x 3 m 10% SP1200/1% H_3PO_4 on Chromosorb/WAW column. Samples of the separated organic phases are analyzed for C_5-C_{40} hydrocarbons, and any contribution from the initial slurry oil is subtracted from the analysis.

The analytical data is collected and temporarily stored in the Sigma 10 integrator, before direct transfer to the Tektronix disc system. After compilation into matrix format, the six data files for each sample point are assembled by the computer into an overall product matrix, and weight percent, mole percent and Schulz-Flory distributions, selectivity and conversion fractions, and C and H material balances are calculated. The Tektronix graphics routines provide immediate plots of the hydrocarbon weight and Schulz-Flory product distributions.

The total analysis of the Fischer-Tropsch product routinely provides material balances to within 1-3%.

(c) Catalyst Preparation

With the objective of maximizing selectivity and activity for transportation fuels range hydrocarbons, precipitated, exchanged and supported "conventional" catalysts, and novel, supported molecular cluster catalysts have been prepared and studied in the slurry reactor systems. Coprecipitated catalysts are prepared at constant pH and temperature in a flow-through, tubular, stirred precipitation reactor of the type described by Kolbel (3) and Deckwer (5).

2.3 Sintered Fe_2O_3 - Baseline Slurry Catalyst

Initial slurry tests were made with an ammonia synthesis catalyst, sintered Fe_2O_3 promoted with 2% Al_2O_3, 0.5% K_2O and 0.7% CaO, to provide baseline information. Prior to use, the catalyst was ground to <200 mesh and reduced with H_2 at 1 atm, 450°C and a GHSV of 380 h^{-1} for 72 hours in a gas/solid tubular reactor. The reduced, pyrophoric catalyst was then slurried under N_2 in a deoxygenated C_{25}-C_{35} oil, and contacted with 0.5, 1.4 and 2.8:1 CO/H_2 at ~3.2 MPa, stir speeds of 800-1600 min^{-1}, space velocities of 150-300 h^{-1}, and temperatures of 220-300°C.

Selected results, obtained over a continuous operating period of 311 to 646 hours, are listed in Table 3. Hydrocarbon weight fractions of n-alkanes, 1-alkenes and branched isomers are plotted against carbon number for CO/H_2 ratios of 0.5, 1.4 and 2.8 in Figures 5-7.

The CH_4 yield decreased and the hydrocarbon product moved to increasing molecular weight as the CO/H_2 ratio was increased. At CO/H_2 = 2.8, the CH_4 yield was a low 4.7 wt%, but the catalyst showed a decreased activity. A small trend to higher molecular weight product was also observed with increasing temperature at a constant CO/H_2 ratio. However, as Table 3 indicates, the relative amounts of n-alkanes, 1-alkenes and branched isomers in the total product varied little with temperature for CO rich syngas, and were mainly dependent on the CO/H_2 ratio. The largest 1-alkene content occurred at CO/H_2 = 1.4.

The slurry tests of the baseline sintered Fe_2O_3 catalyst fulfilled three functions. The first was to thoroughly test the analytical and data handling systems. The need to quantitate and analyze all parts of the Fischer-Tropsch product, including heavier molecular weight hydrocarbons that build up in the slurry reactor, in order to obtain good carbon/hydrogen material balances, has already been emphasized.

The second function was to determine the mass transfer limitations of the stirred, three phase test reactor. This function is 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. To study mass transfer effects, space velocity and stir speed were varied as a function of temperature. With $CO/H_2 > 1$, and $T > 280°C$, evidence was observed for significant mass transfer limitation of the observed overall conversion.

Using the baseline results, a totally backmixed stirred reactor model was developed to deconvolute the effects of mass transfer and kinetic resistances and obtain activation energies and kinetic parameters.

The rate constant and activation energy obtained with the Fe_2O_3 baseline catalyst are compared in Table 4 with those derived for similar catalysts in both bubble column and CSTR operation. The agreement between CSTR activation energies is good; the rate constant, however, may have been reduced by sulfur poisoning.

The third function was to provide a baseline selectivity profile for slurry phase operation.Table 3 shows that the values of α obtained from the slurry baseline Fe_2O_3 catalyst are independent of temperature in the range 250-280°C, but depend strongly on the CO/H_2 ratio. In Figure 7, the hydrocarbon product distributions are plotted on a Schulz-Flory basis. For H_2 rich synthesis gas, i.e. $CO/H_2 = 0.5$, the hydrocarbon product very closely follows a straight line Schulz-Flory distribution with a value of $\alpha = 0.71$ over the range C_1-C_{23}. For CO rich syngas with $CO/H_2 = 1.4$, the product distribution still closely approximates a straight line Schulz-Flory distribution, at least up to C_{23}, but with a higher values of $\alpha = 0.78$, reflecting the shift of the overall product to higher molecular weights. However, for the highest CO ratio syngas, $CO/H_2 = 2.8$, the hydrocarbon distribution plotted on a Schulz-Flory basis falls into two distinct regions separated at $\sim C_{10}$, with the C_{10}-C_{30} hydrocarbons following a separate line with a high α value of 0.93.

The phenomenon of two α values for the Schulz-Flory distribution observed with CO rich syngas, may be due to the participation of olefinic products in a secondary polymerization process.

2.4 Catalyst A

A method of preparing and activating Catalyst A has been evolved to produce a FT catalyst that is

o selective for diesel fuel (C_9-C_{25} hydrocarbons), and produces low yields of methane,

o operates with $CO/H_2 = 1.5$, producing nearly equal feed and usage ratios,

o has a low deactivation rate (<6% of initial activity over 800 hours at 240°C and a ~4% over 460 h at 260°C), and

o gives ~3 times the space time yield of diesel fuel under simulated Rheinpreussen conditions.

The catalyst has been tested in a sequence of fixed bed and stirred reactor tests, including an extended slurry test period of up to 1800 h. Typical results are listed in Table 5. Results that have been obtained with this catalyst can be summarized as follows:

o The catalyst is selective for diesel fuel and produces low yields of methane. At 240°C with 1.5 CO/H_2 and a time on stream of 800 hours, methane yields were low (2.6-3.1%), while the C_9-C_{25} product fraction was in the range of 50-55%. The amount of hydrocarbon produced in the range C_{18}-C_{35} was 73% higher than the Schulz-Flory maximum. At 260°C and a time on stream of 350 hours, the methane yield was 4%, with 48% C_9-C_{25}. The C_{18}-C_{35} range contained 42% of the product, 15% higher than the Schulz-Flory maximum. These selectivity profiles are illustrated in Figure 8, while Figure 9 plots them on a log W_i/C_i basis, which clearly shows the deviations from the Schulz-Flory distribution in the range C_9-C_{25}. Results from the standard, sintered Fe_2O_3 catalyst are shown for comparison, at a higher CO partial pressure; conditions which would favor selectivity.

- o Low deactivation rates were measured in extended slurry tests. At 240°C, the activity decreased by less than 6% of its initial value over 800 hours, and at 260°C by approximately 4% over 460 hours. The catalyst operated continuously with $CO/H_2 = 1.5$, producing nearly equal feed and usage ratios.
- o In a simulation of Rheinpreussen conditions, using kinetic constants derived from the CSTR data, at 260°C the catalyst produced approximately 3 times the space time yield of diesel fuel reported by Kolbel.

Without further optimization, these results show that the precipitated Catalyst A, prepared by a procedure developed by Air Products, can produce yields in the fuel range C_9-C_{25} equal to or greater than the Schulz-Flory maximum. Further investigation, utilizing combined slurry phase tests and advanced surface analysis techniques, e.g. ESCA (electron spectroscopy chemical analysis) and SAM (scanning Auger microscopy), will shortly be underway to characterize the surface of catalyst samples, correlate surface composition with activity and selectivity, and maximize the selectivity in the C_9-C_{25} region.

2.5 Catalyst B

A supported metal cluster catalyst has been developed which is:

- o <u>the most selective for diesel fuel</u> (C_9-C_{25} hydrocarbons) of any catalyst that has been reported to date,

- produces a high selectivity for diesel fuel with $CO/H_2 = 2.0$ (as produced by a Shell-Koppers gasifier),

- has a low deactivation rate, and

- shows a high activity.

In the slurry phase test of this catalyst, the product selectivity was again observed to depend on the CO partial pressure. Typical results are listed in Table 5.

- When the CO/H_2 ratio was increased from .97 to 1.98, at 300 psi and 250°C, the selectivity for diesel fuel increased dramatically to 67.3 wt% C_9-C_{25}.

- Simultaneously, the yield of CH_4 was reduced to 6.5%, while $C_{26}+$ remained low at 5.4%.

- The catalyst shows a high activity, and a low deactivation rate, under constant process conditions. However, the activity for the water-gas shift reaction is low.

The enhancement of product selectivity in the C_9-C_{25} region by an increase in the CO/H_2 ratio, coupled with a product cut-off above the $C_{26}+$ region, is illustrated in the carbon number distribution plots in Figure 10. On a log W_i/C_i diagram, Figure 11, the deviation from a straight line SF distribution can be observed as a function of CO/H_2 ratio. This figure also includes the sintered Fe_2O_3 catalyst for comparison at a higher CO partial pressure, where selectivity to higher hydrocarbons is favored.

These results show again that it is possible to overcome the SF limitations of product selectivity. Using novel supports and catalysts of this type, selectivity can be tailored to the diesel fuel range.

2.6 Catalyst C

The supported Catalyst C also showed a CO pressure dependent product selectivity - Figures 12 and 13.

- An increase in CO partial pressure by increasing the operating pressure and the CO/H_2 ratio gave good selectivity to a mixed fuel range, and also decreased the yield of CH_4, e.g. 14-11% CH_4, 51% C_5-C_{11}, 32% C_9-C_{25}, 0.2% C_{26}+.
- A product cut-off at ~C_{28} was observed - the slurry showed very little accumulation of higher hydrocarbons.
- High activity (but a low water-gas shift activity) was observed. The catalyst was stable and did not deactivate, provided a critical temperature in the slurry phase was not exceeded.

3.0 Simulation of Bubble Column Operation

Using the backmixed, stirred reactor model, it was determined that the slurry tests were subject to minimal diffusion limitations from gas to liquid mass transfer. It was therefore possible to determine kinetic parameters from the tests, and these are listed in Table 6 for Catalysts A, B and C.

The activation energies are in good agreement with the baseline Fe_2O_3. Although the Rheinpreussen catalyst's rate constant is apparently higher, the value derived by Deckwer from Kolbel's data is very dependent on the assumptions made in Deckwer's model of the column hydrodynamics.

The kinetic parameters were then utilized in a computer model of the three phase bubble column, to predict conversion and space time yield in a bench scale column and one the size of Rheinpreussen, under both the quiescent and churn turbulent regimes. The results are listed in Tables 7 for a 4" x 30' bench scale unit, operated in the quiescent regime, and in Table 8 for the 1.5 m x 8 m Rheinpreussen column, operated in the churn turbulent regime.

- At 0.1 ft/sec (the quiescent regime), the predicted conversions are similar and high (>93% for the bench scale column). Space time yields are also similar under these conditions. Under these conditions, the Air Products catalysts compare favorably with Kolbel's catalyst and other published data.

- At 0.3 ft/sec (the churn turbulent regime, in which Rheinpreussen operated), differences in conversion between catalysts can be observed. Higher space time yields are also evident.

- The space time yield of the current Catalyst B is limited by a lack of water gas shift activity, and therefore by H_2 consumption. For comparison, the Tables contain the conversions that are predicted if water gas shift activity can be built into this catalyst.

- The differences in kinetic constants in Table 6 are reproduced under Rheinpreussen operating conditions by lower predicted conversion for Air Products' catalysts than observed by Kolbel. An achievable increase in activity by a factor of ~2 would give higher conversions than Kolbel's.

The space time yields predicted under Rheinpreussen operating conditions were then compared with the product selectivities determined in the lab CSTR tests, to predict the space time yields of fuel fractions. These are illustrated in Figure 14.

- Without further increase in catalyst activities, the space time yield of diesel fuel product under Rheinpreussen conditions is predicted to be 3-5 times higher than that observed by Kolbel.

4.0 Slurry Catalyst Development Conclusions

- The diesel fuel selectivity of catalysts developed in this work approaches or exceeds the SF maximum. Greater yields have been measured than at Rheinpreussen.

- High CO partial pressure generally increases the diesel fuel selectivity. Therefore, the slurry phase reaction system is particularly well suited to maximize the yield of liquid fuels obtainable from CO rich syngas.

- The slurry reactor is able to produce continuously in this region, without plugging or increased pressure drop.

- CO rich syngas can be continuously accepted by the slurry reactor.

- Syngas feed and usage ratios were near equal for $CO/H_2 = 1.5$ with catalysts exhibiting water gas shift activity.

- Deactivation rates are lower than those reported at Rheinpreussen.

- An increase in catalyst activity by ~2 is required to exceed the conversion reported at Rheinpreussen.

- Currently, 3-5 times the diesel space time yield is predicted in a simulated Rheinpreussen operation than was observed by Kolbel.

- It is important in any further work to be able either to access in a bubble column, or model and predict accurately on the computer, the flow regime that maximized space time yields, i.e. the churn turbulent regime at ~0.3 ft/sec as used at Rheinpreussen. This implies a diameter >4" for modelling or operating purposes.

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TABLE 1

SCHULZ-FLORY PRODUCT FRACTIONS

	α	C_1 wt%	C_5-C_{11} wt%	C_9-C_{25} wt%	C_{26}+ wt%
Schulz-Flory Maxima					
gasoline range	0.76	5.8	47.6	31.8	0.7
diesel range	0.88	1.4	31.9	54.1	12.9

TABLE 2

A COMPARISON OF COMMERCIAL SASOL AND PRIOR SLURRY PHASE FISCHER-TROPSCH DATA

Reaction	Sasol(7, 9) Arge fixed bed	 Synthol gas entrained solid	Rheinpreussen(3, 8) slurry 1.6 id x 8.6 m	Kolbel Bench Scale Slurry(8) Low MW	 Medium MW	 High MW
CO/H_2	0.6	0.5	1.5	1.5		
T °C	220-250	320	268	268		
P MPa	2.6	2.0	1.2	1.1		
Conversion %	70	85	89	88		
Recycle	2.5	2	0	0		
Space Time Yield kg/m^3/h	50-70	90	41	32		
C_1 wt%	5	10	† 6.8 ($C_1 + C_2$)	6.3 ($C_1 + C_2$)		
Approx. Gasoline Range Wt%	22	39 (C_5-C_{12})	53.6 (40-180°C)	68.1	40.0	7.1 (C_5 - 190°C) *
Approx. Diesel Range Wt%	21	6 (C_{13}-C_{21})	10-12 (180-320°C)	13.3	44.0	41.2 (190-450°C)
Higher Hydrocarbons Wt%	35	5 (C_{22}+)	1.9 (>320°C)	0.6	9.1	49.5 (>450°C)

† Storage tank sample

* Wt% of C_3+ products

TABLE 3

THE DEPENDENCE OF α AND PRODUCT TYPE ON CO/H_2 RATIO

SLURRY PHASE, BASELINE Fe_2O_3 †

Slurry conc. wt%	P MPa	T °C	CO/H_2	Conv. mol %	α	Wt% of Hydrocarbon			Oxygenates mol % of product
						n-alkanes	1-alkenes	branched isomers	
19.3	3.34	260	0.5	30.4	0.72	46.1	34.4	19.5	0.2
19.3	3.31	280	0.5	43.4	0.71	41.6	46.4	12.1	0.1
14.7	3.17	248	1.4	24.7	0.78	25.4	50.1	24.5	7.1
14.7	3.14	277	1.4	50.8	0.78	24.9	49.0	26.1	1.2
14.7	3.17	251	2.8	9.0	0.70, 0.93*	40.7	40.5	19.1	2.2
14.7	3.10	281	2.8	27.7	0.70, 0.93*	40.0	44.2	15.8	2.8

* For $>C_{10}$ hydrocarbons

† Mean material balance for tabulated data: $\begin{cases} C & 98.9 \pm 1.5\% \\ H & 98.6 \pm 2.1\% \end{cases}$

TABLE 4

	k_o (260°C) sec^{-1} $wt\%^{-1}$	E_{act} kJ/mol
APCI Fe_2O_3 Slurry (Stirred Reactor)	1.4×10^{-3}	108.4
Deckwer's Analysis(12) of Fe_2O_3 Slurry (Bubble Column)	4.0×10^{-3}	81
Satterfield & Huff's(13) Analysis of Fe_2O_3 Slurry (Stirred Reactor)	6.1×10^{-3}	100

TABLE 5

SUMMARY OF SELECTED SLURRY PHASE, FISCHER-TROPSCH RESULTS

Catalyst	P MPa	T °C	GHSV h^{-1}	CO/H_2	Activity mol syngas/ kg/h	Selectivity wt%			
						C_1	C_5-C_{11}	C_9-C_{25}	C_{26}^+
Fe_2O_3 (baseline)	3.31	280	250	0.5	26.2	17.4	37.6	17.3	0.1
	3.17	248	146	1.4	10.2	7.4	39.9	30.3	1.7
	3.14	277	145	1.4	20.8	6.8	41.1	36.2	2.7
	3.10	281	183	2.8	14.3	4.7	23.8	39.9	12.7
A	2.11	239	298	1.6	15.7	3.1	9.5	55.4	29.4
	2.11	260	295	1.6	31.2	4.3	22.4	48.1	20.0
B	2.07	247	325	1.0	44.9	10.7	38.8	44.7	7.8
	2.08	250	348	2.0	30.6	6.5	28.9	67.3	5.4

TABLE 6

KINETIC PARAMETERS

	k_o [10^{-3} sec^{-1} wt% (catalytic metal)$^{-1}$]				E_{act}
	240°C	250°C	260°C	268°C	kJ/mol
Rheinpreussen(5)				(19.0)†	70
Baseline Fe_2O_3		0.93	1.42	2.28	108.4
Catalyst A	2.03	3.14	4.68	6.50	94.7
Catalyst B		22.1			
Catalyst C		28.2		52.8	82.0

†depends on column hydrodynamic assumptions

TABLE 7

BENCH SCALE COLUMN SIMULATION

Regime	Quiescent			
Catalyst	Base	A	B	B with shift
Inlet gas velocity, cm/sec	3.44	3.44	3.44	3.44
Gas holdup	0.108	0.129	0.156	0.128
Interfacial area, cm^2/cm^3	9.18	10.94	13.26	10.85
Temperature, °C	260.2	260.3	260.4	260.3
Rate Constants:				
Pre-exponential factor (sec wt% in slurry)	1.12×10^5	9.03×10^6	1.15×10^7	1.15×10^7
Activation energy, kJ/mol	70	94.7	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98	1.98
[illegible] ratio, mol CO/mol H_2	1.5	1.5	0.65	1.98
Hydrogen conversion, %	100.0	92.7	97.8	93.7
Rel. mass transfer resistance	0.623	0.236	0339	0.239
Space time yield, mol CH_2/hm^3	2137	1982	1158	2005
<u>Constants in Case Study</u>				
Reactor length, ft (cm)	30 (914)	→	→	→
Reactor diameter, in (cm)	4 (10.1)	→	→	→
Contraction factor	-0.5	→	→	→
Particle diameter, µm	10	→	→	→
Reactor pressure, psig (bar)	300 (21)	→	→	→
Weight fraction catalyst in slurry	0.2	→	→	→
Specific heat transfer area, cm^2/cm^3	0.1	→	→	→

TABLE 8

RHEINPREUSSEN SIMULATION

Regime	Churn Turbulent			
Catalyst	Base*	A	B	B with shift
Inlet gas velocity, cm/sec	9.0	9.0	9.0	9.0
Gas holdup	0.385	0.149	0.171	0.146
Interfacial area, cm^2/cm^3	32.66	36.06	41.43	35.39
Temperature, °C	260.2	260.4	260.4	261.1
Rate Constants:				
Pre-exponential factor (sec wt% in slurry)	1.12×10^5	9.03×10^6	1.15×10^7	1.15×10^7
Activation energy, kJ/mol	70	94.7	94.7	94.7
Inlet ratio, mol CO/mol H_2	1.5	1.5	1.98	1.98
Usage ratio, mol CO/mol H_2	1.5	1.5	0.65	1.98
Hydrogen conversion, %	80.4	55.9	62.9	58.5
Rel. mass transfer resistance	0.106	0.043	0.069	0.048
Space time yield, mol CH_2/hm^3	2937	2042	1273	2135
Constants in Case Study				
Reactor length, ft (cm)	26.3 (800)	→	→	→
Reactor diameter, in (cm)	59 (150)	→	→	→
Contraction factor	-0.5	→	→	→
Particle diameter, μm	50	→	→	→
Reactor pressure, psig (bar)	174 (12)	→	→	→
Weight fraction catalyst in slurry	0.20	→	→	→
Specific heat transfer area, cm^2/cm^3	0.10	→	→	→

* Operating conditions at Rheinpreussen

+ Cold flow model gas holdup correlation

FIGURE 1

VARIATION OF HYDROCARBON FRACTION WITH α: Schulz-Flory Distribution

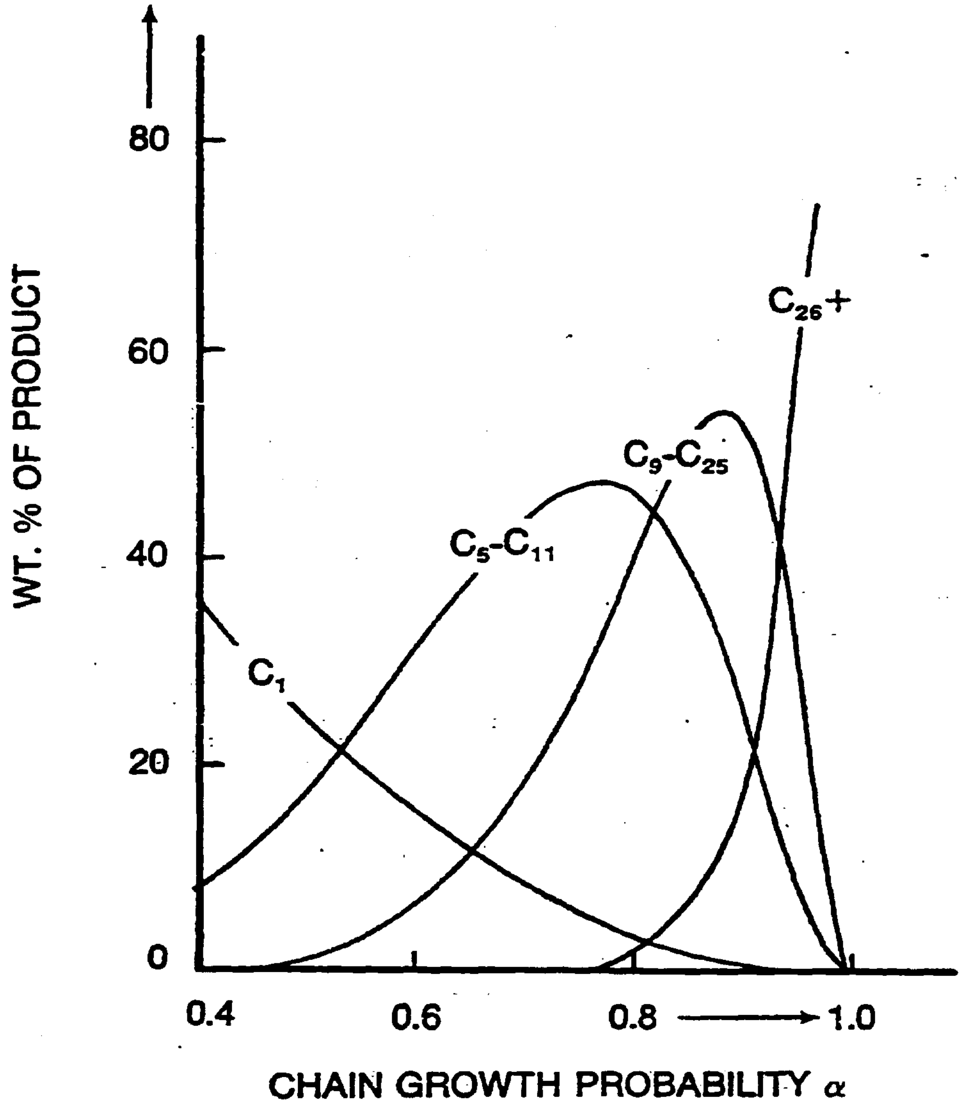


FIGURE 2

SELECTIVITY TO FUEL FRACTIONS

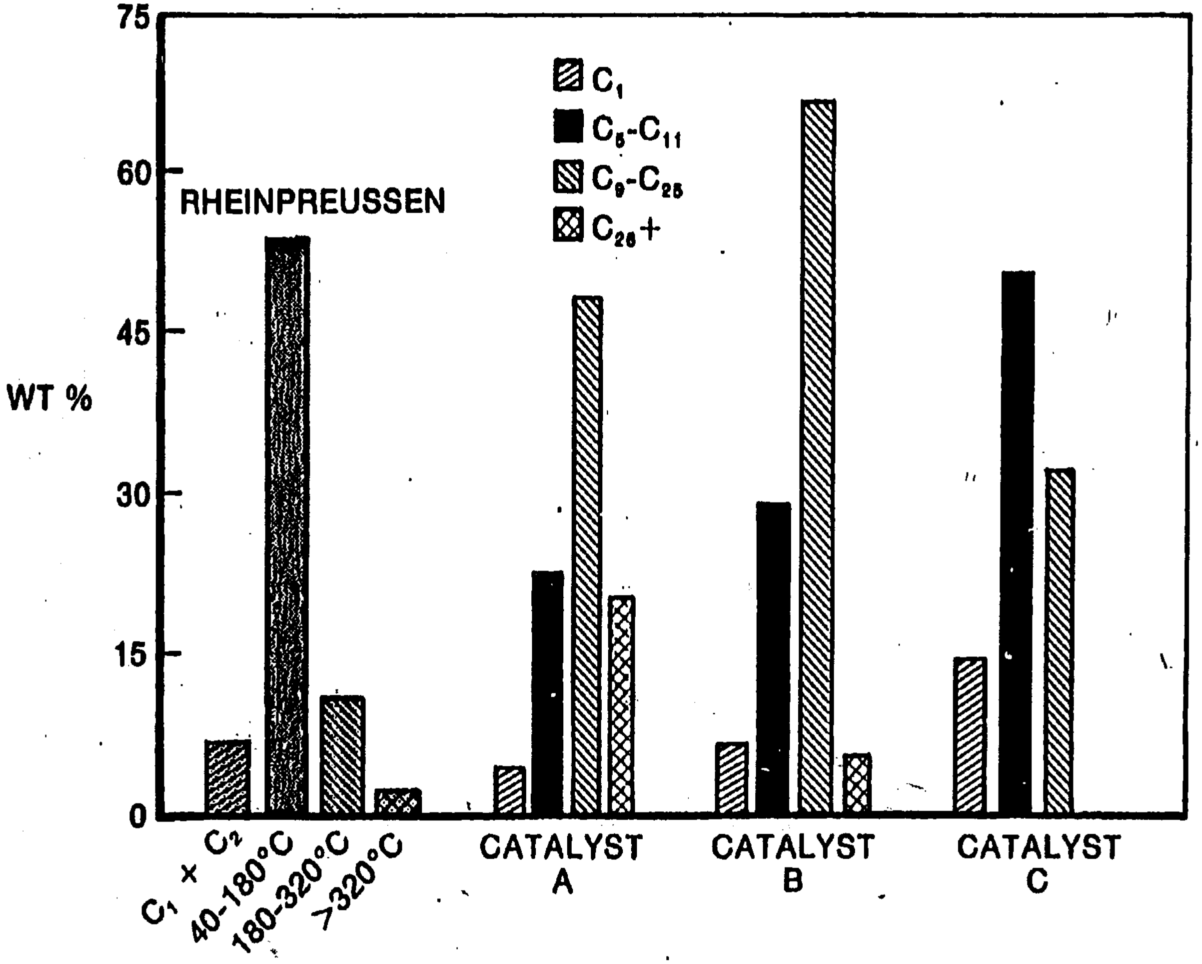


Figure 3

CONTINUOUS, AUTOMATED FISCHER-TROPSCH SLURRY REACTOR

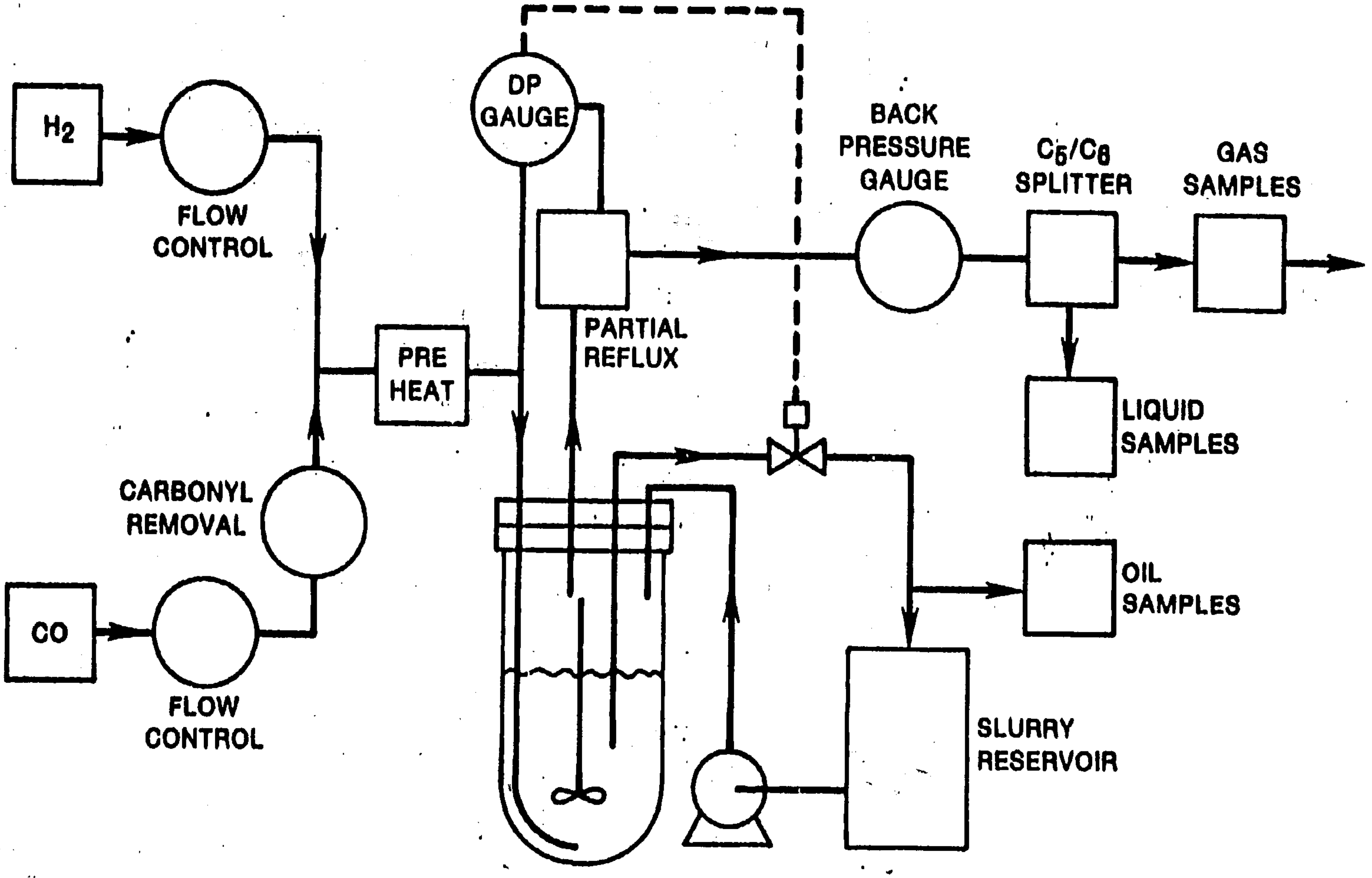


Figure 4

PRODUCT ANALYSIS AND DATA ACQUISITION SCHEME

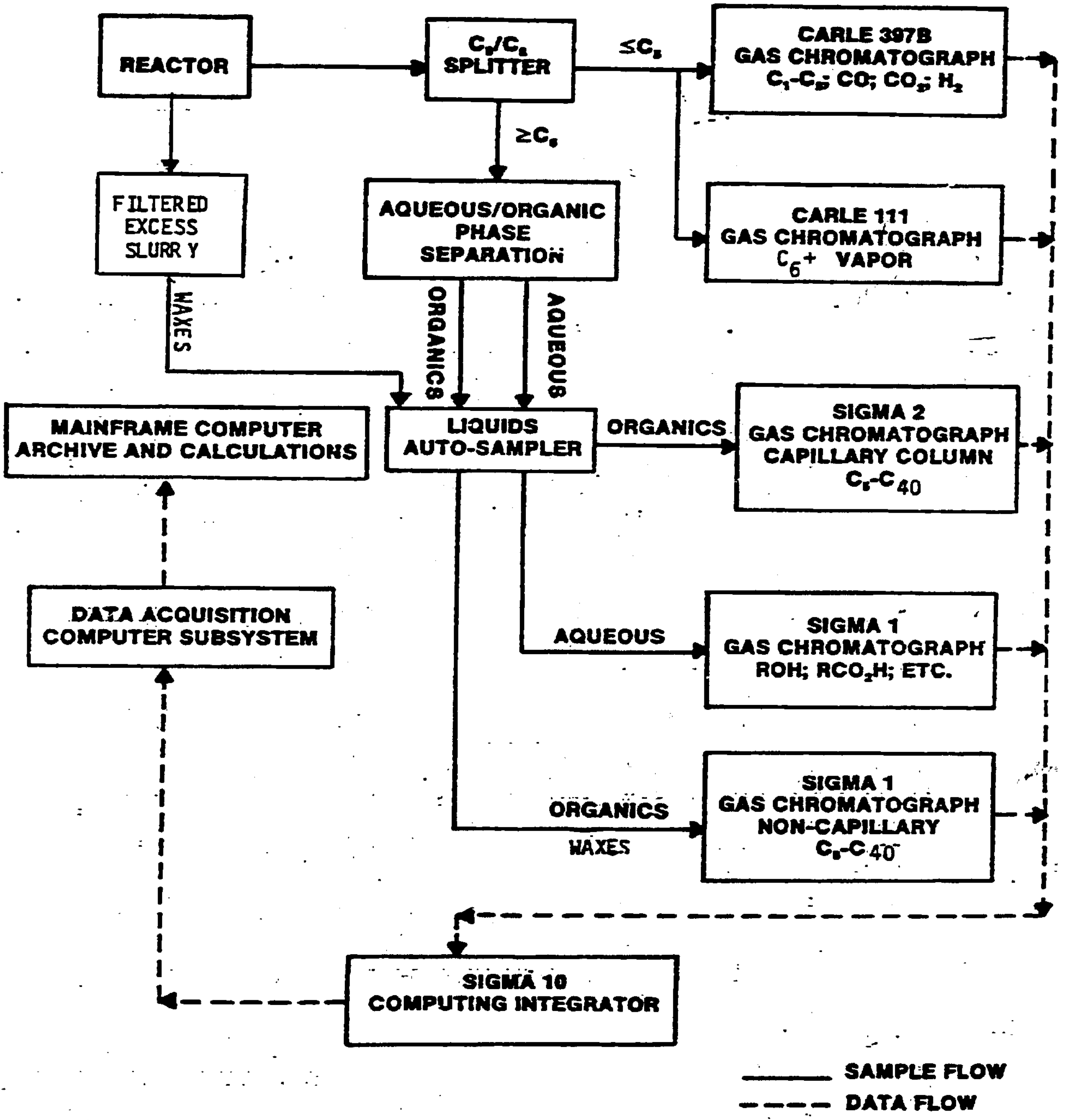


FIGURE 5

HYDROCARBON WEIGHT DISTRIBUTION
Fe_2O_3

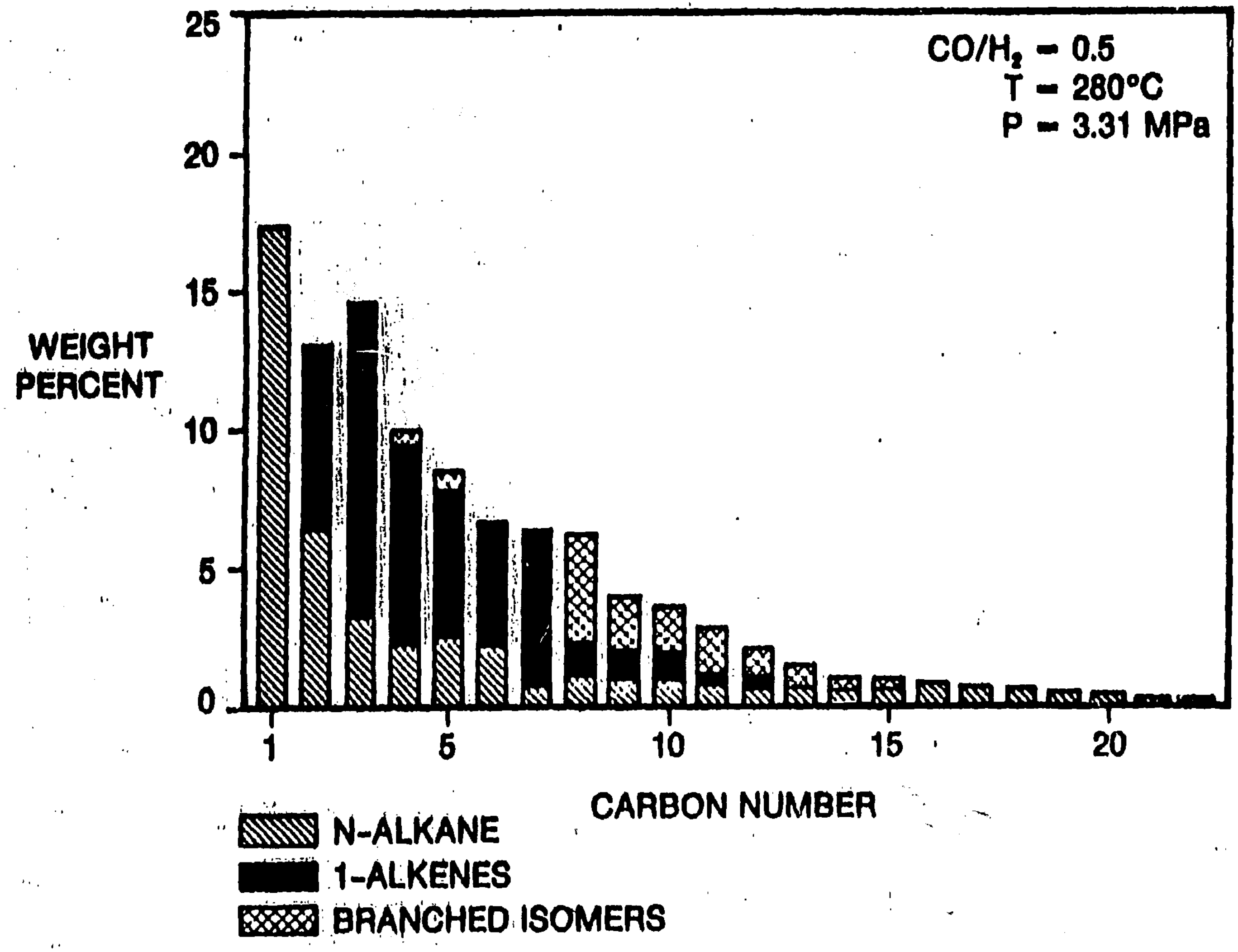


FIGURE 6

HYDROCARBON WEIGHT DISTRIBUTION
Fe_2O_3

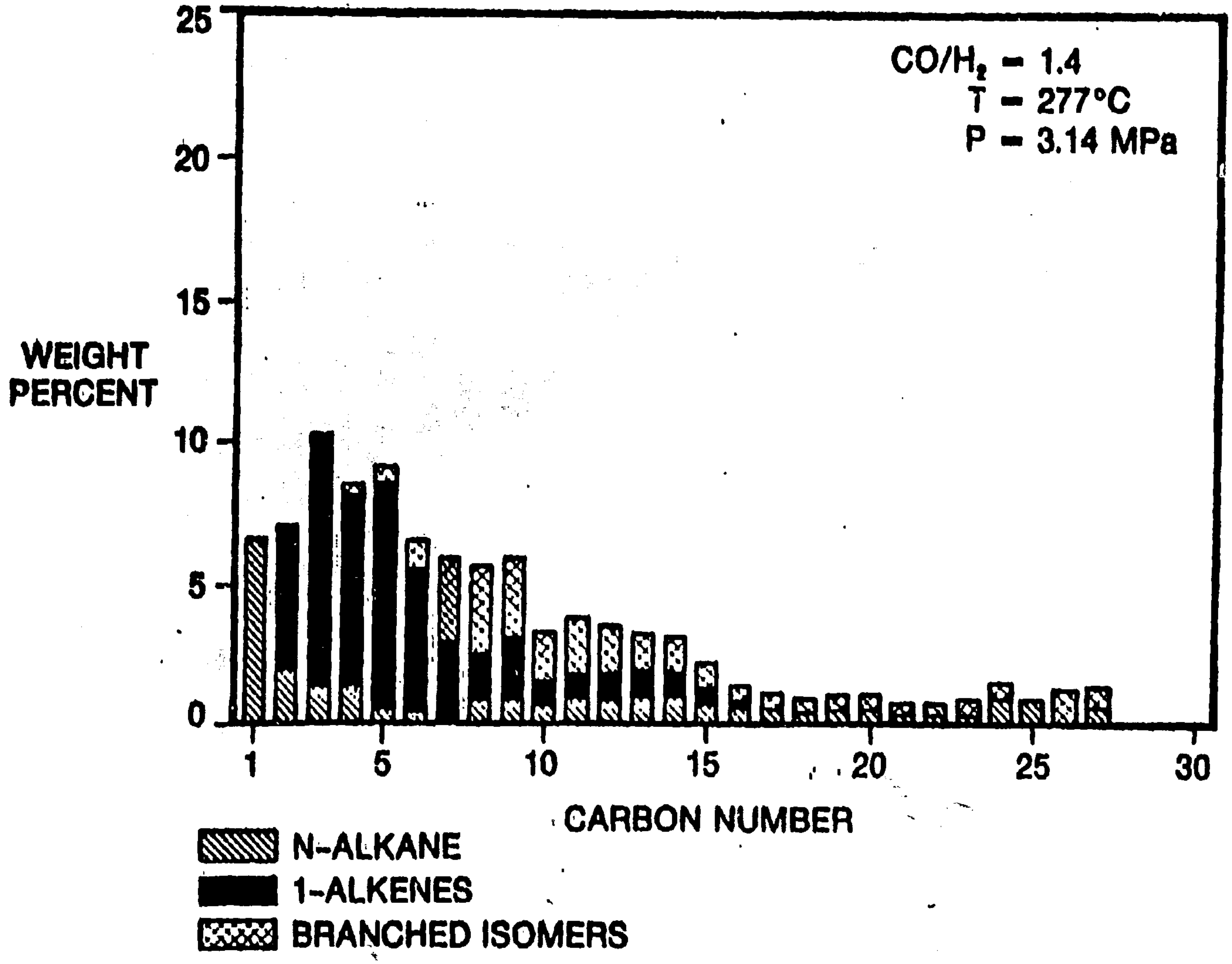


FIGURE 7

HYDROCARBON SCHULZ-FLORY DISTRIBUTION
Fe_2O_3

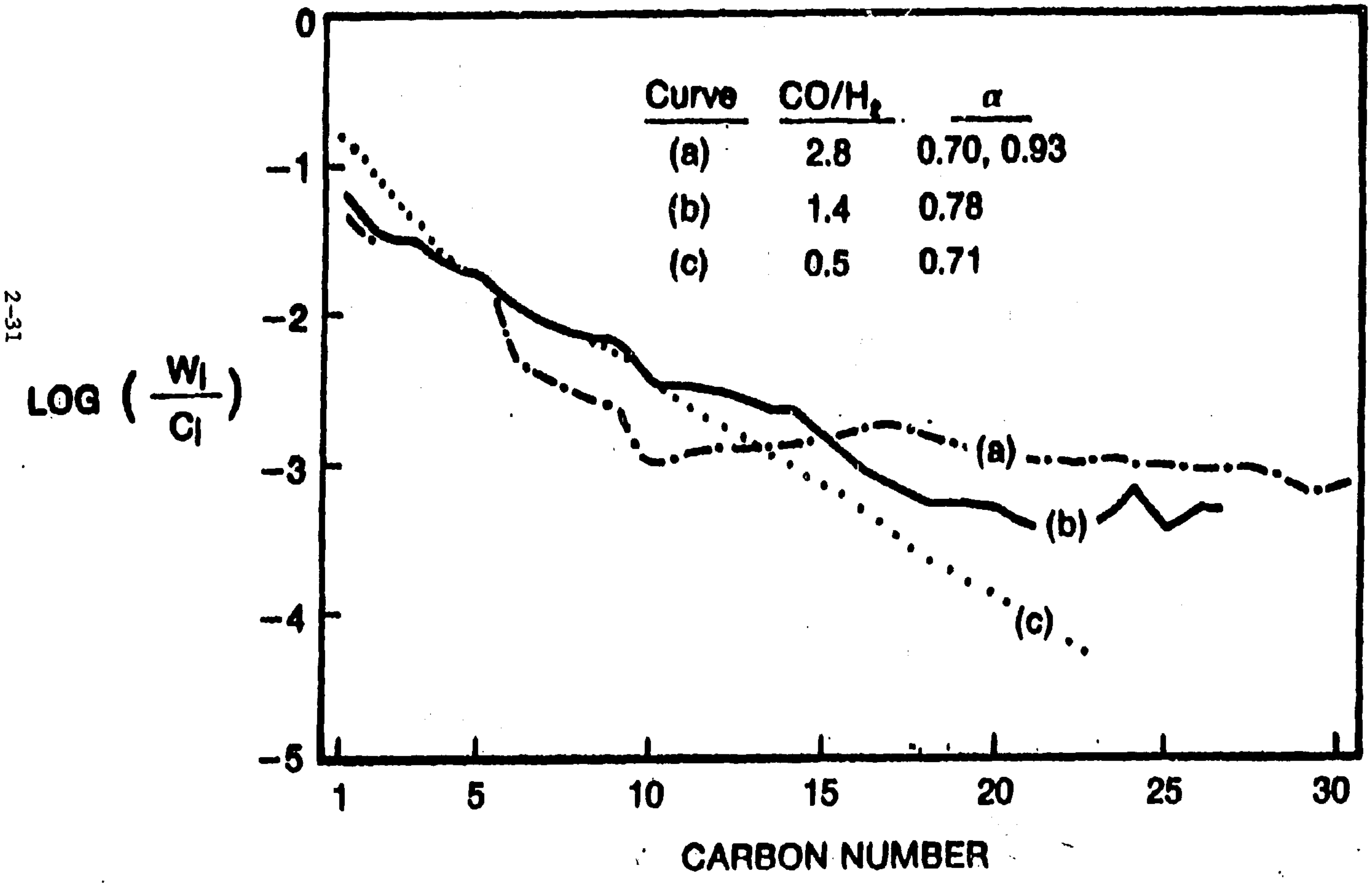


FIGURE 8

HYDROCARBON WEIGHT DISTRIBUTION EXTENDED SLURRY TEST, CATALYST A

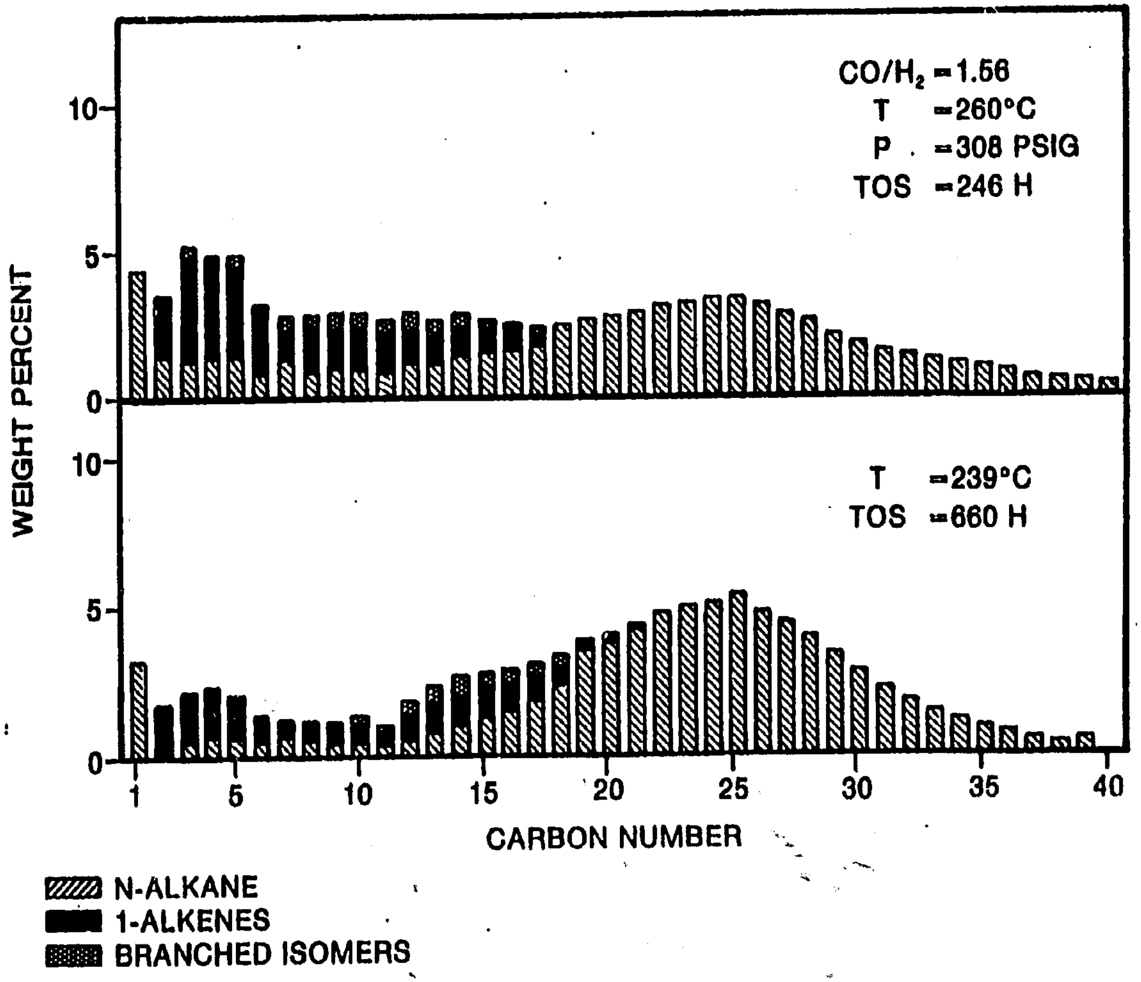


FIGURE 9

HYDROCARBON SCHULZ-FLORY DISTRIBUTION EXTENDED SLURRY TEST, CATALYST A

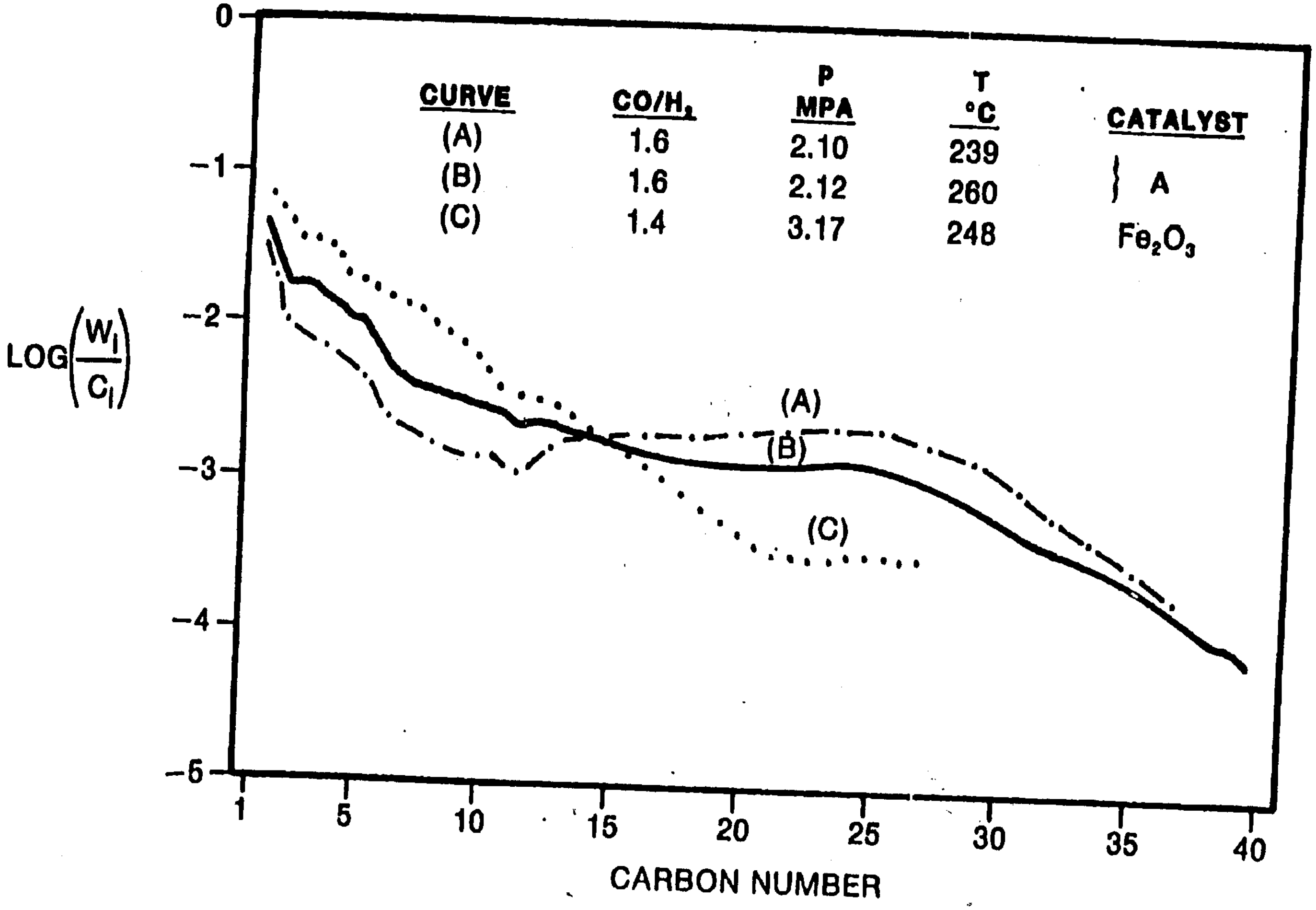


FIGURE 10

HYDROCARBON WEIGHT DISTRIBUTION
CATALYST B

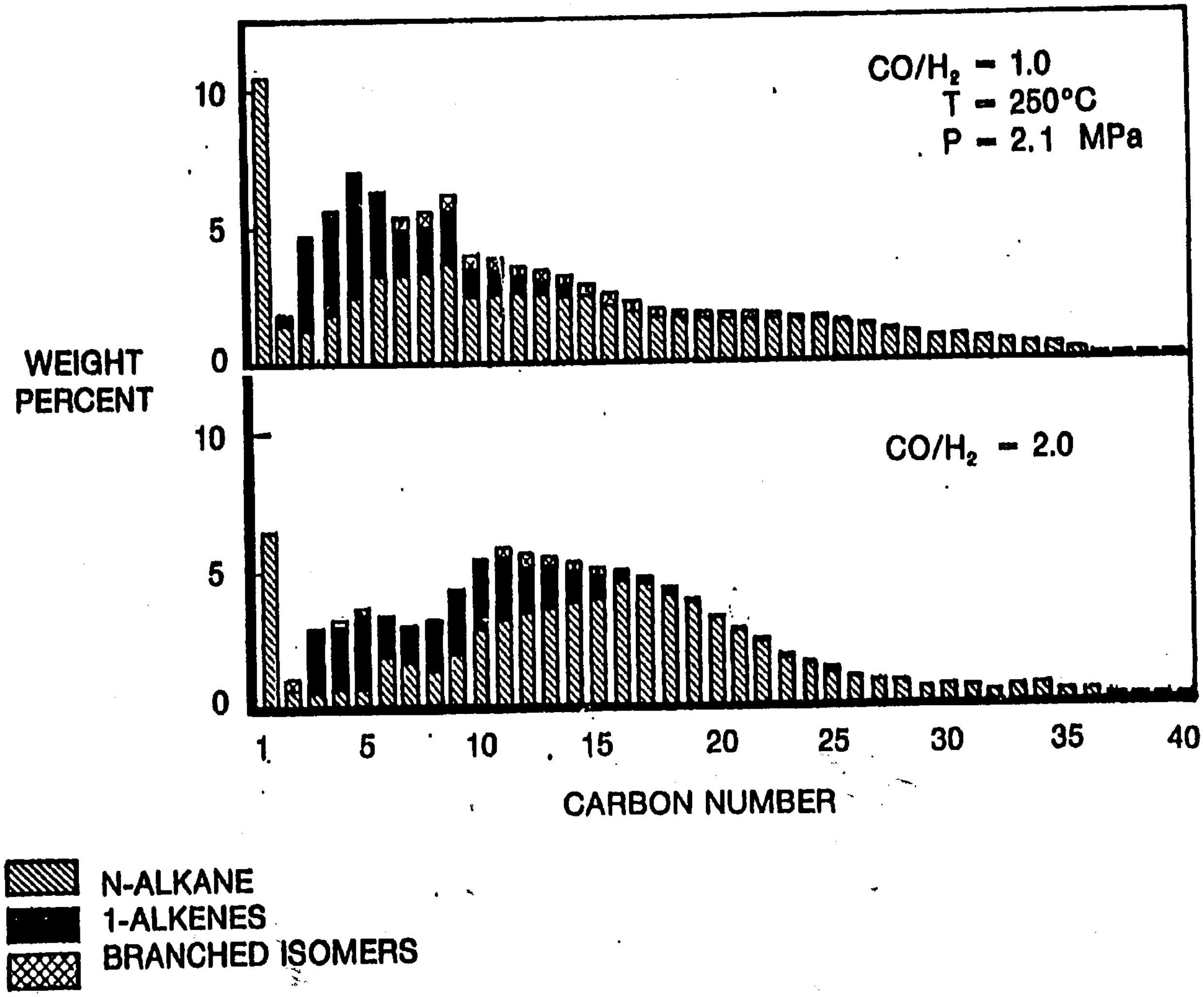


FIGURE 11

HYDROCARBON SCHULZ-FLORY DISTRIBUTION

CATALYST B

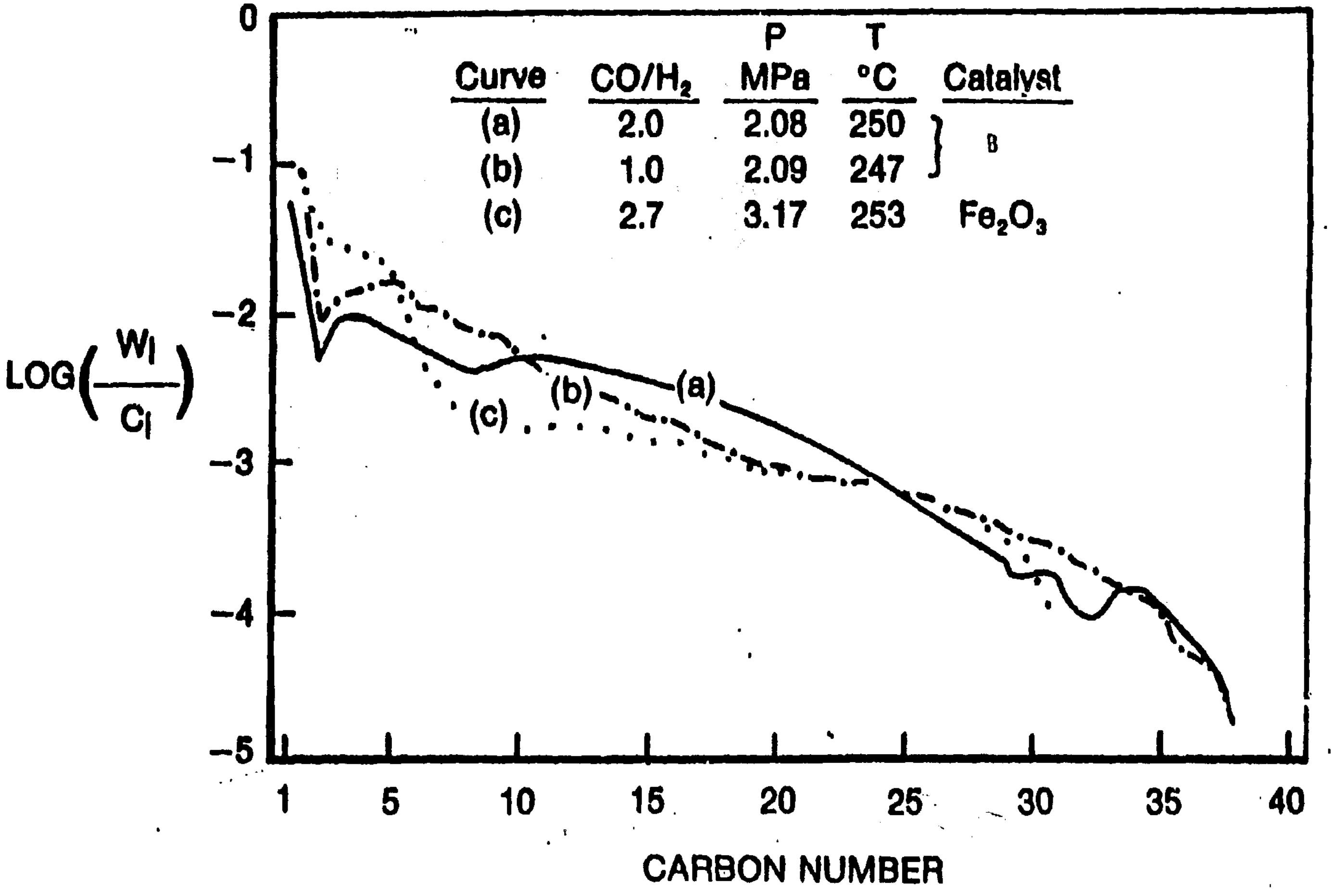
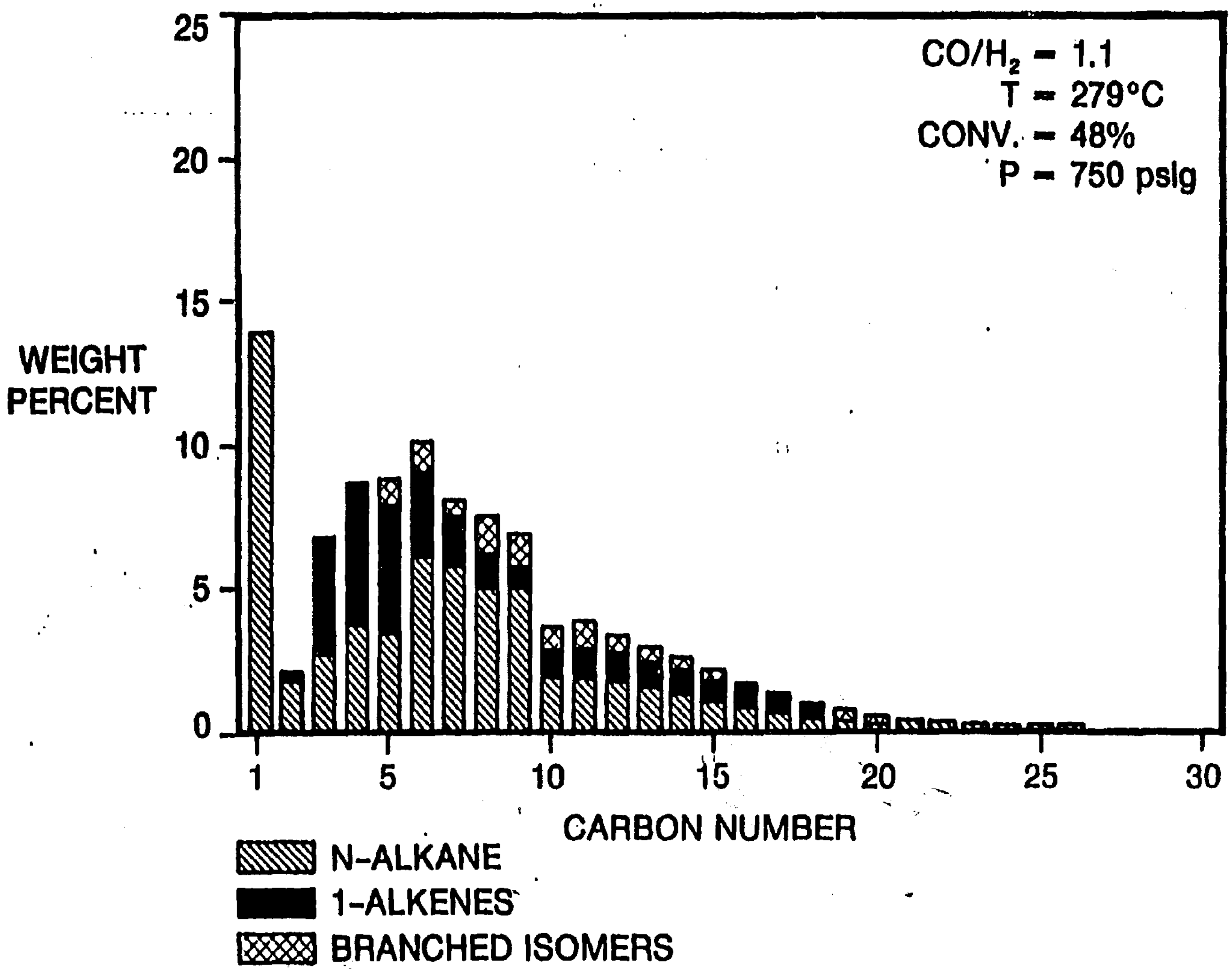


FIGURE 12

HYDROCARBON WEIGHT DISTRIBUTION
CATALYST C



FIGURE

HYDROCARBON SCHULZ-FLORY
DISTRIBUTION
CATALYST C

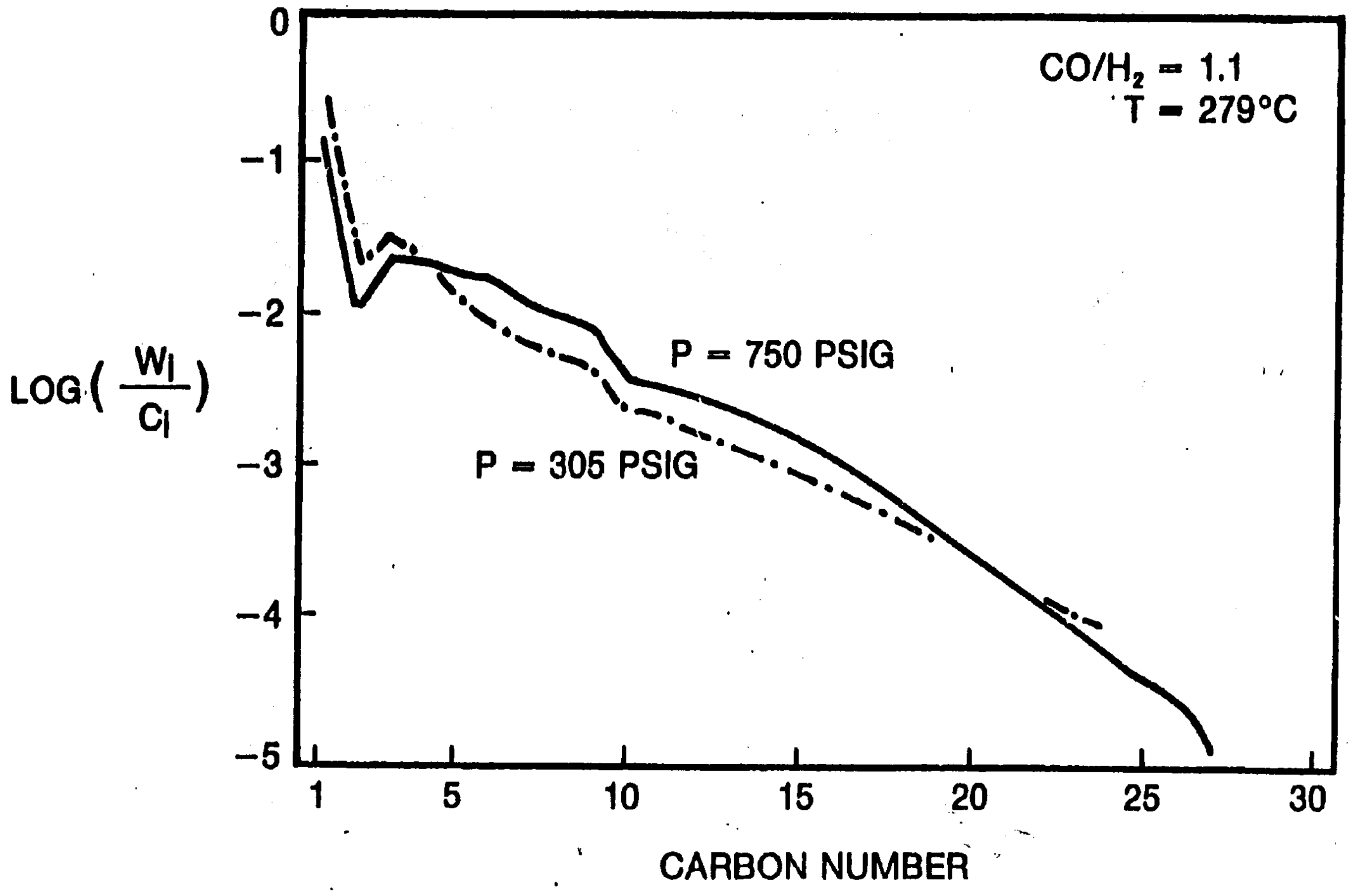


FIGURE 14

SPACE-TIME YIELD
AT RHEINPREUSSEN CONDITIONS