I. Fluid Catalysts - Plexiglass Model Flow Studies

A plexiglass model of the bench-scale, fluid bed reactor was used to simulate process conditions with fluid catalysts entered in the program. The model was used to observe any elutriation or particle entrainment; to determine velocities necessary for good fluidization; and to visually evaluate the quality of fluidization.

The plexiglass model consisted of a 3/4" ID tube approximately 44" long, with a 17" disengaging zone. Gas exiting this zone passed successively through a knock-out vessel, 40-60 micron filter disk and water bubbler. The distributor assembly slid into the plexiglass tube and was sealed at the distributor chamber itself (asbestos packing), as well as at the gas inlet via a 3/4" Swagelok fitting. The distributor plate was attached with a #50-40 machine screw or could easily be modified, eliminating the screw by using epoxy to attach the plate. Pressure drops through the bed were not measured. Photographs of the model depicting settled and expanded catalyst beds are shown in Figure 3.

To observe the proper flow dynamics in the model, it was necessary to use gases having properties at ambient conditions similar to those of the total bench-scale unit charge at operating pressure (200-300 psig) and temperature (∿500°F). This was done by using a gas having the same Reynolds number ($Re_p = d_p u_o \rho_g / \mu_g$) as the bench scale charge. Since particle diameter (d_p) and superficial linear velocity (u_o) were the same for both the model and bench-scale unit, the gas density/viscosity ratio (ρ_g/μ_g) determined the gas to use at ambient conditions.

Assuming a diluted H_2/CO charge (0.9 H_2/1.0 CO/0.3 CO/ 3.4 CH_4) to the bench-scale unit at 500°F and 200-300 psig, the gases selected were Freon-22 and sulfur hexafluoride. Both are non-toxic and unreactive at ambient conditions and were readily available. The data in Table 44 show why these gases were selected. Freon-22 and SF_6, thus, simulate 200 and 300 psig operation, respectively. Air is shown to illustrate the large differences in transport properties and would give quite misleading results if such a gas is used.

An approximate superficial velocity operating range before entrainment was determined for each catalyst by(46)

$$u_{mf} = \frac{d_p^{\,2} (\rho_s - \rho_g) g}{1650 \mu} \qquad Re_p < 20$$

$$u_t = \left[\frac{4}{225} \frac{(\rho_s - \rho_g)^2 \; g^2}{\rho_g \mu} \right]^{1/3} d_p \qquad 0.4 < Re_p < 500$$

TABLE 44

SELECTION OF FREON-22 AND SILICON HEXAFLUORIDE FOR PLEXIGLASS MODEL STUDIES

	Density, ρ gm/cc	Viscosity, μ gm/cm sec	Ratio of ρ gm/liter to μ centipoise
Bench Scale Unit Charge, 500°F			
200 psig	5.78×10^{-3}	2.00×10^{-4}	289
300 psig	8.46×10^{-3}	2.01×10^{-4}	421
Air, 70°F, 1 atm	1.21×10^{-3}	1.8×10^{-4}	67
SF_6, 70°F, 1 atm	6.41×10^{-3}	1.53×10^{-4}	419
Freon-22, 70°F, 1 atm	3.64×10^{-3}	1.27×10^{-4}	287

TABLE 45

SOME PROPERTIES OF FLUID SYNTHESIS GAS CONVERSION CATALYSTS

	Catalyst			
	SGF-B-1	SGF-A-2	SGF-A-3	SGF-A-4
Pore Volume (cc/gm)	0.64	0.54	0.91	0.48
Real Density	2.56	2.7	2.65	2.72
Particle Density	0.970	1.098	0.777	1.180
Packed Density	0.50	0.50	0.35	0.50
Size Distribution, wt %				
Microns				
0-20	4.9	4.3	2.2	0.6
0-30	14.9	10.6	4.3	9.6
0-40	27.2	19.4	9.1	28.2
0-60	50.4	40.3	28.8	61.1
0-80	67.3	59.6	56.4	78.1
0-100	78.3	74.3	79.3	86.2
Mean Particle Diameter, Microns	59.7	69.8	75.6	53.0

The average particle diameter (d_p) was used to calculate the minimum fluidization velocity (u^p_{mf}), whereas 30 microns (a size present in appreciable quantity) was used in estimating terminal velocities (u_t).

Four fluid catalysts were examined in the plexiglass model. Their properties are listed in Table 45. The particle densities, needed to estimate minimum fluidization and terminal velocities, were backed out using the real density and pore volumes $\left(\frac{1}{\rho_{Particle}} - \frac{1}{\rho_{Real}} = V_{Pore}\right)$. The particle densities shown are the corrected values and yield a consistent set of density values.

Particle size distributions showed that none of the four catalysts contained more than 5% of fines (0-20 microns). Mean particle diameters ranged from 53 microns for SGF-A-4 to 76 microns for SGF-A-3. All catalysts appeared to be attrition resistant.

Calculated values of minimum and terminal velocities are given in Table 46. The data show a factor of over 50 (i.e., 0.0034 to 0.24 ft/sec) in superficial linear velocity range before fines might be entrained. In fact, linear velocities many times the terminal velocity can be used for bubbling fluidized bed systems without severe entrainment. During actual runs in the plexiglass model, no measurable quantity of catalyst was lost via elutriation or entrainment, although small quantities were noted visually at times.

1. SGF-B-1

Four distributor assemblies were tested in the plexiglass model with catalyst SGF-B-1: P-300 and P-650 filter disks attached by a machine screw, an ASTM 40-60 micron glass frit epoxied in place, and a plate type distributor. Based on fluidization studies in the plexiglass model, the P-300 filter disk and the glass frit were unsatisfactory. The P-650 filter disk and plate distributors were identical to those used in the bench-scale fluid bed unit. Based on these studies and results from the bench scale unit, the plate distributor was used for all subsequent runs.

A P-650 (∿60 micron) filter disk attached via a machine screw was tried in the model with Freon-22 to simulate operation with 150 cc of catalyst at 200 psig and 500°F.

ft^3/hr	ft/sec	Bed Height, cm
0.61	0.055	80-85
0.95	0.086	89-95
1.26	0.11	88-97
2.00	0.18	96-110
3.14	0.28	102-120
7.77	0.70	-
0	-	62

TABLE 46

MINIMUM AND TERMINAL VELOCITIES OF FLUID BED CATALYSTS*

	Catalyst							
	SGF-B-1		SGF-A-2		SGF-A-3		SGF-A-4	
Velocity, ft/sec	u_{mf}	u_t	u_{mf}	u_t	u_{mf}	u_t	u_{mf}	u_t
Syngas Charge at								
500°F, 200 psig	0.0034	0.24	0.0052	0.26	0.0044	0.20	0.0032	0.27
500°F, 300 psig	0.0034	0.21	0.0052	0.23	0.0043	0.18	0.0032	0.24
Freon-22, 70°F, 1 atm	0.0053	0.32	0.0082	0.35	0.0069	0.28	0.0051	0.37
SF_6, 70°F, 1 atm	0.0044	0.25	0.0068	0.27	0.0056	0.21	0.0042	0.28

*u_{mf} = minimum fluidization velocity

u_t = terminal velocity

TABLE 47

CATALYST FLUIDIZATION USING THE PLATE DISTRIBUTOR AND FREON-22

SGF-B-1					
100 cc			150 cc		
ft^3/hr	ft/sec	Bed Height, cm	ft^3/hr	ft/sec	Bed Height, cm
0.73	0.066	41-45	0.90	0.081	81-92
0.90	0.081	51-58	0.99	0.090	81-93
1.28	0.116	53-61	1.20	0.11	89-97
1.36	0.123	57-62	1.54	0.14	92-101
1.71	0.15	59-65	1.75	0.16	87-102
2.62	0.24	61-69	1.89	0.17	92-106
3.56	0.32	66-80	2.88	0.26	101-118
4.59	0.42	69-86	0	-	64
0	-	41			

At the lower rates (0.055-0.086 ft/sec), the bed did not cease fluidizing: 0.055 ft/sec gave poor mixing near the inlet while 0.086 ft/sec appeared to give adequate circulation even at the inlet. At both 0.086 and 0.11 ft/sec, channeling along the walls was apparent. At 0.18 ft/sec and greater, mixing was excellent with violent bubbling. The bed height just reached the disengager zone at 0.28 ft/sec while at 0.70 ft/sec fluidization extended several inches into the disengaging zone with some solids being carried over to the knock-out pot. Conclusions were that the lower limit of linear velocity for the bench-scale unit would be ∿0.06 ft/sec while at >0.18 ft/sec bypassing may be too severe.

The above P-650 disk readily dispersed gas through the surface with little bypassing radially to the wall or along the machine screw. However, the P-650 disk removed from the unit after 13 days operation at 500°F and 200 psig passed most of the gas radially and by the screw - only at rates much higher than practical did appreciable gas emerge from the surface. This indicates that even the 60 micron openings could plug with fines or coke during processing.

A new distributor was fabricated and tested in the model. It consisted of a 100 mesh screen sandwiched between two drilled plates each containing 19 holes. The upper plate's 5/64-inch holes were centered over the 0.025-inch holes in the bottom plate. This distributor was run in the model with both 100 and 150 cc of catalyst SGF-B-1 while using Freon-22 (Table 47). The data are plotted in Figure 50 along with those obtained with the P-650 disk. At the low rates, circulation of particles appeared poorer with the plate distributor. At 0.066 ft/sec the bed would stagnate unless tapped or the flow pulsed. A minimum rate of ∿0.09 ft/sec would be necessary to ensure fluidization in the model, but would be less in the bench scale reactor. Channeling along the wall was still apparent with the plate distributor and is inherent in such a small diameter tube without baffles.

2. SGF-A-2

Studies with catalyst SGF-A-2 were limited to Freon-22 and the plate distributor described above. Experimental results are summarized below and plotted as Figure 51.

ft^3/hr	ft/sec	Bed Height, cm
0.50	0.045	67-79
0.97	0.088	67-72
1.64	0.15	72-77
2.32	0.21	76-82
2.64	0.24	79-87
3.30	0.30	82-91
5.05	0.46	92-105
0	0	52

Figure 50

EXPANSION RATIO FOR SIMULATION OF FLUID BED OPERATION WITH SGF-B-1 AND FREON 22

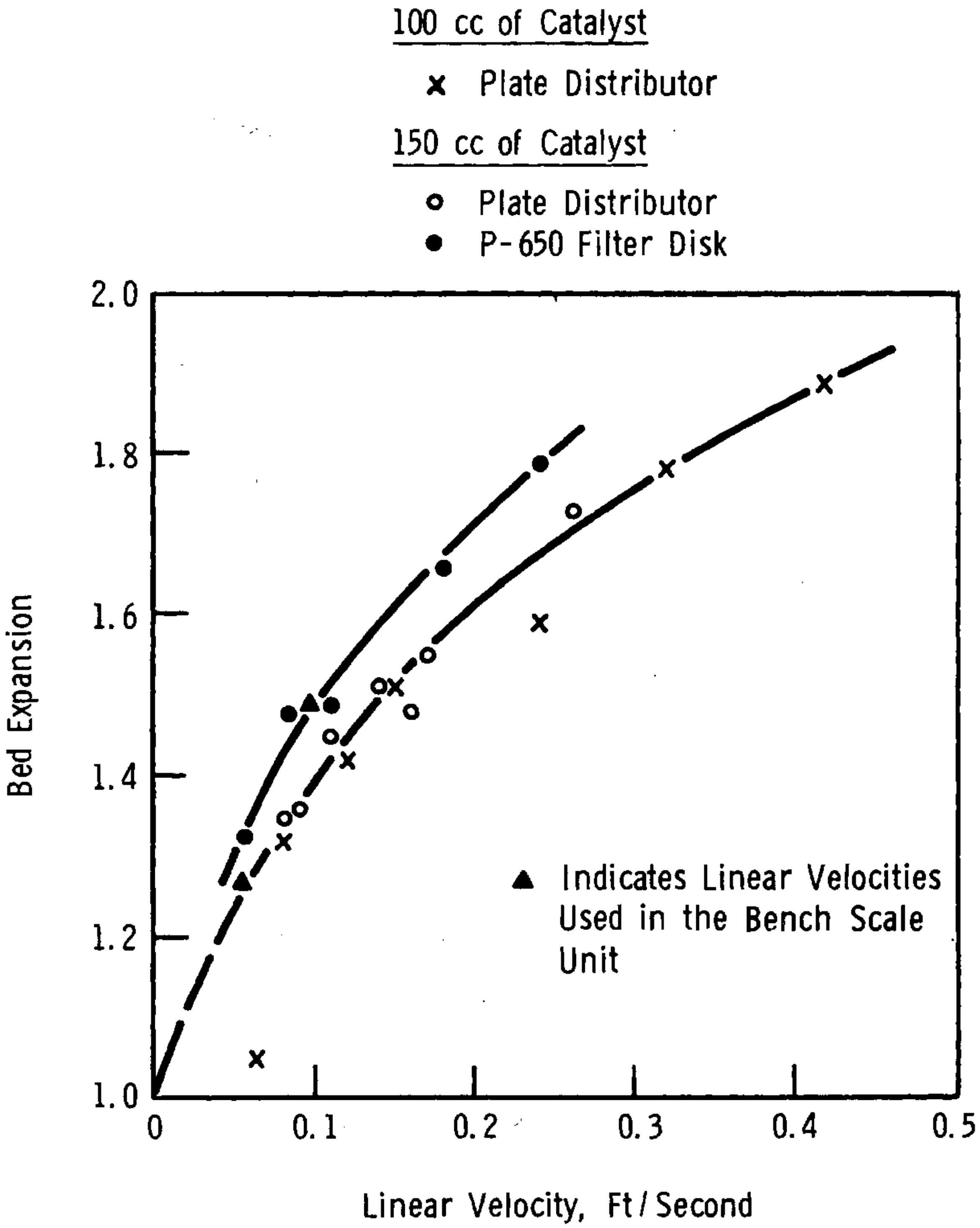
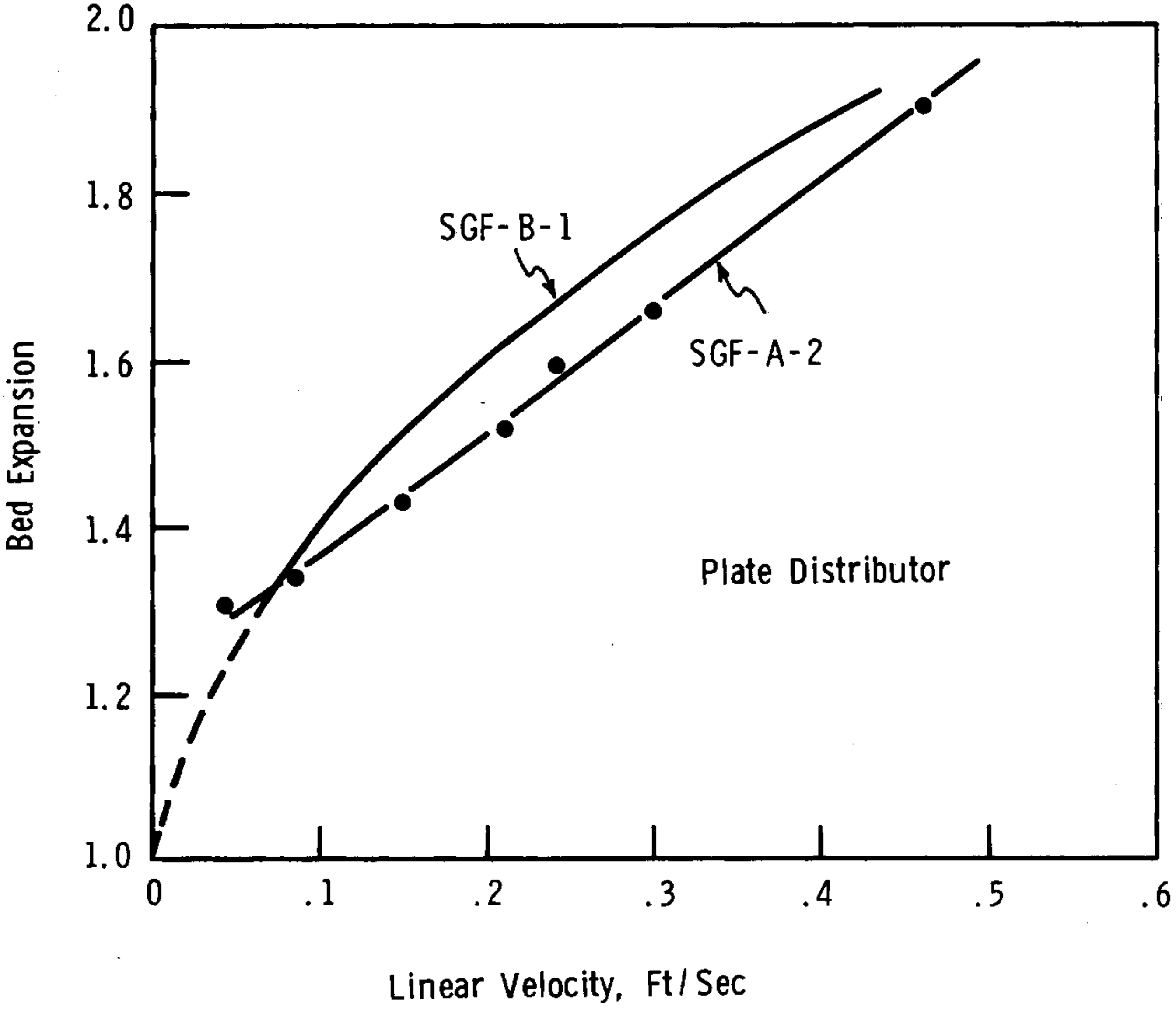


Figure 51

EXPANSION RATIO FOR SIMULATION OF BENCH-SCALE UNIT OPERATION WITH FREON-22



Upon start-up at 0.21 ft/sec, some entrainment occurred. However, once the fines had been elutriated, after several hours at various rates, entrainment was observed only at the highest rates. It should be noted that the plexiglass model did not contain filters in the disengaging zone, thus loss of catalyst would be no problem in the bench-scale unit.

Particle circulation was good at 0.088 ft/sec with satisfactory fluidization even at 0.045 ft/sec. Fluidization did not cease as it did for SGF-B-1 at low rates. Figure 51 compares results for 150 cc of each catalyst. Results for SGF-A-2 are linear over the entire range and would permit more catalyst loading due to reduced bed expansion. Also since mixing appeared better, lower velocities could also be used.

3. SGF-A-3

Both fresh and spent SGF-A-3 were studied with the plate distributor. It should be mentioned that fresh catalyst refers to an untreated uncalcined version. Activation prior to processing in the bench-scale unit very likely could alter the physical properties so as to affect the fluidization characteristics. This was apparent with the spent sample of this catalyst.

Experimental results with fresh SGF-A-3 were:

ft^3/hr	ft/sec	Bed Height, cm
0.43	0.039	61-63
0.90	0.081	65-68
1.42	0.13	66-71
2.00	0.18	69-74
2.39	0.22	72-79
3.00	0.27	74-84
3.96	0.36	81-92
0	0	53

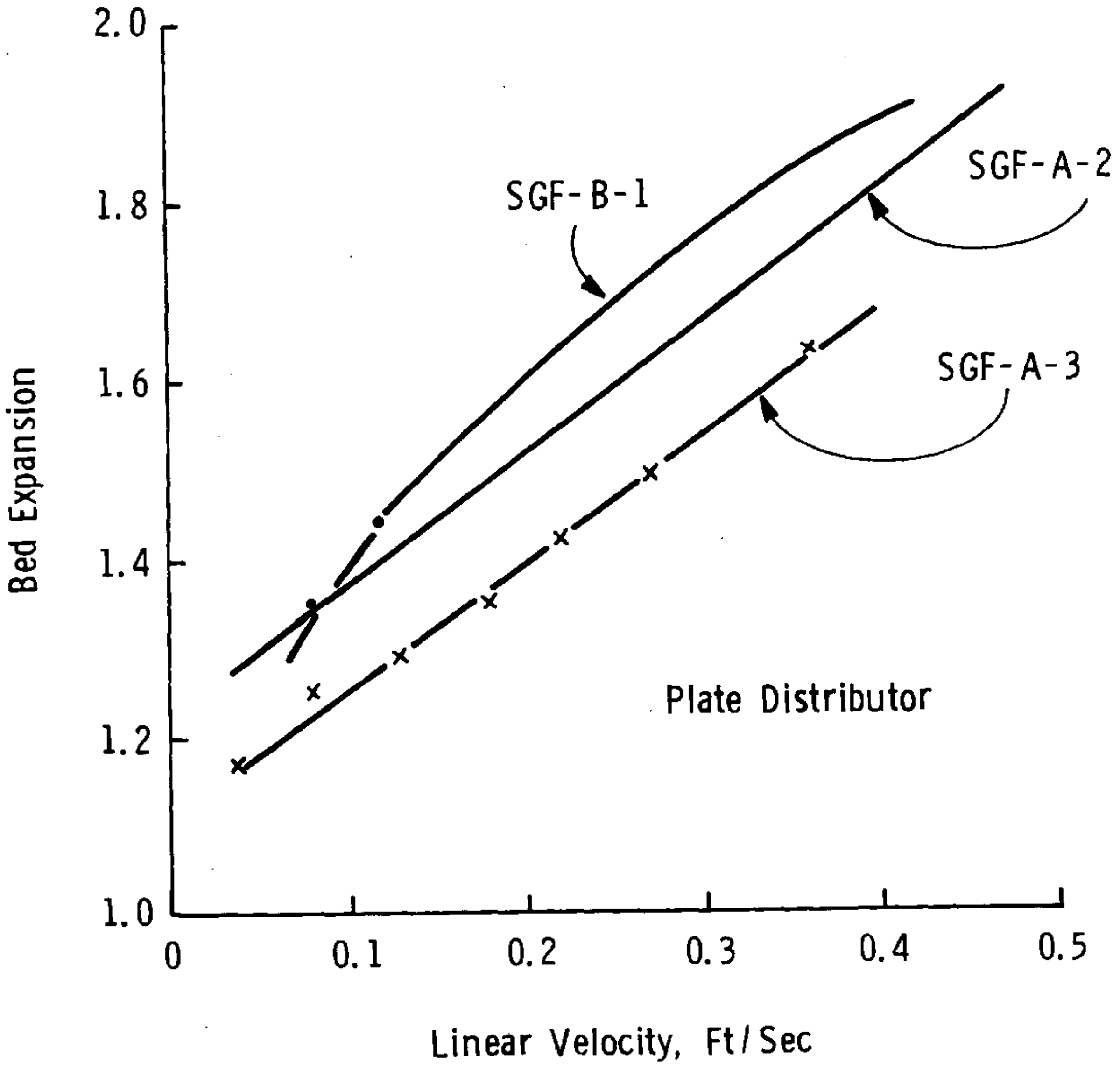
This catalyst had a great tendency to adhere to the walls of the plexiglass model. Wetting the catalyst reduced this, but is still felt to have contributed to the poor mixing observed at the inlet. Even at the highest rates, catalyst circulation was not good near the distributor. Some entrainment of fines was observed at 0.36 ft/sec.

Results are shown in Figure 52 which also includes data for SGF-B-1 and SGF-A-2. Despite being the lightest catalyst, bed expansion for SGF-A-3 was the least. Since bed expansion for a given catalyst decreases with increasing particle diameter (at constant velocity), the particle size distribution indicates that SGF-A-3 should expand least.

	Average diamter, microns
SGF-B-1	60
SGF-A-2	70
SGF-A-3	76

Figure 52

EXPANSION RATIO FOR SIMULATION OF BENCH-SCALE UNIT OPERATION WITH FREON-22



Agglomeration and adherence to the walls also will reduce bed expansion by leading to an increased particle diameter and gas bypassing, respectively.

Catalyst SGF-A-3 presented some problems in operation of the bench-scale fluid unit. After activation and processing for several days, the catalyst contained large amounts of coke. In the loosely packed state it appeared much lighter than the fresh unactivated catalyst. Diligent tapping revealed both to have approximately equal packed densities.

Upon examining the used catalyst in the plexiglass model, possible causes of the bench scale reactor operational problems were observed. The spent catalyst had a tendency to agglomerate and form large particles in stagnant areas. This could be near the inlet or in stagnant areas in the disengaging zone. The catalyst also formed slugs when flow was started and was observed to move as a large slug into the disengaging zone where it could remain, especially if wet.

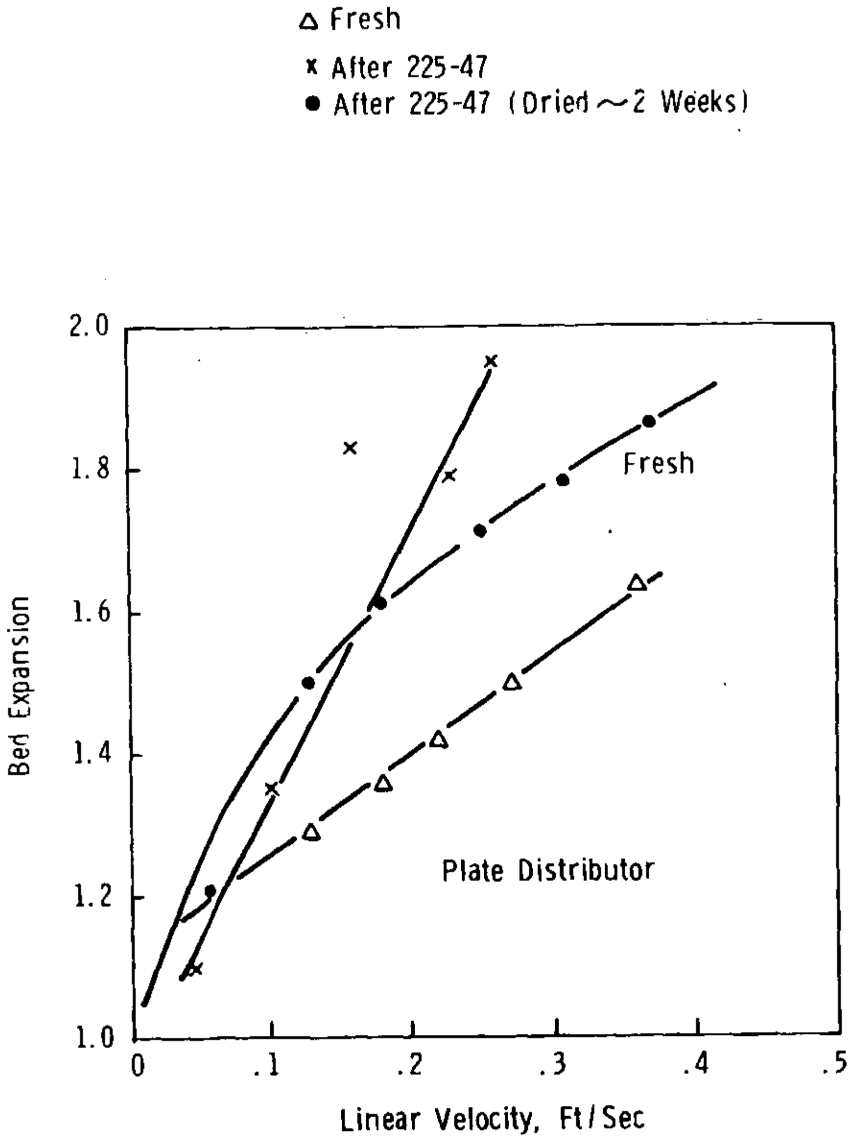
Results from the flow study are given in Figure 53. The fresh catalyst curve lies below those of the used catalyst for two major reasons -- it was apparently heavier than the activated catalyst; and it was electrically charged resulting in much gas bypassing during the study. The upper curve is the used catalyst upon first being removed from the reactor. It had a greater tendency to slug and remain in the disengager than did the "dried" catalyst. Smoother operation of the bed would be attained by increasing flows quickly to the desired rate and using a rate of at least about 0.2 ft/sec.

4. SGF-A-4

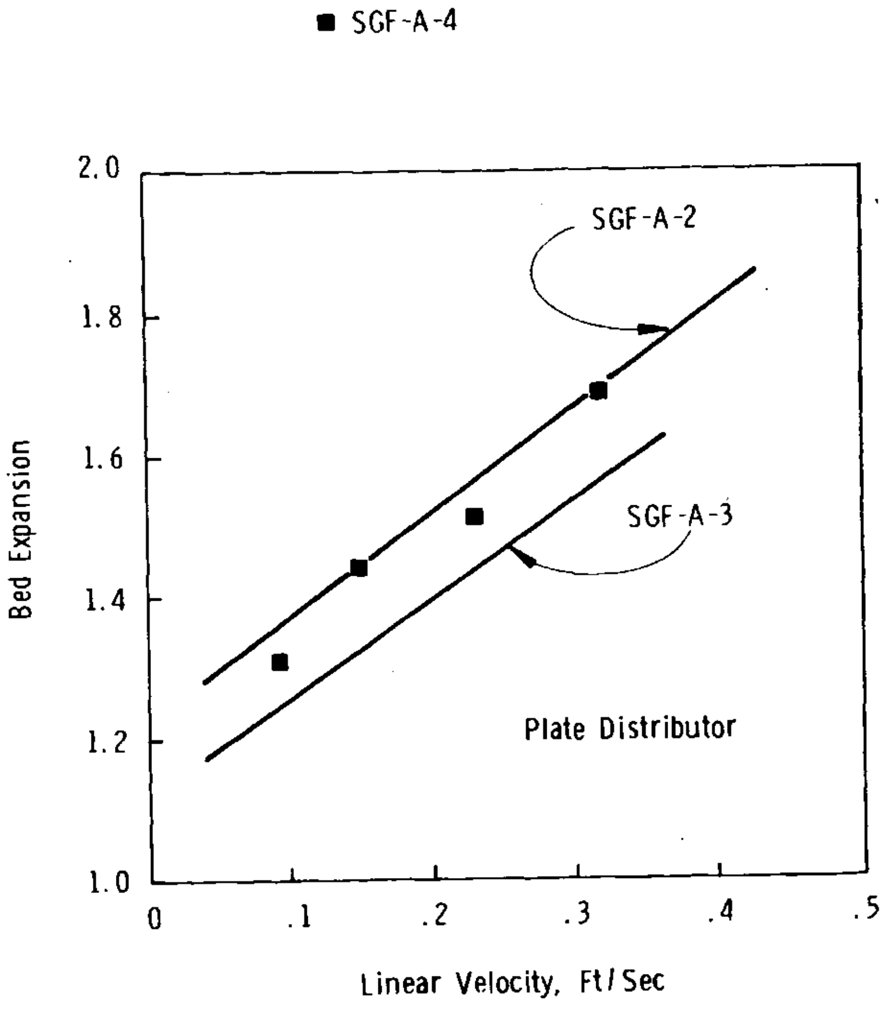
Catalyst SGF-A-4 was denser than SGF-A-3 and was expected to present fewer fluidization problems. It did behave better in the plexiglass model, presenting fewer problems with static electricity and did not entrain as did the A-3 at higher rates. However, bypassing was still appreciable with poor particle circulation near the distributor inlet.

Results are plotted in Figure 54 and show a greater bed expansion than did SGF-A-3. In fact it is comparable to SGF-A-2 despite the differences in average particle size.

EXPANSION RATIO FOR FRESH AND USED SGF-A-3 FLUID CATALYST USING FREON-22



EXPANSION RATIOS FOR FRESH SGF-A SERIES FLUID CATALYSTS USING FREON-22



J. Studies with Developmental Fluid Catalyst SGF-B-1

In addition to the studies in the bench-scale unit, the various fluid catalysts, introduced into the contract work, were pelletted, crushed and sized for fixed bed experiments in the micro reactor units. These "simulated fluid catalysts" were used to obtain qualitative data on activation and regeneration procedures, optimum temperature and pressure, cycle times, etc. It is recognized that the fixed bed, micro reactor unit results will not always translate directly to the fluid, bench-scale unit. However, this compromise enabled more rapid progress, and established limits in which the fluid unit could operate. In general, the agreement between micro reactor and bench-scale results was very good.

1. Task 1 - Exploratory Process Research

The experiments were made with catalyst SG-B-3, which is chemically identical to fluid catalyst SGF-B-1. The performance of catalyst SG-B-3 was extensively evaluated in the micro reactor units regarding activation, process studies, aging and regeneration. Related detailed data are given in Appendix D.

a. Process Studies

Catalyst SG-B-3 was quite active for converting synthesis gas of H_2/CO composition at 485-515°F, 540 GHSV and 200 psig (Table 48). During the initial 8.8 days of processing, the activity was good, declining less than one percent in carbon monoxide conversion per day. The hydrocarbon selectivities were also good with >65% C_5^+ and about 20% C_1+C_2. The liquid product was mainly olefinic, with very little aromatics, but extended outside the defined gasoline boiling range (90% point >400°F).

The high boiling points and good C_5^+ selectivity are related to the process temperature, long contact time, and inability of the catalyst to produce branched olefins at 485°F. Increasing the temperature to 515°F lowered the boiling range, increased olefin branching and reduced gasoline yield. Even with the increased olefin branching at 515°F, the boiling range was at best marginal. However, this same catalyst was found to give acceptable 90% points at 515°F, 200 psig, and 1000 GHSV with a H_2/CO charge, as well as with a diluted charge (0.9 H_2/1.0 CO/0.3 CO_2/3.1 CH_4) at 200 psig, 1000 GHSV and temperatures varying from 460-525°F (pretreat at 600°F). The diluted charge gave methylbutene contents found with previous catalysts (Table 49). The H_2/CO charge, although making fewer methylbutenes than found in 159-139-9 and -10 (Table 48), still gave an acceptable boiling range, most likely due to the decreased contact time at 1000 GHSV.

Product quality was improved by pretreating SG-B-3 at 950°F overnight rather than at 600°F (Table D4). At a process temperature of 515°F selectivity was good with a high methylbutene content and a 90% point <400°F. At 485°F the product was significantly lower boiling than that obtained by pretreating at 600°F. However, several factors tended to negate this improvement while processing at 485°F.

TABLE 48

ACTIVITY AND SELECTIVITY OF SG-B-3

Run 159-139-	2	4	7	9	10
Days	1.8	4.8	8.8	11.8	12.9
Temperature, °F	487	487	486	516	517
Conversion CO, % wt	39	35	32	38	40
Selectivity, % wt					
C_1+C_2	16	18	20	24	28
C_5+	73	71	68	61	58
Olefins in C_5, % wt	85	86	85	84	84
Methylbutenes in $C_5^=$,%wt	43	38	36	66	69
90% OH, °F	504	500	500	450	390

TABLE 49

FEED COMPOSITION EFFECTS WITH SG-B-3

Charge $H_2/CO/CO_2/CH_4$	1/1/0/0	0.9/1.0/0.3/3.1			
Temperature, °F	514	460	485	508	525
GHSV	1009	1039	1047	1057	1063
Conversion CO, % wt	36	27	29	32	32
Selectivity, % wt					
C_1+C_2	22	37	23	38	41
C_5+	64	51	58	46	40
Olefins in C_5, % wt	85	87	80	72	71
Methylbutenes in $C_5^=$,%wt	61	81	83	84	83
90% OH, °F	396	368	365	367	341

TABLE 50

EFFECT OF CO PARTIAL PRESSURE AND CONTACT TIME

Run	143-64-2	159-139-8	143-66-2
$H_2/CO/CO_2/CH_4$	1/1/0/0	1/1/0/0	0.9/1.0/0.3/3.1
Partial Pressure CO, psia	107	107	41
GHSV	1001	539	1084
GHSV on CO	500	270	205
Contact Time, sec	26.7	52.0	24.6
CO Conversion, % wt	40	42	32
HC Selectivity, % wt			
C_1+C_2	21	22	39
C_3+C_4	14	12	16
C_5+	65	65	45
Olefins in C_5, % wt	85	84	75
Methylbutenes in $C_5^=$, % wt	65	66	84
90% OH, °F	366	450	339

- The methylbutene content was decreasing rapidly with a corresponding increase in boiling range.
- The increase in boiling range was accompanied by a drop in C_5^+ gasoline and a corresponding increase in C_4's.
- Hydrocarbon yields were significantly less at 485°F following the 950°F pretreatment -- 150-160 gm HC/m^3 CO versus 180-200 gm HC/m^3 CO (Table D1) -- due to lower conversion.

In the process of improving branched olefin formation by pretreating at 950°F, catalyst activity and even selectivity were also altered. The latter was expected to have been affected by processing at 515°F before going to 485°F, but it should not have lowered the activity.

This same effect of pretreatment temperature was observed for processing the H_2/CO charge at 400 psig and 500°F (Table D5). This increased pressure was used as a starting point for examining such items as the effect of carbon monoxide partial pressure. Earlier studies with catalyst SG-B-3 indicated that decreasing the contact time (with H_2/CO) or CO partial pressure (by diluting with CH_4 and CO_2) gave a lower boiling range product and affected the selectivity significantly at 515°F and 200 psig (catalyst pretreated in H_2 at 600°F). Lowering the CO partial pressure at constant contact time greatly increased light gas make. Increasing the contact time at constant partial pressure did not affect C_5^+ make, yet yielded a higher boiling product (Table 50).

The effect of pretreating at 950°F versus 600°F is shown in Table 51 for 400 psig operation. Increasing the pretreat temperature from 600 to 950°F significantly increased the methylbutene content and lowered the 90% point. At the same time the conversion and C_5^+ selectivity decreased. Lowering the contact time at 400 psig had a much greater affect than it did at 200 psig (Table 52).

One short study considered the activation of catalyst SG-B-3 in flowing synthesis gas of H_2/CO composition (Table 53). The catalyst was first evaluated for 24 hours at 500°F, 200 psig, and a GHSV of 500. The activity for CO conversion was practically negligible (1%).

Next the activation temperature was raised to 600°F for two hours, after which catalyst activity was measured at 500°F. The CO conversion was negligible. This procedure was repeated with the same result. After exposure for 8 hours to synthesis gas at 600°F an evaluation at 500°F showed CO conversion was still only 1%. A final material balance run was made at 600°F for 24 hours. This resulted in a CO conversion of only 7% and a hydrogen conversion of only 13%. It appears that at 600°F and prolonged times (>36 hours) SG-B-3 slowly activates. No additional work using synthesis gas activation was done.

TABLE 51

EFFECT OF PRETREAT TEMPERATURE AND PROCESS PRESSURE ON SG-B-3 PERFORMANCE

Run	159-141-2	159-142-2	159-144-2	159-144-4
Pretreat, H_2, °F	950	600	950	950
Pressure, psig	200	400	400	400
Partial Pressure CO, psia	107	207	207	207
GHSV	527	531	506	1003
GHSV on CO	263	265	253	502
Contact Time, sec	53.2	101.9	107.1	54.3
CO Conversion, % wt	40	43	37	25
HC Selectivity, % wt				
C_1+C_2	22	17	24	27
C_3+C_4	11	12	12	13
C_5+	68	71	63	60
Olefins in C_5, % wt	80	82	78	80
Methylbutenes in $C_5^=$, % wt	81	42	69	66
90% OH, °F	395	554	465	432

TABLE 52

EFFECT OF CONTACT TIME AND PROCESS PRESSURE ON SG-B-3 ACTIVITY

Run	143-64-2	159-139-8	159-144-2	159-144-4
Pretreat, °F	600	600	950	950
Pressure, psig	200	200	400	400
Contact Time, sec	26.7	52.0	107.1	54.3
CO Conversion, % wt	40	42	37	25

TABLE 53

SYNTHESIS GAS ACTIVATION OF SG-B-3 AT 600°F

(200 psig; 500 GHSV)

Run CT 158-105-	1		2		3		4		5
Processing Temp., °F	500	H_2/CO 2 Hr. 600°F	500	H_2/CO 2 Hr. 600°F	500	H_2/CO 4 Hr. 600°F	500	H_2/CO 4 Hr. 600°F	600
CO Conversion, % wt	1		1		1		1		7
H_2 Conversion, % wt	5		8		5		4		13

TABLE 54

EFFECT OF PRESSURE AND CONTACT TIME ON SELECTIVITY

	15 sec.			29 sec.			55 sec.		
PSIG	C_1+C_2	C_3+C_4	C_5^+	C_1+C_2	C_3+C_4	C_5^+	C_1+C_2	C_3+C_4	C_5^+
50	41	15	44	44	11	45	-	-	-
100	29	14	57	26	13	61	31	15	54
200	27	14	59	21	14	65	24	11	65
400	-	-	-	20	17	63	18	12	70

The lower activation temperature of 600°F was chosen arbitrarily for the process variable studies. Both 1/1 and 2/1 H_2/CO charge stocks were examined at 50-400 psig. A process temperature of 515°F was used since this gave good conversion and selectivity at 200 psig.

Complete data for these studies are given in Tables D6-D9 of Appendix D and plotted in Figures 55-59. Figure 55 shows the catalyst activity for converting CO as a function of contact time at various pressure levels. Unlike the SG-A-type catalysts that were relatively inactive for converting $2H_2/CO$ at low pressures, SG-B-3 had good activity at 50 and 100 psig. Activity at 200 psig was greater than that at 400 psig (constant contact time), but did not show a maximum around 200 psig as did the SG-A catalysts. Points were selected from the curves in Figure 55 and are plotted in Figure 56 to illustrate the effect of pressure at constant contact time.

The effects of pressure on hydrocarbon selectivity are shown in Figures 57, 58 and 59 for contact times of 15, 29, and 55 seconds, respectively. The data indicate a preference for higher pressure for C_5^+ gasoline production. The selectivity for C_3+C_4 was remarkably constant, with C_5^+ increasing at the expense of light gas as pressure was increased from 50 to 400 psig. Although not shown in Table 54, increasing contact time further to 100 seconds still gave 70% C_5^+ and 20% C_1+C_2 at both 200 and 400 psig.

In addition to good carbon monoxide conversion and C_5^+ selectivity, it is desirable to have a high octane product boiling within the gasoline range. The octane can be attained with an aromatic product or one that contains highly branched olefins in good quantity. Catalyst SG-B-3 generates octane by producing the latter type product (R+0 ∿85). Data (Table 55) illustrate the effects of pressure and contact time on "product quality." Except for the 400 psig points, the products are all satisfactory. At constant contact time, the products are higher boiling with reduced olefin branching as one proceeds to higher pressure. Increasing contact time at constant pressure also gives a higher boiling liquid product. The product from processing at 400 psig can be improved (lower 90% OH and greater olefin branching) by using a somewhat more severe pretreatment.

Based on the above work with H_2/CO, it appears that pressures greater than 100 psig are necessary for the best C_5^+ selectivity. Although activity was somewhat lower at 200 and 400 psig, the greatly enhanced selectivity for C_5^+ gasoline more than compensated.

Data for the process variable study with $2H_2/CO$ are given in Tables D10-D12 of Appendix D and Figures 60-61. The study was not as detailed as was that for the 1/1 charge, but did cover the range of 50-400 psig at temperatures ranging from 485 to 550°F. The effect of temperature on catalyst activity is depicted in Figure 60 for four pressure levels and a constant gas hourly space velocity.

Figure 55

EFFECT OF CONTACT TIME AT CONSTANT PRESSURE ON THE ACTIVITY OF CATALYST SG-B-3

(H_2/CO Charge, 515°F)

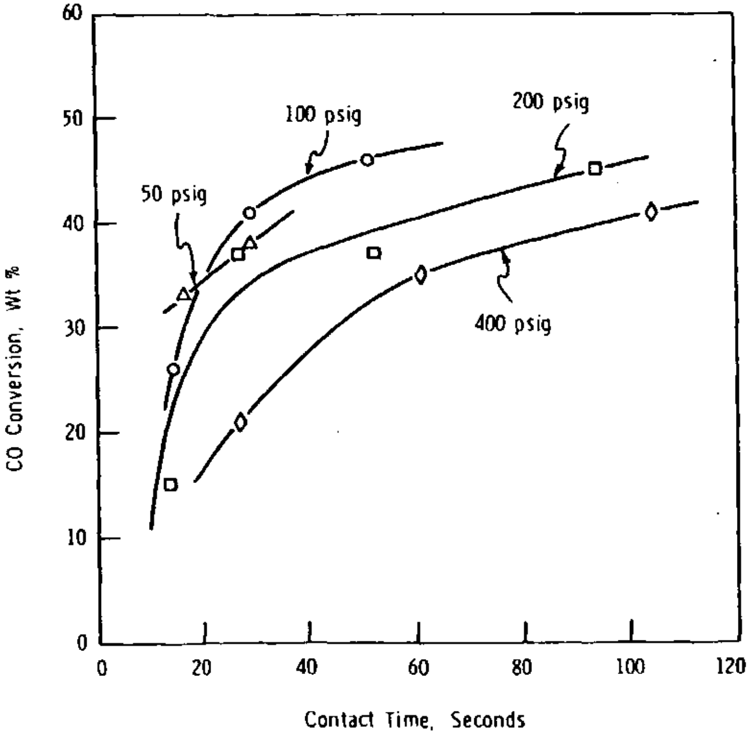


Figure 56

EFFECT OF PRESSURE AT CONSTANT CONTACT TIME ON THE ACTIVITY OF CATALYST SG-B-3

(H_2/CO Charge, 515°F)

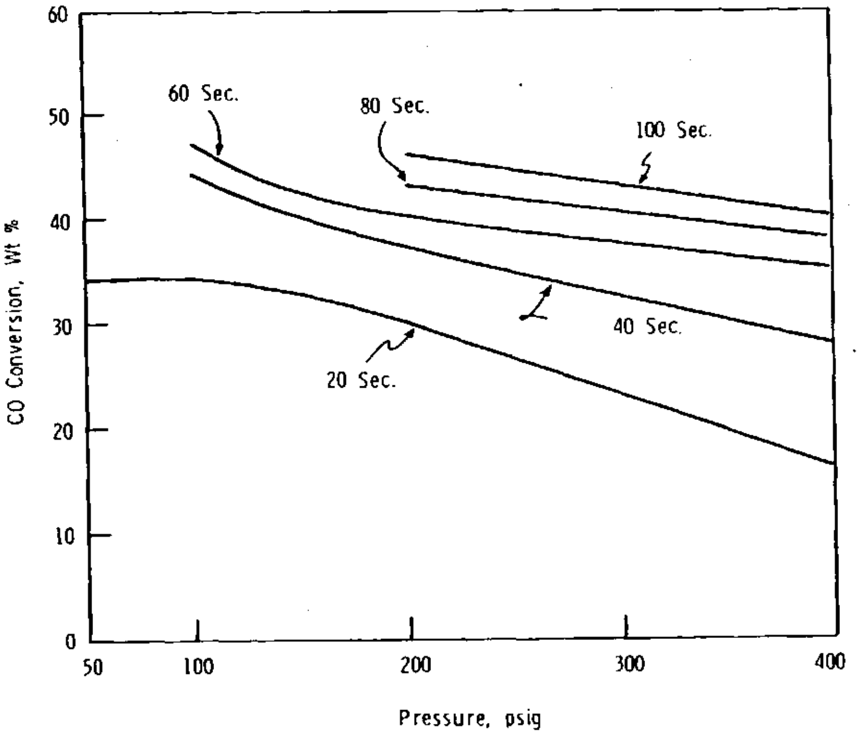


Figure 57

EFFECT OF REACTION PRESSURE ON HYDROCARBON SELECTIVITY WITH H_2/CO OVER SG-B-3 AT 515°F, τ 15 SEC

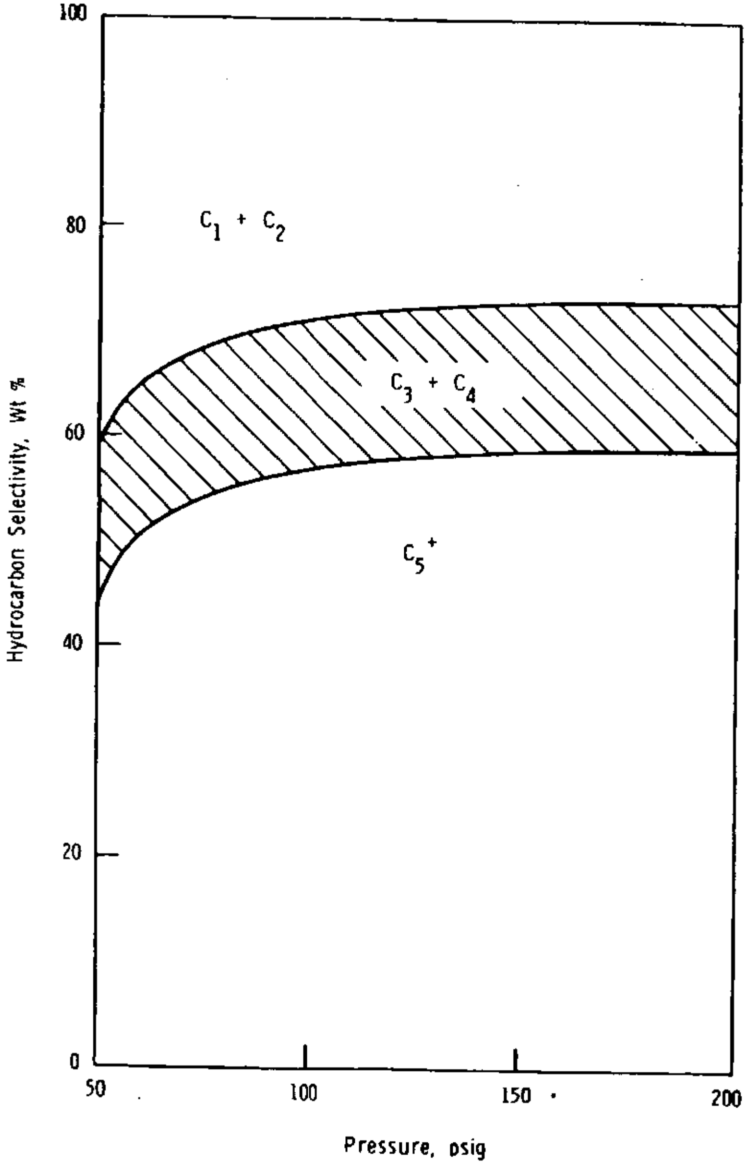


Figure 58

EFFECT OF REACTION PRESSURE ON HYDROCARBON SELECTIVITY WITH H_2/CO OVER SG-B-3 AT 515°F, τ 29 SEC

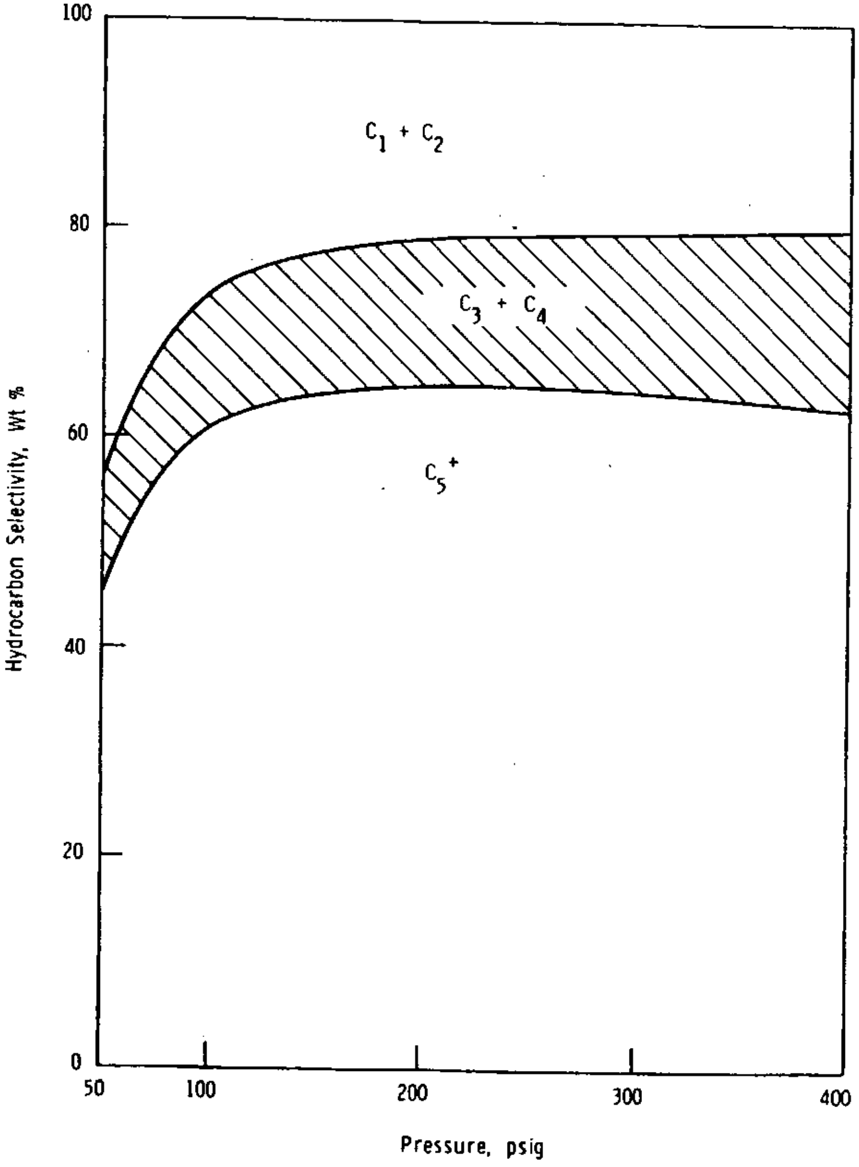


Figure 59

EFFECT OF REACTION PRESSURE ON HYDROCARBON SELECTIVITY WITH H_2/CO OVER SG-B-3 AT 515°F, τ 55 SEC

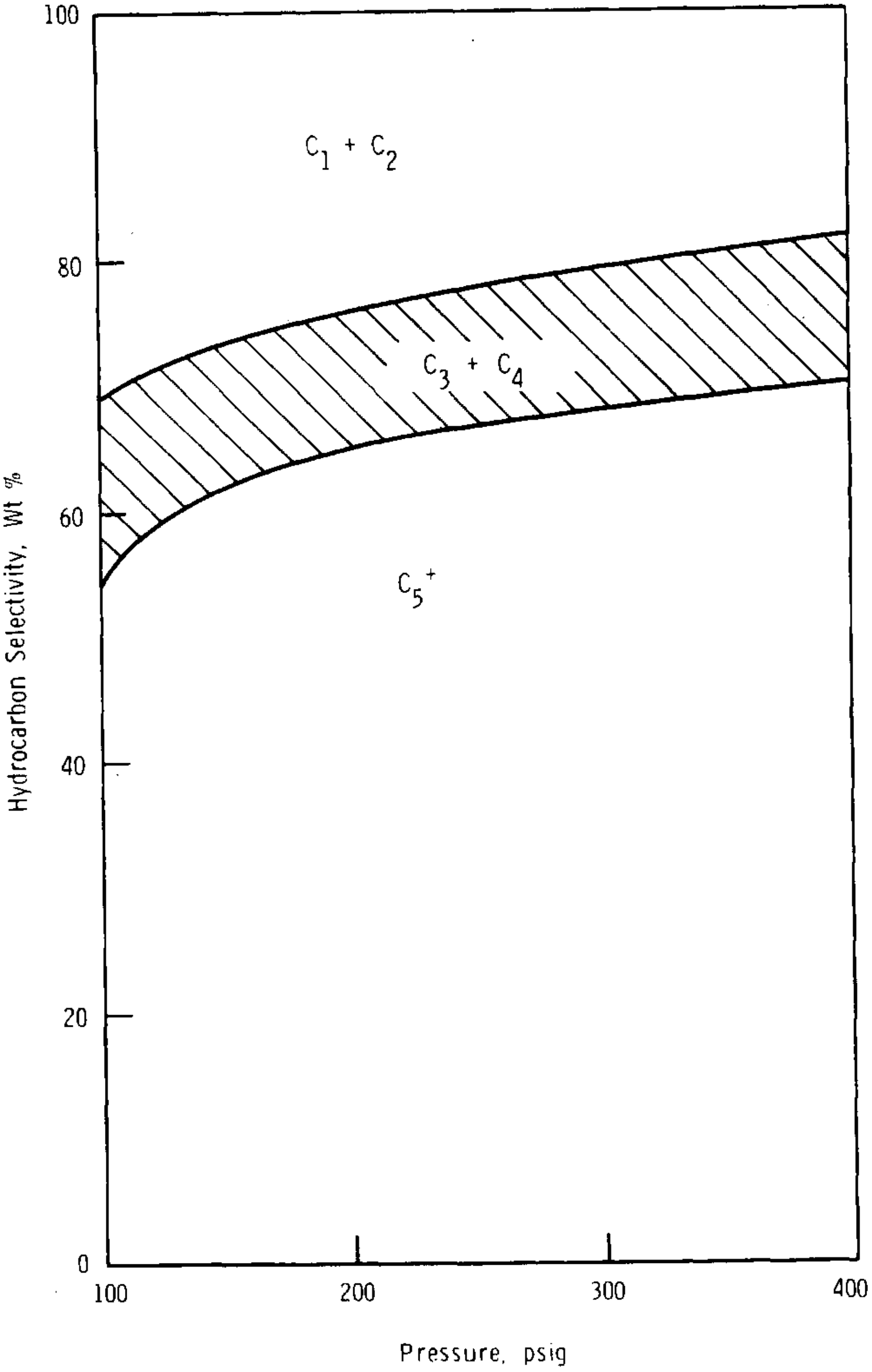


Figure 60

EFFECT OF TEMPERATURE ON ACTIVITY OF CATALYST SG-B-3 WITH 2 H_2/CO AT 500 GHSV

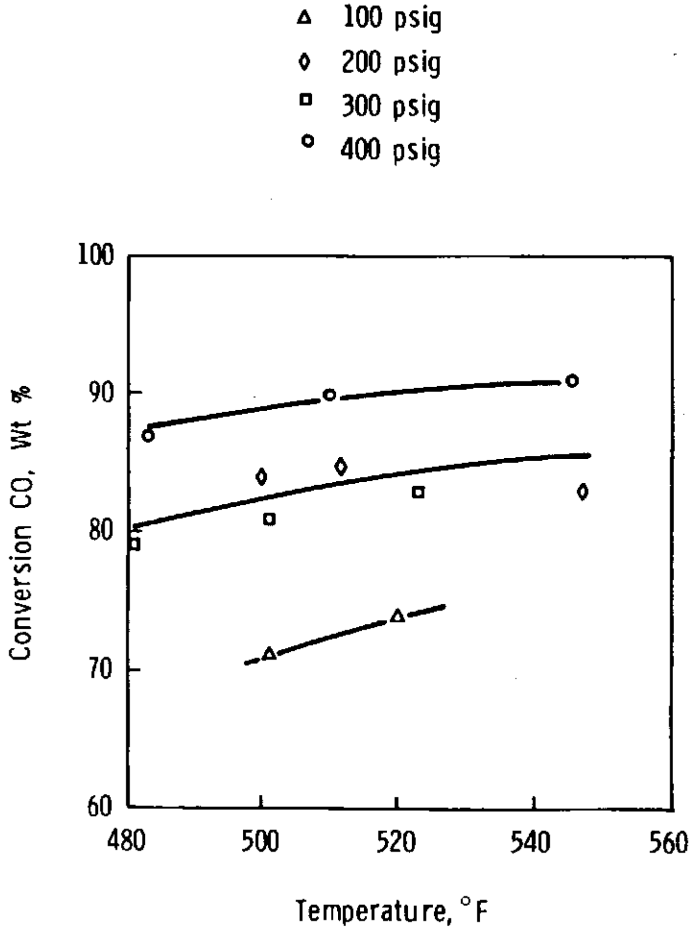
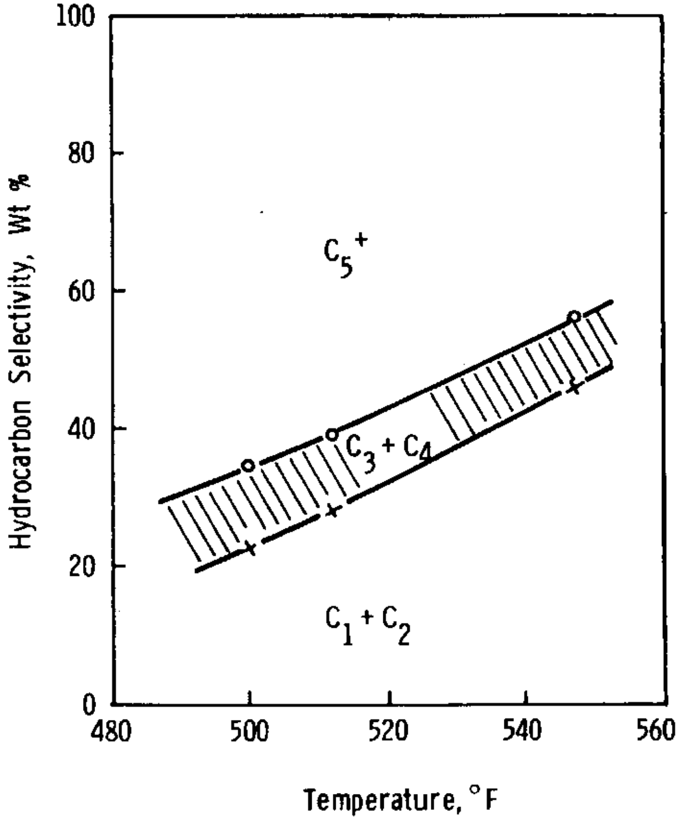


Figure 61

EFFECT OF TEMPERATURE ON HYDROCARBON SELECTIVITY OF CATALYST SG-B-3 WITH 2 H_2/CO AT 500 GHSV

Pressure: 200 psig



As the pressure increased from 100 to 400 psig, conversion of CO rose from the 70% to the 90% level. This was in large part due to the increased contact time as pressure increased. The results for 200 and 300 psig are shown as a single line since such variations as 81 to 84% CO conversion can occur from run to run with fresh catalyst at identical conditions.

A rough estimate of the effect of contact time at different pressures can be obtained from the tables.

Effect of Pressure at 500°F for A Constant 80% CO Conversion

Pressure, psig	100	200	400
Contact Time, sec	40	50	85
GHSV	380	570	647
Selectivity to C_1+C_2, % wt	35	23	22
C_5^+, % wt	53	65	66

Although the catalyst is apparently more active as the pressure is lowered, it is not feasible to operate at 50-100 psig due to poor selectivity and low feed rates needed to attain the optimum contact time.

Despite the increasing conversion with temperature (Figure 60), a ceiling of 500 to 510°F should be maintained to keep light gas (C_1+C_2) make below 30% and C_5^+ gasoline above 60% of the hydrocarbon product. This is illustrated for 200 and 300 psig in Figure 61. At 50 and 100 psig, light gas always exceeded 30%, making it necessary to operate at higher pressures for good gasoline yields.

The results also indicated accelerated aging as space velocity was increased (i.e., 1000 versus 500 GHSV). Thus, with SG-B-3 and $2H_2/CO$, temperatures should be maintained below 510°F, pressures at 200-400 psig, and a space velocity higher than 500 GHSV.

Product quality varied during the studies. As pressure increased, the 90% overhead boiling point of the liquid rose above 500°F. This indicated 200 psig as the compromise pressure resulting in recommended process conditions such as 500°F, 200 psig, and 500 GHSV.

b. Regeneration of Catalyst SG-B-3

Regeneration of catalyst SG-B-3 was studied extensivly. Various schemes were tried, including simple hydrogen treatments, low and high temperature oxidative "burns," as well as solvent extraction. All of this work was complicated by the fact that the catalyst might regenerate successfully several times before performance began to deteriorate. This necessitated longer multiple cycle studies for each method. Adding to the difficulty was a difference in catalyst regenerability when processing a 2/1 versus a 1/1 H_2/CO charge.

High Temperature Oxidative Regeneration of Catalyst SG-B-3

This regeneration scheme is a standard type procedure for burning coke on petroleum processing catalysts. The initial step was a 700°F hydrogen purge at 100 psig followed by introduction (after an inert gas purge) of a 1% oxygen in nitrogen gas mixture and lining out at 750°F. Temperatures were then raised in 50°F increments to 900°F where full air was introduced. Final burning was at 950°F. The catalyst was then pretreated in flowing hydrogen before resuming the syngas charge.

In one experiment the fresh catalyst was activated at 600°F and 200 psig in flowing hydrogen. After 13 days of processing with H_2/CO (Table D1), regeneration was performed as described above with a 1 hour burn at 950°F and a 16 hour H_2 treat at 600°F and 200 psig. A comparison of the data (Tables D1 and D13) show that catalyst activity and selectivity were recovered. In addition, branched olefin formation (methylbutenes) was enhanced and 90% overhead boiling points lowered. The improvement in methylbutene content and 90% point are attributable to the 950°F temperature attained during regeneration compared to the 600°F seen by the catalyst during initial activation.

The same type of regeneration was tried after processing a 2/1 H_2/CO charge at 500°F (Appendix D, Tables D14 and D15). Neither attempt was successful. Increasing the burn in full air from 1 to 5 hours did not improve catalyst performance. Several reasons for the failure to regenerate can be advanced. Initial pretreatment and H_2 treatments following air burns were at 950°F compared to 600°F for the successful regeneration. However, catalyst SG-B-3 has been successfully regenerated using these steps, for a H_2/CO charge (discussed below). The $2H_2$/CO charge may make a coke more difficult to remove and thus recover good activity-selectivity.

Another loading of catalyst SG-B-3 which had been preaged for six days processing a methane diluted synthesis gas, 0.9 H_2/ 1.0 CO/0.3 CO_2/3.1 CH_4, at temperatures between 435 and 460°F was followed by runs with H_2/CO (Table D16). The regeneration procedure used here differed from that given above only in that the pressure was atmospheric rather than 100 psig, and air diluted with helium was used in place of oxygen diluted with nitrogen. Pertinent data gleaned from Table D16 are summarized in Table 56. Both activity and selectivity were recovered.

It is evident that at a process temperature of 485°F no benefit was obtained by catalyst air regeneration, either for two hours at 900°F or two hours at 950°F. High 90% O.H. temperatures and low methylbutenes indicate a low octane C_5^+ gasoline product. Regeneration of the catalyst for sixteen hours at 950°F in air and raising the reaction temperature to 515°F again produced gasoline range 90% overhead points and near equilibrium methylbutene values. Both are indicators of an increased octane number product.

TABLE 55

EFFECT OF PRESSURE AND CONTACT TIME ON PRODUCT QUALITY

PSIG	Contact Time, sec.	Olefins in C_5, % wt	Methyl $C_4^=$ in $C_5^=$, %wt	90% OH, °F	C_5^+ Selectivity, % wt
50	15	71	83	328	44
100		84	82	343	57
200		88	76	367	59
50	29	61	82	360	45
100		76	82	378	61
200		85	63	381	65
400		83	43	456	63
100	55	63	82	393	54
200		84	75	400	65
400		82	35	505	70

TABLE 56

REGENERATION OF CATALYST SG-B-3*

Regeneration	Days Stream Time	Temp., °F	Conv., % CO	90% OH, °F	Selectivity, % wt		
					$MeC_4^=$	C_5^+	C_1+C_2
	6.0	485	34	492	24	70	20
2 Hr-Air-900°F	0.9	485	36	522	54	74	15
	3.9	485	31	545	35	68	21
2 Hr-Air-950°F	0.9	485	36	509	64	75	15
	3.9	485	32	523	53	73	17
16 Hr-Air-950°F	0.9	515	39	389	80	71	19
	3.9	515	35	372	79	64	25
	5.9	515	33	381	77	60	29
	7.9	515	30	380	77	58	31
	8.9	515	29	380(est)	77	56	32

*Activation, H_2 for 16 hours @ 600°F and 200 psig. Processing, 500 GHSV and 200 psig.

Side-by-side multiple cycle studies were carried out to check unit reproducibility while further defining catalyst regenerability. Processing was at 200 psig, 500°F, and 525 GHSV with a H_2/CO charge. Regenerations were carried out as described above with the final burn with full air at 950°F for 16 hours. The procedures did differ in that 143 unit utilized air diluted with helium at 0 psig while 158 unit was regenerated at 100 psig using oxygen diluted with nitrogen.

Data for the first 3 cycles are presented in Tables 57 and 58 and show good unit reproducibility for catalyst activity and selectivity.

A third regeneration was then carried out at 950°F for 16 hours on each catalyst. Subsequent processing was at 200 psig, 515°F and 1030 GHSV with a H_2/CO charge. The catalyst after three regenerations had lost about 20% of its activity for carbon monoxide conversion, most of the loss being encountered during the third regeneration (Appendix D - Table D17). However, product quality remained high, with good C_5^+ gasoline yields, high branched olefin content, and satisfactory 90% overhead boiling points.

Following the above studies, each catalyst was run two additional cycles following 16 hour 950°F air regenerations and 600°F hydrogen activations. Unit 158 was used to study a $2H_2/CO$ charge while 143 unit continued with H_2/CO, both at 525 GHSV.

Data for the runs with $2H_2/CO$ are summarized in Table 59 and plotted in Figure 62. Process conditions were 200 psig, 500°F and 525 GHSV. The data show that catalyst activity was decreased 10% at 2.9 and 20% at 6.9 days on stream. Although catalyst activity had been lost and aging accelerated after these multiple regenerations, performance of SG-B-3 during the cycle following the 5th regeneration showed little change over that after four regenerations.

Data for the fourth, fifth and sixth regeneration of catalyst SG-B-3 while processing H_2/CO are summarized in Figure 63. Catalyst activity showed a decline with each cycle. Following the fifth regeneration, a 20% loss in activity had been sustained versus that for fresh catalyst. This is a significant drop over that observed for the first 3 cycles where catalyst performance appeared stabilized.

Data taken from Tables 57, D17, D20-D24 comparing fresh catalyst performance with regenerated (six times) catalyst at 1.9 and 6.9 days on stream, are shown in Table 60. At 1.9 days on stream and after six regenerations, catalyst activity decreased 23%. At 6.9 days on stream the activity of the regenerated catalyst showed an accelerating aging, resulting in a 40% activity decrease.

The catalyst stream time in this study was 42 days and included seven cycles of operation (six regenerations). It is

TABLE 57

AGING AND REGENERATION OF CATALYST SG-B-3* - 143 UNIT

(H_2/CO at 200 psig)

	Fresh						First Reg.							Second Reg.		
Run CT 143-68-	1	2	3	4	6		7	8	9	10	11	12		13	14	15
Days On Stream	0.9	1.9	2.9	4.9	6.9		1.9	2.9	3.9	4.9	5.9	6.9		1.9	2.9	3.9
Temperature, Inlet, °F	481	487	486	487	489	A	485	486	488	489	488	489	A	484	486	488
Average, °F	488	493	492	493	495	I	490	492	493	494	493	494	I	490	492	493
Maximum, °F	497.	502	500	501	502	R	497	499	500	501	500	501	R	501	501	500
Outlet, °F	475	481	480	481	482		478	480	481	483	482	483		477	480	482
GHSV	530	530	529	540	523	R	501	507	509	510	513	524	R	531	531	530
WHSV	0.7	0.7	0.7	0.8	0.7	E	0.7	0.7	0.7	0.7	0.7	0.7	E	0.8	0.8	0.8
Material Balance, %	105	105	105	102	103	G	101	100	102	103	103	105	G	102	100	100
CO Conversion, % wt	36	35	34	34	32	E	36	34	31	31	30	30	E	37	34	32
To HC, % wt	99	99	99	99	99	N	99	99	99	99	99	99	N	99	99	99
H_2 Conversion, % wt	77	78	77	72	73	E	75	75	71	71	68	69	E	75	74	69
To HC, % wt	56	58	58	58	59	R	57	58	59	59	59	60	R	51	52	56
						A							A			
Total Conversion, % wt	39	38	37	37	35	T	39	37	34	34	33	33	T	40	37	35
g HC/m^3 Charge (CO)	208	199	190	199	185	I	209	194	177	173	175	174	I	208	185	190
HC Selectivity, % wt						O							O			
C_1	13	17	17	17	20	N	15	17	19	19	19	21	N	15	18	19
C_2	2	1	2	2	3		2	2	2	2	3	2		2	2	2
C_3	2	3	4	5	5	950°F	3	4	4	4	4	4	950°F	3	3	4
C_4	7	5	7	7	7		7	7	7	6	8	6		8	6	7
C_5	11	9	8	10	8	16 Hr.	11	9	8	7	9	8	16 Hr.	12	10	8
C_6^+	65	65	62	59	57		62	61	60	62	57	59		60	61	60
						1 Atm.							1 Atm.			
Olefin Selectivity, % wt																
C_2	39	65	41	40	33	then	50	26	50	50	39	50	then	38	41	40
C_3	39	62	66	68	70		54	62	63	62	62	62		54	57	62
C_4	66	68	73	75	74	950°F	67	69	73	69	76	76	600°F	68	69	68
C_5	80	81	82	82	83		79	81	82	82	82	83		80	81	82
						16 Hr.							16 Hr.			
C_5 Olefin Selectivity, % wt																
1-Pentene	2	2	3	4	4	H_2	2	3	3	3	3	3	H_2	2	3	3
2-Pentene	21	25	31	36	38		21	25	28	30	32	32		22	27	29
Methylbutenes	77	73	66	60	58	1 Atm.	77	72	69	67	65	65	1 Atm.	76	70	68
C_6^+ Aromatics, % wt	7	<1	<1	<1	<1		<1	<1	<1	<1	<1	10		7	8	<1
90% OH, °F	416	406	435	478	498		395	398	372	426	433	427				
C_5^+ Octane Number (R+0)	-	-	-	81	-		-	-	-	-	-	-		84	-	-

*Activation of fresh catalyst - 950°F, 16 Hr., H_2

TABLE 58

AGING AND REGENERATION OF CATALYST SG-B-3* - 158 UNIT

(H_2/CO at 200 psig)

Run CT 158-106-	1	2	3	4	5	6		7	9	10	11	12		13	14	15
Days On Stream	0.8	1.9	3.0	3.8	5.9	6.9		0.9	3.9	4.9	5.9	6.9		0.8	2.9	3.8
Temperature, Inlet, °F	482	487	489	489	491	491	A	482	490	490	490	491	A	486	489	492
Average, °F	483	487	489	489	491	491	I	484	490	491	491	492	I	488	491	493
Maximum, °F	498	500	501	499	502	501	R	497	500	500	501	501	R	499	501	502
Outlet, °F	473	477	478	478	481	481		476	481	482	482	483		478	484	485
GHSV	547	526	537	534	540	536	R	542	540	540	543	547	R	507	516	527
WHSV	0.8	0.8	0.8	0.8	0.8	0.8	E	0.8	0.8	0.8	0.8	0.8	E	0.7	0.7	0.7
Material Balance, %	95	102	102	104	104	102	G	98	101	104	103	105	G	96	100	106
CO Conversion, % wt	37	37	36	35	34	33	E	39	34	31	34	31	E	35	35	34
To HC, % wt	99	99	99	99	99	99	N	99	99	99	99	99	N	99	99	99
H_2 Conversion, % wt	81	80	78	75	76	74	E	70	73	63	70	69	E	75	70	68
To HC, % wt	53	54	54	55	59	56	R	52	54	52	53	55	R	53	52	60
							A						A			
Total Conversion, % wt	40	40	39	38	37	36	T	41	37	31	36	37	T	38	38	36
g HC/m^3 Charge (CO)	196	204	197	192	204	182	I	198	191	167	185	173	I	190	192	185
HC Selectivity, % wt							O						O			
C_1	16	17	18	19	20	22	N	17	20	18	20	23	N	18	17	20
C_2	2	3	2	2	3	2		2	2	2	3	3		2	2	2
C_3	3	3	4	4	4	5	950°F	3	3	4	4	5	950°F	4	3	3
C_4	8	8	8	8	9	9		7	8	9	9	8		11	9	8
C_{5+}	12	12	12	11	11	11	16 Hr.	12	12	14	11	11	16 Hr.	12	13	11
C_6	59	57	56	56	53	51		59	55	53	53	50		53	56	56
							1 Atm.						1 Atm.			
Olefin Selectivity, % wt																
C_2	41	33	39	41	33	40	then	41	40	50	33	39	then	48	50	40
C_3	55	55	61	62	64	65		56	56	56	61	54		37	48	49
C_4	65	68	69	74	76	75	950°F	63	69	71	71	72	950°F	50	63	69
C_5	77	80	81	81	82	83		76	80	81	81	82		72	76	78
							16 Hr.						16 Hr.			
C_5 Olefin Selectivity, % wt																
1-Pentene	2	2	3	4	3	3	H_2	2	3	3	3	3	H_2	2	2	2
2-Pentene	19	20	23	26	28	30		19	22	24	24	25		17	18	19
Methylbutenes	79	78	74	70	69	67	1 Atm.	79	75	73	73	73	1 Atm.	81	80	79
C_6^+ Aromatics, % wt	<1	1	<1	<1	<1	<1		7	7	6	7	7		8	7	8
90% OH, °F	394	368	391	395	390	380		391	373	371	373	376		404	388	382
C_5^+ Octane Number (R+O)	-	-	-	-	87	-		-	-	-	-	-		-	87	-

*Activation of fresh catalyst - 950°F, 16 Hrs., H_2

TABLE 59

PROCESSING $2H_2/CO$ AFTER AIR REGENERATION OF CATALYST SG-B-3

			Selectivities % wt			
Catalyst SG-B-3	Stream Days	CO Conv., % wt	C_1+C_2	C_5^+	90% OH, °F	Methylbutenes in $C_5^=$
Fresh	2.9	79	22	64	431	70
After 4th Reg.	2.9	71	32	54	364	79
After 5th Reg.	2.9	68	30	54	-	85
Fresh	6.9	71	30	57	427	64
After 4th Reg.	6.9	57	37	52	369	84
After 5th Reg.	6.0	58	37	49	-	85

TABLE 60

PERFORMANCE OF SG-B-3 AFTER MULTIPLE AIR REGENERATIONS

			Selectivities % wt			
Catalyst SG-B-3	Stream Days	CO Conv., % wt	C_1+C_2	C_5^+	90% OH, °F	Methylbutenes in $C_5^=$
Fresh	1.9	35	18	74	406	73
After 1st Reg.	1.9	36	17	73	395	77
After 2nd Reg.	1.9	37	17	72	-	76
After 4th Reg.	1.9	31	21	69	398	79
After 5th Reg.	2.8	31	21	65	367	80
After 6th Reg.	1.9	27	19	68	385	81
Fresh	6.9	32	23	65	-	58
After 1st Reg.	6.9	30	23	67	427	65
After 2nd Reg.	6.9	-	-	-	-	-
After 4th Reg.	6.9	26	25	62	363	76
After 5th Reg.	6.8	24	28	59	-	78
After 6th Reg.	6.9	19	27	60	374	80

Figure 62

AGING AND REGENERATION OF SG-B-3 WITH 2 H_2/CO

(Process Conditions: 2 H_2/CO, 525 GHSV, 500°F, 200 psig)
(Regeneration: Air, 16 Hr, 950°F, 100 psig)

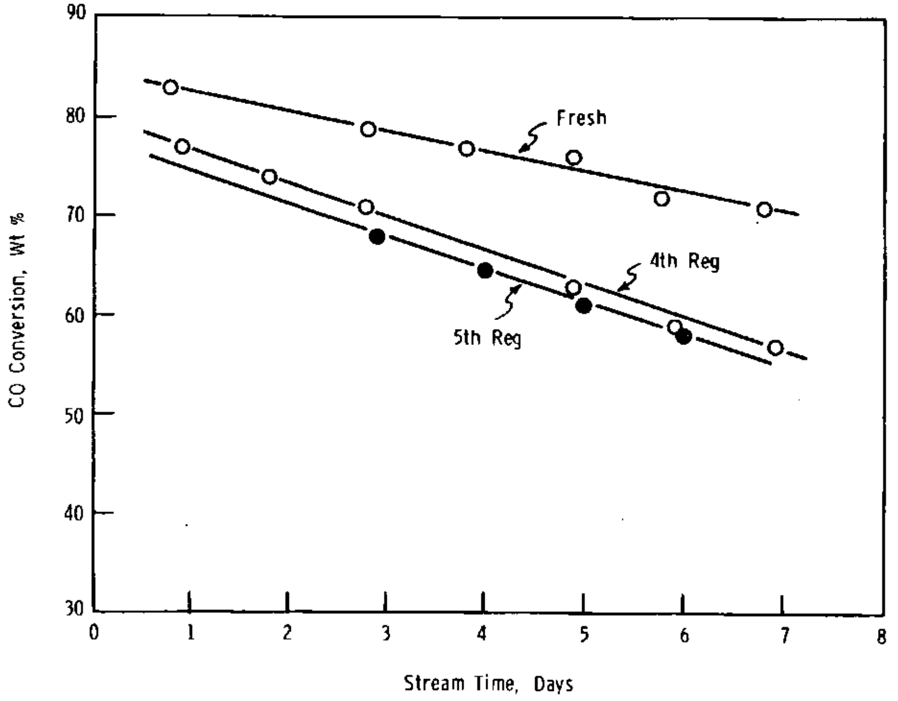


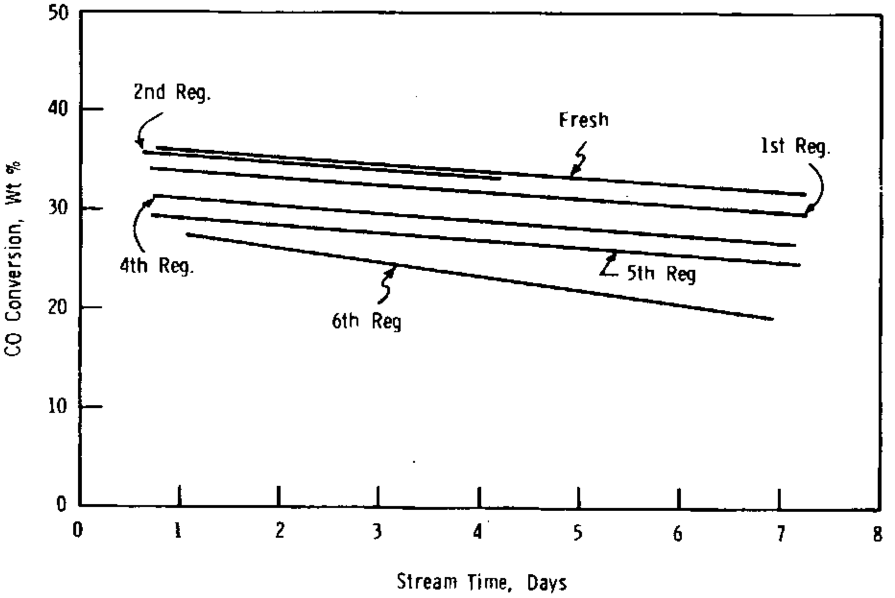
Figure 63

AGING AND REGENERATION OF SG-B-3 WITH H_2/CO

(Process Conditions: H_2/CO, 525 GHSV, 500°F, 200 psig)

Regenerations: Air, 16 Hrs, 950°F, 0 psig

Pretreat: After Regen. 1, 6, H_2, 16 Hrs, 950°F, 0 psig
After Regen. 2, 4, and 5 - H_2, 16 Hrs, 600°F, 0 psig



evident that catalyst SG-B-3 cannot withstand the oxidative regeneration conditions (16 hrs-air-950°F) used in this study beyond about 3 or 4 cycles of operation without sustaining appreciable losses in activity for CO conversion.

Hydrogen Regeneration of Catalyst SG-B-3

Hydrogen regenerations would be simple operations to carry out commercially since they would be at conditions quite similar to those used during processing. Several studies were made to determine the feasibility of this type regeneration following processing with 1/1 and 2/1 H_2/CO charge stocks.

1/1 H_2/CO

A total of 15 cycles were completed with the H_2/CO charge at 500 GHSV, 200 psig, and 515°F. During the study 12 hydrogen and two oxidative regenerations were performed. Hydrogen rejuvenations were at ∿3000 GHSV at temperatures ranging from 600° to 900°F and pressures from 0 to 200 psig. Oxidative regenerations consisted of consecutive burns in 1% oxygen and then air (Appendix D, Tables D25 and D26 and Figures D1-D4).

Hydrogen treatments at 600°F and 200 psig did not restore catalyst activity. Conversion of carbon monoxide declined linearly during the 19 days of processing. However, hydrocarbon selectivity was restored through these four cycles with C_5^+ gasoline varying between 55 and 75% of the hydrocarbons produced.

Treatments at 750 and 900°F still maintained this selectivity as well as restoring CO conversion activity to the 37% level at start of cycle (Cycles 6-8). Problems in the unit off-gas sampling and measurement system precluded calculation of activity and selectivity data for Cycle 5. However, charge rates and process conditions were maintained so subsequent catalyst performance was not affected.

All 16 cycles are summarized in Table 61. Aging was consistent through the first seven cycles, but increased dramatically upon extending the H_2 treat to 40 hours. Activity was not restored for cycles 9 and 10, but was returned to near fresh activity by an air regeneration. However, the aging rate after the oxidative regeneration was equivalent to or greater than that for the two previous cycles. A second air regeneration again restored catalyst activity, but the aging rate had increased again.

To examine the possibility of extended time at high temperatures causing accelerated aging, a run was made where fresh SG-B-3 was treated for 66 hours at 950°F and 200 psig in hydrogen. The results (Appendix D, Table D24) were not unusual, with the aging being about 0.8 wt % loss in carbon monoxide conversion per day. Thus, aging while converting synthesis gas may be a prerequisite for a dramatic increase in aging following treatments at high temperature for extended times. Regardless, extended H_2 treats should be avoided.

TABLE 61

REGENERATION OF CATALYST SG-B-3*

			Start of Cycle			
Cycle	Regeneration	CO Conv. Aging Slope (%/Day)	CO Conv., % wt	Selectivity, %wt C_1+C_2	Selectivity, %wt C_5^+	Days to 55% C_5^+ Selectivity
1	Fresh	0.5	43	18	77	5
2	H_2, 600°F, 16 Hr, 200 psig	0.5	42	18	77	6
3	H_2, 600°F, 16 Hr, 200 psig	0.5	40	20	68	7
4	H_2, 600°F, 16 Hr, 200 psig	0.5	36	22	69	5
6	H_2, 750°F, 16 Hr, 200 psig	0.6	38	20	70	9
7	H_2, 900°F, 16 Hr, 200 psig	0.8	38	20	69	8
8	H_2, 750°F, 40 Hr, 200 psig	2.0	41	22	65	5
9	H_2, 900°F, 66 Hr, 200 psig	1.3	36	24	62	4
10	H_2, 750°F, 16 Hr, 0 psig	1.1	34	24	63	4
11	Air, 750°F, 1 Hr, 100 psig	1.3	42	21	70	6
12	H_2, 700°F, 16 Hr, 200 psig	1.7	40	-	-	4
13	H_2, 750°F, 16 Hr, 200 psig	1.5	36	19	66	5
15	Air, 750°F, 1 Hr, 100 psig	2.4	38	19	69	4

*Total time on stream was 44 days.

From the above results it appears that catalyst life in single pass operation would be about 3 months with cycle lengths of 4-6 days. Conversions would be greater than 30 percent with a high yield of C_5^+ (>55%) olefinic gasoline.

$2H_2/CO$

A similar study was carried out using a $2H_2/CO$ charge at 500 GHSV, 200 psig, and 500°F with SG-B-3. A total of six cycles were run with results presented in Appendix D (Table D25 and Figure D5). Points extracted from Appendix D are summarized in Table 62.

Initial activity and selectivity declined throughout cycles 1 through 5. Cycle times to 55% C_5^+ gasoline were also decreasing. Again, as with the H_2/CO charge, higher temperatures for H_2 regeneration appeared to be harmful to catalyst aging (cycles 4-5). An air regeneration (cycle 6) restored much activity and returned the catalyst to fresh selectivity. This latter point was not observed in previous oxidative regenerations following processing of $2H_2/CO$ and was probably related to the 900-950°F regeneration temperatures used in those studies.

The results show a significant difference from the H_2/CO study. Aging rates were greater and H_2 regenerations did not prevent large decreases in start-of-cycle activity. The higher aging rates with $2H_2/CO$ are attributable to the higher CO conversion attained per unit time. It was hoped that decreasing on-stream times to about four days would make hydrogen regenerations more effective, thus, reducing this aging rate of 2-3% CO conversion/day.

Results are summarized in Appendix D (Tables D26 and D27 and Figures D6-D9). Two micro reactor units, CT 158 and 159, were used and the two studies were identical for the first several cycles with the major difference being the greater initial activity for the 159 unit study. Aging rates were about 1.2%/day for both studies, which is less than the 2-3% day observed above. However, the shortened on-stream times did not increase the effectiveness of H_2 regeneration to the point where fresh activity was recovered. The activity loss was steady for 3-4 cycles at which time both studies showed some recovery of activity. The conclusions still remained that, for once through operation, hydrogen regenerations would permit at best one month of operation before activity losses become too great (∿60% conversion). Hydrogen regenerations did restore catalyst selectivity each time. Increasing processing temperature fo 510°F improved the activity, but dramatically increased the aging rate.

Low Temperature Oxidative Regeneration of Catalyst SG-B-3

During the high temperature oxidative regenerations described above, the only exotherms observed were at 750°F with 1% oxygen. No evidence of burning was observed at higher temperature, although heat was released when switching to full air. Thus, it was felt that a low temperature "burn" might be sufficient to regenerate the catalyst.

TABLE 62

REGENERATION OF SG-B-3 WHILE PROCESSING $2H_2/CO$

Cycle	Regeneration	CO Conv. Aging Slope (%/Day)	Start of Cycle			Days to 55% C_5^+ Selectivity
			CO Conv., % wt	Selectivity, %wt		
				C_1+C_2	C_5^+	
1	Fresh	2.6	90	18	71	4
2	H_2, 700°F, 16 Hr, 200 psig	2.2	83	24	63	4
3	H_2, 700°F, 16 Hr, 200 psig	2.0	75	19	66	4
4	H_2, 800°F, 16 Hr, 200 psig	3.0	74	25	62	3
5	H_2, 800°F, 16 Hr, 200 psig	3.0	68	25	59	2
6	Air, 750°F, 1 Hr, 100 psig	2.7	83	19	67	4

TABLE 63

MILD OXIDATIVE REGENERATION OF CATALYST SG-B-3 AFTER PROCESSING $2H_2/CO$

Run CT-159-	Regen. Temp., °F	Start of Cycle		Aging %/Day
		CO Conv., %wt	C_1+C_2, %wt	
181	-	93	26	2.2
182	600	95	28	3.2
183	525	90	30	3.7
184	750	86	27	3.2
185	750	82	25	3.3
186	750	77	25	3.2

TABLE 64

MILD OXIDATIVE REGENERATION OF CATALYST SG-B-3 FOLLOWING A HELIUM PURGE

Run CT-158-	Aging Rate % CO Conv. Loss/Day	Initial Activity % CO Conversion	Selectivity	
			C_1+C_2	C_5^+
136	2.5	83	24	64
137	2.5	86	24	69
138	2.4	84	24	70
139	2.5	81	20	69
140	2.4	77	-	-
141	2.5	79	21	66
142	3.4	77	21	70
143	3.4	75	19	68
144	3.4	72	23	66
145	3.4	64	21	65

Data are summarized in Appendix D (Tables D28-D29) and plotted as Figure 64. Initial catalyst activation was in flowing hydrogen for 16 hours at 600°F and 200 psig. Regenerations consisted of a 1 hour hydrogen purge at 700°F and 100 psig followed by successive 1 hour burns at 750°F (100 psig) with 1% oxygen in nitrogen and then air. Before resuming H_2/CO charge, the catalyst was again treated 16 hours at 600°F, 200 psig with hydrogen.

As shown by data plotted in Figure 64, the regenerations were successful. Activity and selectivity were both recovered. The selectivity did, however, decline more rapidly after regeneration with the loss in C_5^+ gasoline being 1% per cycle. Aging of CO conversion activity could not be distinguished for the three cycles.

Unfortunately, this study was ended before the deleterious effects of multiple regenerations had been established. The catalyst was reloaded in a micro unit, after being stored several weeks in a closed vial, and regenerated as above. The results, given in Appendix D - Table D31, showed that the catalyst did not regenerate as selectivity was the same as at the end of the previous cycle.

The effects of multiple low temperature regenerations were then examined in studies that utilized only 1% oxygen, eliminating the burn in full air. One of these studies is detailed in Appendix D (Table D32 and Figures D10-D11) and summarized in Table 63. Following a hydrogen purge, regenerations were for 1/4 hour at 100 psig using one percent oxygen in nitrogen with temperatures varied from 525 to 750°F. The enhanced carbon monoxide conversion activity and higher C_1+C_2 make compared to other runs were probably just a start-up variable. Part of the increased carbon monoxide conversion was due to slightly higher shift activity observed during these runs. Aging rates were constant for all cycles at 3-3.5%/day. The loss in activity at the start of each cycle would still limit this catalyst life in single pass operation. The most interesting point in this study is the extent of the selectivity and activity recovery at these mild conditions.

In all of the above, the catalyst was purged with hydrogen following processing, and prior to regeneration. Since hydrogen alone did not restore catalyst activity and may be detrimental, another study was started using helium as the purge gas. Results are given in Appendix D (Table D33 and Figure D12). These data are summarized in Table 64 and Figure 65. The first 4 cycles were equivalent to those obtained with hydrogen as the purge gas, i.e., aging rates of 2.4-2.5% loss/day, with the same selectivity and initial activities. This study then appeared to maintain activity at a higher level for the next 2 cycles, although these also were less than fresh activity. At this point the aging rate apparently increased to >3% loss/day with further losses in initial activity. Again, 1 month appeared to be the total stream time before CO conversions fell to the 60% level.

Figure 64

LOW TEMPERATURE OXIDATIVE REGENERABILITY OF SG-B-3

(Process Conditions: H_2/CO, 500 GHSV, 515°F, 200 psig)

(Regeneration: Air, 1 Hr, 750°F, 100 psig Followed by
H_2, 16 Hr, 600°F, 200 psig)

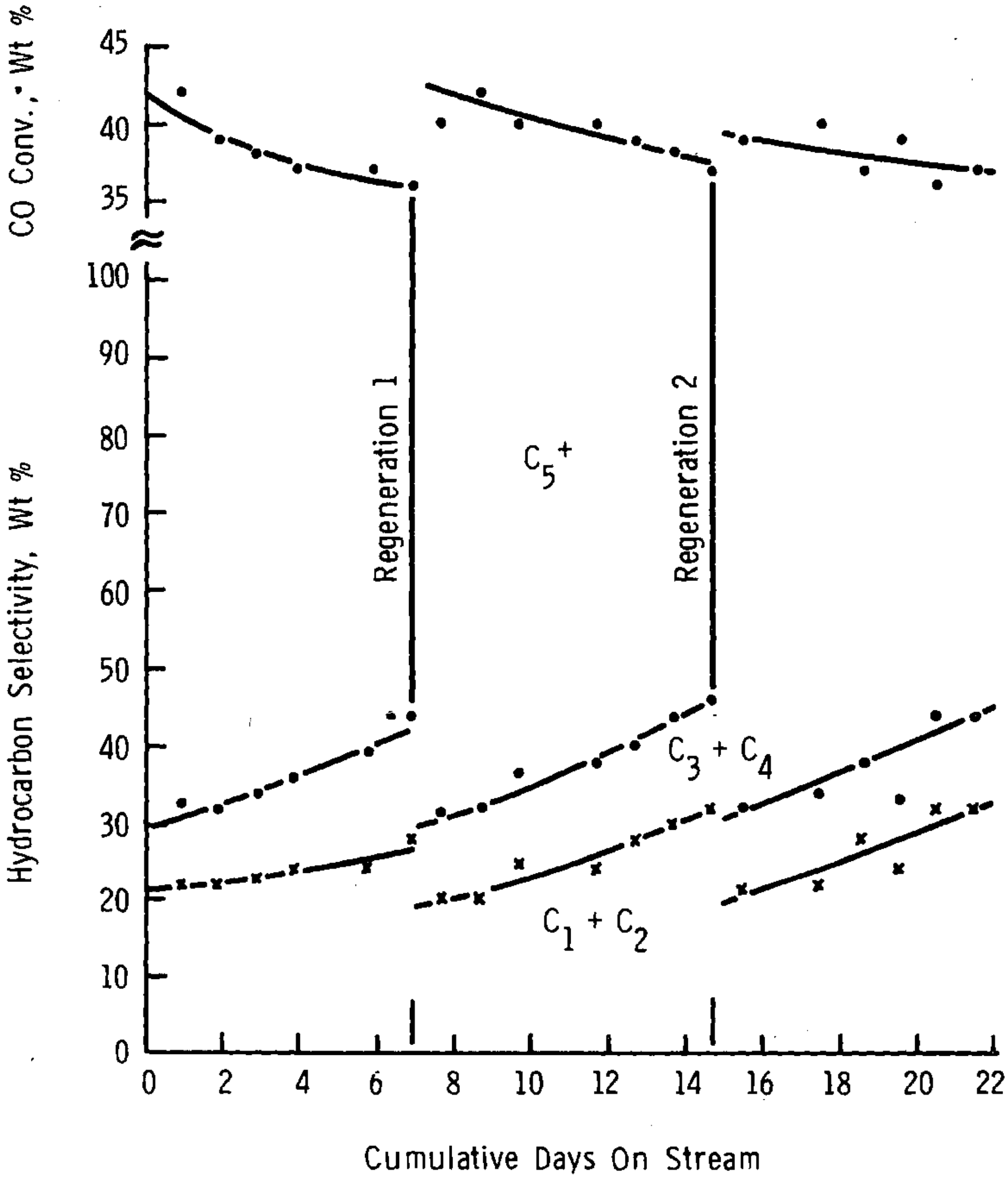
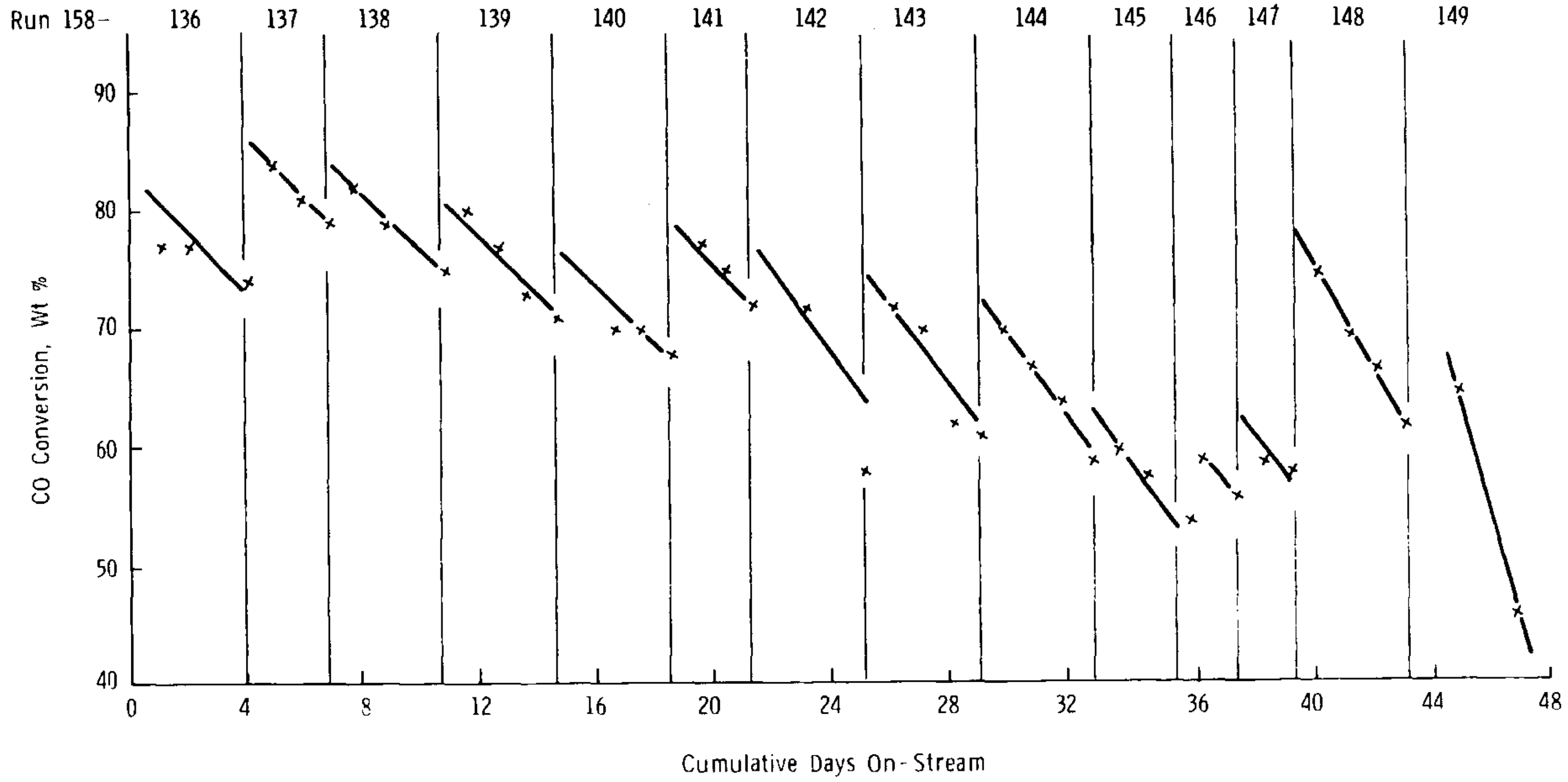


Figure 65

EFFECT OF REGENERATION ON ACTIVITY OF CATALYST SG-B-3

(Pretreatment: H_2, 950°F, 0 psig, 16 Hr)
(Process Conditions: Thru 158-147 2 H_2/CO 500 GHSV, 200 psig, 500°F, 158-148 280 GHSV, 200 psig, 158-149 280 GHSV, 400 psig

(Regeneration: Thru 158-143 and 146, 148, 149 Helium Purge Followed by 1% O_2 at 700°F, 100 psig for 1 Hour – H_2 for 1 Hour at 700°F, 200 psig.
158-144 Also Treated 4 Hours 850°F With 10% O_2 Before H_2, 1 Hour 700°F
158-145 Same as 158-144 With H_2 for 4 Hours at 700°F
158-147 Same as 158-144 With 42 Hours Soak With 2% O_2, 100 psig, 675°F)



With hydrogen purges, the C_5 olefin content remained constant at about 50%, whereas with helium purges it decreased with each cycle.

Hydrogen Purge

CT-158-	128	129	130	131	132	133	134	135
Initial CO Conv.	87	89	83	81	77	71	68	67
Olefins in C_5	52	52	53	50	47	45	52	50

Helium Purge

CT-158-	136	137	138	139	140	141	142	143	144	145
Initial CO Conv.	83	86	84	81	77	79	77	75	72	64
Olefins in C_5	62	58	56	55	56	48	46	43	42	36

Regenerations after 158-143 and 158-144 used 10% oxygen at 850°F in an attempt to increase the C_5 olefin content and also the catalyst activity. However, both olefin content and activity continued to decline.

A 42 hour soak in 2% oxygen at 675°F following regeneration (158-147) did not restore catalyst activity and the C_5 olefin content remained at the 40% level. At this point, standard regeneration procedures (one percent oxygen) were resumed and process conditions were changed in an attempt to improve catalyst activity. Lowering space velocity to 280 GHSV (158-148) gave an initial conversion of 78%, comparable to performance at 15 days. Aging rate was about 4%/day, but C_5 olefin content was only 25% which indicates an unsatisfactory gasoline with respect to octane number. Increasing pressure to 400 psig while at 280 GHSV (158-149) was detrimental to aging as well as product quality.

Regeneration of Catalyst SG-B-3 by Solvent Extraction

A brief study was made using solvent extraction followed by heating in flowing hydrogen as a method of regeneration for catalyst SG-B-3. For this study, a sample of fresh SG-B-3 was activated in hydrogen for 16 hours at 600°F and 200 psig. The activated catalyst was used to process H_2/CO at 500°F, 200 psig, and 525 GHSV for 7.9 days. After this time the catalyst had lost 17% of its activity for converting carbon monoxide.

The aged catalyst was then continuously extracted with n-decane (five LHSV) and the reactor effluent monitored. When a GLC analysis showed the effluent was pure n-decane, the reactor was purged with helium and then heated at 750°F and 200 psig for 16 hours in flowing hydrogen. Following the hydrogen treatment the catalyst was used to process H_2/CO synthesis gas at the conditions given above. A total of three n-decane extractions were performed. The first two were at 250°F and atmospheric pressure while the third extraction was at 500°F. In this case a pressure of 300 psig was used to insure liquid phase conditions.