

Langmuir-Hinshelwood equation were tried, and the best of these turned out to be (equation 4):

$$\text{Rate CO} = \frac{\text{SQRT}(p_{H_2}) * (p_{CO})^{**2}}{B1 * (1 + B2 * p_{CO})^{**4}}$$

milli-gm mole CO  
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hr. gm catalyst

The constants, B1 and B2, from the same previously described 32 data points (corrected for 240 deg. C. with the same activation energy of 25.427 kcal/gmole) are:

$$B1 = 902.8516$$

$$B2 = 0.011400751$$

The percent difference between the experimental CO rate and the value from the fitting was again computed as a measure on the goodness the fit. The statistics on the percent difference was computed with the results below:

Eqn (4)	32 data points	Mean of %Difference	-0.0668 %
		Std deviation	+/- 4.723 %
		Std Error	+/- 0.835 %

Both the Power Law and the Langmuir-Hinshelwood forms fit equally well. I would hesitate to read too much into the physical significance of the Langmuir-Hinshelwood form. On practical grounds, we prefer using the Power Law form, because it better suit our existing computer calculations.

Figure C5 shows how well equation (4) fits the experimental CO rate data. The Langmuir-Hinshelwood form employs only two constants as compared to three constants for the Power Law form at constant temperature.

#### V. The Usage Ratio Correlation for Co/X11/TC-123

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In the Fischer-Tropsch synthesis, there are actually two reactions involved, the additional one being the water gas shift reaction. To do a proper reactor simulation, we have to know the extent of this second reaction:



Cobalt-based catalysts are known to have very little water gas shift activity, and this was found true for the catalyst 45 with the finding of only a little CO<sub>2</sub> among its products. With water as the primary by-product of the FT reaction, the consumption of H<sub>2</sub> bears a fairly constant relation to the consumption of carbon monoxide by virtue of the stoichiometry involved. Because of this, the reactor simulation program can compute the H<sub>2</sub> consumption from the CO consumption with a constant usage ratio. We only need to correlate the CO consumption from the relevant process variables.

It should be mentioned, however, that we did get a correlation on the usage ratio. Based on the same Run 45 data set, we started the regression fitting with the full set of the variables of  $FT(=1000/RT)$ ,  $LRHC(= \ln(H_2/CO))$ ,  $SV$ (space velocity) and  $PSIG$ . The pressure variable  $PSIG$  got kicked out in the backward elimination of the regression variables, an event which was not surprising, since the water gas shift reaction does not involve any change in the number of moles. All the other variables were found to be valid. Considering the free energy expression for the reactants involved, it was quite logical that the temperature, the log of the ratio  $(H_2/CO)$  and the space velocity were found to be the significant variables.

$$\Delta G = RT \cdot \ln(K_p) = RT \cdot \ln \left[ \frac{H_2 \cdot CO_2}{H_2O \cdot CO} \right]$$

$$USAGE = 4.37130878 - 2.5551154 \cdot FT + 0.19579258 \cdot LRHC + 0.00021829 \cdot SV$$

Although we found a good and valid correlation for the usage ratio, we chose not to use it in the reactor simulation at this time. The experimental usage ratio data (52 points) had a range of 1.69 to 2.14, with the following statistics:

Usage ratio (52 points):	mean	1.9414
	std deviation	0.0817
	std error	0.0113

Since it did not change much, we kept the usage ratio as a constant (1.94 in this case) in the reactor simulation program. It is much simpler that way, since using the usage ratio correlation would require another time consuming dimension in the computer's iteration procedure.

## VI. Product Selectivity

The Fischer-Tropsch synthesis produces hydrocarbons as its main product and the water and carbon dioxide as its by-products. The relative amount of the water and  $CO_2$  in the by-products depends on the water gas shift activity. Since cobalt does not have too much shift activity, the by-product will be mostly water.

Due to the stoichiometry involved, there is a one to one correspondance between the moles of by-products ( $H_2O+CO_2$ ) and the moles of main products, the hydrocarbons, as expressed in terms of a symbolic methylene molecule,  $CH_y$ .

The distribution of the hydrocarbons has been reasonably well represented by the Schulz-Flory distribution. The theory assumes that the hydrocarbon chain grows one carbon atom by one

carbon atom, that at each stage the chain can either terminate or add one more carbon atom, and that the rate of growth and termination at any stage remain the same regardless of the carbon number. Based on these assumptions, the following relationship, usually referred to as the Schulz-Flory distribution, holds:

$$W_n = n * (1-\alpha)^2 * \alpha^{(n-1)}$$

where

$W_n$  - wt. fraction of hydrocarbon fraction of carbon number  $n$   
 $\alpha$  - chain growth probability, growth / (growth + termination)  
 $\alpha$  - exp(slope) of  $\ln(W_n/n)$  vs.  $n$  plot (Schulz-Flory plot)

The validity of this equation is shown by a straight line relationship if the logarithm of  $(W_n/n)$  is plotted against carbon number  $n$ . The product distribution usually conforms to this general scheme for all carbon numbers except methane. With a cobalt catalyst the methane production usually exceeds that predicted by the Schulz-Flory distribution, so that the methane must be separately calculated. Figure C3 shows a typical Schulz-Flory plot of  $\ln(W_n/n)$  vs carbon number  $n$  using one of the samples from the Run 45.

The methane make itself, as well as the value of  $\alpha$  that must be used with the Schulz-Flory equation to describe the  $C_2+$  product distribution, were found to correlate with the  $H_2:CO$  ratio, temperature, pressure and space velocity. The following functional form was used in the backward elimination regression procedure on the data from run 45 with the full data set of 52 samples.

$$\begin{aligned} W_{tCH_4} \\ \text{or} \\ \alpha \end{aligned} = B_1 + B_2 * LHC + B_3 * PT + B_4 * PSIG + B_5 * SV$$

where  $LHC = \ln(H_2/CO)$   
 $PT = 1000/(1.98726 * T_k)$ , a temperature function, deg K.  
 $PSIG = \text{pressure, psig}$   
 $SV = \text{space velocity, vol fresh syngas feed/vol cat./hr.}$

## VII. The Methane Correlation

For the methane make correlation, the following values of the parameters were found for the various stages of the backward elimination procedure.

A. with all variables entered:

	B value	Std Error	F	PROB>F
Intercept	69.81544			
LHC	9.58478	0.600697	254.60	0.0001

FT	-59.76776	15.328388	15.20	0.0003
PSIG	-0.0132184	0.00202695	42.53	0.0001
SV	0.0039068	0.00200398	3.80	0.0572

B. with variable SV removed (its probable error exceeded the 5% confidence level):

	B value	Std Error	F	PROB>F
Intercept	75.87977			
LHC	9.568084	0.617910	279.67	0.0001
FT	-65.039663	15.521898	17.56	0.0001
PSIG	-0.0123202	0.00203067	36.81	0.0001

Hence the following expression (set D) was adopted for the wt% methane make:

$$WCH4 = 75.8798 + 9.56808 \cdot LHC - 65.03966 \cdot FT - 0.01232 \cdot PSIG \quad (D)$$

#### VIII. The Alpha Correlation

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Similarly, for the alpha correlation, the following values of the parameters were found for the various stages of the backward elimination procedure.

A. with all variables entered:

	B value	Std Error	F	PROB>F
Intercept	0.73997			
LHC	-0.035875	0.0039318	83.25	0.0001
FT	0.131421	0.108613	1.46	0.2428
PSIG	0.00007254	0.00001307	30.80	0.0001
SV	-0.00001917	0.00001152	2.77	0.1144

When we followed the backward elimination procedure for the 95% confidence criteria, both the variables FT and SV were eliminated with the following result:

	B value	Std Error	F	PROB>F
Intercept	0.864595			
LHC	-0.0336896	0.0040103	70.57	0.0001
PSIG	0.00006830	0.00001342	25.90	0.0001

However, most of the literature sources indicated that the temperature does influence the chain length of the hydrocarbon product, the fact that the variable FT got kicked out in the elimination step is probably due to the narrow range of the temperature variable in the input data; so it was decided to let the variable FT stay in the correlation. There is also logical ground to let the variable SV stay in; it is reasonable to believe that the hydrocarbon product becomes lighter with higher space velocity or less contact time. However the value of the

parameter is quite small and its inclusion in the correlation would complicate the reactor simulation computation, so it was decided to leave the variable SV out. Hence we ended up with a correlation for alpha as a function of H2/CO ratio, temperature and pressure with following constants:

	B value	Std Error	T	PROB>F
Intercept	0.694295	0.108239	6.414	0.0001
LHC	-0.035949	0.0041203	-8.725	0.0001
FT	0.174206	0.110593	1.575	0.1326
PSIG	0.000065801	0.000013024	5.052	0.0001

The use of these constants leads to the following expression (set D) for alpha:

$$\text{ALPHA} = 0.694295 - 0.035949 \cdot \text{LHC} + 0.174206 \cdot \text{FT} + 0.000065801 \cdot \text{PSIG} \quad (\text{D})$$

#### IX. The Previous Rate and Product Selectivity Correlation on a simple cobalt catalyst on UCC-101 support

The reaction rate expression and the product selectivity expressions on Wt%CH4 and alpha calculated for the Co/UCC-101 catalyst developed under the previous contract (ref.1) are presented here for the ease in comparison against the latest expressions for catalyst 45. The same power law rate expression on CO conversion and the Arrhenius activation temperature function were used in the correlations for both catalysts. These expressions for the early Co/UCC-101 catalyst were:

$$R_{CO} = 0.01515617 \cdot \frac{1.6515671 \cdot (\text{pH}_2)^{1.6515671} \cdot \text{TCOE}^F}{0.466108 \cdot 1000.0} \cdot \frac{\text{gm moles CO}}{\text{hr, gm catalyst}}$$

$$\text{TCOE}^F = \exp \left[ \frac{30114.78 \cdot (t_c - 250)}{1.98726 \cdot 523.15 \cdot (t_c + 273.15)} \right] \cdot \frac{\text{Arrhenius Temp. Coeff. with 250 C as base temp.}}{1.98726 \cdot 523.15 \cdot (t_c + 273.15)}$$

where  $R_{CO}$  = rate of CO conversion, gm mole CO/hr, gm catalyst  
 $\text{pH}_2$  = partial pressure of hydrogen, psia  
 $\text{pCO}$  = partial pressure of carbon monoxide, psia  
 $\text{TCOE}^F$  = Arrhenius temperature coefficient with 250 C as reference  
 $t_c$  = temperature in deg. C.

$$\text{Wt\%CH}_4 = 147.791 + 15.1143 \cdot \ln \left\{ \frac{\text{pH}_2}{\text{pCO}} \right\} - 128.4976 \cdot \frac{1000.0}{1.98726 \cdot (t_c + 273.15)}$$

$$\alpha = 0.78124 - 0.048725 \ln\left\{\frac{p_{H_2}}{p_{CO}}\right\} + 0.031305 \frac{1000.0}{1.98726(tc+273.15)}$$

Figures C6 and C7 use the above-described correlations to compare the Wt%CH<sub>4</sub> make for the early and the present catalysts at 240 C. and 270 C. respectively.

#### X. Potential Performance of the Co,X11-TC-123 Catalyst in a Fixed-Bed Reactor

The most important difference between the old and the new catalysts is the low methane make of the new catalyst formulation. Because of this, the new catalyst can operate with a higher H<sub>2</sub>/CO ratio feed to permit a higher space velocity while suppressing the methane make to a reasonable amount. For instance, if we had a feed stream with a 1.8 H<sub>2</sub>/CO ratio and we wanted to estimate sets of process conditions for an 85% conversion of CO with less than a 10 Wt%CH<sub>4</sub> make in a single stage fixed-bed reactor with a 2.3 recycle ratio, the computer simulation containing correlations for catalyst 45 would yield:

#### SUMMARY OF REACTOR SIMULATION WITH Co,X11-TC-123 CATALYST (85% Conversion in Single Stage Fixed-Bed Arge-Type Reactor).

	CASE I	CASE II
RF, Feed H <sub>2</sub> /CO	1.80	1.80
Usage Ratio, H <sub>2</sub> /CO consumed	1.94	1.94
SA (Spec.Activity req'd)	1.0	1.0
PSIG	400	500
TEMP C.	250	260
SV, Space Velocity	471	808
CVCO, % CO Conversion	85 %	85 %
CVSG, % Syngas Conv.	89.25 %	89.25
Wt%CH <sub>4</sub>	9.70 %	9.64 %
alpha	0.88327	0.88672
Cost, \$/gal. gasoline	\$ ?	\$ ?

As one can see, the through-put in terms of the space velocities for a slightly higher conversion are 471 and 808 as compared to the previous estimate (tabulated under "Introduction") of 300 and 360 respectively. Only part of the improvement stems from the net effect of a beneficial increase in pressure which is partly counterbalanced by a lower temperature. These lower space velocities are a significant improvement in the capital investment cost for an equally-sized production plant.

The fixed-bed reactor simulation computer program has already been documented in the 15-th Quarterly Report of the previous contract, DE-AC22-81PC40077.

- Ref. 1 15-th Quarterly Report under previous DOE contract DE-AC22-81PC40077, issued Feb. 21, 1986, appendix B, and Fig. B1 & B9.
- Ref. 2 MITRE Corp. Working Paper No. 85W00031, April 12, 1985  
A Techno-Economic Assessment of Fischer-Tropsch Catalyst Development at Union Carbide, by A. El Sawy, D. Gray, M. Neuworth and G. Tomlinson.

FIGURE C1

**SCHEMATIC DIAGRAM OF UNION CARBIDE  
TUBULAR REACTOR SIMULATION PROGRAM  
INPUT/OUTPUT RELATIONS**

THE BERTY REACTOR, a CSTR (CONTINUOUS-FEED STIRRED TANK REACTOR) operates under steady state conditions with a high internal recycle rate, causing the catalyst to be exposed to a known and unvarying gas phase composition

↓  
YIELDS DATA

↓

DATA CORRELATION by MULTIPLE REGRESSION FOR:

1. CO Conversion Rate as a function of partial pressures of H<sub>2</sub>, CO and Temp.
2. Wt%CH<sub>4</sub> as a function of H<sub>2</sub>/CO ratio and Temp.
3. Schulz-Flory alpha as a function of H<sub>2</sub>/CO ratio and Temp.

↓  
is put into

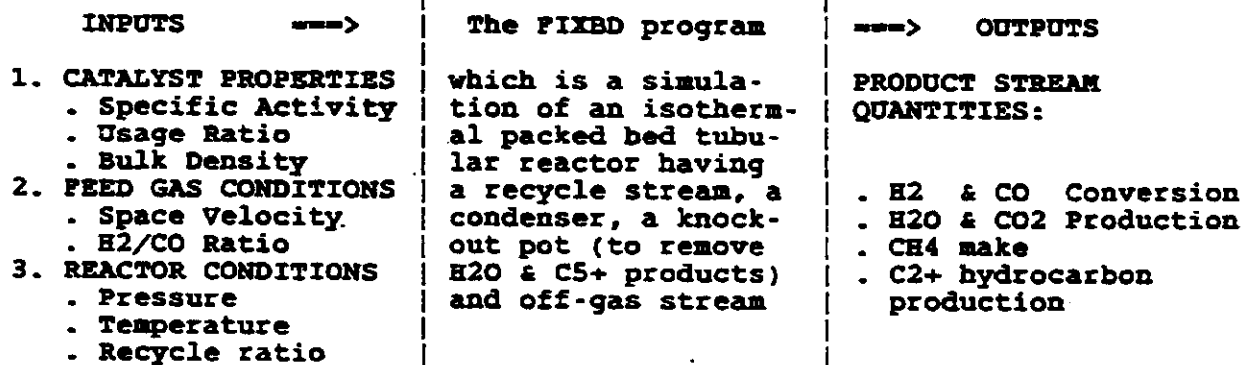




Figure C2. Schematic diagram of the P-T reactor system.

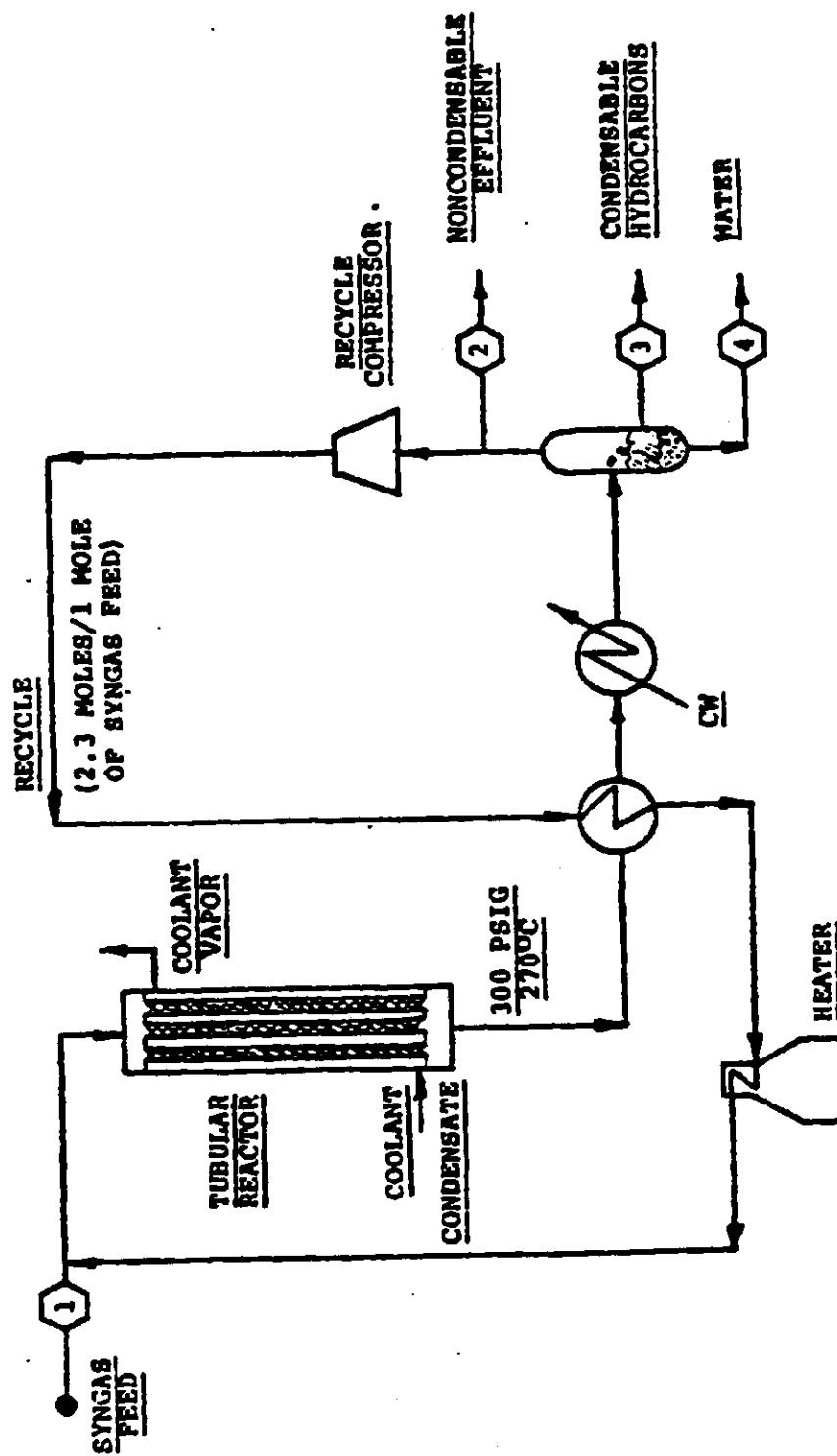


Figure C3. Schulz-Flory Distribution Plot

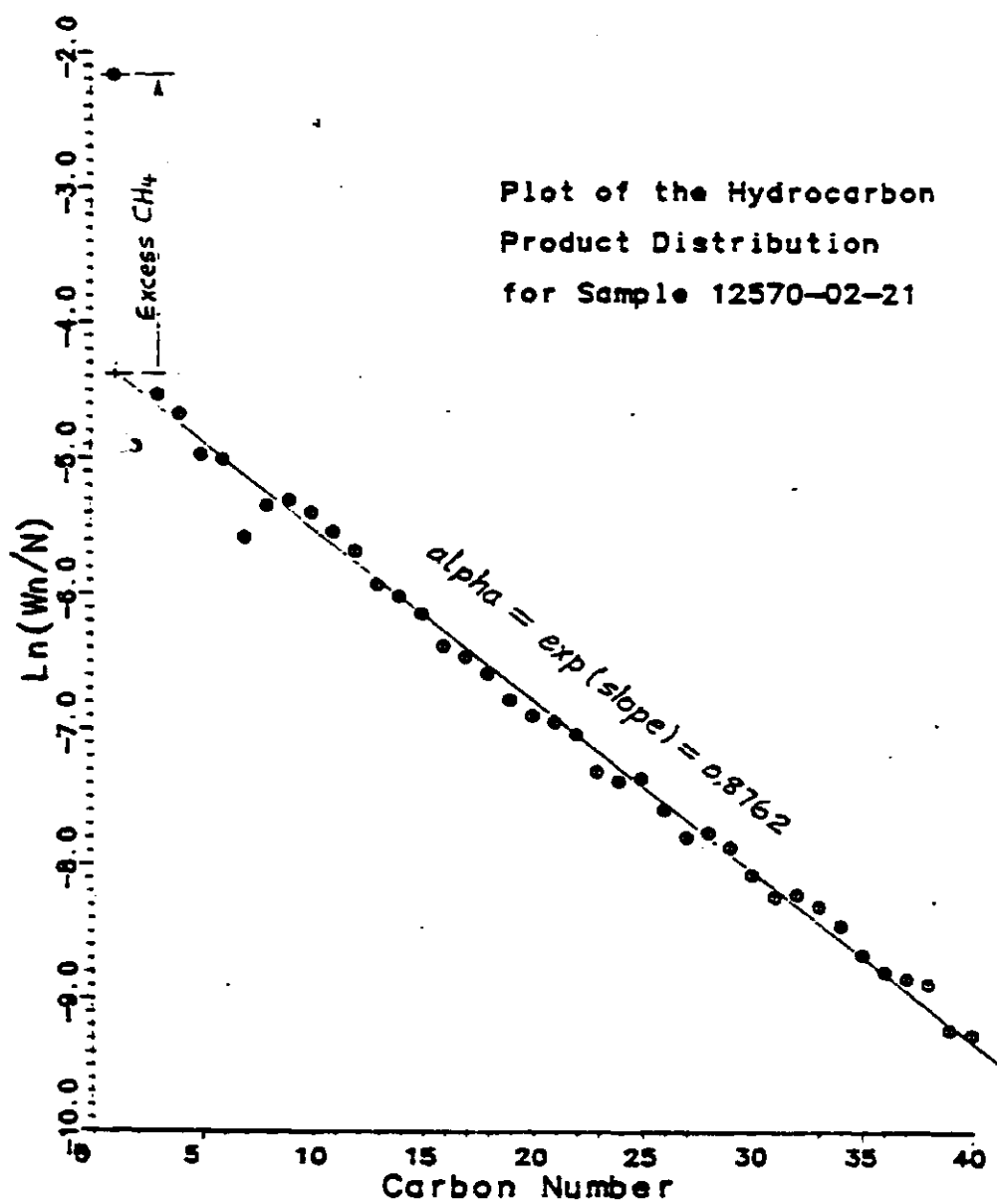


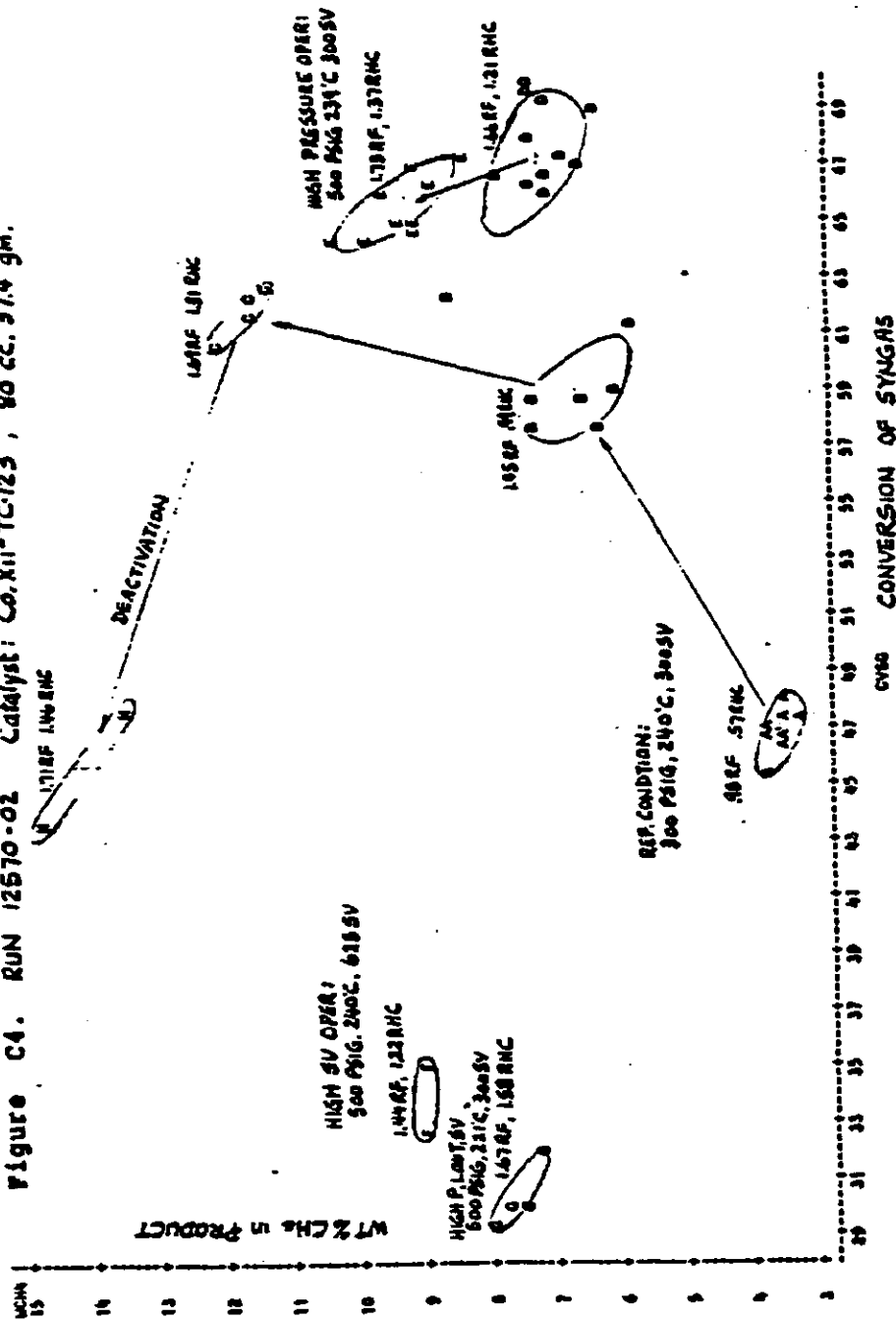
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PLOT OF Wt% C<sub>2</sub>H<sub>4</sub> vs. VALUE OF SAMPLE

Figure C4. RUN 12570-02 Catalyst: Co.Xi-TC-123, 80 cc. 37.4 gm.



NOTE: 5 088 H100EN RF, Feed Ratio = (H<sub>2</sub>/CO) feed  
RHC, Residual (H<sub>2</sub>/CO) ratio in Berty Reactor

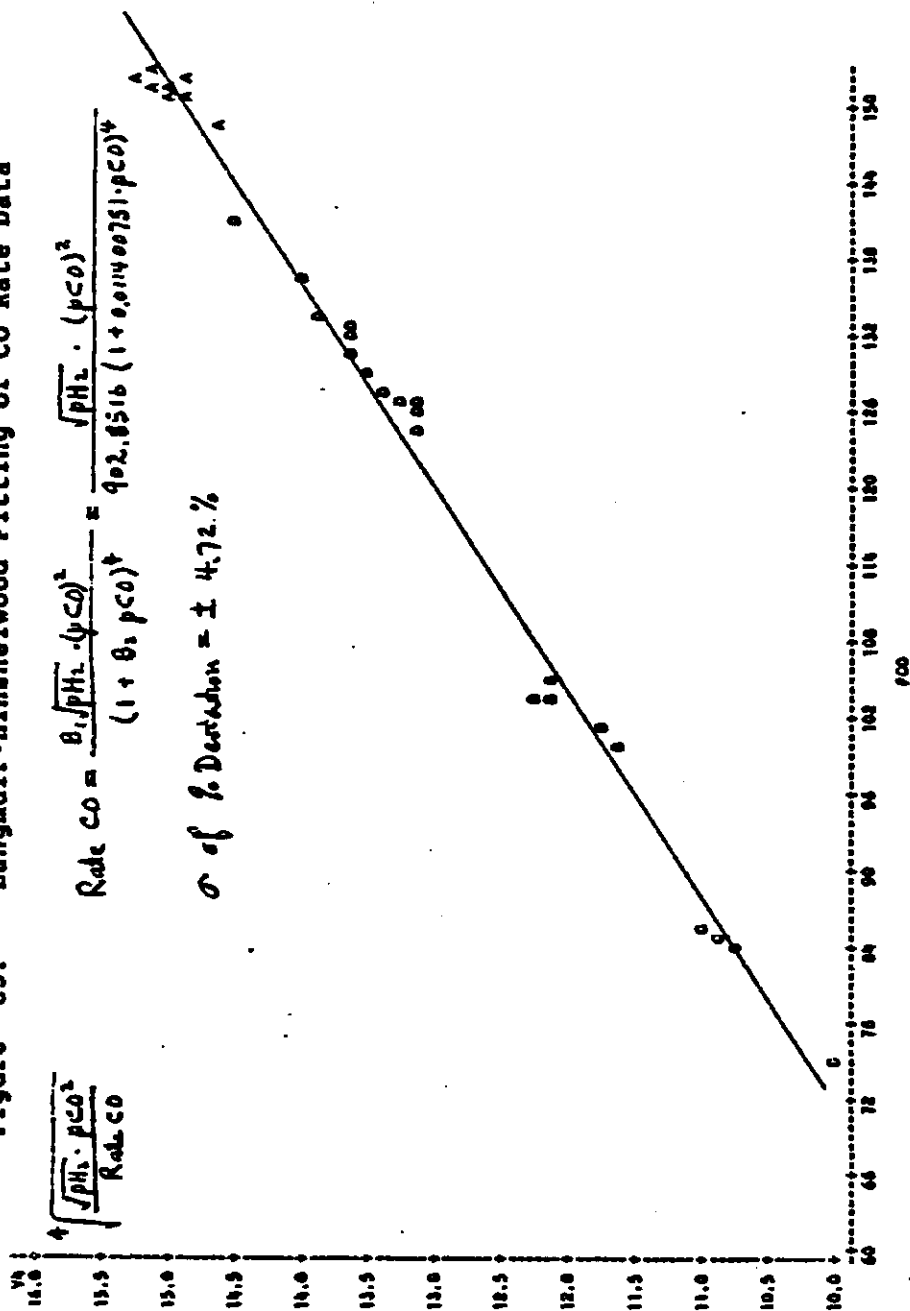
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Figure C5. Langmuir-Hinshelwood Fitting of CO Rate Data

$$\text{Rate CO} = \frac{B_1 \sqrt{P_{H_2}} \cdot (p_{CO})^2}{(1 + B_1 \sqrt{P_{H_2}} \cdot (p_{CO})^2)} = \frac{\sqrt{P_{H_2}} \cdot (p_{CO})^2}{902.8516 (1 + 0.011400751 \cdot p_{CO})^4}$$

$\sigma$  of fit Deviation =  $\pm 4.72\%$



NOTES: 3 OBS W/DOUBT

Figure C6.

CH<sub>4</sub> Selectivity of Three Different Catalysts  
at 240 °C.

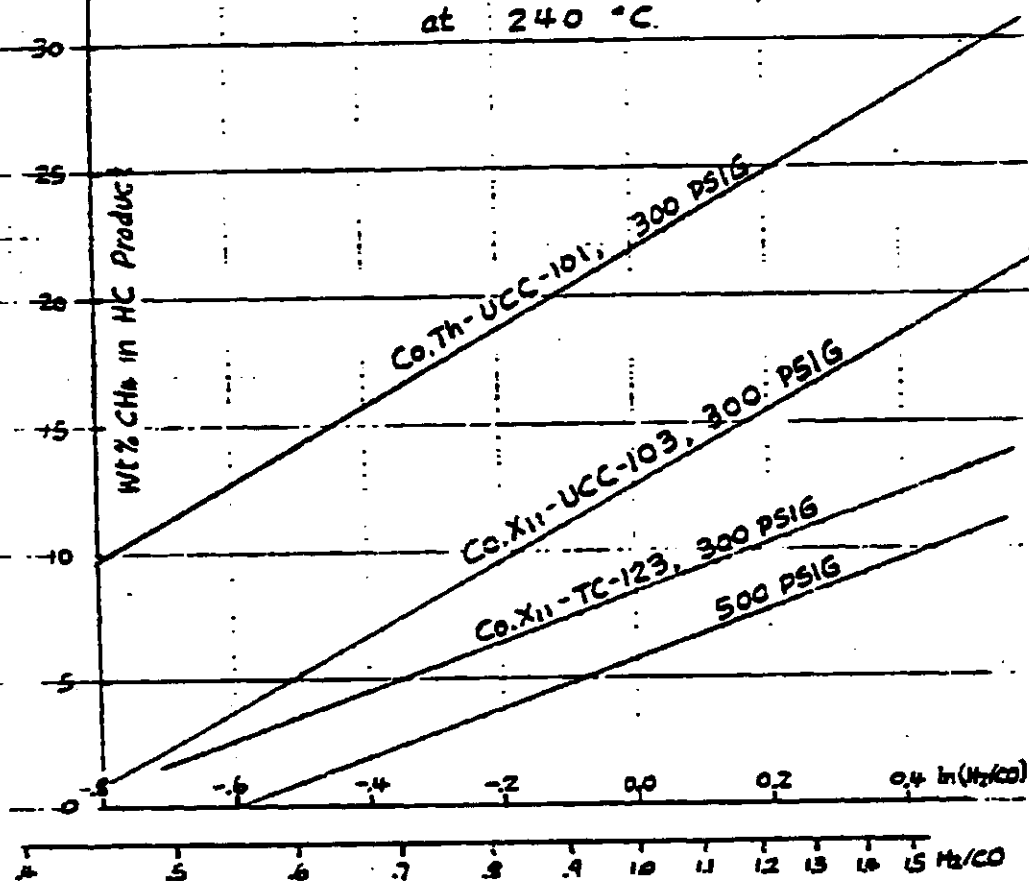


Figure C7.

