K.  Studies with Developmental Fluid Catalyst SGF-A-3

Catalyst SGF-A-3 has water-gas shift activity, and can effectively convert low $H_2$/CO ratio synthesis gas. Anticipating that low ratio gas will be cheaper than high ratio, synthesis gas with a $H_2$/CO ratio of one was used, almost exclusively, in studies with catalyst SGF-A-3. Experimental work was done in both the fixed bed micro reactor units and in the fluid bed bench-scale unit. Fluid catalyst SGF-A-3 was pelletted, crushed and sized, and designated SG-A-4 for the fixed bed work.

1.  Task 1 - Exploratory Process Research

The experiments in Task 1 were made with SG-A-4 which is chemically identical to SGF-A-3. The performance of catalyst SG-A-4 was evaluated in micro reactor units with respect to activation procedures, process studies, and especially aging and regeneration. Related detailed data are given in Appendix E.

a.  Activation

A 16 hour pretreatment in flowing synthesis gas of 1/1 $H_2$/CO composition at 610°F and 0 psig was used as the standard activation procedure for catalyst SG-A-4. The effect of pretreating in hydrogen or in carbon monoxide on activity was compared with the standard procedure.

Pretreatment in flowing hydrogen proved detrimental. Summarized in Table 77 are results obtained on sequentially treating one SG-A-4 catalyst loading with hydrogen at 0 psig, hydrogen at 200 psig, synthesis gas and finally air followed by synthesis gas. Processing was performed after each treating step. Note that hydrogen treatment, either at zero or 200 psig, completely deactivates the catalyst. Further, the standard activation procedure of $H_2$/CO synthesis gas at 610°F, fails to activate the catalyst after exposure to hydrogen. However, an oxidative treatment (initial temperature 750°F in 10% air, final conditions 16 hr-100% air-950°F) of this deactivated catalyst, followed by the standard pretreat in synthesis gas yields an active catalyst. A comparison with fresh catalyst shows a 14% higher carbon monoxide conversion (78 vs 64%).

As part of a multiple regeneration study of catalyst SG-A-4, a brief investigation was made on pretreatment in carbon monoxide as an activation method. Table 78 summarizes the comparison between synthesis gas and carbon monoxide as pretreatment gases. The early on stream data indicate that the carbon monoxide treatment yields a more active catalyst. However, at about four and six days on stream, there is little or no difference between the two pretreatment methods. Also, the hydrocarbon selectivities are essentially the same. The conclusion is that catalyst SG-A-4 can be activated by pretreatment in either synthesis gas or carbon monoxide.

# TABLE 77

## HYDROGEN PRETREATMENT OF CATALYST SG-A-4 [a]

| Run CT-143-77 | -1 | -2 | -3 | -5 [b] |
|---|---|---|---|---|
| Stream Days | 0.9 | 0.9 | 1.8 | 1.9 |
| Treatment, 16 Hr | 0 psig $H_2$-950°F | 200 psig $H_2$-950°F | 0 psig $H_2$/CO-610°F | Air-950°F-0 psig + $H_2$/CO-610°F |
| CO Conversion, wt % | <1 | <1 | <1 | 78 (64) |
| $H_2$ Conversion, wt % | <1 | <1 | <1 | 65 (59) |
| Selectivity, wt % | | | | |
| $C_1$+$C_2$ | - | - | - | 31 (29) |
| $C_5^+$ | - | - | - | 50 (54) |

(a) Process conditions - 200 psig, 575°F, $H_2$/CO, 575 GHSV.

(b) () indicates fresh catalyst data using standard activation with $H_2$/CO at 610°F.


# TABLE 78

## CARBON MONOXIDE PRETREATMENT OF CATALYST SG-A-4 [a]

### (Processing $H_2$/CO at 575°F, 200 psig and 580 GHSV)

| | | Pretreat for 16 Hrs at 610°F and 0 psig | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | $H_2$/CO | | | | CO | | |
| Run CT-143-80- | R [b] | 24 | 25 | 26 | R [b] | 31 | 32 | 33 |
| Days On Stream | E G E | 1.9 | 3.9 | 5.9 | E G E | 1.9 | 3.9 | 5.9 |
| Conversion, wt % | N | | | | N | | | |
| CO | E | 71 | 67 | 73 | E | 80 | 71 | 75 |
| $H_2$ | R A | 61 | 59 | 62 | R A | 63 | 59 | 61 |
| Selectivity, wt % | T | | | | T | | | |
| $C_1$+$C_2$ | I | 35 | 34 | 35 | I | 36 | 33 | 36 |
| $C_5^+$ | O N | 49 | 50 | 44 | O N | 47 | 51 | 49 |

(a) Catalyst had previously 41 days on stream.

(b) Conditions: 5 hrs $H_2$ @ 750°F; 1 hr 10% air @ 750°F; 4 hrs 100% air @ 850°F.

TABLE 79

REGENERATION OF CATALYST SG-A-4[a,b]

(Activation: 16 Hrs, $H_2/CO$, 610°F, 0 psig)

(Processing at 575°F, 200 psig, 575 GHSV, $H_2/CO$)

| | Cycle | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 Fresh | | 2 | | 3 | | 4 | | 5 | |
| Run #143- | 75-1 | 75-3 | 75-11 | 75-13 | 75-18 | 75-20 | 75-21 | 75-23 | 75-24 | 75-26 |
| Days On Stream | 1.9 | 5.9 | 1.9 | 5.9 | 1.9 | 5.9 | 1.9 | 5.9 | 1.9 | 5.8 |
| **% Conversion** | | | | | | | | | | |
| CO | 64 | 64 | 65 | 65 | 59 | 57 | 51 | 49 | 68 | 71 |
| $H_2$ | 59 | 58 | 61 | 62 | 60 | 59 | 53 | 58 | 62 | 63 |
| **% HC Selectivity** | | | | | | | | | | |
| $C_1 + C_2$ | 29 | 34 | 33 | 37 | 32 | 35 | 31 | 37 | 36 | 38 |
| $C_5^+$ | 54 | 59 | 59 | 58 | 52 | 49 | 52 | 45 | 45 | 44 |
| % $C_5^=$ in $C_5$ Fraction | 13 | 39 | 12 | 30 | 13 | 30 | 14 | 24 | 15 | 21 |
| % $MeC_4^=$ in $C_5^=$ | 87 | 82 | 80 | 80 | 79 | 78 | 79 | 76 | 80 | 78 |
| % $C_6^+$ Aromatics | 43 | 21 | 41 | 26 | 44 | 26 | 43 | 35 | 45 | 40 |

(a) Regeneration after Cycles 1-3 - air, 16 hrs, 950°F, 0 psig followed by standard activation.
(b) Regeneraiton after Cycle 4 - air, 16 hrs, 950°F, 0 psig; $H_2$, 16 hrs, 950°F, 0 psig; air, 16 hrs, 950°F, 0 psig followed by standard activation.

Figure 78

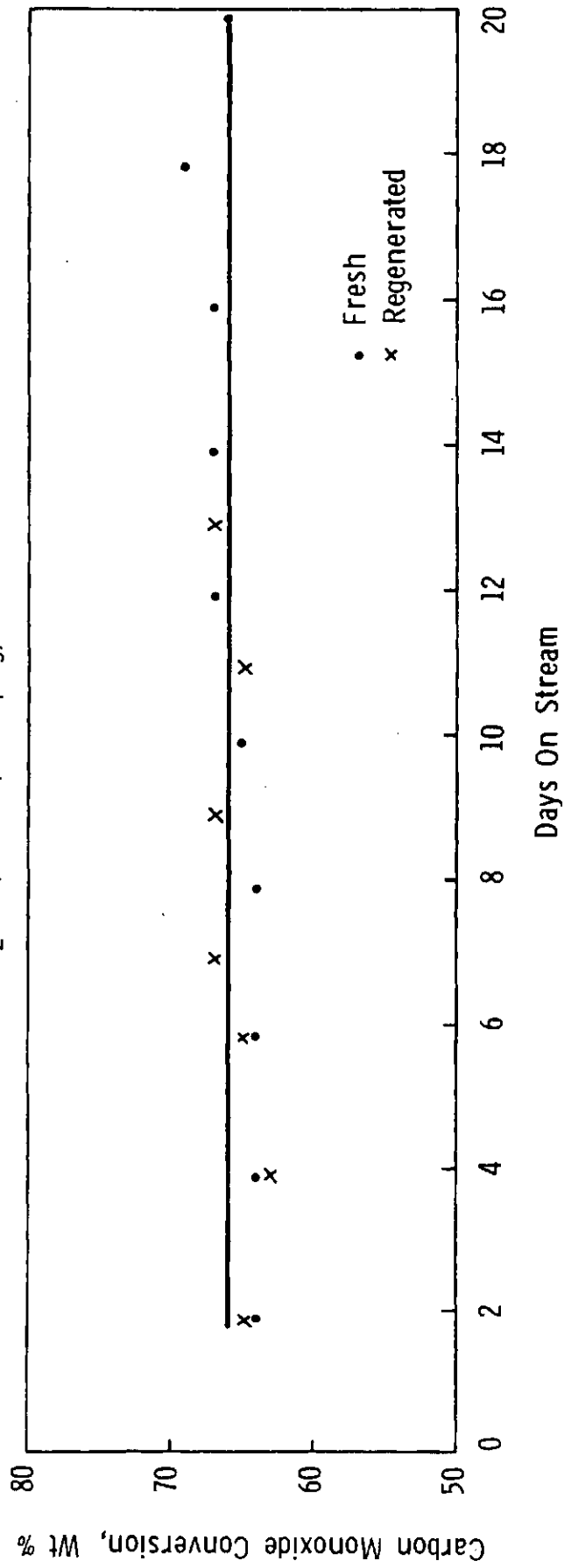AGING AND REGENERATION OF SG-A-4
($H_2$/CO, 575°F, 200 psig, 575 GHSV)

Figure 79

SELECTIVITY AGING OF SG-A-4
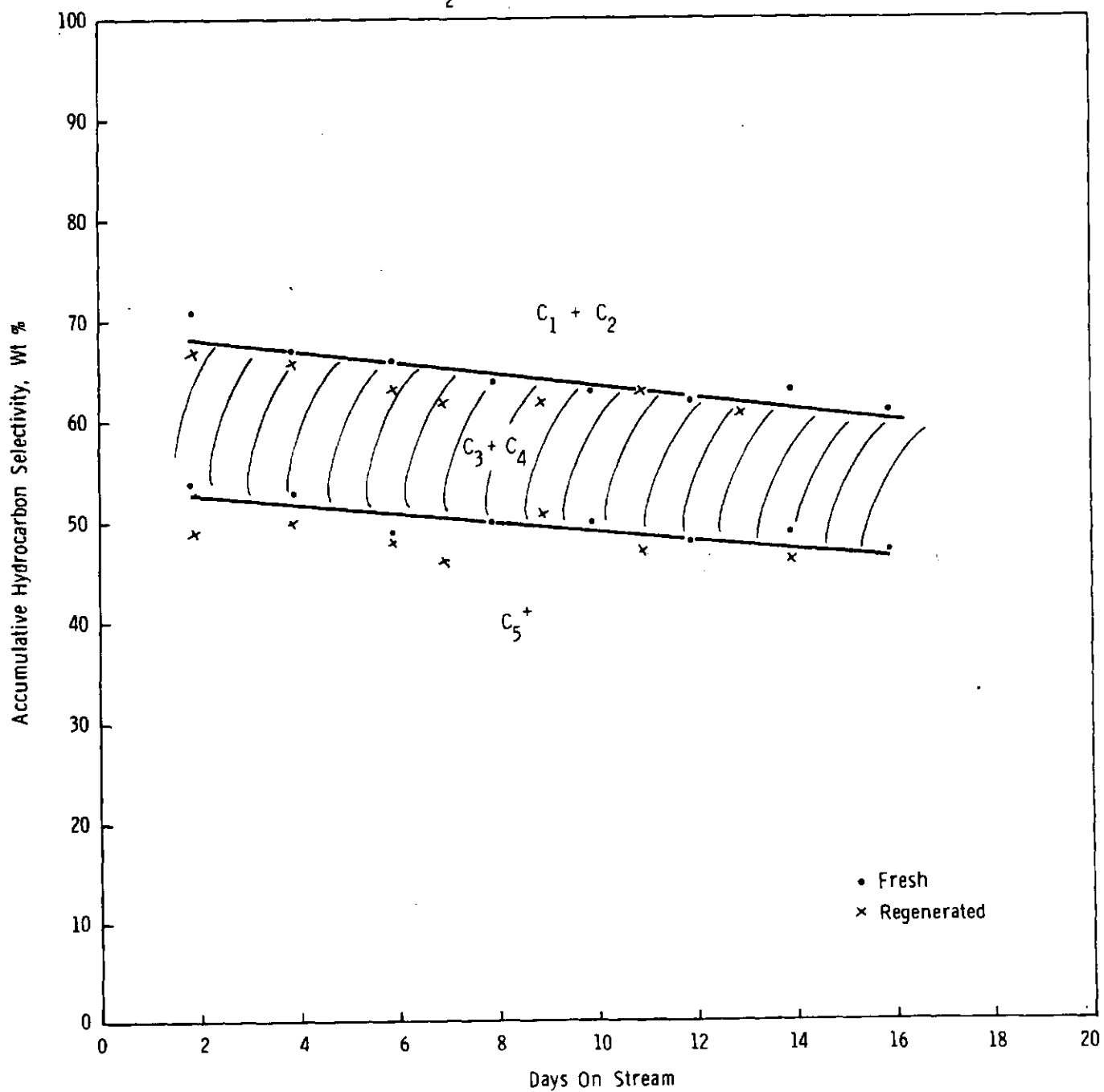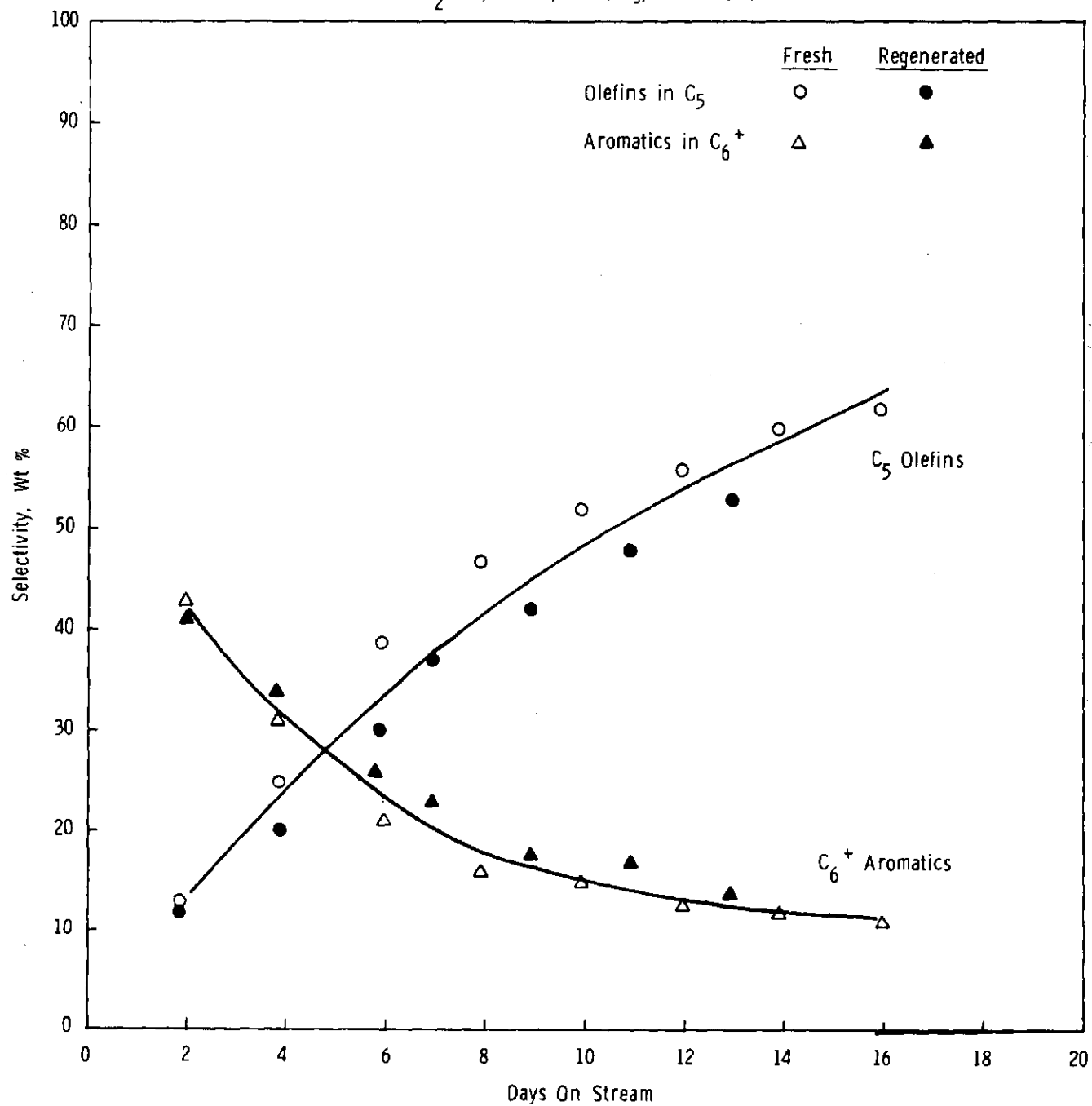($H_2$/CO, 575°F, 200 psig, 575 GHSV)



- Fresh
× Regenerated

Figure 80

OLEFIN AND AROMATIC PRODUCTION ON AGING AND REGENERATION OF SG-A-4
$(H_2/CO,\ 575°F,\ 200\ psig,\ 575\ GHSV)$

Comparisons in Table 79 are made at 1.9 and 5.9 days on stream for the fresh, regenerated and the rejuvenated catalyst. After three air regenerations, catalyst carbon monoxide conversion activity dropped to 51% from 64% (fresh). After the rejuvenation treatment, shown above, carbon monoxide conversion increased to 68% which is higher than the 64% conversion produced by the fresh catalyst. However, the reactivated catalyst shows $(C_1+C_2)$ levels slightly higher while $C_5^+$ yields are somewhat lower than those obtained with fresh catalyst.

### c.  Process Variables

This study measured the effect of temperature, pressure and space velocity on catalyst SG-A-4 performance. Since the catalyst appeared stable to multiple regenerations, an effort to optimize the regeneration procedure and to obtain data to support an estimate of catalyst life, was incorporated into this study.

### Temperature

For the initial experiments, one loading of catalyst was used and the temperature was varied between 530° and 575°F. The runs were made in descending order and the highest temperature experiment was repeated at the end of the sequence. Processing was with synthesis gas of $H_2$/CO composition at 200 psig and 600 GHSV.

As shown in Figure 81, carbon monoxide conversion decreases about 7% for each 10°F lowering of the process temperature. However, the $C_5^+$ gasoline selectivity remains constant at 57% for each condition. The repeat experiment at 575°F, indicates no catalyst aging with respect to activity and $C_5^+$ gasoline selectivity. Although the $C_5^+$ gasoline selectivity remains constant, Figure 80 shows that its composition does vary with time as olefins increase and aromatics decrease. Experiments at each process condition, with a fresh or regenerated catalyst, would have more realistically represented the effect of temperature on catalyst performance.

The cross-over of the aromatic and olefin selectivities (Figure 80) occurs at about five to six days on stream. At this point the $C_6^+$ aromatics and $C_5$ olefin selectivities are both about 30%. A six day cycle time was selected for further experiments with catalyst SG-A-4. The catalyst loading used in the previous sequence was regenerated by purging with hydrogen for 16 hours at 750°F, heating in 10% air at 750°F for one hour and finally heating in 100% air at 850°F for four hours. A temperature study at 575°, 560° and 545°F was started. The catalyst was held at each temperature for six days, and then regenerated, as above, before moving to the new condition.

Complete data are shown in Appendix E (Table E6) and selected data in Table 80. As in the earlier study, carbon monoxide conversion decreases about 7% for each 10°F lowering of temperature. The $C_1+C_2$ selectivity is constant at 28%. However, the changes in

Figure 81

EFFECT OF TEMPERATURE ON ACTIVITY AND $C_5^+$ SELECTIVITY
WITH CATALYST SG-A-4

(Processing $H_2$/CO at 200 psig and 600 GHSV)
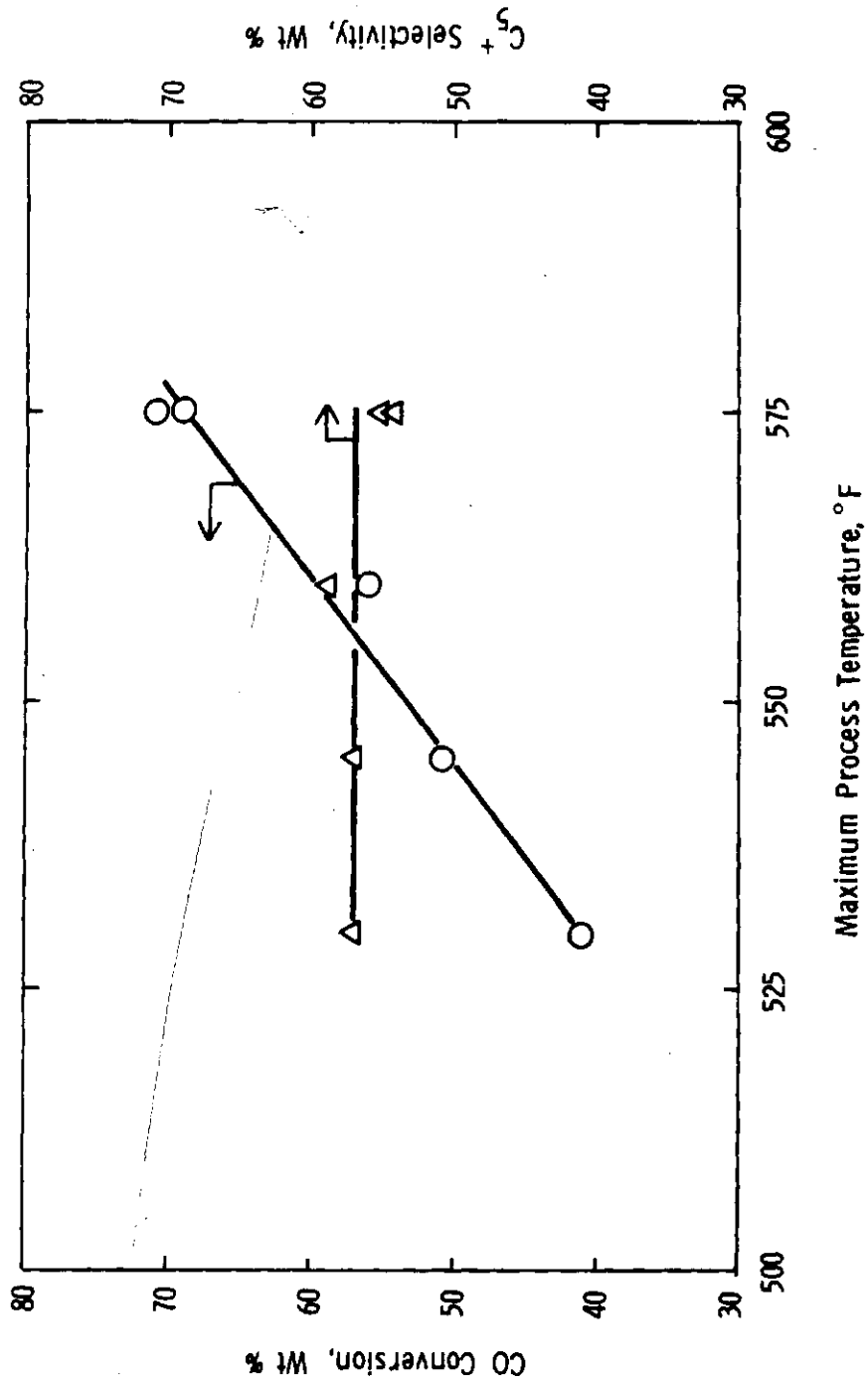
$C_5^+$ gasoline selectivity cannot be explained. As expected, the $C_5$ olefin selectivity is highest at the lowest temperature while the $C_6^+$ aromatic selectivity is highest at the high temperature. Of interest, the point of identical concentration for $C_5$ olefins and $C_6^+$ aromatics is constant at about 30% over the temperature range studied (Figure 82). Also, this point occurs at shorter on stream times as reaction temperature is decreased.

The total on stream time for this catalyst loading is now 27 days.

### Pressure

Catalyst SG-A-4 performance was compared at 100, 200 and 400 psig. Processing was with $H_2$/CO synthesis gas at constant temperature, 575°F, and contact time, 44 seconds. The catalyst loading from the temperature study was used.

The detailed data are shown in Table E7 of Appendix E. The data plotted in Figure 83 indicate that carbon monoxide conversion decreases linearly with increasing process pressure. Selected data taken at 3 to 4 days on stream are shown in Table 81. At 100 psig increased carbon monoxide conversion is obtained at the expense of throughput rate, and lower $C_5^+$ gasoline selectivity. As expected, aromatic formation increases at lower pressure. Decreasing space velocity at 400 psig to improve the carbon monoxide conversion would probably give increased $C_1+C_2$ selectivity at the expense of gasoline. For catalyst SG-A-4, an operating pressure of 200 psig is the best compromise between activity and selectivity.

The catalyst loading has now been on stream for 44 days or seven cycles (six regenerations). It appears to fully recover activity following each regeneration, however, small losses in $C_5^+$ gasoline selectivity are apparent. The raw $C_5^+$ gasoline produced during this time has a 90% overhead boiling point <400°F and an octane number of 91-92 (R+0).

### Space Velocity

Several runs were made to study the effect of changes in space velocity and temperature on catalyst performance. The objective was to increase the single-pass carbon monoxide conversion to 90%. The data are given in Appendix E (Table E9).

Data extracted from Appendix E, and presented in Table 82, show the effect on activity and selectivity while processing $H_2$/CO at 200 psig and 280 GHSV at temperatures from 560° to 580°F. The results indicate that it is possible to obtain high, single-pass carbon monoxide conversions with reasonable $C_5^+$ gasoline selectivities. At these conditions, low olefin and high aromatic selectivities are observed. Operational data obtained at a constant temperature of 575°F and 200 psig, while varying space velocity, are also shown in Table 82. Doubling the space rate

# Figure 82

### EFFECT OF TEMPERATURE AND STREAM TIME ON
### YIELDS OF $C_6{}^+$ AROMATICS AND $C_5$ OLEFINS
### PRODUCED BY SG-A-4

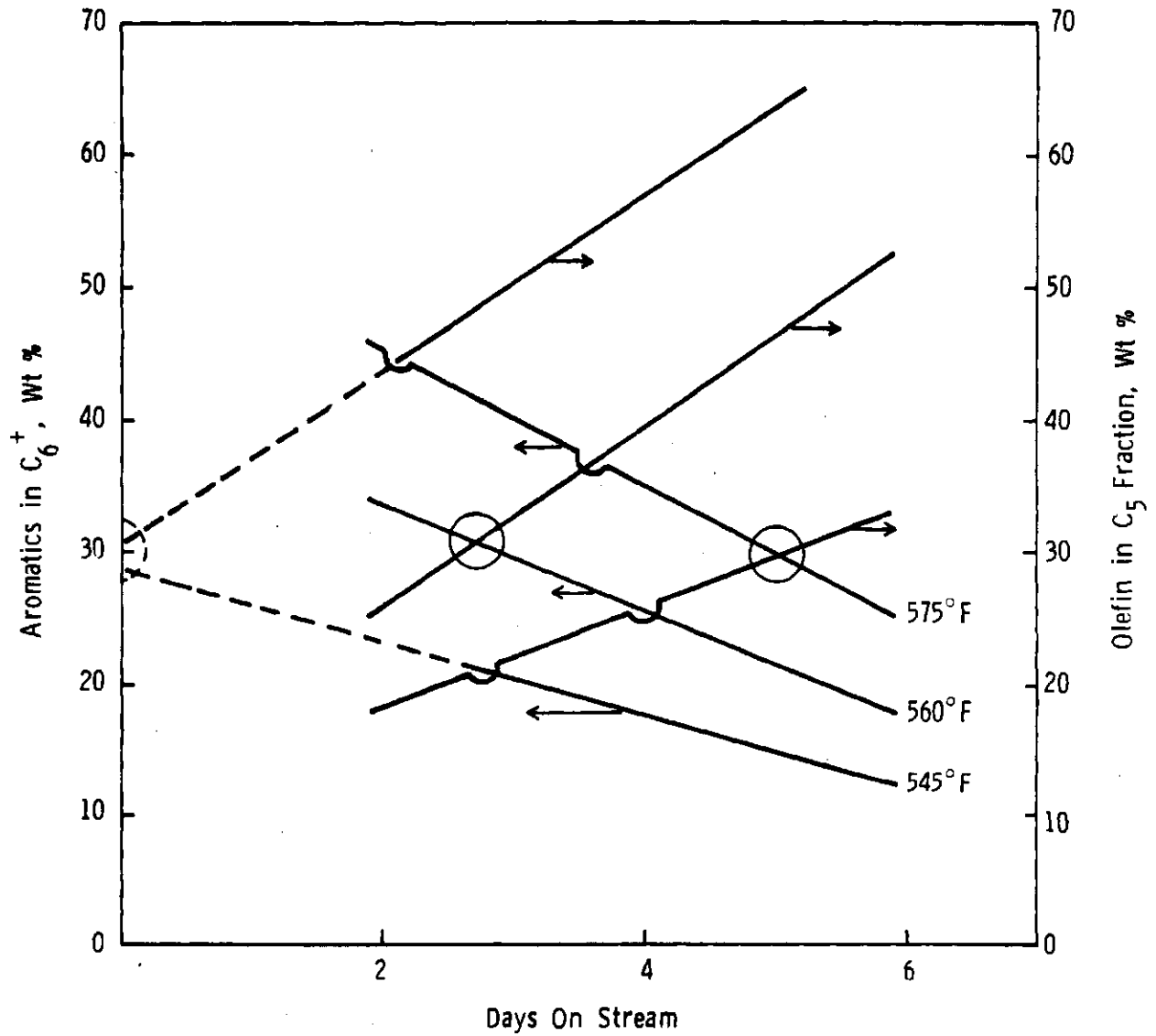($H_2$/CO at 200 psig and 600 GHSV)

Figure 83

EFFECT OF REACTION PRESSURE ON ACTIVITY OF SG-A-4

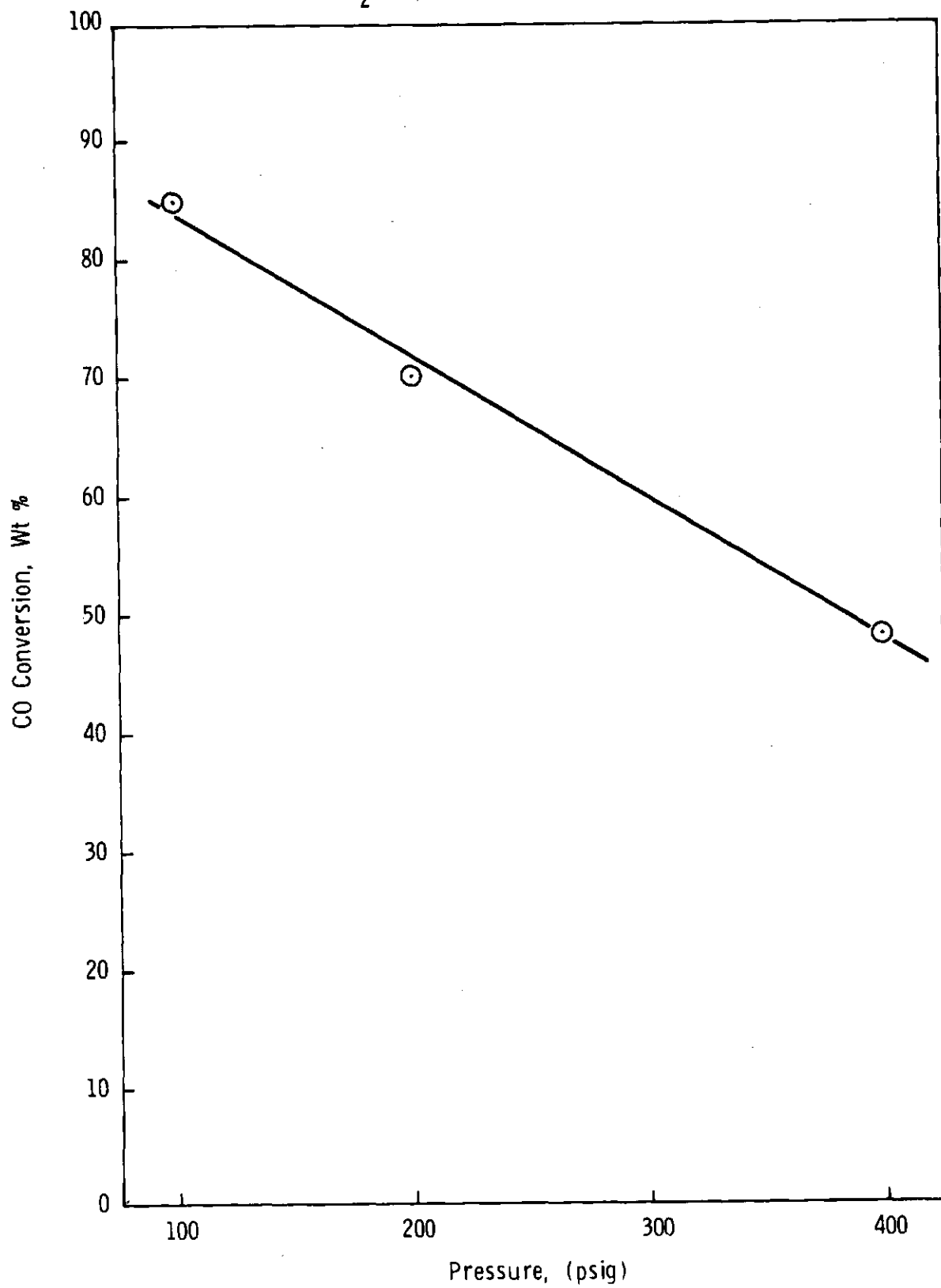(H$_2$/CO, 575°F and $T$ = 44 Seconds)

TABLE 80

EFFECT OF TEMPERATURE ON
CATALYST SG-A-4 ACTIVITY AND SELECTIVITY

(Processing $H_2$/CO at 200 psig and 600 GHSV)

| | Temperature, °F at Two Days On Stream | | |
|---|---|---|---|
| | 575 | 560 | 545 |
| Conversion, wt % | | | |
| CO | 70 | 63 | 48 |
| $H_2$ | 62 | 61 | 58 |
| Selectivity, wt % | | | |
| $C_1$+$C_2$ | 28 | 28 | 28 |
| $C_5$+ | 53 | 49 | 58 |
| Olefins in $C_5$ | 13 | 25 | 43 |
| Aromatics in $C_6$+ | 46 | 34 | 24 |


TABLE 81

EFFECT OF PRESSURE ON
CATALYST SG-A-4 ACTIVITY AND SELECTIVITY

(Processing $H_2$/CO at 575°F and 44 sec contact time)

| | Pressure | | |
|---|---|---|---|
| | 100 | 200 | 400 |
| Days On Stream | 3.9 | 3.9 | 2.9 |
| GHSV | 308 | 590 | 1140 |
| Conversion, wt % | | | |
| CO | 78 | 70 | 48 |
| $H_2$ | 64 | 66 | 54 |
| Selectivity, wt % | | | |
| $C_1$+$C_2$ | 42 | 36 | 38 |
| $C_5$+ | 39 | 46 | 47 |
| Olefins in $C_5$ | 6 | 22 | 65 |
| Aromatics in $C_6$+ | 60 | 35 | 15 |


TABLE 82

COMBINED EFFECT OF SPACE RATE AND TEMPERATURE ON
CATALYST SG-A-4 PERFORMANCE

| | GHSV | | | Temperature | |
|---|---|---|---|---|---|
| Temperature, °F | 560 | 566 | 580 | 574 | 574 |
| GHSV | 280 | 280 | 272 | 585 | 1160 |
| Conversion, wt % | | | | | |
| CO | 88 | 87 | 94 | 68 | 45 |
| $H_2$ | 65 | 69 | 71 | 59 | 46 |
| Selectivity, wt % | | | | | |
| $C_1$+$C_2$ | 35 | 36 | 43 | 37 | 34 |
| $C_5$+ | 46 | 43 | 33 | 47 | 51 |
| Olefins in $C_5$ | 9 | 8 | 4 | 38 | 70 |
| Aromatics in $C_6$+ | 44 | 45 | 57 | 26 | 11 |

from 585 to 1160 decreases carbon monoxide conversion from 70 to 45%. As expected, the $C_5^+$ gasoline selectivity is higher at the lower conversion level.

This study has demonstrated that identical $C_5^+$ gasoline selectivities can be obtained at different conversion levels, by adjustments in the space rate and temperature, as:

| | | |
|---|---|---|
| Temperature, °F | 560 | 575 |
| GHSV | 280 | 585 |
| Conversion, wt %, CO | 88 | 68 |
| Selectivity, wt %, $C_5^+$ | 46 | 47 |

### Long Term Aging

The identical charge of catalyst SG-A-4 used in the process studies, had a total on stream time of 56 days (ten cycles, nine regenerations). All processing used synthesis gas having a $H_2$/CO ratio of one. Periodically throughout the studies, the operating conditions were returned to 575°F, 200 psig and 600 GHSV to check long term catalyst aging. Detailed data covering the 56 days of operation are given in Appendix E. The activity and selectivity of the catalyst during this period are shown in Figures 84 and 85, respectively. The activity data are represented by a horizontal line at about 70% carbon monoxide conversion. The $C_5^+$ gasoline selectivity decreases from about 54% initially to about 47% after 56 days. The $C_5^+$ gasoline quality remains constant, and has an octane number and 90% overhead boiling point of 91 R+O and 370°F, respectively.

### 2. Task 2 - Process Development

Studies with catalyst SGF-A-3 in the fluid bench-scale unit were concurrent to those with its fixed bed analog, SG-A-4, in the micro reactor units. All experiments were made using synthesis gas with a $H_2$/CO ratio of one. Areas briefly examined include: catalyst pretreatment, catalyst regeneration, and the effect of temperature, pressure and GHSV on catalyst performance. Fluid, bench-scale experiments with catalyst SGF-A-3 encompassed Runs 225-42 through -50 and 225-56 through -67. Data from significant runs are given in Appendix E, Tables E10-E24.

Start of cycle process conditions for the initial experiment, 225-42, were:

| | |
|---|---|
| Fresh Feed Composition, mol ratio $H_2$/CO | 1/1 |
| GHSV (on fresh feed), $hr^{-1}$ | 1000 |
| Pressure, psig | 200 |
| Temperature, °F | 560 |
| Recycle Ratio | 2/1 |
| Approx. Superficial Lin. Vel., ft/sec | 0.2 |
| Catalyst Volume, cc | 150 |

Figure 84

ACTIVITY OF CATALYST SG-A-4 DURING LONG TERM
AGING-NINE CYCLES
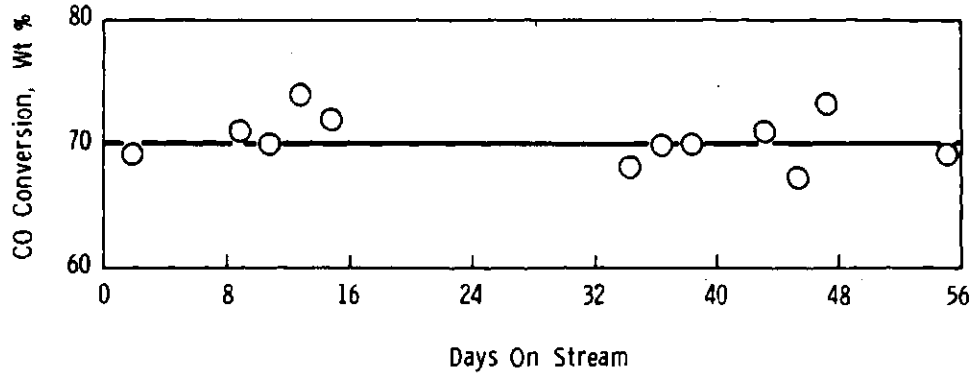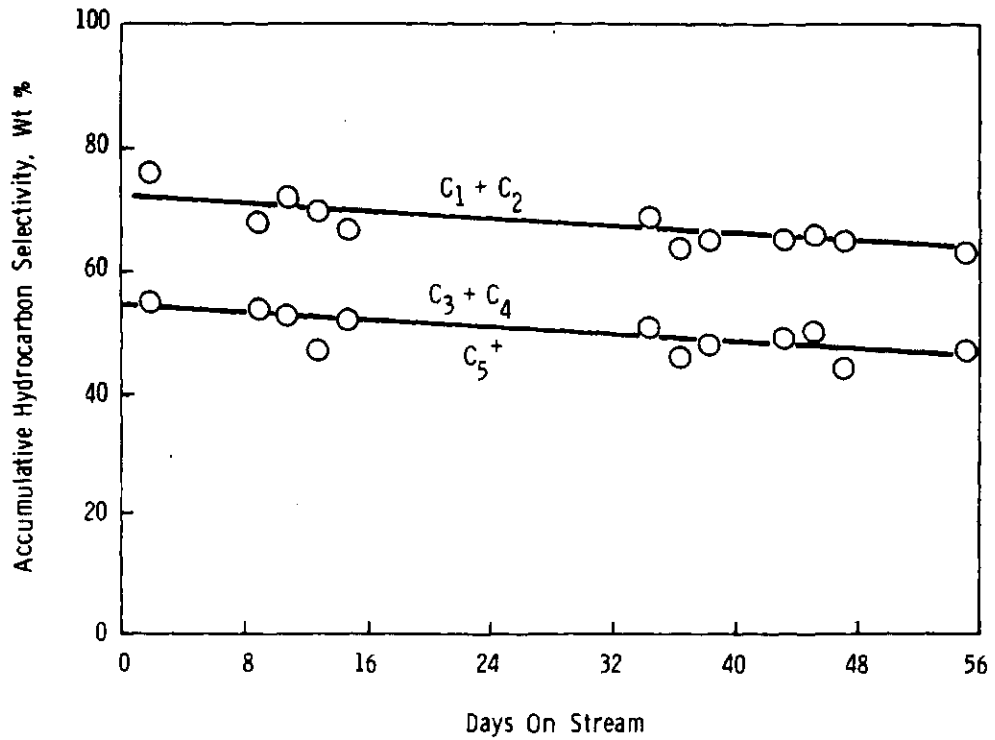(Processing $H_2/CO$ at 575°F, 200 psig and 600 GHSV)



Figure 85

SELECTIVITY OF CATALYST SG-A-4 DURING LONG TERM
AGING-NINE CYCLES
(Processing $H_2/CO$ at 575°F, 200 psig and 600 GHSV)



- 196 -

The experiment ran continuously for 23 days. During this time the reactor temperature was held at 560°F for five days, dropped to 540°F for three days, raised to 580°F for about four days, and then lowered to 560°F for the remainder of the run. Reactor pressure was raised from 200 psig to 300 psig for the last four balances. The following reactor parameters were calculated for these conditions.

|  | Pressure, 200 psig | | | Pressure, 300 psig |
| --- | --- | --- | --- | --- |
|  | 540°F | 560°F | 580°F | 560°F |
| Active Bed Height, ft | 3.0 | 3.0 | 3.0 | 2.8 |
| Sup. Gas Lin. Vel., ft/sec | 0.19 | 0.19 | 0.20 | 0.13 |
| Res. Time, sec | 15 | 15 | 15 | 21 |

### Effect of Temperature

Selected data from Run 225-42, which show the effect of temperature on catalyst SGF-A-3 performance, are given in Table 83. Although some catalyst aging was evident during the 23 days on stream, the effects of temperature observed are directionally valid. The $H_2$+CO conversions, and the $C_1$+$C_2$ and $C_5^+$ selectivities for all the material balances are plotted in Figure 86. During the first five days at 560°F, the $H_2$+CO conversion rose from 52 to 73%, and the $C_5^+$ gasoline selectivity increased from about 55 to 60%.

When the reactor temperature was lowered 20° to 540°F, the $H_2$+CO conversion was reduced from 73% to 67%. However, methane decreased from 17 to 13.5% and $C_5^+$ increased from 59 to 64%. This resulted also in a reduction in $C_5^+$ paraffins (from 16 to 12%) and in aromatics (from 8 down to 0.4%), and an increase in $C_5^+$ olefins (from 21 to 31%) and gasoline range hydrocarbons of unknown structure. Unfortunately, this selectivity shift resulted in a reduction of about 3 octane numbers for the clear raw product. However, the product distribution is such, that a gain of more than 1% by weight and 3% by volume was realized at 540°F versus 560°F, when alkylation products are considered.

When the temperature was raised to 580°F, $H_2$+CO conversion rose to about 80%. But $CH_4$ and other light hydrocarbons rose also, to levels somewhat higher than at 560°F. Selectivity to $C_5^+$ fell to about 53%, as against 60% at 560°F. Although the octane number increased to the same level as at 560°F, the $C_5^+$ plus alkylate dropped by about 5% by weight and volume. The $C_5^+$ olefins decreased a bit while operating at 580°F, but $C_5^+$ paraffins and aromatics seemed to be at about the level that would be expected if the catalyst were aging normally at 560°F.

## TABLE 83

### MATERIAL BALANCES FROM FLUID BENCH-SCALE UNIT WITH CATALYST SGF-A-3

| RUN NUMBER 225- | 42- 3 | 42- 7 | 42-10 | 42-12 | 42-18 |
|---|---|---|---|---|---|
| RUN DAYS-ON-STREAM | 3.3 | 8.3 | 12.3 | 15.3 | 23.3 |
| CUM. DAYS-ON-STREAM | 3.3 | 8.3 | 12.3 | 15.3 | 23.3 |
| FRESH FEED H2/CO RATIO | 1.1 | 1.0 | 1.0 | 1.0 | 1.0 |
| GHSV, HR⁻1 (CHG BASIS) | 995 | 994 | 1003 | 1003 | 995 |
| RECYCLE RATIO | 1.98 | 2.01 | 2.00 | 1.98 | 2.00 |
| REACT. PRESS., PSIG | 201 | 201 | 201 | 200 | 300 |
| REACT. INLET TEMP., °F | 446 | 418 | 426 | 413 | 449 |
| NOM. REACT. TEMP., °F | 560 | 540 | 580 | 560 | 560 |
| CONVERSIONS, MOL °/° | | | | | |
| H2 | 78.4 | 81.3 | 85.0 | 85.2 | 87.3 |
| CO | 62.0 | 53.4 | 76.7 | 73.1 | 82.5 |
| H2+CO | 70.4 | 67.3 | 80.9 | 79.2 | 84.9 |
| YIELDS, WT °/° | | | | | |
| HYDROGEN | 1.6 | 1.3 | 1.1 | 1.0 | 0.9 |
| WATER | 16.1 | 16.8 | 12.0 | 12.2 | 9.5 |
| CO | 35.5 | 43.7 | 21.7 | 25.1 | 16.3 |
| CO2 | 24.5 | 18.8 | 41.5 | 38.9 | 48.8 |
| TOTAL HYDROCARBON | 22.4 | 19.5 | 23.8 | 22.8 | 24.6 |
| HC SELECTIVITY, WT °/° | | | | | |
| METHANE | 18.3 | 11.8 | 21.2 | 18.8 | 25.1 |
| ETHENE | 0.4 | 0.6 | 0.5 | 0.5 | 0.5 |
| ETHANE | 9.6 | 7.1 | 11.2 | 10.3 | 13.7 |
| PROPENE | 0.7 | 2.0 | 1.1 | 1.3 | 1.2 |
| PROPANE | 4.8 | 3.6 | 4.9 | 5.1 | 6.9 |
| BUTENES | 2.4 | 5.2 | 3.5 | 4.0 | 3.1 |
| I-BUTANE | 4.8 | 1.0 | 2.9 | 2.4 | 2.9 |
| N-BUTANE | 3.5 | 2.3 | 2.9 | 3.1 | 3.7 |
| TOTAL C4- | 44.5 | 33.6 | 48.3 | 45.6 | 57.0 |
| C5+ PARAFFINS | 17.5 | 11.0 | 13.4 | 11.7 | 11.7 |
| OLEFINS | 15.2 | 33.5 | 21.4 | 25.9 | 17.0 |
| NAPHTHENES | 2.5 | 1.5 | 1.7 | 1.3 | 1.4 |
| AROMATICS | 10.4 | 0.6 | 5.1 | 4.3 | 5.4 |
| OTHERS | 9.9 | 19.8 | 10.2 | 11.2 | 7.5 |
| TOTAL C5+ | 55.5 | 66.4 | 51.7 | 54.4 | 43.0 |
| YIELDS, G/SCM CONV CO+H2 | | | | | |
| TOTAL HC | 206 | 193 | 192 | 192 | 192 |
| C5+ | 114 | 128 | 100 | 104 | 83 |
| OLEFINS, WT °/° BY C NO. | | | | | |
| C2 | 4.5 | 8.3 | 4.4 | 4.8 | 3.4 |
| C3 | 12.1 | 35.6 | 18.8 | 19.8 | 15.0 |
| C4 | 22.3 | 61.4 | 37.5 | 42.5 | 31.8 |
| C5 | 34.7 | 72.3 | 50.1 | 57.1 | 46.0 |
| 90 PCT OH, RAW PROD., °F | - | 378 | 366 | 365 | 369 |
| OCTANE NO. ON RAW PROD. | | | | | |
| R+O | 92.3 | 87.5 | 91.3 | 90.0 | 90.1 |
| R+3 | 96.6 | 96.2 | - | 97.0 | 97.5 |
| OXYGENATES, WT °/° | - | - | - | 0.1 | 0.1 |

Figure 86

PERFORMANCE OF CATALYST SGF-A-3 IN THE FLUID BENCH-SCALE UNIT

A. Activity

B. $(C_1 + C_2)$ and $C_5^+$ Selectivity

Accumulated Days On Stream
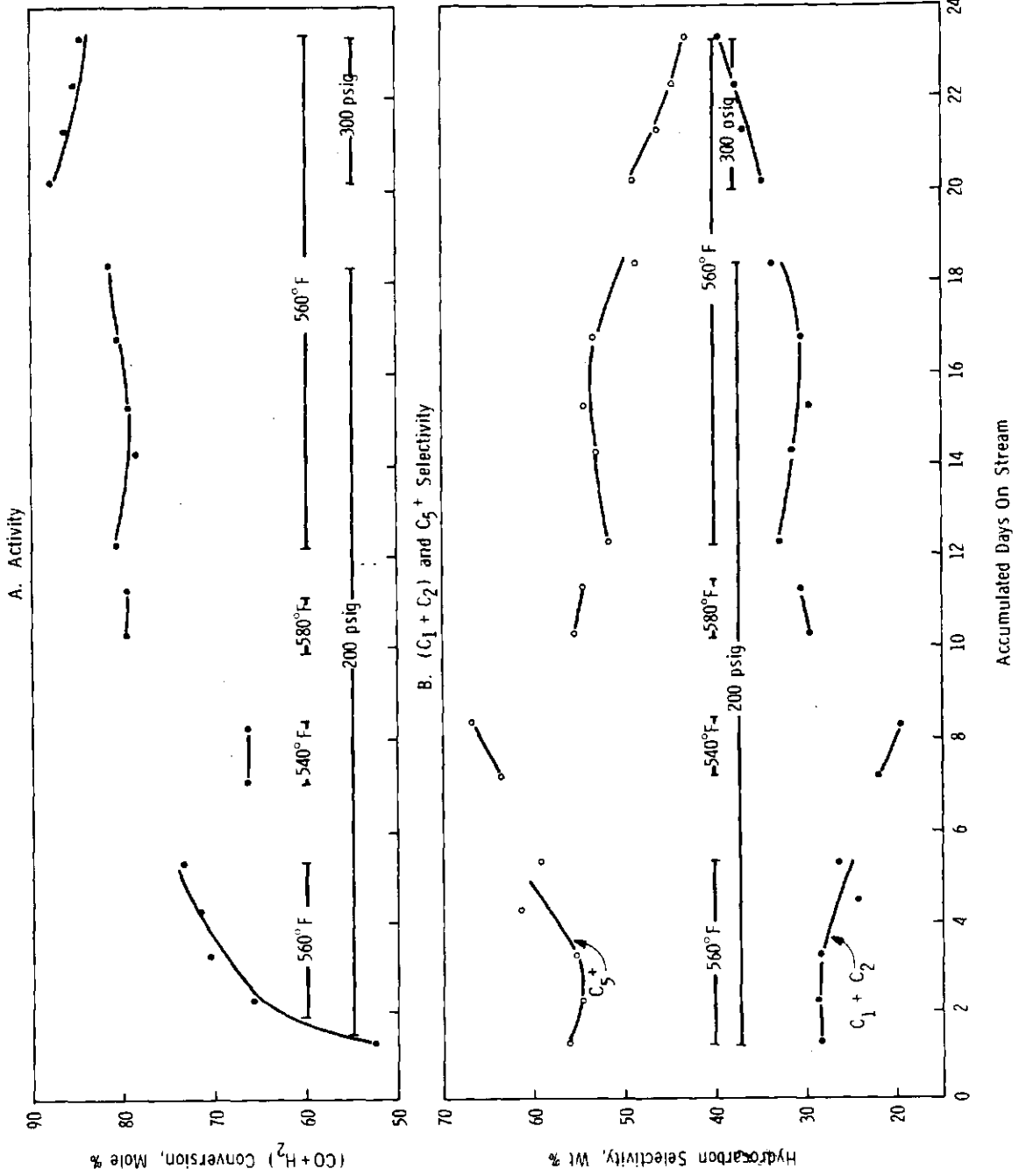
At about 13 days on stream, the reactor temperature was brought back to conditions at the start of the run. The $H_2$+CO conversion at 560°F dropped slightly below that at 580°F, but was higher than it had previously been at 560°F. Therefore, either the activity would have been increasing slowly if the catalyst had been maintained at 560°F, or the activity increased because of the periods of time at 540°F and/or 580°F. Production of $C_5^+$ gasoline, however, decreased from the initial rate at 560°F, and light hydrocarbon selectivity increased.

Although catalyst activity remained high, at about 18 days on stream some aging in selectivity was apparent. The $C_5^+$ paraffins and aromatics were lower and the olefins were higher. This resulted in a loss of two octane numbers.

### Effect of Total Pressure

Increasing the process pressure from 200 to 300 psig (longer contact time), improved the $H_2$+CO conversion by about 5%. During the three days at this condition, the selectivity to $C_5^+$ gasoline fell from 49 to 43%.

### Effect of GHSV

Using a fresh loading of catalyst SGF-A-3, a ten day run (225-67) was made during which the fresh GHSV was varied. The total gas linear velocity over the catalyst was held constant by adjusting the recycle. Thus, the contact time was constant. However, the gas composition over the catalyst varied considerably.

| GHSV (fresh feed) | Recycle Ratio | $H_2$/CO |
|---|---|---|
| 500 | 7 | 0.43 |
| 1000 | 3 | 0.72 |
| 2000 | 1 | 0.79 |

Data for run 225-67 are given in Table 84. The $H_2$+CO conversion and the selectivities are significantly affected by changes in the fresh feed GHSV. However, most results are as expected. The $H_2$+CO conversion and $C_5^+$ selectivity are inversely proportional to the space velocity. The selectivity to olefins increases, while selectivities to paraffins, naphthenes and aromatics decrease with increasing space velocity.

### Pretreatment

In an attempt to improve the start of cycle activity of catalyst SGF-A-3, several catalyst pretreatment procedures were tried. Fresh catalyst was used and all processing was with $H_2$/CO at 560°F, 200 psig and 1000 GHSV. The light gas to fresh feed recycle ratios for these experiments were between 2 and 3.8. Thus, the $H_2$/CO ratio of the gas passing over the catalyst varied between 0.70 and 0.86. The data are in Table 85.

## TABLE 84

### MATERIAL BALANCES FROM FLUID BENCH-SCALE UNIT WITH CATALYST SGF-A-3

| | 67- 2 | 67- 4 | 67- 6 | 67- 8 |
|---|---|---|---|---|
| RUN NUMBER 225- | | | | |
| RUN DAYS-ON-STREAM | 2.2 | 4.9 | 6.9 | 9.0 |
| CUM. DAYS-ON-STREAM | 2.2 | 4.9 | 6.9 | 9.0 |
| FRESH FEED H2/CO RATIO | 1.1 | 1.0 | 1.0 | 1.0 |
| GHSV, HR⁻1 (CHG BASIS) | 1014 | 504 | 2021 | 1031 |
| RECYCLE RATIO | 2.94 | 6.95 | 0.99 | 2.94 |
| REACT. PRESS., PSIG | 200 | 200 | 200 | 200 |
| REACT. INLET TEMP., °F | 420 | 423 | 419 | 418 |
| NOM. REACT. TEMP., °F | 560 | 560 | 560 | 560 |
| CONVERSIONS, MOL °/° | | | | |
| H2 | 77.4 | 88.7 | 66.2 | 81.4 |
| CO | 55.9 | 65.3 | 55.5 | 69.2 |
| H2+CO | 67.1 | 77.0 | 60.9 | 75.3 |
| YIELDS, WT °/° | | | | |
| HYDROGEN | 1.6 | 0.8 | 2.3 | 1.2 |
| WATER | 15.3 | 17.3 | 9.8 | 13.8 |
| CO | 41.0 | 32.4 | 41.5 | 28.8 |
| CO2 | 23.4 | 27.9 | 29.3 | 34.9 |
| TOTAL HYDROCARBON | 18.6 | 21.6 | 17.0 | 21.3 |
| HC SELECTIVITY, WT °/° | | | | |
| METHANE | 24.2 | 20.7 | 27.7 | 25.6 |
| ETHENE | 0.3 | 0.2 | 0.5 | 0.3 |
| ETHANE | 12.7 | 10.6 | 14.9 | 14.0 |
| PROPENE | 0.7 | 0.7 | 1.8 | 0.8 |
| PROPANE | 7.5 | 6.2 | 8.8 | 8.1 |
| BUTENES | 1.9 | 1.2 | 4.6 | 2.5 |
| I-BUTANE | 5.2 | 6.0 | 2.7 | 3.6 |
| N-BUTANE | 4.2 | 4.0 | 4.4 | 4.4 |
| TOTAL C4- | 56.8 | 49.6 | 65.4 | 59.5 |
| C5+ PARAFFINS | 13.8 | 17.1 | 9.4 | 13.1 |
| OLEFINS | 7.6 | 8.4 | 9.4 | 10.6 |
| NAPHTHENES | 2.2 | 3.2 | 1.0 | 1.9 |
| AROMATICS | 12.3 | 13.7 | 5.4 | 7.6 |
| OTHERS | 7.2 | 7.9 | 9.3 | 7.3 |
| TOTAL C5+ | 43.2 | 50.4 | 34.6 | 40.5 |
| YIELDS, G/SCM CONV CO+H2 | | | | |
| TOTAL HC | 179 | 187 | 185 | 189 |
| C5+ | 77 | 94 | 64 | 77 |
| OLEFINS, WT °/° BY C NO. | | | | |
| C2 | 2.4 | 1.7 | 3.3 | 1.9 |
| C3 | 9.0 | 9.5 | 17.1 | 9.4 |
| C4 | 16.7 | 10.7 | 39.4 | 23.7 |
| C5 | 21.7 | 17.8 | 44.1 | 31.9 |
| 90 PCT OH. RAW PROD., °F | 388 | 383 | 371 | 376 |
| OCTANE NO. ON RAW PROD. | | | | |
| R+O | - | - | - | - |
| R+3 | 97.5 | 99.2 | 98.6 | - |
| OXYGENATES, WT °/° | 0.1 | 0.1 | 0.4 | - |

## TABLE 85

### PRETREATMENT OF CATALYST SGF-A-3 IN THE FLUID BENCH-SCALE UNIT

(Processing $H_2/CO$ at 560°F, 200 psig and 1000 GHSV)

| Run 225- | Pretreatment at 0 psig Gas/°F/Hours | Recycle Ratio | Gas Over Catalyst, $H_2/CO$ | Days On Stream | Conv., Mole % $H_2+CO$ | Selectivity, wt % | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $C_1+C_2$ | $C_5+$ | Aromatics in $C_5+$ |
| 42 | $H_2/CO/610/16$ | 2.0 | 0.74 | 1.3 | 52 | 28 | 56 | 16 |
| | | | | 2.3 | 66 | 29 | 55 | 12 |
| 49 | $H_2/CO/610/16$ | 3.8 | 0.86 | 1.4 | 71 | 35 | 48 | 19 |
| | | | | 2.4 | 75 | 32 | 52 | 18 |
| 65 | $CO/610/16$ | 3.0 | 0.70 | 1.5 | 56 | 28 | 56 | 15 |
| | | | | 2.5 | 68 | 25 | 60 | 13 |
| 58 | (a) 2% $O_2/850/1$ | | | | | | | |
| | (b) Air/850/4 | | | | | | | |
| | (c) $H_2/CO/610/16$ | 2.9 | 0.67 | 1.2 | 57 | 47 | 30 | 9 |
| | | | | 2.1 | 64 | 36 | 44 | 13 |
| 67 | (a) $H_2/750/16$ | | | | | | | |
| | (b) 2% $O_2/850/1$ | | | | | | | |
| | (c) Air/850/4 | | | | | | | |
| | (d) $CO/610/16$ | 3.0 | 0.70 | 1.5 | 58 | 34 | 46 | 15 |
| | | | | 2.2 | 67 | 37 | 43 | 12 |

For 225-42 and -49, pretreatment was with $H_2/CO$ at 610°F, 0 psig for 16 hours. The higher activity and lower $C_5^+$ gasoline selectivity noted in 225-49 are attributable to the higher hydrogen concentration of the gas passing over the catalyst. The effect obtained on substituting carbon monoxide for synthesis gas in the pretreatment step is illustrated by comparing 225-42 with -65. The catalyst pretreated with carbon monoxide is slightly more active; the selectivities are about the same. Oxidation with air, prior to pretreatment with either synthesis gas or carbon monoxide, marginally increases catalyst activity. However, in both instances the $C_5^+$ gasoline selectivity is lower. These results are in variance with micro reactor studies with catalyst SG-A-4, the fixed bed analog of SGF-A-3. Also, the multistep pretreatment procedure used for 225-58 was very effective in the micro reactor units. These discrepancies, plus the fact that in every case catalyst activity increases with time on stream, clearly shows that additional work is needed to establish a satisfactory pretreatment procedure for the activation of this catalyst composition in a fluid bed unit.

## Regeneration

Several unsuccessful attempts were made to regenerate catalyst SGF-A-3 in the fluid, bench-scale unit. This includes the multistep procedure used successfully to regenerate this chemical composition in the micro reactor units. Contributing to the failure on regeneration was the lack of a suitable pretreatment procedure for activation of the catalyst. Regenerated catalyst performance paralleled that of fresh catalyst, that is, increasing activity with time on stream.

## Overall Performance of Catalyst SGF-A-3

Several operational problems were encountered with catalyst SGF-A-3 in the fluid, bench-scale unit. Carbon formation was a main contributor to the problems. For those experiments considered valid, coke on catalyst was as high as 30 wt %. This resulted in decreasing the density of the catalyst, and in changes in its fluidization characteristics. At times, during unit upsets or at high temperature operation, copious amounts of carbon were formed. This caused the catalyst to agglomerate and move upward into the reactor disengager section, probably as slugs of catalyst and coke. The slugging phenomenon was demonstrated in the plexiglass model of the bench-scale reactor, using coked catalyst recovered from the operating unit. In those cases, catalyst attrition was evident. The operational problems encountered in this research could probably be minimized by redesign of the fluid, bench-scale reactor.

Despite the operational problems, catalyst SGF-A-3 processed synthesis gas with a $H_2/CO$ ratio of one for 23 continuous days in the fluid, bench-scale unit (225-42). During that time, the $H_2$+CO conversion ranged between 52 and 88%, with an average conversion of 76%. The $C_5^+$ gasoline selectivity ranged from 43 to 66%, with an average selectivity of 54%. During the entire 23 day operation, the 90% overhead boiling point was about 375°F and the octane number about 91.

3.  **Task 4 – Theoretical Studies in Support of Process Research**

    a.  **Kinetic Characterization of Catalyst SG-A-4**

    A kinetic study on catalyst SG-A-4, the pelleted form of fluid catalyst SGF-A-3, was conducted in micro reactors. The experimental results indicate a clear linear dependence of the synthesis gas, $H_2$+CO, conversion rate on the partial pressure of hydrogen. The conversion rate is inhibited by the carbon monoxide partial pressure, probably due to the strong adsorption of carbon monoxide on the catalyst surface. The kinetic data from this study can be correlated by the rate expression,

    $$r = k\, P_{H_2}/P_{CO}^{0.5}$$

    where $P_{H_2}$ and $P_{CO}$ denote the partial pressures of hydrogen and carbon monoxide. From the temperature dependence of the rate constant k, the activation energy is 19.6 kcal/g-mole.

    A set of experiments was designed to explore the kinetic characterization of catalyst SG-A-4. The objective was to develop a start-of-cycle rate expression for synthesis gas conversion within a broad range of process conditions. Fresh catalysts were used for every set of experiments. The material balances were usually taken the first day on stream following catalyst pretreatment to minimize any effect of catalyst deactivation. The range of process conditions included:

    ●  Temperature – 500°F to 575°F

    ●  Pressure – 200 psig to 530 psig

    ●  $H_2$/CO ratio – 1 to 4

    At every fixed process condition, the space velocity was varied so that the reaction rate could be deduced from a conversion versus contact time curve. To simplify data analyses, the space velocity was adjusted so that the conversion could be kept below 20%, and in most cases between 5 to 15%. Conversions lower than the above range were not attempted due to a concern that experimental error might be overwhelmingly significant. The main advantage of keeping the conversion low is that the reactant concentration does not vary much along the catalyst bed. This allows the assumption of a constant rate throughout the reactor and permits treatment as an ideal differential reactor. The possible error introduced by this assumption can be illustrated by considering the special case of a first order reaction in a plug flow reactor. It can be shown that in this case the conversion, Y, is given by

    $$Y = 1 - e^{-k\frac{V}{F}}$$

where k is the first order rate constant; V and F are the reactor volume and volumetric flow rate, respectively. For an ideal differential reactor, the rate constant k can be obtained from the conversion divided by the contact time V/F because

$$k = \lim_{V/F \to 0} \frac{Y}{V/F}$$

However, for the case of finite conversion, this ratio is related to k by

$$\frac{Y}{V/F} = \frac{Y}{-\ln(1-Y)} k$$

Accordingly, if a reactor of finite conversion is treated as a differential one, an error of magnitude depending on the degree of conversion is introduced. For the case where the conversion is equal to 10%, around which most of our experiments were operated,

$$\frac{Y}{V/F} = \frac{0.1}{-\ln(1-0.1)} k \cong 0.95 k$$

This indicates that the assumption of differential reactor only results in a 5% underestimate of the rate constant.

Note that the above error estimate was based on first order kinetics. In the case of a zero order reaction, there should be no error at all. The synthesis gas reaction being considered, assumed an overall order of less than one. This means that the actual error due to the assumption of a differential reactor should be smaller than the above estimate. In fact, the actual error should be even less, because the formation of hydrocarbon results in a volume contraction. In consequence, the drop in reactant concentration (partial pressure) is less than what the conversion implies.

Another reason to keep the space velocity high and the conversion low is to minimize the secondary water-gas shift reaction along the reactor. Under the process conditions of the present experiments, the oxygen in carbon monoxide is mostly rejected as water. Only small amounts of carbon dioxide are formed. The examination of a typical material balance illustrates the extent of water gas reaction and the change of reactant concentration across the reactor (CT-158-155). The process conditions were:

| | |
|---|---|
| Temperature, °F | 525 |
| Pressure, psig | 310 |
| Hours on Stream | 10 |
| GHSV | 14380 |

and the feed and product structure were:

|  | Feed (in moles) | Product (in moles) | Mole % Product (Neglecting Hydrocarbon) |
|---|---|---|---|
| $H_2$ | 68.3 | 62.2 | 66.3 |
| CO | 31.7 | 28.0 | 29.9 |
| $CO_2$ | 0 | 0.15 | 0.2 |
| $H_2O$ | 0 | 3.4 | 3.6 |
| Hydrocarbons | 0 | (Not Available) | - |
| Total | 100.0 | 93.75 | 100.0 |

The low yield of carbon dioxide indicates that the extent of the water-gas reaction is insignificant. It is also remarkable that the mole % (or partial pressures) of hydrogen and carbon monoxide only drop 3 and 5%, respectively, across the reactor, in contrast to the averaged $H_2$+CO conversion of about 10%. This reflects that the assumption here of a constant rate across the reactor should indeed be a good approximation.

To analyze the experimental data, the reactor is assumed to be of plug flow. This leads to,

$$-F \frac{dc}{dV} = r$$

where, F = volumetric flow rate in cc/sec

c = reactant concentration in g-mole/cc

V = catalyst bed volume in cc

r = reaction rate per volume of catalyst in g-mole/cc-sec

By assuming a constant reaction rate along the reactor, the above equation can be integrated to give

$$r = \frac{C_o Y}{\tau}$$

where, $C_o$ = initial reactant concentration in g-mole/cc

Y = conversion

$\tau$ = V/F = superficial contact time in sec.

Table 86 lists the relevant information from experiments in two micro reactors (Unit 158 and 159). The $H_2$+CO converted per volume of catalyst can be calculated from the measured conversion, and plotted against superficial contact time as shown in Figure 87A, in which four sets of data at different hydrogen partial pressures are included. Based on the assumption of constant rate across the

## TABLE 86

## SYNTHESIS GAS CONVERSION VERSUS SUPERFICIAL CONTACT TIME

| Run No. | $P_{H_2}$ psia | $P_{CO}$ psia | Temp., °F | Contact Time, sec | $H_2+CO$ Conv. % |
|---------|------|------|------|------|------|
| 158-154 | 168 | 52 | 525 | 3.1 | 15.3 |
|         |     |    | 525 | 2.3 | 12.0 |
|         |     |    | 523 | 1.8 | 10.4 |
|         | 345 | 110 | 528 | 3.9 | 13.5 |
|         |     |    | 527 | 2.5 | 8.1 |
| 158-155 | 222 | 103 | 525 | 4.7 | 16.2 |
|         |     |    | 526 | 3.6 | 13.6 |
|         |     |    | 525 | 2.8 | 9.8 |
|         |     |    | 525 | 2.1 | 7.1 |
| 159-201 | 109 | 106 | 551 | 4.7 | 16.2 |
|         |     |    | 526 | 4.9 | 10.3 |
|         |     |    | 528 | 9.0 | 20.3 |
|         |     |    | 499 | 9.2 | 12.7 |
| 159-202 | 109 | 106 | 502 | 5.0 | 7.4 |
|         |     |    | 525 | 9.1 | 17.5 |
|         |     |    | 525 | 4.9 | 11.1 |
|         |     |    | 525 | 3.2 | 8.4 |
|         |     |    | 551 | 4.8 | 18.0 |
|         |     |    | 551 | 3.1 | 9.2 |
|         |     |    | 575 | 4.7 | 25.9 |
|         |     |    | 575 | 3.0 | 18.9 |
| 159-204 | 218 | 107 | 551 | 4.8 | 22.8 |
|         |     |    | 547 | 3.7 | 19.2 |
| 159-207 | 344 | 111 | 502 | 19.6 | 30.5 |
|         |     |    | 500 | 10.1 | 19.9 |
|         |     |    | 500 | 6.6 | 14.1 |
|         |     |    | 549 | 6.3 | 27.6 |
|         |     |    | 547 | 4.8 | 21.9 |
| 159-208 | 147 | 68 | 528 | 4.7 | 17.3 |
|         |     |    | 525 | 3.1 | 12.8 |
|         |     |    | 525 | 2.3 | 10.6 |
|         | 222 | 103 | 527 | 3.1 | 13.2 |
| 159-209 | 175 | 40 | 526 | 3.1 | 17.1 |
|         |     |    | 527 | 2.2 | 15.9 |
|         |     |    | 527 | 1.8 | 14.2 |
|         | 443 | 102 | 528 | 4.7 | 18.6 |
|         |     |    | 529 | 3.5 | 16.4 |

## SYN GAS CONVERSION VS. CONTACT TIME



TEMPERATURE : 525 oF
$P_{CO}$ : ~ 105 PSIA
$P_{H2}$ : o : 109 PSIA
           □ : 222 PSIA
           ▲ : 345 PSIA
           ▼ : 443 PSIA

y-axis: $10^5 \times$ H2+CO CONVERTED (G-MOLE/CC CATALYST)
x-axis: SUPERFICIAL CONTACT TIME (SEC)

FIGURE 87B

## DEPENDENCE OF CONVERSION RATE ON H2 PARTIAL PRESSURE



$P_{CO}$ : ~ 105 PSIA
TEMPERATURE :
  o : 500 oF
  □ : 525 oF
  ▲ : 550 oF

y-axis: $10^5 \times$ H2+CO CONVERSION RATE (G-MOLE/SEC-CC CATALYST)
x-axis: H2 PARTIAL PRESSURE (PSIA)
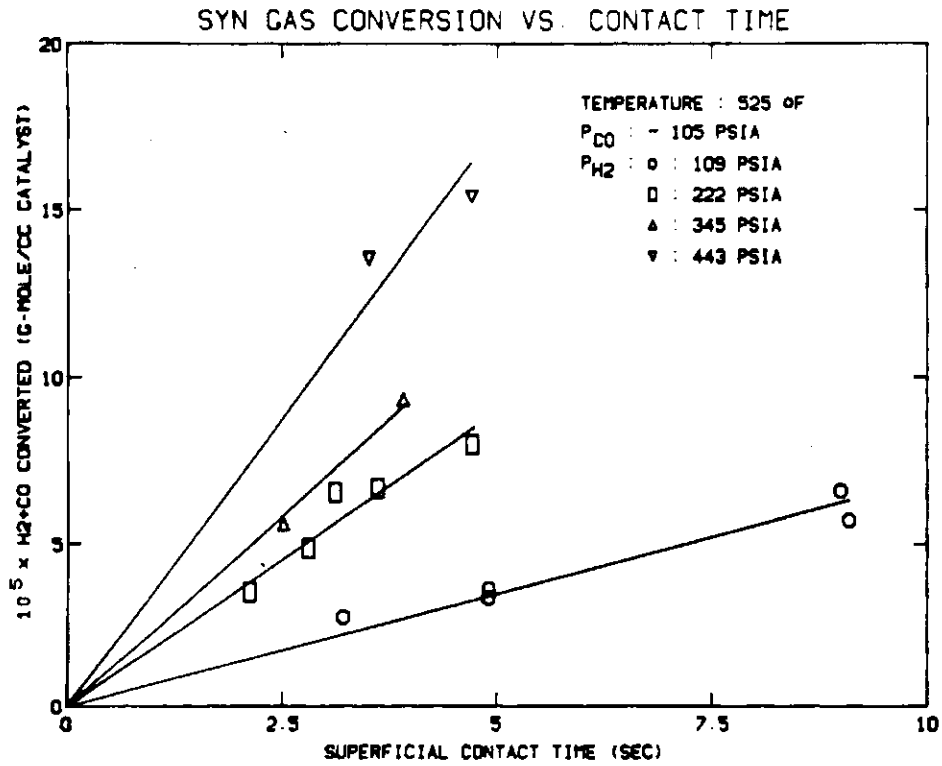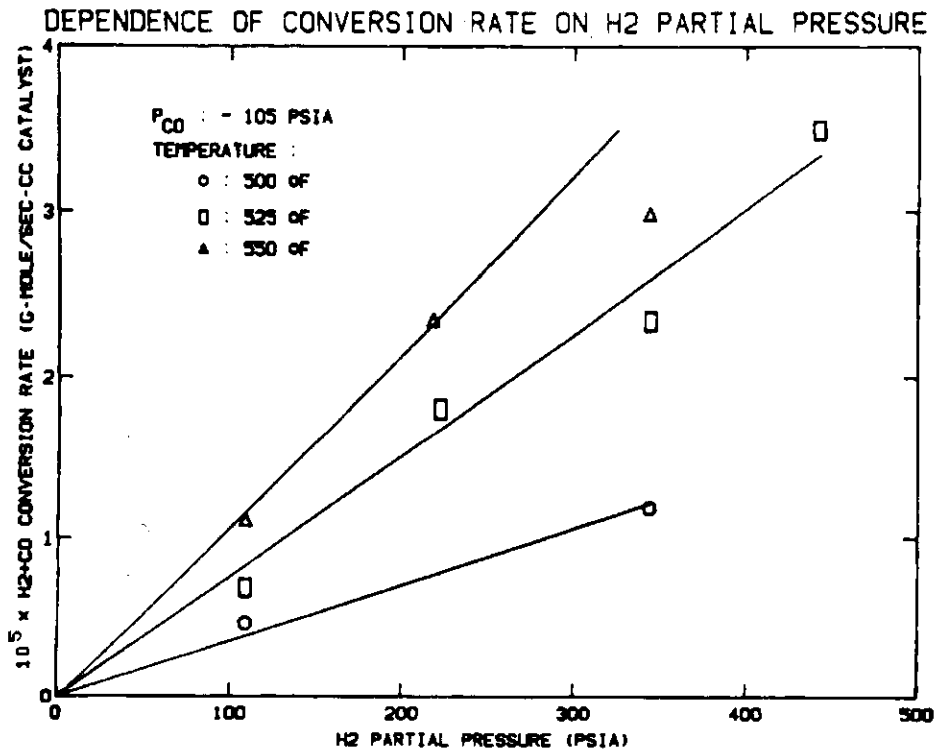
reactor, a straight line can be fitted through every set of points and its slope gives the correspondent reaction rate. The reaction rates thus calculated for different process conditions are listed in Table 87.

To study the effect of hydrogen partial pressure, the carbon monoxide partial pressure was fixed at about 105 psia and the reaction rate was plotted versus $H_2$ partial pressure at three temperature levels (Figure 87B). It can be seen clearly that a linear relationship exists between the reaction rate and hydrogen partial pressure.

Having established the linear dependence of the reaction rate on the hydrogen partial pressure, the role of carbon monoxide in synthesis gas conversion can be examined. In Figure 88, are plotted the rate/$P_{H_2}$ at 525°F against $P_{CO}$ on a log-log scale. This reveals a negative correlation and can be well fitted by a straight line with a slope equal to -0.5. All together, the conversion rate of synthesis gas ($H_2$+CO) can be expressed as

$$r = k \, P_{H_2}/(P_{CO})^{0.5}$$

Indeed when r is plotted versus $P_{H_2}/(P_{CO})^{0.5}$ (Figure 89), all of the points fall along a straight line.

From the rate expression derived above, it can be seen that the carbon monoxide partial pressure has an inhibiting effect on the synthesis gas conversion. This can probably be explained by the fact that the adsorption of carbon monoxide is much stronger than that of hydrogen and the hydrogen molecules have to compete with carbon monoxide for active sites. Indeed, a Langmuir type of adsorption kinetics is capable of exhibiting a rate dependence on a negative power of carbon monoxide and approximating the present rate expression under special conditions. Due to its singularity at $P_{CO}$ = 0, the present rate expression is not expected to be valid at low pressures. Instead, a more complicated kinetic model, perhaps of the Langmuir type, should be used to cover the whole pressure range. Further experimentation is obviously needed to discriminate among various models.

It is interesting to note that at a fixed $H_2$/CO feed, the reaction rate is proportional to the 0.5 power of the total pressure, P. From the previous discussion on the differential reactor, the rate is also proportional to $C_0 Y/\tau$ or $PY/\tau RT$. Accordingly, the conversion Y should be proportional to $(P)^{-0.5}$. This is consistent with an earlier observation that at a fixed feed composition and contact time, the conversion actually drops with increasing total pressure, as shown previously in Figure 83.

## TABLE 87

### SYNTHESIS GAS CONVERSION RATE

| Temperature, °F | $P_{H_2}$ psia | $P_{CO}$ psia | $10^5 \times (H_2+CO)$ Conversion Rate (g-mole/sec-cc catalyst) |
|---|---|---|---|
| 500 | 109 | 106 | 0.468 |
|  | 344 | 111 | 1.191 |
| 525 | 175 | 40 | 2.093 |
|  | 168 | 52 | 1.699 |
|  | 147 | 68 | 1.282 |
|  | 109 | 106 | 0.695 |
|  | 222 | 103 | 1.804 |
|  | 345 | 110 | 2.345 |
|  | 443 | 102 | 3.490 |
| 550 | 109 | 106 | 1.111 |
|  | 218 | 107 | 2.356 |
|  | 344 | 111 | 2.990 |
| 575 | 109 | 106 | 1.781 |

FIGURE 88

## DEPENDENCE OF CONVERSION RATE ON CO PARTIAL PRESSURE



FIGURE 89

## DEPENDENCE OF CONVERSION RATE ON FEED COMPOSITION
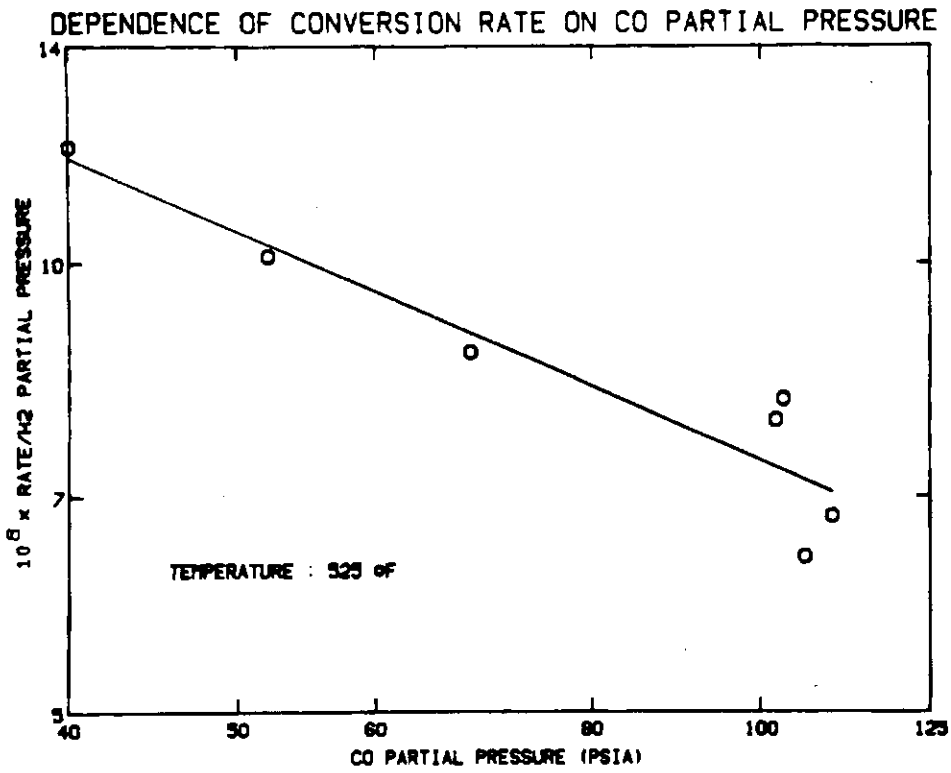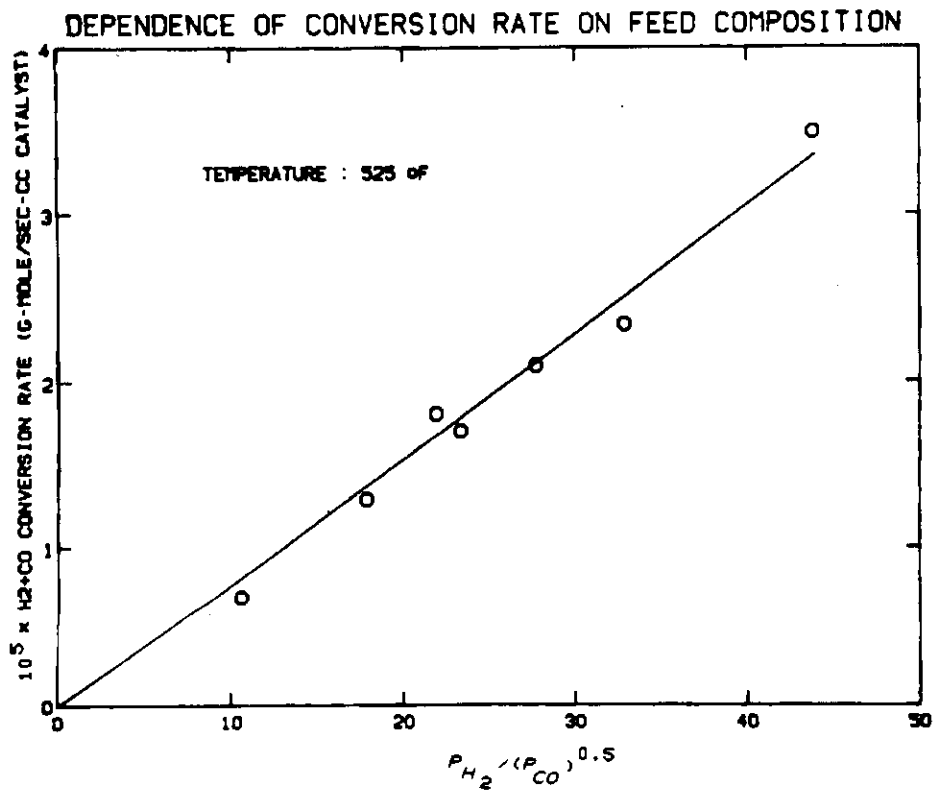
The dependence of the reaction rate on temperature was studied using synthesis gas with a $H_2/CO$ ratio of 1.03, a pressure of 200 psig, and temperatures from 500°F to 575°F. Relevant results from experiments were included in Table 86 and the conversion versus contact time data are plotted in Figure 90. Again, the slopes of the straight lines fitted through the data correspond to the rates which were listed in Table 87. Figure 91 gives the Arrhenius plots of reaction rate versus temperature. A straight line can be drawn through all the points, with its slope corresponding to an activation energy of 19.6 kcal/g-mole.

### b. Experimental Procedure Used in the Kinetic Characterization

Data obtained for the kinetic study over catalyst SG-A-4 are presented in Appendix E, Table E25. Runs were made in the micro reactors with the catalyst pretreated 16 hours with 1/1 $H_2/CO$ at 0 psig and 610°F. Catalyst charge consisted of one gram of SG-A-4 rather than the customary two grams used in other studies. This smaller quantity of catalyst gave the desired low conversions at more reasonable charge rates.

Runs were made at conditions ranging from 500 to 575°F at 200 to 530 psig for $H_2/CO$ ratios varying between 1 and 4. Contact times were varied two to three-fold for each condition.

A data point was obtained simply by measuring the off-gas rate for one hour (following a one hour equilibration period), and analysis of this gas by mass spectrometry. This eliminated the need for large quantities of charge gas, as well as reduced any effects of aging on catalyst performance. No measurable amount of liquid was observed during any runs due to the high rates, low conversion, and short sample times. However, the amount of liquid could be calculated by assuming a 100% material balance. This permitted calculation of conversions and the fraction of carbon in CO converted to hydrocarbon. An oxygen balance allowed further calculation of light gas selectivity and the fraction of hydrogen converted to hydrocarbon. These latter numbers will not. be as precise and should be used judiciously.
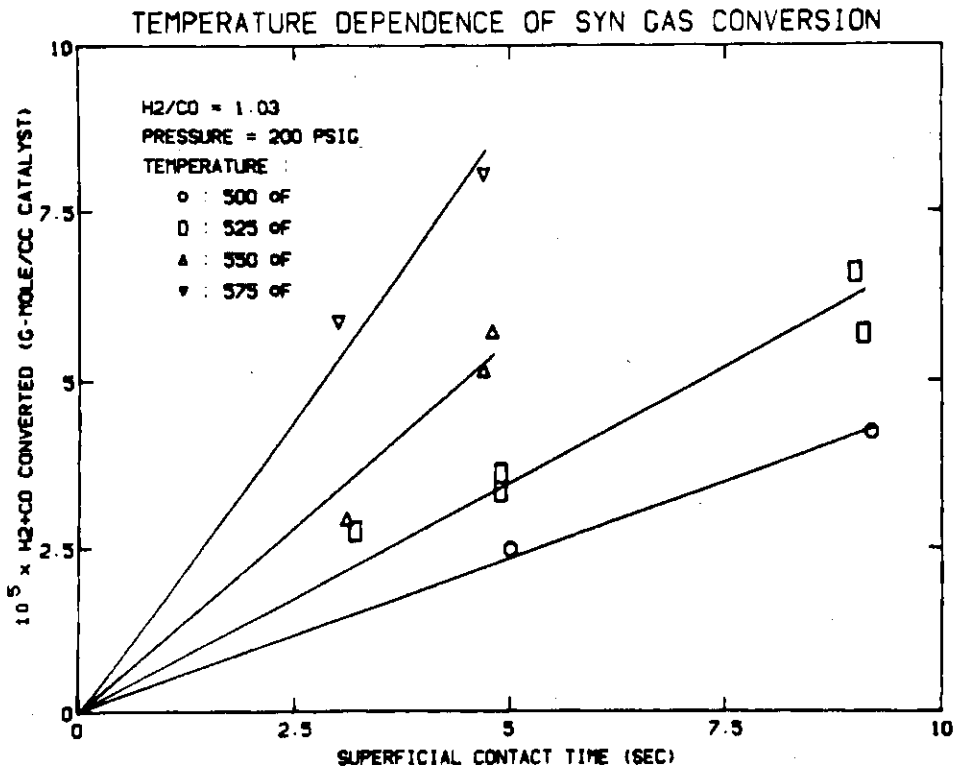
FIGURE 90

## TEMPERATURE DEPENDENCE OF SYN GAS CONVERSION



H2/CO = 1.03
PRESSURE = 200 PSIG
TEMPERATURE :
o : 500 oF
□ : 525 oF
▲ : 550 oF
▼ : 575 oF

SUPERFICIAL CONTACT TIME (SEC)

$10^5$ x H2+CO CONVERTED (G-MOLE/CC CATALYST)

FIGURE 91

## TEMPERATURE DEPENDENCE OF CONVERSION RATE



H2/CO = 1.03
PRESSURE = 200 PSIG

ACTIVATION ENERGY
= 18.6 KCAL/G-MOLE

$10^5$ x H2+CO CONVERSION RATE (G-MOLE/SEC-CC CATALYST)

TEMPERATURE (oF)