results indicated a very rapid drop in conversion which was subsequently attributed to a loss in catalyst from the reactor. A missing hold down plate was ~~responsible for this. The situation was corrected and Run~~ Series 16 completed. The results for these extrudates are encouraging in light of the fact that the relative activity in the liquid phase, compared to the standard catalyst, Catalyst A, improved over that trend in the vapor phase, up to a value of 0.8, as indicated in Table 4-19. In addition, it must be noted that these activity ratios are obtained with only one-half the actual active catalyst. The α-alumina function only as a bulking agent to improve the extrudate physical properties. Based on these results, it is apparent that through further development there is a real opportunity for activity enhancement for these catalyst/α-alumina composite extrudates.

Modified Tablet Composition

Past attempts by several manufacturers to produce a small (1/16") extrudate form of catalyst based on the Catalyst A composition powder were unsuccessful. French Patent Application No. 76-16432 details the manufacture of an active methanol catalyst (tablet form) which incorporates a hydraulic alumina cement (Secar 80) into the support matrix, thereby imparting exceptional physical strength to the tablets. It was thought that this alumina cement could also be used to modify the basic Catalyst A formula in order to improve the physical strength properties when the mixture was formulated into an extrudate.

Various mixtures of Catalyst A, alumina cement, and water were investigated in order to define a composition region for which the mixture has the proper consistency for extrusion. No reaction tests were conducted. The particles were formed by manually extruding the mixture out of a 10 cc syringe. Strength characteristics of the dried particles were only fair. However, it should be noted that these hydraulic cement containing materials need rigid control of humidity and temperature in order to develop their optimum strength properties during curing. This was beyond the scope of this preliminary investigation. Different methods of incorporating the water were attempted: (1) adding water to the blended powder and (2) adding water to one, or both, of the

individual powders prior to blending. In either case, the properties of the resultant mixture depended primarily on its overall composition, and not on the blending sequence.

Figure 4-32 is a ternary diagram for the catalyst-cement-water system. Compositions 1, 2, 3, and 4 define the workable range for the binary, catalyst - water and cement - water mixtures. Compositions 5, 6, 7, and 8 further define the workable range for the ternary mixtures (see Table 4-21). Mixtures in the central portion of the ternary diagram had the proper consistency for extrusion. Mixtures above were too dry, while mixtures below were too watery. Because of the simple test apparatus used, some water was pressed out of the mixture during the initial stages of extrusion. Therefore, the extrusion became more difficult as the extrudate bead was being layed down.

Future work, should concentrate on: (1) determining the minimum amount of cement required for strength and, (2) developing curing techniques for the catalyst-cement-water ternary mixtures. Cured materials would be quantitatively tested for strength. When the desired strength properties are obtained, vapor phase reaction tests could be used to screen the candidates for base level activity prior to any liquid phase tests.

Tests At Lehigh University

Eight catalyst samples were evaluated at Lehigh University by Dr. Kamil Klier's group. The samples, which were evaluated, include:

1. Fresh mini-tablets (prepared from Catalyst A powder), which were used in the bench scale life test and the first two continuous PDU tests. (See Section 6).

2. Fresh commercial Catalyst A tablets as received from the manufacturer.

3. Used 16 x 20 mesh catalyst product from the third PDU run.

4. Used mini-tablets from the second PDU continuous run.

5. Used mini-tablets from the first PDU continuous run.

FIGURE 4-32

MIXTURE CONSISTENCIES
FOR THE CATALYST A:
SECAR 80: WATER SYSTEM
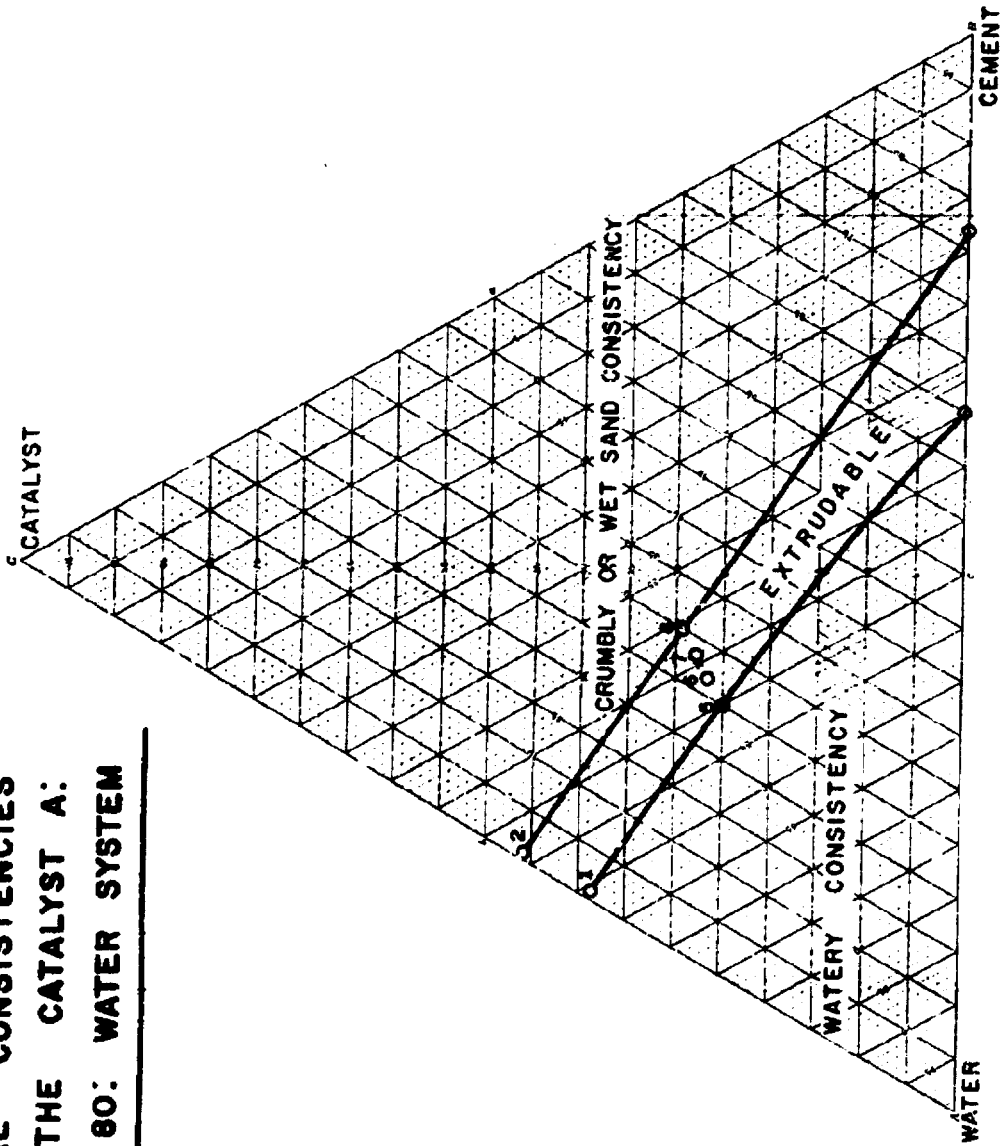
TABLE 4-21

DATA FOR CATALYST-WATER-CEMENT TERNARY DIAGRAM

Blend No.	Compositions (wt %)			Observation
	Cement	Catlayst	Water	
1	--	39	61	Very thin paste, watery - Marginally Extrudable
2	--	46	54	Dry, sandy - Not Extrudable
3	65	35	---	Very thin paste, watery - Marginally Extrudable
4	82	18	--	Dry, sandy - Not Extrudable
5	25	25	50	Thin paste - Marginally Extrudable
6	26	26	48	Workable mixture - Extrudable
7	28	28	44	Workable mixture - Extrudable
8	29	29	42	Dry, very sandy - Not Extrudable

6. Used mini-tablets from the 30-day bench scale continuous life test.

7. Poisoned catalyst from the chlorine poisoning test (commercial Catalyst A used).

8. Poisoned catalyst from the sulfur poisoning test (commercial Catalyst A used).

The catalysts which had been used in the liquid phase synthesis system (catalysts 3, 4, 5, and 6) were solvent extracted with cyclohexane and then petroleum ether. Following these extractions, the catalysts were dried. This procedure assured that the mineral oil used in the synthesis process was removed from the catalyst.

The fresh catalyst (1 and 2) were reduced with hydrogen prior to testing. The inspections included the following:

1. Auger and x-ray photoelectron spectroscopic analysis for Cu, Zn, O, Cr, Al, Ni, Fe, C, S, Cl, Na, and Ca.

2. Surface and pore distribution.

The detailed results of these inspections are reported separately(*) though the conclusions are summarized below.

The measured surface areas are given in Table 4-22. The only clear correlation is that the intentionally poisoned catalysts (chlorine and sulfur) have substantially reduced surface area compared to the fresh catalyst. No such trend is apparent to correlate activity as a function of surface area for the samples from the continuous bench scale and PDU runs.

* Klier, K., "Study of Deactivation of Methanol Synthesis Catalysts", EPRI AF-694, December 1977.

TABLE 4-22

SURFACE AREAS OF CATALYST SAMPLE

Sample	Surface Area M^2/g)
1. Fresh mini-tablets	99.8
2. Fresh commercial catalyst	88.0
3. Used 16 x 20 catalyst from third PDU run	90.6
4 Used mini-tablets from second PDU run	95.6
5. Used mini-tablets from first PDU run	83.7
6. Used mini-tablets from 30-day bench scale run	85.7
7. Used commercial catalyst from chlorine poisoning test	45
8. Used commercial catalyst from sulfur poisoning test	67

The Auger spectrograms were not remarkable. The intentionally poisoned samples (chlorine and sulfur) showed the particular poison as a major constituent. In the chlorine poisoned sample there was a notable deficiency of alumina, apparently due to volatization of $AlCl_3$. This is probably why this sample has such a low surface area (alumina normally providing a major portion of the surface area). Loss of surface alumina was noted to a small extent in all of the used samples.

Traces of sulfur and chlorine were reported on all of the used catalysts. Trace nickel was also noticed, though this could not be quantified due to peak overlap. Bulk analysis of the catalyst (Table 4-23) by atomic absorption revealed concentrations of nickel as high as 0.15 percent. This is well below the quantifiable threshold for the Auger unit.

Contaminant Metals Analysis

The various catalysts from the bench scale life test and the PDU tests were analyzed (atomic absorption) for metallic impurities. The results (Table 4-23) show a significant elevation in iron and nickel as compared to the fresh catalyst levels. In particular, nickel seems to correspond well with the rapid deactivation in the first two PDU tests.

Nickel could derive from traces of methanation catalyst left in the PDU from previous operations. Iron is probably deposited from the carbonyl, which is present to some extent in high pressure CO gas cylinders.

TABLE 4-23

CATALYST CONTAMINANT LEVELS

Description	Fe (ppm)	Ni (ppm)
Fresh Catalyst	90	15
Used Catalyst - Third PDU	143	229
Used Catalyst - Second PDU	196	1,275
Used Catalyst - First PDU	186	1,555
Used Catalyst - Bench Scale Life Test	414	52

Section 5

TESTING OF PROCESS VARIATIONS

SLURRY PHASE OPERATION

An experimental test program was set up to obtain reaction data for very fine size catalyst particles, since these particles should have a high effectiveness factor due to the larger surface area for mass transfer. The Bench Scale Unit was used for these initial slurry experiments. However, in the event that future work is contemplated, the Process Development Unit, with its reactor γ-ray density detector should be the unit of choice.

The Catalyst A 3/16" Ø tablets were hand crushed and sieved to obtain a -50 +70 size fraction (0.21 - 0.30 mm Ø). This is about one-fourth the size of the regular -16 +20 mesh cut (0.85 - 1.20 mm Ø). The intent for this series of runs was to start at the lowest operable circulating liquid flow rate and slowly increase it, step by step, in order to find the point at which the flow rate was sufficient to smoothly fluidize the catalyst bed, but not be so great as to carry over solids due to excess bed expansion. The catalyst was used in conjunction with Witco 40 mineral oil and a Lurgi feed gas. The results for this variable scan are presented in Table 5-1. Based on the extraordinary increase in conversion between runs 130-1 and 130-2, it was concluded that smooth fluidization had occured at a liquid flow rate between 8-15 gpm/ft^2 (at reaction conditions). This compares with a normal operating value of about 50 gpm/ft^2 for the -16 +20 mesh particles. Having established the minimum flow rate necessary to fluidize the bed, the process liquid flow rate was raised incrementally to establish an upper operating bound. On three consecutive days, increased flow rate resulted in significantly increased conversion levels (compare runs 131-1 and 132-2, and 133-1 and 133-2). However, when the test conditions were repeated on the fourth day, a lower conversion was obtained. These incremental losses in activity at the higher liquid flows were due to catalyst solids lost during start-up. This was substantiated at the end of the variable

TABLE 5-1

SIMULATED SLURRY OPERATION IN THE BENCH SCALE UNIT
COMMERCIAL CATALYST A[1] (50 x 70 MESH)/WITCO 40/LURGI FEED GAS[2]

RUN NO.	TEMP. C	PRESSURE psig	VHSV Hr^{-1}	CIRCULATING PROCESS OIL FLOW RATE[3] GPH	CO CONVERSION TO $MeOH$[4] PERCENT
129-1	230	500	1030	1.3	20.6
129-2	230	500	2420	1.3	13.8
130-1	230	500	2515	1.3	13.8
130-2	230	500	2480	2.6[5]	20.1
131-1	230	500	2450	2.6	18.8
131-2	230	500	2420	3.9	22.4
132-1	230	500	2470	3.9	20.5
132-2	230	500	2440	5.2	23.2
133-1	230	500	2360	5.2	19.2
133-2	230	500	2450	6.5	23.4
134-1	230	500	2470	6.5	18.3
134-2	230	1000	3380	6.5	40.1
135-1	230	1000	3840	6.5	38.8
135-2	230	1000	1550[6]	6.5	47.9

[1]Catalyst Loading = 235 grams = 210 cm^3

[2]Nominal Composition: 50% H_2, 25% CO, 10% CO_2 and 15% CH_4

[3]Normal flow rate for 16 x 20 mesh particles is 7.8 GPH at the pump

[4]Includes small selectivity to higher alcohols (< 2%).

[5]Fluidization is assumed to have occurred over this range.

[6]After shutdown, it was found that 40% of catalyst was entrained from the system.

scan, when only 60 percent of the original catalyst inventory was recovered. Based on weight of catalyst recovered, the conversion level at the adjusted space velocities are 30 - 40 percent greater than those levels obtained with the larger, -16 + 20 mesh particles (see Table 5-2).

COMBINED WATER-GAS SHIFT/METHANOL SYNTHESIS REACTIONS

The purpose of this experiment was to examine the feasibility of simultaneously effecting the water gas-shift and methanol synthesis reactions by the direct addition of steam to the synthesis reactor. If successful, this technique would increase the H_2/CO molar ratio of a hydrogen deficient synthesis gas, eg., a Koppers-Totzek feed gas (H_2/CO = 0.60-0.65), to the stoichiometric level of H_2/CO = 2, in situ, and thereby increase methanol reactor productivity in a once-through process. Alternatively, it might be possible to reduce the size of the shift conversion section of a total conversion methanol plant.

Catalyst A (-16 +20 mesh) and Exxon Aromatic 150 oil were used with both a Lurgi and Koppers-Totzek feed gas. The results, presented in Table 5-3 and Figure 5-1 indicate that Catalyst A is such an effective shift catalyst that the steam-carbon monoxide reaction takes place preferentially, at the expense of the methanol synthesis reaction. This reduces methanol productivity, especially so for gases that already have the required H_2/CO stoichiometry, eg., Lurgi. For non-stoichiometric synthesis gases, eg., Koppers-Totzek, the fall off in productivity is relatively slow. The combination of reactions results in an unreacted product gas stream differing significantly from the feed in its H_2/CO ratio (i.e., H_2/CO_{eff} > 2 for Run 118-2). It would thus be possible to carry out integrated total conversion (with recycle) of an unbalanced gas without a separate shift conversion step and without a substantial reduction in reactor productivity.

CO_2 REACTIVITY

The purpose of these experiments was to investigate the relative reactivities of CO_2 and CO. Most of the past work had been performed with Lurgi and KT type synthesis gases, and equilibrium considerations show that under virtually all reaction conditions CO_2 should not

TABLE 5-2

COMPARISON OF METHANOL PRODUCTIVITY FOR 16 x 20 AND 50 x 70 MESH CATALYST A

| | | | 50 x 70 MESH[1] | | | 15 x 20 MESH [2] | |
| | | | VHSV (Hr⁻¹) | | | | |
RUN NO.	TEMP. (°C)	PRESS. (psig)	BASED ON CATALYST LOADED	BASED ON CATALYST RECOVERED	CO CONVERSION (%)	VHSV (Hr⁻¹)	CO CONVERSION (%)
133-2	230	500	2450	4080	23.4	4100	14 - 16
134-1	230	500	2470	4115	18.3		
134-2	230	1000	3380	5635	40.1	5700	32 - 35
135-1	230	1000	3480	5800	38.8		

[1] See Table 5-1

[2] See EPRI Report AF-202, August 1976, Section VI.

TABLE 5-3

EFFECT OF STEAM ADDITION ON METHANOL SYNTHESIS REACTION
COMMERCIAL CATALYST A[1] (16x20 MESH)/EXXON AROMATIC 150

| RUN NO. | FEED GAS[2] | TEMP. (°C) | PRESS. (psig) | VHSV[3] (Hr^{-1}) | MOLES STEAM / MOLES DRY GAS | MOLES STEAM / MOLE CO | % CO CONVERSION | % SELECTIVITY | | H_2/CO EXIT |
								TO CO_2	TO MeOH[4]	
112-1	Lurgi	230	1000	4760	0.145	0.58	51.2	85	15	
113-1	Lurgi	230	1000	4900	---	---	35.4	0	100	
114-1	Lurgi	230	1000	1000	---	---	35.3	0	100	
115-1	KT	230	1000	3760	---	---	14.5	10	90	0.45
116-1	KT	230	1000	3760	0.087	0.145	25.0	50	50	0.68
117-1	KT	230	1000	3760	---	---	15.2	10	90	0.44
117-2	KT	230	1600	3760	0.174	0.290	35.0	75	25	1.11
118-1	KT	230	1000	3760	0.174	0.290	35.0	70	30	1.03
118-2	KT	230	1000	3760	0.261	0.435	60.0	85	15	2.41

[1]Catalyst Loading = 219.6 gm.

[2]Lurgi Feed Gas: 50% H_2, 25% CO, 10% CO_2, and 15% CH_4. KT Feed Gas: 3C% H_2, 60% CO, and 2% CO_2.

[3]Dry gas basis.

[4]Includes small selectivity to higher alcohols.

FIGURE 5-1

EFFECT OF DIRECT STEAM ADDITION
ON METHANOL PRODUCTIVITY
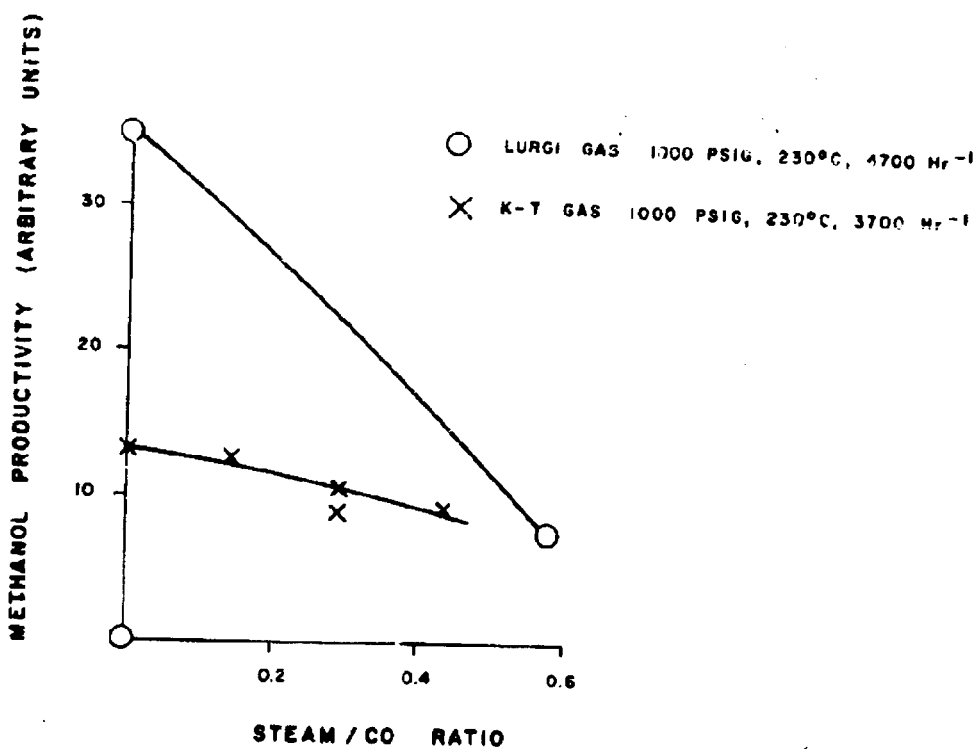
react. (This has been repeatedly confirmed by experimental evidence.) For this reason, feed gas compositions were chosen that would lead to substantial conversion of both CO_2 and CO at equilibrium, as shown below.

Feed Gas Composition; %

Gas	CO	CO_2	Inerts*	H_2
A	9.2	7.3	7.6	Balance
B	14.3	9.5	4.1	Balance
C	2.7	13.9	5.6	Balance

* Used to aid in closing the mass balance.

A series of experiments were conducted over a practical range of temperature, pressure, and gas flow.

The high H_2 feed composition, coupled with the reaction stoichicmetry, allowed a reasonably constant H_2 pressure to be maintained across the reactor. The results for these three gases are presented in Tables 5-4, -5 and -6, and Figures 5-2, -3 and -4, respectively.

While the original equilibrium calculations had been done for gases of slightly different compositions (a result of limitation in the gas blending step), the actual equilibrium values are not sufficiently different to change the qualitative nature of the results. In general, both CO_2 and CO are equally reactive. That is, under a given set of reaction conditions, their individual approaches to equilibrium, expressed as a ratio of the actual conversion to the theoretical conversion at equilibrium, are nearly the same. Values of approach to equilibrium on the order of 60-90 percent are readily obtainable. However, whether or not CO_2 reacts directly with H_2 to form methanol, or reacts with H_2 via a reverse water gas shift mechanism to yield CO (which subsequently forms methanol) is not known. (Some of the runs with the third gas composition had spurious analyses). Nevertheless, the data obtained should be useful in future reaction modelling studies.

TABLE 5-4

PROCESS VARIABLE SCAN

CATALYST A*/WITCO 40 MINERAL OIL/GAS BLEND A

RUN NO.	TEMP. °C	PRESSURE psig	VHSV** SCFH GAS/CF CATALYST	% CONVERSION		CONVERSION AS % APPROACH TO EQUILIBRIUM***	
				CO	CO_2	CO	CO_2
161-1	230	1000	2830	70.3	28.0	78.1	65.1
-2	230	1000	5590	55.1	23.0	61.2	53.5
-3	250	1000	1720	63.1	22.8	78.9	76.0
-4	250	1000	5385	52.5	23.1	65.6	77.0
-5	250	1000	2980	58.5	20.3	73.1	67.7
-6	270	1000	1895	50.0	19.1	73.5	79.6
-7	270	1000	2885	48.6	20.5	71.5	85.4
-8	270	500	880	17.7	11.1	59.0	100
-9	270	500	1745	17.2	17.5	57.3	100?
-10	250	500	915	36.9	9.6	76.9	80.0
-11	250	500	3265	25.1	10.9	52.3	90.8
-12	250	500	1695	26.9	7.1	56.0	59.1
-13	230	500	1585	40.9	11.7	68.2	58.5
-14	230	500	2190	30.5	11.4	50.3	57.0
-15	230	1000	2845	64.0	22.3	71.1	51.9

* Catalyst loading - 219.6 grams

** Nominal feed gas composition: 9.2% CO, 7.3% CO_2, 7.6% Inerts and balance H_2.

*** Based on 8.7% CO, 6.8% CO_2, 7.4% Inerts and balance H_2.

TABLE 5-5

PROCESS VARIABLE SCAN
CATALYST A*/WITCO 40 MINERAL OIL/GAS BLEND B

RUN NO.	TEMP. °C	PRESSURE psig	VHSV** SCFH GAS/CF CATALYST	% CO	CONVERSION CO₂	CONVERSION AS % APPROACH TO EQUILIBRIUM*** CO	CO₂
162-1	230	1000	3020	69.6	25.8?	79.1	100?
-2	230	1000	5175	51.3	11.6	58.3	55.2
-3	250	1000	1675	64.4	12.8	81.5	80.0
-4	250	1000	5370	51.8	14.9	65.6	93.1
-5	250	1000	2555	58.6	14.4	74.2	90.0
-6	250	500	805	35.0	8.5	76.1	100
-7	250	500	2760	27.5	10.7	59.8	100
-8	250	500	1650	33.1	7.6	72.0	95.0
-9	230	500	1605	45.2	8.4	66.5	93.3
-10	230	500	2975	35.1	11.4	51.8	100
-11	230	1000	2600	68.8	17.5	78.2	83.3

* Catalyst Loading = 219.6 grams.

** Nominal feed gas composition: 14.3% CO, 4.1% Inerts and balance H_2.

*** Based on 15% CO, 9% CO_2, 3% Inerts and balance H_2 equilibrium.

TABLE 5-6

PROCESS VARIABLE SCAN

CATALYST A*/WITCO 40 MINERAL OIL/GAS BLEND C

RUN NO.	TEMP. °C	PRESSURE psig	VHSV** SCFH GAS/CF CATALYST	% CONVERSION		CONVERSION AS % APPROACH TO EQUILIBRIUM***	
				CO	CO_2	CO	CO_2
163-1	230	1000	2725	30.7	28.3	45.6	50.0
-2	230	1000	5540	22.3	25.1	33.0	44.3
-3	250	1000	1690	35.6	28.6	61.4	59.6
-4	250	1000	5270	04.9	28.2	25.7	58.8
-5	250	1000	2845	28.3	32.4	48.3	67.5
-6	250	500	3140	0 ?	19.8	---	NA****
-8	250	500	1820	0 ?	22.8	---	NA****
-9	230	500	1715	14.9	22.5	NA****	NA****
-10	230	500	3105	0 ?	17.9	---	NA****
-11	230	1000	2745	36.7	27.4	54.5	48.4

* Catalyst loading = 219.6 grams.

** Nominal feed composition: 2.7% CO, 13.9% CO_2, 5.6% Inerts and balance H_2.

***Based on 3% CO, 13% CO_2, 6% Inerts and balance H_2.

****Not calculated due to spurious analytical results.

FIGURE 5-2

PROCESS VARIABLE SCAN

CATALYST A / WITCO # 40 MINERAL OIL

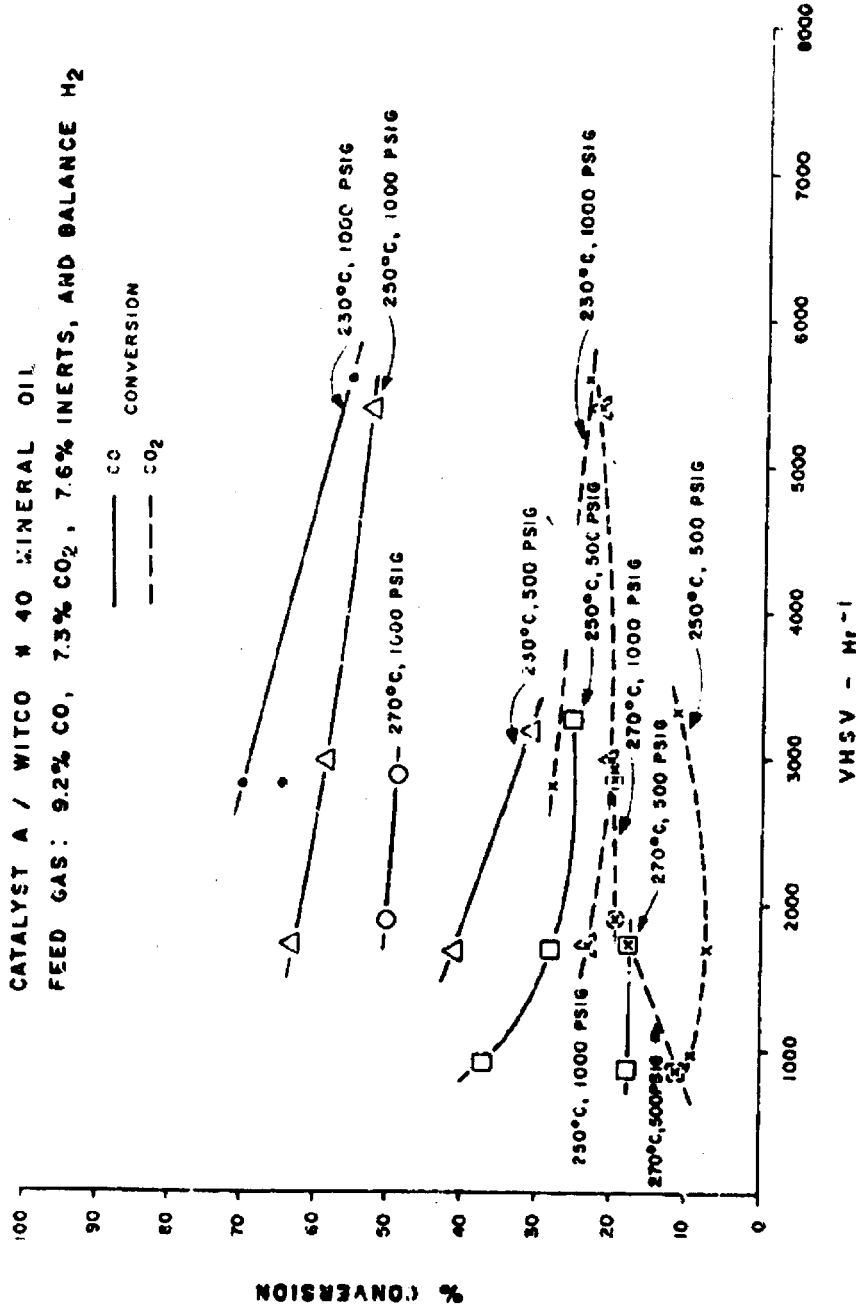FEED GAS: 9.2% CO, 7.3% CO_2, 7.6% INERTS, AND BALANCE H_2

CO CONVERSION

CO_2

VHSV – Hr^{-1}

% CONVERSION

230°C, 1000 PSIG
250°C, 1000 PSIG
270°C, 1000 PSIG
230°C, 1000 PSIG
250°C, 500 PSIG
230°C, 500 PSIG
270°C, 1000 PSIG
250°C, 500 PSIG
250°C, 1000 PSIG
270°C, 500 PSIG
270°C, 500 PSIG

FIGURE 5-3

PROCESS VARIABLE SCAN

CATALYST A / WITCO # 40 MINERAL OIL

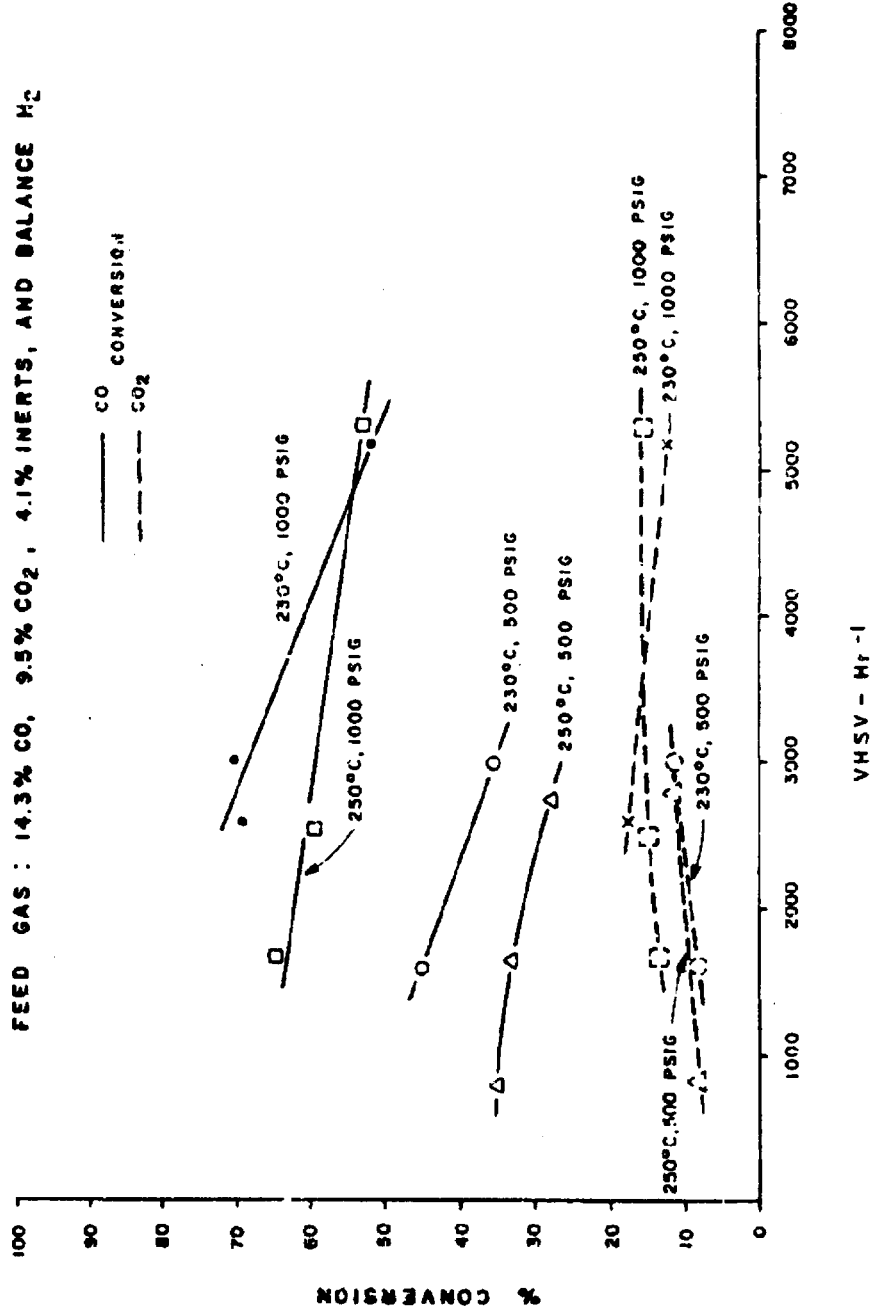FEED GAS : 14.3% CO, 9.5% CO_2, 4.1% INERTS, AND BALANCE H_2

FIGURE 5-4

PROCESS VARIABLE SCAN

CATALYST A / WITCO * 40 MINERAL OIL
FEED GAS : 2.7% CO, 13.9% CO$_2$, 5.6% INERTS, AND BALANCE H$_2$