Run data are summarized in Appendix D (Tables D34 and D35). CO activity data at 1.9 days on stream as a function of the number of decane extractions are shown in Figure 66. Catalyst activity for carbon monoxide conversion declines linearly with the number of extractions performed on the catalyst. Compared with fresh catalyst activity, after the first extraction carbon monoxide conversion activity decreases by 16% and after the third extraction carbon monoxide conversion is down 38%.

An oxidative regeneration (one hour air at 750°F plus one hour air at 950°F) following the n-decane extractions did little toward reactivating this catalyst. At 1.9 days on stream carbon monoxide conversion activity was only 29%.

The data show that spent catalyst SG-B-3 cannot be regenerated by solvent extraction at these conditions.

2. Task 2 - Process Development

The experiments with catalyst SGF-B-1 in the bench-scale unit were made concurrently with those with the chemically equivalent catalyst SG-B-3 in the micro reactor units. As a result, some repetition occurred. However, the repetition served the purpose of illustrating in which areas micro reactor, fixed bed data could be used to complement the fluid bed, bench-scale reactor results.

The detailed data, with catalyst SGF-B-1 in the fluid, bench-scale unit, are given in Appendix D (material balances are in Tables D36-D46 and gas compositions in Tables D47-D57).

The initial experiment, 225-17, was made at the following conditions:

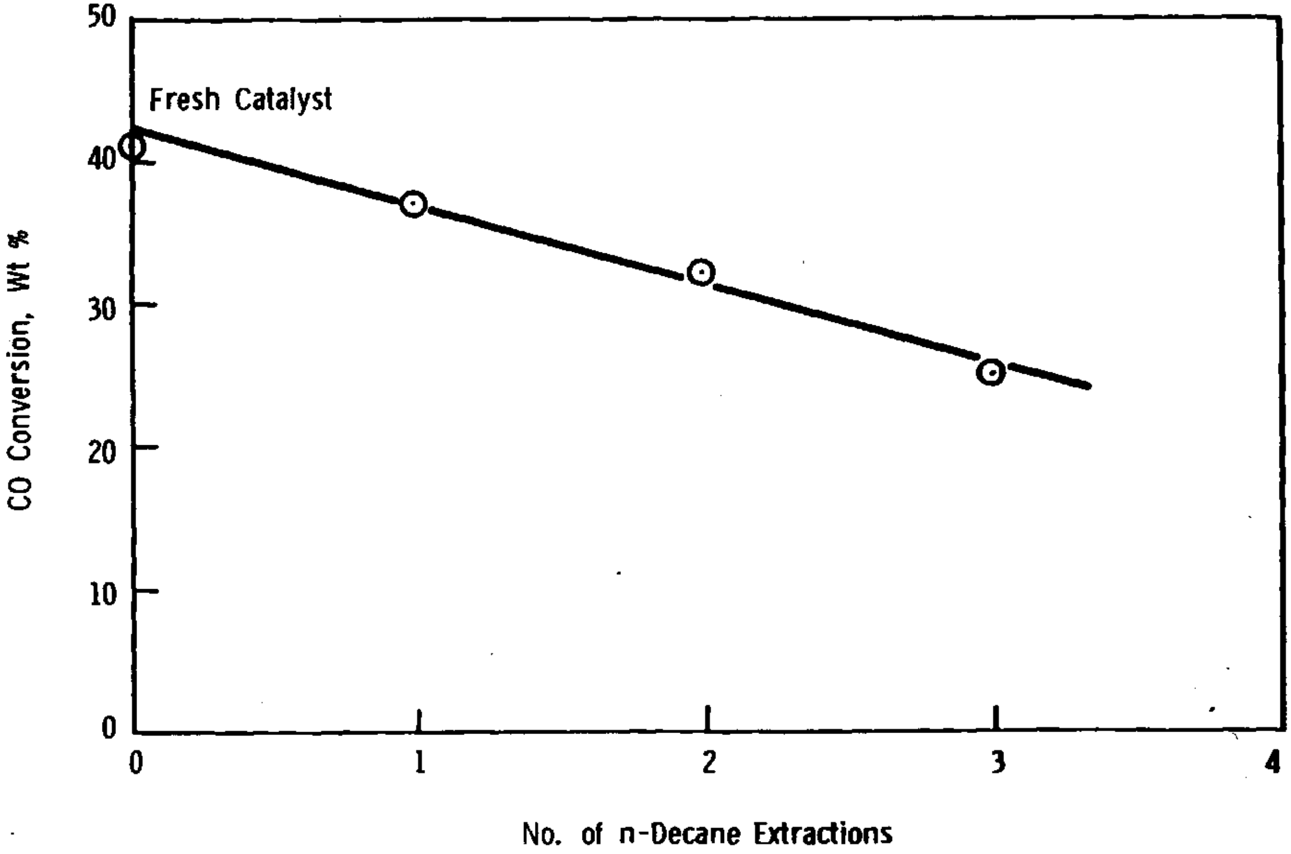
Fresh Feed, H_2/CO	2/1
GHSV, Fresh Feed	500
Pressure, psig	200
Inlet Temperature, °F	400
Maximum Temperature, °F	500
Recycle Ratio	2.0
Superficial Gas Velocity, ft/sec	0.06
Catalyst Charge, cc (g)	100 (50)

With a catalyst charge of 100 cc, the catalyst bed height in the 3/4"-ID reactor was 13.8". Based on studies done in the plexiglass model of the reactor (Task 1), the bubbling bed height would be about 21". The gas velocity selected (0.06 ft/sec) is the lower limit for operation with this catalyst in the bench-scale unit. This velocity was chosen to keep the recycle ratio low. Model studies indicated that pulsing, vibrations, and other physical factors associated with the bench-scale unit should result in reasonable fluidization.

In contrast with the fixed bed runs, where the temperature showed a gradual increase across the catalyst bed, the fluid

Figure 66

EFFECT OF n-DECANE EXTRACTIONS ON THE ACTIVITY OF SG-B-3 WHILE PROCESSING H_2/CO AT 500 GHSV, 500°F AND 200 psig
(Data at 1.9 Days On-Stream)



bed showed a rapid temperature rise in the first couple of inches to within 10-15°F of the maximum in the reactor. Since the fluidized bed height is 20 inches or more, the reactor is operating, essentially, in an isothermal manner; therefore, conversion and selectivity should be relatively insensitive to inlet temperature.

During this run, the recycle ratio was about 2/1 in the fluid reactor as opposed to about 10-15/1 in the fixed-bed reactor. Because the recycle ratio is low in the fluid bed, the composition of the fresh/recycle mix over the catalyst is sensitive to small changes in the recycle ratio.

During the 12-day run, balances were made at 500 and at 725 GHSV on fresh feed. Increasing the space velocity gave a sharp decrease in conversion and a lower selectivity to gasoline.

After about 9 days on stream, an increasing ΔP was noted across the porous sintered metal distributor at the bottom of the reactor. This indicated partial plugging of the distributor disk. Concomitant with this, would be a change in the gas distribution pattern, which probably caused a loss of conversion efficiency.

When the run was completed, after approximately 12 days on stream, the distributor was removed, disassembled, and inspected. It was found to be partially plugged with what appeared to be coke. The heated gas transfer line between the external preheater and the distributor was also found partially plugged with coke. These deposits could have originated from easily decomposed olefins in the recycle stream.

On the basis of this information, a new distributor, which was less subject to plugging, was fabricated and installed in the fluid bed reactor for use during subsequent runs. This new distributor was constructed of 200-mesh stainless steel screen sandwiched between two perforated metal plates. Distribution patterns for the new design, which was tested in the plexiglass model of the reactor, was better than the previous porous metal distributor.

After installation of the new distributor, the reactor was charged with 150 cc of fresh catalyst SGF-B-1, and the bench-scale unit was brought on stream for run 225-18. The run was aborted, however, after only one day because two heater elements burned out. The catalyst was held on standby with flowing hydrogen while repairs were made. The reactor was brought on stream for run 225-19 which was identical to 225-17 except that 225-19 used 150 cc of catalyst and a GHSV of 463, rather than the 100 cc of catalyst and 500 GHSV of 225-17. The data in Table 65 show that the two distributors gave strikingly similar results. However, there was no sign of plugging in over 17 days of operation with the new distributor, while signs of plugging appeared at about 6 days into the 12-day run (225-17). The only significant differences in the runs were the use of a lower recycle ratio to control

TABLE 65

MATERIAL BALANCES FROM FLUID BENCH-SCALE UNIT WITH CATALYST SGF-B-1

RUN NUMBER 225-	17- 2	19- 2
RUN DAYS-ON-STREAM	2.6	2.6
CUM. DAYS-ON-STREAM	2.6	2.6
FRESH FEED H_2/CO RATIO	2.0	2.0
GHSV, HR^{-1} (CHG BASIS)	500	463
RECYCLE RATIO	1.93	1.09
REACT. PRESS., PSIG	200	201
REACT. INLET TEMP., °F	400	422
NOM. REACT. TEMP., °F	500	500
CONVERSIONS, MOL °/°		
H_2	96.2	96.6
CO	87.0	86.6
H_2+CO	93.1	93.3
YIELDS, WT °/°		
HYDROGEN	0.5	0.4
WATER	47.0	47.1
CO	11.4	11.7
CO_2	2.9	3.2
TOTAL HYDROCARBON	38.2	37.6
HC SELECTIVITY, WT °/°		
METHANE	26.6	24.5
ETHENE	0.0	0.0
ETHANE	3.8	3.5
PROPENE	0.1	0.3
PROPANE	2.2	2.0
BUTENES	1.1	1.5
I-BUTANE	1.9	1.8
N-BUTANE	2.1	2.2
TOTAL C4-	37.8	35.8
C5+ PARAFFINS	18.3	20.0
OLEFINS	27.5	27.4
NAPHTHENES	1.6	1.1
AROMATICS	0.6	0.3
OTHERS	14.2	15.4
TOTAL C5+	62.2	64.2
YIELDS, G/SCM CONV CO+H_2		
TOTAL HC	195	191
C5+	121	123
OLEFINS, WT °/° BY C NO.		
C2	0.9	1.3
C3	6.0	12.8
C4	22.1	26.8
C5	42.2	47.2
90 PCT OH, RAW PROD., °F	384	381
OCTANE NO. ON RAW PROD.		
R+0	84.3	82.3
R+3	94.1	-
OXYGENATES, WT °/°	-	0.4

temperatures with the new distributor versus the old one, and a consequent higher H_2/CO ratio in the gas going over the catalyst.

During run 225-19 the temperature was varied between 475° and 525°F. The effects of temperature were masked somewhat by catalyst aging. Nevertheless, the results show that catalyst SGF-B-1 can operate efficiently in only a relatively narrow temperature range near 500°F. At 475°F, conversion was low and the 90% overhead boiling point exceeded 400°F. At 525°F, the process produced large amounts of methane and other light products.

Because linear gas velocities over the catalyst in Run 225-19 were on the borderline of good mixing (as shown by experimental work in the plexiglass model of the reactor), a run was made at a higher recycle ratio, keeping the fresh feed GHSV about the same. The gas velocity was increased in this way from about 0.06 ft/sec to about 0.15 ft/sec. Process conditions for a comparison of the two runs were:

	225-19	225-20
Fresh Feed Composition	$2H_2/CO$	$2H_2/CO$
GHSV (on fresh feed), hr^{-1}	465	500
Pressure, psig	200	200
Maximum Reactor Temp., °F	500	500
Recycle Ratio	1/1	4/1

The results at about the same on-stream times are shown in Table 66. Near the beginning of each run (19-1 and 20-1), the results were equivalent. However, there seems to be somewhat less C_4^- and more C_5^+ for the higher velocity run (225-20). This may be attributable to the different gas composition over the catalyst caused by the different recycle ratios (1.3 H_2/CO versus 0.7 H_2/CO for 225-19 and 225-20, respectively), or possibly by better mixing.

Table 67 gives the composition of the gas passing over the catalyst for these runs. It is immediately obvious that recycle ratio has a major effect on gas composition and, since gas composition affects conversions and selectivities, it is not surprising that product compositions differ. Even so, conversions of H_2 and CO are remarkably similar at about 97 and 87 percent, respectively, for the early runs. After the catalysts had been aged for about 8 days, however, significant differences are evident (Table 66).

These differences show up primarily as somewhat lower CO conversion and lower olefin selectivities at the higher recycle ratio (Run 225-20-8). Methane make was higher. More significantly, the C_5-olefin distribution was closer to equilibrium concentrations, another indication of better mixing at the higher velocity. Essentially, although the higher gas velocity does indicate improvement in mixing, the results do not invalidate previous data obtained at the lower recycle ratio and, therefore, lower gas velocity.

TABLE 66

MATERIAL BALANCES FROM FLUID BENCH-SCALE UNIT WITH CATALYST SGF-B-1

RUN NUMBER 225-	19- 1	20- 1	19- 6	20- 8
RUN DAYS-ON-STREAM	1.8	1.3	8.4	8.3
CUM. DAYS-ON-STREAM	1.8	1.3	8.4	8.3
FRESH FEED H_2/CO RATIO	2.0	2.1	2.0	1.9
GHSV, HR^{-1} (CHG BASIS)	463	493	463	504
RECYCLE RATIO	1.07	4.20	1.07	4.04
REACT. PRESS., PSIG	201	200	200	201
REACT. INLET TEMP., °F	424	416	425	420
NOM. REACT. TEMP., °F	500	500	500	500
CONVERSIONS, MOL °/°				
H_2	97.1	97.5	93.0	91.6
CO	87.6	86.7	79.0	75.8
H_2+CO	93.9	94.0	88.2	86.3
YIELDS, WT °/°				
HYDROGEN	0.4	0.3	0.9	1.0
WATER	46.6	47.7	43.1	42.6
CO	10.9	11.5	18.5	21.3
CO_2	3.8	2.0	2.7	1.3
TOTAL HYDROCARBON	38.3	38.4	34.5	33.8
HC SELECTIVITY, WT °/°				
METHANE	25.5	19.9	28.7	31.6
ETHENE	0.0	0.0	0.1	0.1
ETHANE	3.6	2.6	4.5	4.3
PROPENE	0.2	0.1	0.7	0.2
PROPANE	2.3	1.9	3.4	2.9
BUTENES	1.2	0.9	2.6	1.4
I-BUTANE	2.3	3.3	0.6	1.4
N-BUTANE	2.2	2.0	2.6	2.4
TOTAL C_4-	37.4	30.7	43.1	44.4
C_5+ PARAFFINS	22.1	24.9	14.4	15.6
OLEFINS	26.6	25.7	29.8	23.7
NAPHTHENES	1.7	2.6	0.9	1.2
AROMATICS	0.5	0.6	0.4	0.3
OTHERS	11.8	15.6	11.5	14.7
TOTAL C_5+	62.6	69.3	56.9	55.6
YIELDS, G/SCM CONV CO+H_2				
TOTAL HC	195	189	188	189
C_5+	122	131	107	105
OLEFINS, WT °/° BY C NO.				
C_2	1.2	1.4	1.5	1.3
C_3	6.4	6.0	17.7	7.6
C_4	21.6	14.2	45.4	27.4
C_5	39.8	30.5	62.3	45.5
90 PCT OH, RAW PROD., °F	381	381	402	458
OCTANE NO. ON RAW PROD.				
R+O	81.7	83.2	80.9	83.4
R+3	-	94.0	93.3	-
OXYGENATES, WT °/°	0.4	0.3	0.3	0.2

TABLE 67

GAS COMPOSITION OVER CATALYST SGF-B-1, MOL PCT

RUN NO., 225-	19- 1	20- 1	19- 6	20- 8
HYDROGEN	38.24	24.08	43.43	33.16
CO	28.63	32.73	31.14	35.91
CO2	3.39	2.96	1.66	1.24
NITROGEN	0.00	0.00	0.00	0.00
METHANE	25.30	34.00	20.04	25.27
ETHENE	0.02	0.03	0.02	0.02
ETHANE	1.87	2.24	1.54	1.82
PROPENE	0.02	0.03	0.12	0.08
PROPANE	0.76	1.07	0.73	0.77
I-BUTANE	0.46	1.04	0.07	0.27
1-BUTENE	0.12	0.11	0.12	0.14
N-BUTANE	0.37	0.52	0.32	0.40
TRANS-2-BUTENE	0.04	0.04	0.10	0.06
CIS-2-BUTENE	0.02	0.03	0.06	0.04
UNKNOWN C4-MONOOLEFINS	0.00	0.00	0.00	0.00
C4-DIOLEFINS (DIENES)	0.00	0.00	0.00	0.00
3-METHYL-1-BUTENE	0.00	0.00	0.00	0.00
I-PENTANE	0.26	0.49	0.08	0.18
1-PENTENE	0.00	0.00	0.01	0.00
2-METHYL-1-BUTENE	0.03	0.03	0.04	0.04
N-PENTANE	0.14	0.19	0.12	0.16
TRANS-2-PENTENE	0.02	0.02	0.04	0.03
CIS-2-PENTENE	0.01	0.01	0.02	0.01
2-METHYL-2-BUTENE	0.12	0.12	0.15	0.15
UNKNOWN C5-MONOOLEFINS	0.00	0.00	0.00	0.00
C5-DIOLEFINS (DIENES)	0.00	0.00	0.00	0.00
CYCLOPENTANE	0.00	0.01	0.01	0.00
C6+ HC	0.18	0.25	0.19	0.23
H2/CO	1.34	0.74	1.39	0.92
RECYCLE RATIO	1.1	4.2	1.1	4.0

After about eight days on stream, the catalyst from 225-20 was regenerated starting with 0.5% oxygen in nitrogen at 750°F, then incrementally raising the temperature to 900°F and the oxygen to 21%, and then holding at these conditions for two hours. The catalyst was pretreated in flowing hydrogen at 900°F for five hours before Run 225-21. The regenerated catalyst had recovered some of its selectivity for gasoline; however, its activity, as measured by the H_2+CO conversion, was slightly lower (85%) compared to the last balance of Run 225-20 (86%).

More severe regeneration conditions of this same catalyst loading were tried. The catalyst was regenerated similarly to Run 225-20, except that it was finally calcined in air (in situ) at 950°F for 16 hours followed by a pretreatment in hydrogen at 950°F for 16 hours. When it was put on stream (Run 225-22), the activity was very low and the run was terminated after only two days. These experiments are summarized in Figure 67.

In order to ascertain whether the treatment alone, and not the treatment plus aging caused the reduction in catalyst activity, a fresh portion of catalyst was calcined at 950°F in air for 16 hours, pretreated at 950°F in H_2 for 16 hours, and brought on stream for Run 225-23. Catalyst activity was lower and its aging rate much higher when compared with Run 225-20 (Figure 68). Pretreatment with hydrogen at 700°F for 10 hours (Run 225-24) yields a catalyst with fresh activity about equivalent to one obtained on heating in hydrogen at 900°F for five hours (Figure 68).

Since the bench-scale unit experiments show that high temperatures for long period of time, in air and/or H_2, seem to damage the catalyst, a series of runs was planned that would avoid these conditions during pretreating and regenerating.

Run 225-24 had been made with fresh catalyst calcined in air at 900°F for 5 hours and pretreated in H_2 at 700°F for 10 hours. After about 6 days on stream, the catalyst was carefully regenerated, in situ, with 0.5% oxygen in nitrogen at 750°F until burning was complete (as judged by G.C. analysis of the effluent regeneration gas). The oxygen content was increased stepwise to 21% (air) and then the temperature was raised in 50°F increments to 850°F and held finally at these conditions for 2 hours. Pretreatment (again in situ) for the run following that (225-25) consisted of heating at 700°F in flowing hydrogen for 10 hours. In Figure 69, is shown the effect of the mild regeneration and pretreatment conditions on the H_2+CO conversion. The catalyst was apparently regenerated successfully since (H_2+CO) conversion increased from about 88.5%, at the end of 6 days for Run 225-24, to about 92% after 1 day on stream for Run 225-25 (catalyst after regeneration and pretreatment). In fact, the regenerated catalyst appears to be better than the fresh catalyst for selectivity to C_5^+. Methane selectivity after about 5 days on stream in Run 225-25 was at about the same level as that for Run 225-24 at the same time on

Figure 67

EFFECT OF AGING AND REGENERATION ON THE ACTIVITY OF SGF-B-1 (UNIT 225)

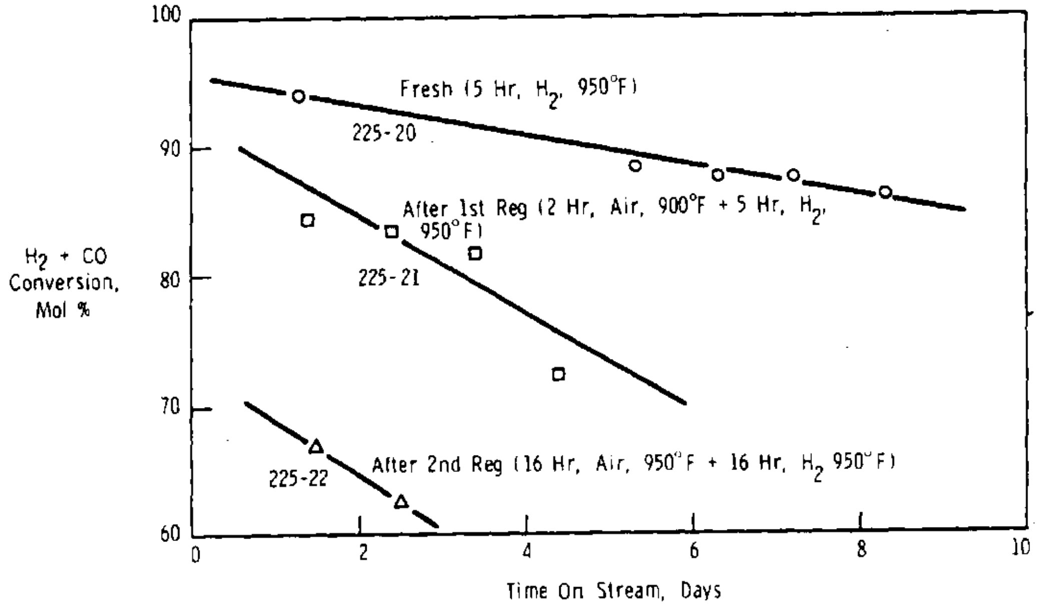


Figure 68

EFFECT OF PRETREATMENT ON H_2+CO CONVERSION BY CATALYST SGF-B-1

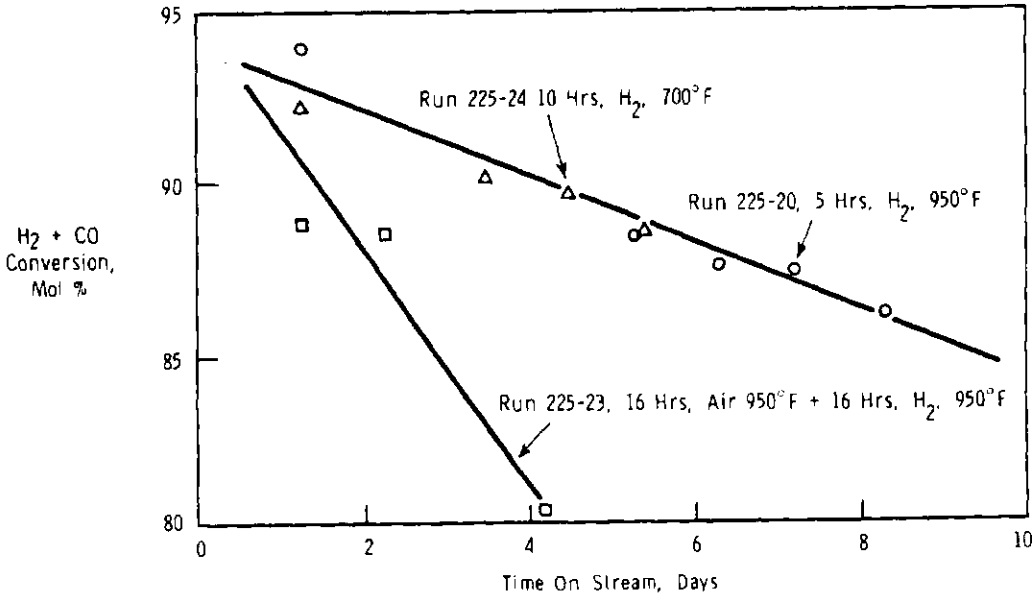
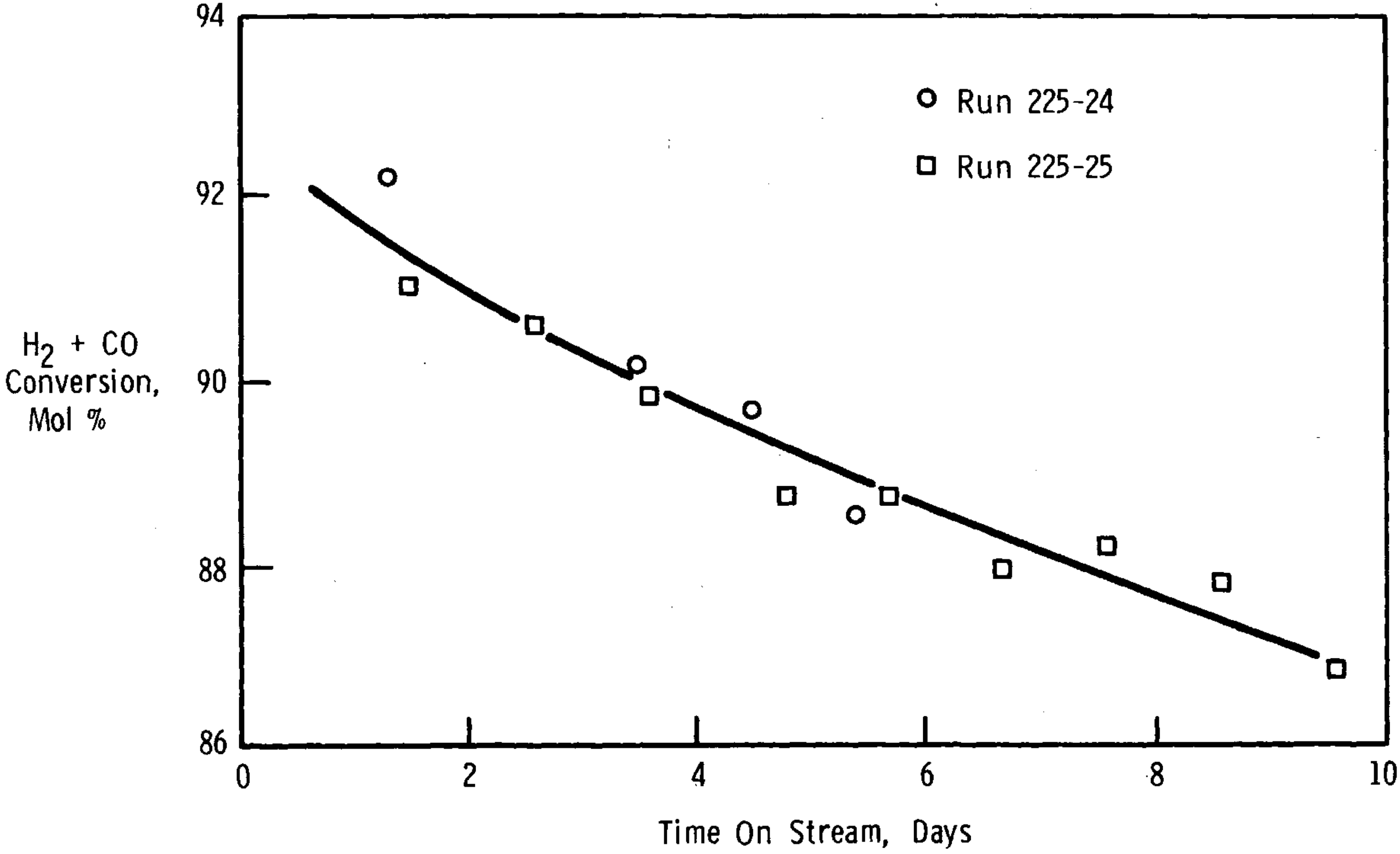


Figure 69

EFFECT ON H_2 + CO CONVERSION OF MILD REGENERATION AND PRETREATMENT ON SGF-B-1 (UNIT 225)



stream, about 24.5% wt. Although this is not inordinately high, it would be desirable to have lower methane make. The C_5 olefin distribution remained essentially at equilibrium throughout both runs. The catalyst was kept on stream for 10 days before being regenerated for run 225-26.

Following the second regeneration, the catalyst was pretreated in hydrogen at 700°F for 10 hours and brought on stream as Run 225-26. The activity, as measured by the H_2+CO conversion was high, however, selectivity to C_5^+ gasoline had not recovered. After the third balance the unit was purged with hydrogen and the catalyst pretreated a second time at 750°F and 0 psig for 10 hours. Dramatic improvement was observed in selectivity. However, the improvement was short-lived and did not bring the catalyst back to the levels of Runs 24 and 25. The catalyst continued aging at a rapid rate. Therefore, Run 26 was terminated, after about seven days on stream, for another regeneration (Table 68).

The catalyst from Run 26 was regenerated in 0.5% oxygen at 750°F and 800°F until evidence of burning diminished, then oxygen was increased in steps to about 1.5%. When burning slowed, the oxygen content was raised incrementally, finally to full air. The temperature was then raised in 50°F-steps to 900°F, held for 1 hour; then raised to 950°F, held for 1 hour; and finally decreased to 750°F under a nitrogen purge. The catalyst was pretreated with hydrogen at 750°F for 10 hours and brought on stream for Run 27. The catalyst did not regenerate.

In the above sequence, the cycle times preceding the first and second regeneration were about 5 and 10 days, respectively. Since the type of coke on the catalyst may vary with time-on-stream, a series of runs with short cycle times was made.

Run 28 was started with fresh SGF-B-1 which was activated in hydrogen at 750°F and 200 psig for 10 hours. The higher pressure for 225-28 was used for several reasons. One was to eliminate the time consuming pressuring and depressuring of the unit as it was switched between operating and regenerating modes. Maintaining the higher pressure also minimized the possibility of lifting the catalyst into the disengaging zone and onto the filters by accidental rapid depressurization as the reactor was switched between modes. Finally, higher gas rates can be used at higher pressure to give the same linear velocity, making it possible to lower the time necessary to complete regeneration.

Conversion and selectivity were good on start-up of Run 28. In fact, perhaps because of the activation at 200 psig, instead of at atmospheric pressure as used previously, initial methane and light hydrocarbons were lower than for Run 24. However, after 2-3 days on stream, they became comparable. During Run 225-28 the GHSV was increased from 500 to 750, and as was found in Run 225-7, the H_2+CO conversion decreased and the C_4^- increased at the higher space rate.

TABLE 68

PRETREATMENT AND REGENERATION OF CATALYST SGF-B-1

			Air Regeneration	
Run 225-	Catalyst Source	H_2 Activation Hrs/°F/psig	Initial - 0.5% O_2 °F/psig	Final - Full Air Hrs/°F/psig
24	Fresh(a)	10/700/0	750/0(b)	2/850/0
25	Run 24	10/700/0	750/0(b)	2/850/0
26	Run 25 25	10/700/0 10/750/0	750/0(c)	1/950/0
27	Run 26	10/750/0	Not Regenerated	
28	Fresh	10/750/200	750/200(d)	~10/800/200
29	Run 28	10/750/200	Not Regenerated	
30	Run 29	10/850/200	750/200(e)	1/950/200
31	Run 30	10/800/200	Not Regenerated	

(a) Calcined in air at 900°F for five hours.

(b) Oxygen gradually increased to full air; the temperature increased in 50°F increments.

(c) Oxygen increased to 1.5%, temperature to 800°F; O_2 increased incrementally to full air; temperature raised to 850°F, then to 900°F; held one hour at each temperature.

(d) Raised temperature to 800°F then increased O_2 incrementally to full air.

(e) 0.5% O_2 at 750, 800, 850 and 900°F, then increased O_2 incrementally to full air.

This same catalyst loading was used in Run 225-28 through -31 with regenerations and/or pretreatments between runs as shown in Table 68. All of these procedures failed to rejuvenate the catalyst.

The data from this series, experiments 225-24 through -31, did not show successful serial regenerations of catalyst SGF-B-1 by oxidative procedures. Therefore, another set of experiments was undertaken to ascertain whether SGF-B-1 could withstand multiple hydrogenative regenerations. The process conditions selected for these experiments were similar to those used previously for SGF-B-1, viz:

Fresh Feed Composition, mol ratio	$2H_2/CO$
GHSV (on fresh feed), hr^{-1}	500
Pressure, psig	200
Nominal Temperature, °F	500
Recycle Ratio	4
Catalyst Volume, cc	150

At the above conditions, the following approximate reactor parameters were calculated:

Active Bed Height, inches	40
Super. Gas Linear Vel., ft/sec	0.15
Catalyst Residence Time, sec	22

The catalyst was initially activated in hydrogen at 700°F and 200 psig for 10 hours.

Regenerations were in flowing hydrogen and were made as follows:

Regeneration After Run No. 225-	Conditions Temp., °F	Pressure, psig	Time, hrs	Treatment Before Regeneration
35, 36, 37 & 38	700	200	24	None
39	700	200	24	H_2, 4 Hr, 0 psig
40	750	200	24	None
41	Not Regenerated			

Total processing for the above series was 40 days. The H_2+CO conversion during this time ranged between 83 and 94%, with an average conversion of 89%. The selectivity to C_5^+ gasoline ranged from about 50 to 75%, with an average of 63% during the 40 days. Alkylation of available olefins and isobutane would add about 3% to the C_5^+ fraction. Data from Runs 35 to 41 are given in Appendix D and summarized in Figures 70 and 71.

Figure 70

ACTIVITY OF SGF-B-1 IN THE FLUID BENCH-SCALE UNIT

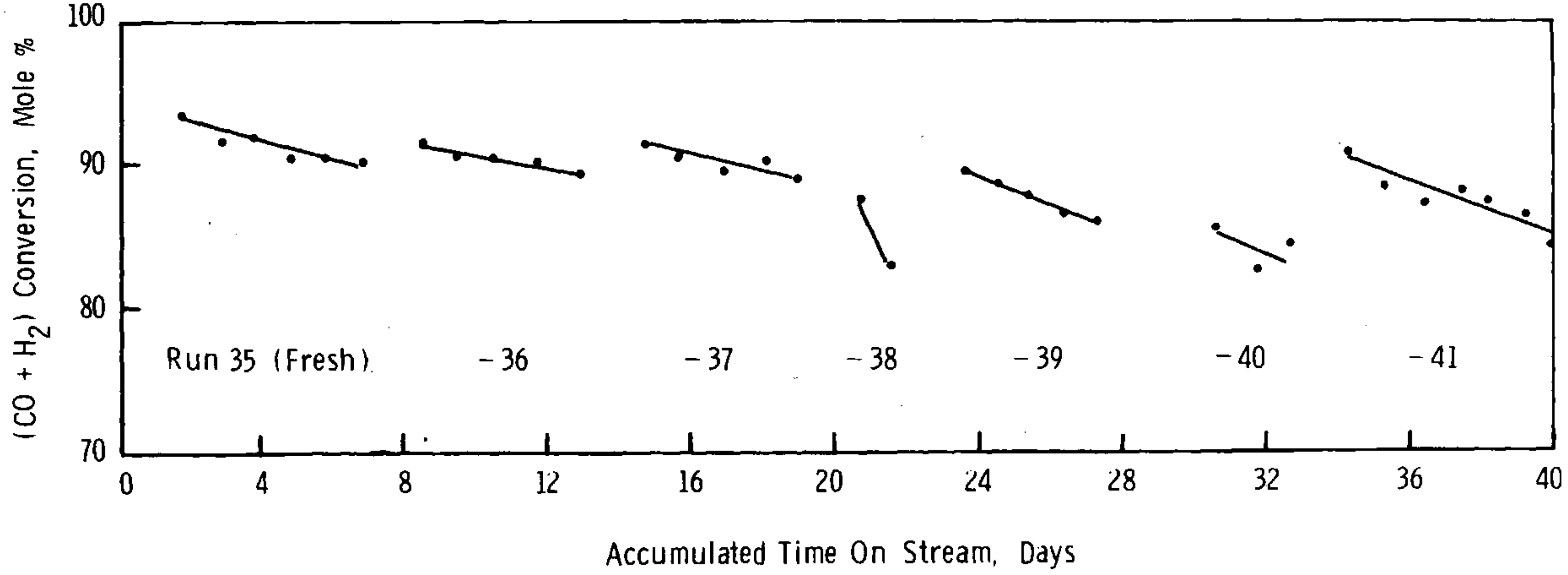
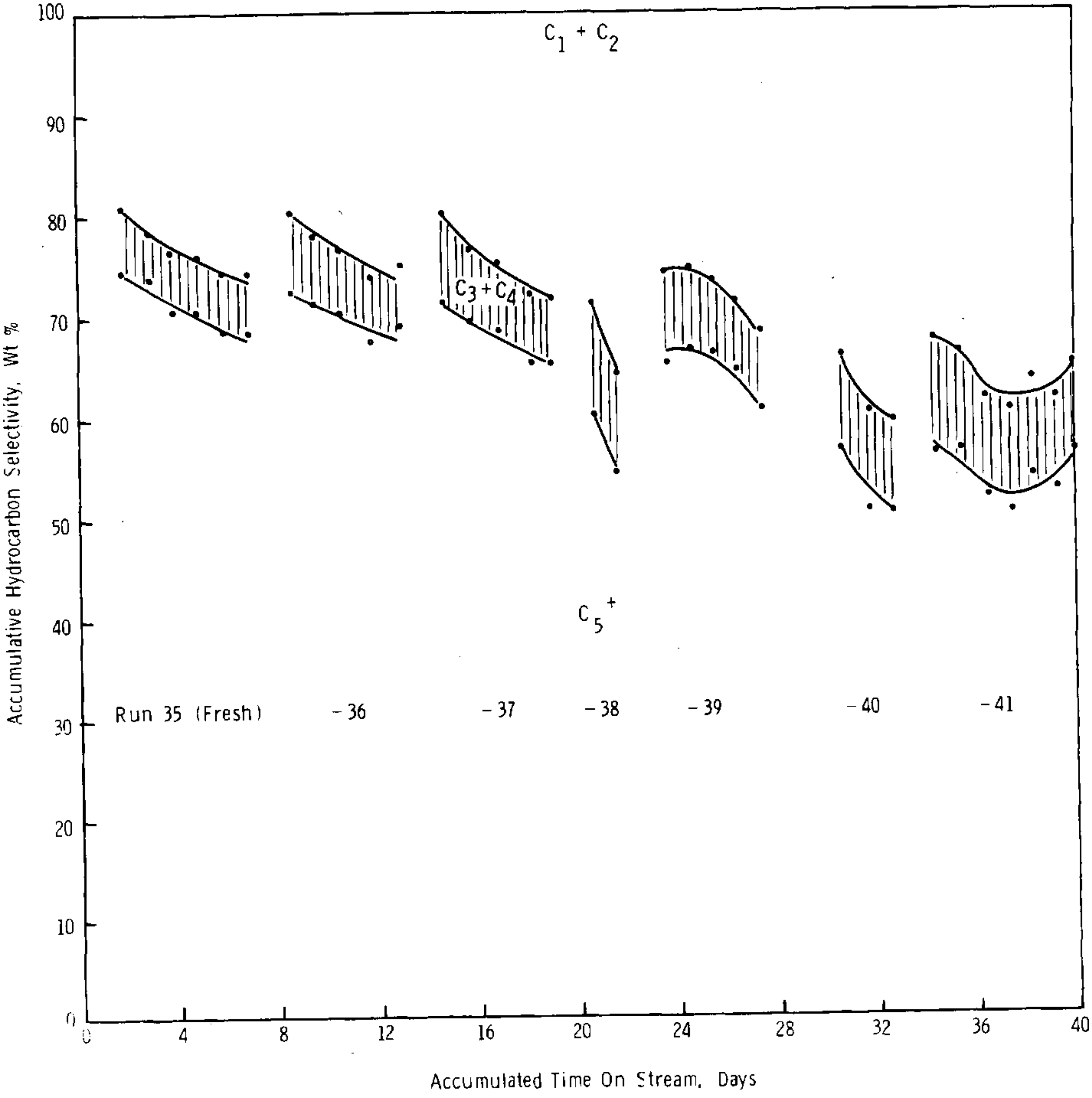


Figure 71

SELECTIVITY OF SGF-B-1 IN THE FLUID BENCH-SCALE UNIT



The 90% overhead boiling point for the raw liquid product shows no general pattern, remaining between 370 and 390°F, except for the last one, Run 41, where it rose to about 410°F. Thus, the boiling range is satisfactory. The octane numbers, likewise, showed no great fluctuations, staying at about 82-83 clear and 94-96 R+3 during the series of runs. Oxygenates remained low, at about 0.2-0.3 wt %.

The results show a recovery of activity after each regeneration. However, the initial activity after each successive regeneration was slightly lower than that of the previous run indicating a slow long-term aging effect. During each evaluation, short-term aging was evident from the reduction of H_2+CO conversion with time. Conversion dropped about 0.5% absolute/day for Runs 35-37, and about 1%/day during Run 39. The catalyst seemed to age much faster during Run 40 (perhaps 3 times as fast), but recovered to the 1% rate in Run 41. For Run 38, which experienced a control malfunction and consequent 150°F over-temperature for 1/2 hour, the aging rate jumped to about 4%/day. (Note that the relative loss is slightly higher than the absolute loss, since the conversion is around 84 to 95%.) The over-temperature did not appear to have a permanent effect on the catalyst.

The four-hour H_2 purge before regeneration of the catalyst from Run 39, was done to determine whether heavy hydrocarbons, which may have deposited on the catalyst during operation, could be removed before regeneration to give a more active catalyst. This purge did not have the desired effect. In fact, the decline in activity during Run 40 appears to be greater than in Run 39. After Run 40, the catalyst was regenerated at 750°F instead of 700°F to test the efficacy of regeneration at a somewhat higher temperature. Start of cycle activity recovered and was comparable to that of Runs 36 and 37. Start of cycle selectivity to C_5^+ gasoline only recovered to that of Run 40.

The compositions of the combined fresh feed and recycle gases are given in Appendix D. Also shown are the H_2/CO in that mixture and recycle ratios for the runs. With the $2H_2$/CO ratio in the fresh feed and a recycle of 4/1, the H_2/CO ratio over the catalyst is initially about 0.7, which increases as the catalyst ages. At the end of the series of runs, the H_2/CO ratio was about 1.2.

In summary, catalyst SGF-B-1 has little or no water-gas shift activity and requires, for high carbon monoxide conversion, a synthesis gas having a H_2/CO ratio of at least two. Based on both the fixed bed micro reactor and the fluid bed bench-scale unit studies, the catalyst is activated in flowing hydrogen. For the bench-scale unit, the best activation procedure consists in heating at 700°F and 200 psig for 10 hours (Table 69). Preferred processing conditions are 500°F, 200 psig and 500 GHSV and for the fluid, bench-scale unit, a superficial gas velocity of about 0.15 ft/sec, attained via light gas recycle. Lower temperatures give low activity, while higher temperatures result in low C_5^+ gasoline

TABLE 69

EFFECT OF PRETREAT CONDITIONS ON FRESH ACTIVITY AND SELECTIVITY OF CATALYST SGF-B-1(a)

Run 225-	Hydrogen Pretreat Hrs/°F/psig	Days On Stream	Conv., mol % (H_2+CO)	Selectivity, wt % C_1+C_2	C_5^+
17	10/700/0	1.5	92.3	27.9	64.1
20	5/950/0	1.3	94.0	22.5	69.3
24	10/700/0(b)	1.3	92.2	32.2	58.3
28	10/750/200	1.7	92.6	23.4	68.3
35	10/700/200	1.9	93.6	19.0	74.6

(a) Processing H_2/CO at 500 GHSV, 500°F and 200 psig.

(b) Following an air calcination at 900°F for five hours.

selectivity. Fresh feed space velocities greater than 500 GHSV also result in lower C_5^+ gasoline selectivity. This last could probably be compensated for by use of a higher processing pressure.

In one series of experiments, with intermittent regenerations, catalyst SGF-B-1 was used to process $2H_2/CO$ for 40 days. The H_2+CO conversion ranged from 83 to 94%, with an average conversion of 89%. The selectivity to C_5^+ gasoline ranged from about 50 to 75% with an average selectivity of 63%. The raw liquid product was low in oxygenates, had a 90% overhead boiling point <400°F and had a R+0 of about 83.

Catalyst SGF-B-1 is amenable to a limited number of oxidative or hydrogenative regenerations. However, conditions at which the catalyst is stable to multiple regenerations, have not been found. Catalyst life is limited to about two months.

3. Task 4 - Theoretical Studies in Support of Process Development - Fluid Bed

a. Heat and Mass Transfer During Synthesis Gas Conversion in the Fluid Bench-Scale Unit

A heat and mass transfer study was made using data obtained with catalyst SGF-B-1 in the fluid bench-scale unit. The analysis is similar to the fixed bed study reported in Section E. Due to the large specific surface area (particle surface area per volume of catalyst) of fluid catalysts, the heat and mass fluxes across the surface of catalyst SGF-B-1 were an order of magnitude lower than that of the fixed bed catalyst, SG-B-2, under similar process conditions. This results in even smaller temperature and concentration differences across the gas-solid interphase for the fluid bed operations.

The process conditions for the fluid bed Run 225-17 using SGF-B-1 are summarized in Table 70, comparing with those for a fixed bed run (225-15) operated in a similar temperature range using SG-B-2. One notable difference is the lower recycle ratio used in the fluid bed operation. This is in consequence of the designed heat loss of the fluid bed reactor in contrast to the adiabaticity of the fixed bed reactor. The resulting differences in conversion, selectivity, and heat and mass fluxes of these same runs are shown in Table 71 by comparing two material balances, 225-15-5 and 225-17-2. The higher conversion achieved in the fluid bed is probably because the bed was uniformly maintained within 10-15°F of the maximum temperature after a rapid temperature rise in the first couple of inches of the reactor (total bed height is 20 inches or more); while in the fixed bed experiment the temperature increased from inlet to outlet condition gradually. The selectivity difference is reflected by the lower amount of C_4^- product formed in the fluid bed.

The fluid catalyst SGF-B-1 has an average particle diameter of 0.006 cm and a specific surface area of approximately 1250 cm^2 per cc of catalyst. In contrast, SG-B-2 catalyst has an effective particle diameter of 0.115 cm and an estimated

TABLE 70

COMPARISON OF CONDITIONS USED IN FIXED AND FLUID BENCH-SCALE OPERATION

	Reactor Type	
	Fixed Bed	Fluid Bed
Run 225-	15	17
Catalyst	SG-B-2	SGF-B-1
H_2/CO in Fresh Feed	2.0-2.2	1.9-3.0
Temperature, °F, Inlet	425	400-440
Maximum	530	500
Pressure, psig	300	200
GHSV	330	490-725
Recycle Ratio	13	1.8-3.9
Catalyst Particle Diameter, cm	0.115	0.006

TABLE 71

COMPARISON OF CONVERSION, SELECTIVITY AND GAS-SOLID INTERPHASE MASS AND HEAT FLUXES DURING FIXED AND FLUID BENCH-SCALE OPERATION

	Reactor Type	
	Fixed Bed	Fluid Bed
Run 225-	15-5	17-2
Catalyst	SG-B-2	SGF-B-1
% Conversion H_2	79	96
CO	68	87
HC Selectivity, % wt		
C_1	31	27
C_2	3	4
C_3	7	2
C_4	13	5
C_5+	47	62
Specific Surface Area, cm^2/cc catalyst	50	1250
Mass Flux of CO(a), mole/sec-cm^2	8.1×10^{-8}	2.3×10^{-9}
Heat Flux(b), cal/sec-cm^2	3.0×10^{-3}	8.6×10^{-5}
Modified Reynolds Number	9.2	0.3

(a) Mole CO diffused into catalyst from the gas stream per sec per cm^2 of catalyst surface.

(b) Assuming 37,500 cal of heat released per mole of CO converted.

specific surface area of about 50 cm^2 per cc of catalyst. Because of this difference in specific surface area, the catalyst-gas interphase heat and mass fluxes for SGF-B-1 catalyst are much lower than those for SG-B-2 catalyst.

Run 225-17 was conducted in a fluid bed of 3/4" ID. The packed volume of the catalyst was 99.7 cc; and there was about 50% volume expansion upon fluidization. The modified Reynolds number based on the average particle diameter was estimated to be about 0.3. Reliable experimental measurements of heat and mass transfer coefficients at such a low Reynolds number are currently unavailable. Extrapolation of some experimental correlations down to this region gives Nu (or Sh) numbers ranging from 0.001 to 0.1 (46). These experiments only measured the overall heat or mass transfer rate in the fluid bed, neglecting such phenomenon as gas bypassing through bubbles. As a consequence, the resulting heat and mass transfer coefficients are too small for the description of local heat and mass transfer between a catalyst particle and its neighboring gas stream. Accordingly, analyses based on these numbers should result in a gross overestimate of the temperature or concentration difference across the solid-gas interphase.

As in the previous studies for fixed bed catalysts, uniform interphase heat and mass fluxes for all catalyst particles were assumed. By doing so, the interphase mass flux could be calculated from the conversion and space velocity. To roughly estimate the heat flux, the heat of reaction, ΔH, was assumed to be about 37,500 cal per mole of CO converted to hydrocarbons. This is a good approximation since there was very little CO converted to CO_2 over this catalyst. In the worst situation, i.e., where methane is the sole product, the ΔH will be 52,000 cal and the interphase temperature difference, ΔT, will be 40% higher. Based on the above assumptions and the Nu number of 0.01, the calculated ΔT's together with the estimated gas and transport properties are listed in Table 72. ΔT's are found to be very small (0.5°F or lower). In each case, ΔT's corresponding to both inlet and outlet conditions are estimated and they are about the same. Since the above estimations were based on roughly the average Nu number from reported experiments, the actual ΔT's should be even smaller as explained above.

Similar analysis for mass transfer based on Sh = 0.01 leads to the conclusion that the concentration differences across the solid-gas interphase are again insignificant as shown in Table 73 in which ΔX_i's represent the mole fraction differences of component i across the interphase, which are very small in comparison with the mole fractions X_i's.

It should be noted that in both the heat and mass transfer cases, the small ΔT's and ΔX_i's are in direct consequence of the low CO (or H_2) flux across the catalyst surface, which is, in turn due to the large specific surface area of SGF-B-1 catalyst.

TABLE 72

GAS PROPERTIES AND INTERPHASE HEAT TRANSFER FOR RUN 225-17 (SGF-B-1, 200 PSIG)

	Balance 225-17			
	2		5	
Charge H_2/CO	2/1		1.91/1	
GHSV (hr^{-1})	500		724	
Recycle Ratio	1.9		2.4	
% CO Conversion	87.0		58.7	
% H_2 Conversion	96.2		68.2	
N_{CO}, mole/sec-cm^2	2.267×10^{-9}		2.304×10^{-9}	
	Inlet	Outlet	Inlet	Outlet
Temperature, °F	400	502	425	504
$\rho \times 10^3$, gm/cc	6.08	6.67	4.08	4.17
$\mu \times 10^4$, gm/sec-cm	2.01	2.04	2.11	2.15
$\lambda \times 10^4$, cal/cm-sec-°C	2.17	1.74	3.29	3.10
Pr	0.51	0.63	0.44	0.47
Re	0.29	0.29	0.32	0.32
$k \times 10^3$, cal/sec-°C-cm^2 (Nu=0.01)	0.36	0.29	0.55	0.52
$\Delta T = 1.8 \times (N_{CO}/h)\Delta H$, °F	0.4	0.5	0.3	0.3

TABLE 73

INTERPHASE MASS TRANSFER FOR RUN 225-17 (SGF-B-1, 200 PSIG)

	Balance 225-17			
	2		5	
Component CO				
N_i, mole/sec-cm^2	2.267×10^{-9}		2.304×10^{-9}	
	Inlet	Outlet	Inlet	Outlet
Dim, cm^2/sec	0.0202	0.0246	0.0330	0.0385
kc, cm/sec (Sh=0.01)	0.0337	0.0410	0.0550	0.0640
Xi	0.3051	0.2518	0.2806	0.2460
$\Delta Xi \times 10^4$	0.86	0.94	0.56	0.59
Component H_2				
N_i, mole/sec-cm^2	5.040×10^{-9}		5.093×10^{-9}	
	Inlet	Outlet	Inlet	Outlet
Dim, cm^2/sec	0.1068	0.1294	0.1161	0.1351
kc, cm/sec (Sh=0.01)	0.1780	0.2157	0.1935	0.2252
Xi	0.3764	0.1907	0.6229	0.5460
$\Delta Xi \times 10^4$	0.54	0.60	0.35	0.37

b. Heat Loss from Fluid Bench-Scale Unit

The fluid bench-scale unit was designed with a large heat loss to the ambient to remove part of the reaction heat. Due to the heat loss, the light gas recycle ratio can be reduced to a commercially manageable level of 2 to 4, in contrast to the large recycle ratio in the adiabatic fixed bed reactor. In an actual commercial operation, the excellent heat transfer characteristics of a fluidized bed facilitates the temperature control and heat removal through the following schemes:

- Cooling coils in the fluid bed;
- Cool feed and recycle gas;
- External catalyst cooling.

Five fluid bed runs using SGF-B-1 and SGF-A-2 catalysts were analyzed to check the reactor heat loss. The results summarized in Table 74 show the heat loss ranging from 73 to 88% of the reaction heat. Table 74 also includes the overall radial heat transfer coefficient between the catalytic bed and the ambient (at 77°F). This coefficient includes the effect from the heating coil and insulation outside of the reactor, which are used to prevent the reactor from losing too much heat.

c. Water-Gas Shift Reaction of Catalyst SGF-B-1

The following conclusions were drawn from the study of the water-gas reaction over SGF-B-1 catalyst:

- Water is the primary product of the synthesis gas conversion and the small amount of CO_2 is produced through the secondary water gas shift reaction.
- SGF-B-1, similar to SG-B-2 (Section E), exhibits little shift reaction activity. At the same temperature range, it shows a lower K/K_E for the reactor effluent than that of SG-B-2. This is probably mainly due to the lower recycle ratio used in the fluid bed runs. Again, this observed small shift activity may be completely due to the catalytic action of the metal surface of the reactor.
- Shift activity increases with reaction temperature.

Run 225-19 was chosen to study the temperature effect on water-gas shift activity because all other runs were operated at about the same temperature (500°F). The process conditions used in Run 225-19 were:

TABLE 74

HEAT LOSS IN FLUID BED BENCH-SCALE UNIT

	Catalyst				
	SGF-B-1			SGF-A-2	
Run CT 225-	17-2	25-2	26-2	32-1	33-4
Fresh Feed, H_2/CO	2.00/1	2.02/1	2.03/1	1.03/1	1.04/1
GHSV, hr^{-1}	500	497	504	1021	1022
Recycle Ratio	1.9	3.9	4.0	2.0	3.0
H_2+CO Conversion, mole %	93.11	90.61	88.56	66.01	68.23
Reactor Temperature, °F					
Inlet	400	418	426	491	447
Outlet	502	498	501	565	577
Adiabatic Temperature, °F	1130	843	821	1068	910
Heat of Reaction, Kcal/mole Feed(a)	11.40	11.04	11.10	8.51	9.46
Heat Loss, Kcal/mole Feed	10.00	9.10	9.14	7.47	6.93
Overall Heat Transfer Coefficient to Ambient(b) BTU/ft^2-hr-°F	0.6	0.8	0.8	1.1	1.1

(a) Based on inlet temperature

(b) In the radial direction, from the catalyst bed to an ambient temperature of 77°F.

- H_2/CO - 2 in fresh feed
- Recycle Ratio - 1.1
- Pressure - 200 psig
- GHSV - 463

and the reactor temperature ranged from 470°F to 530°F.

The extent of reaction expressed as K/K_E were calculated and are listed in Table 75. That all the K/K_E's are smaller than one means that the direction of the water-gas shift reaction is from H_2O to CO_2. The temperature effect is shown in Figure 72, where K/K_E's are plotted against the reactor outlet temperatures. Figure 72 clearly indicates that shift activity increases with reactor temperature.

As compared to SG-B-2 (Run 225-14), which showed little shift activity ($K/K_E \sim 0.01$), SGF-B-1 results in an even lower K/K_E (~ 0.003) in the reactor effluent at the same temperature of about 525°F. This is probably due to the lower recycle ratios used in the fluid bed operation -- Run 19 used a recycle ratio of one while Run 15 used recycle ratios of around 13. As discussed before, the observed small shift activity of these catalysts may also be attributed to the catalytic effect of the metal surface in the reactor.

d. Product Selectivity of Catalyst SGF-B-1

The product selectivity in hydrocarbon synthesis depends on a variety of factors including catalyst, feed composition, temperature, pressure, and residence time. One of the important variables characterizing the hydrocarbon distribution is the H/C atomic ratio. This ratio together with the extent of water gas shift reaction determines the relative conversion of H_2 and CO in the synthesis gas. Data from the fluid bench scale unit using catalyst SGF-B-1 were analyzed to correlate the H/C ratio in hydrocarbon product with various process variables.

The major conclusions drawn on product selectivity with SGF-B-1 in Unit 225 are:

- At 500°F the H/C atomic ratio in the hydrocarbon product increases with the hydrogen partial pressure in the combined feed. This increase is mainly due to the higher yields of C_1 and C_2.
- The selectivity toward methane production increases with reactor temperature.
- Temperature change in the range from 475 to 525°F does not seem to affect the H/C atomic ratio in C_3^+ hydrocarbons.

Only three runs, 225-17, -19, and -20, involving catalyst SGF-B-1 were used in this selectivity study because all the remaining runs were aimed at studying aging and regeneration and,

TABLE 75

WATER GAS SHIFT REACTION OVER SGF-B-1

	Reactor Effluent			
Balance No.	Temperature, °F	K	K_E	K/K_E
19-1	503	0.138	69.9	0.00198
19-2	501	0.137	71.2	0.00192
19-3	475	0.073	91.3	0.00080
19-4	475	0.078	91.3	0.00085
19-5	475	0.083	91.3	0.00091
19-6	502	0.117	70.6	0.00166
19-7	505	0.119	68.7	0.00174
19-8	526	0.160	56.9	0.00281
19-9	525	0.163	57.4	0.00283
19-10	526	0.154	56.9	0.00271
19-11	526	0.159	56.9	0.00279
19-12	526	0.116	56.9	0.00203
19-13	521	0.140	59.4	0.00235
19-14	527	0.157	56.4	0.00279

FIGURE 72

EXTENT OF WATER-GAS SHIFT REACTION OVER SGF-B-1 (Run 225-19)

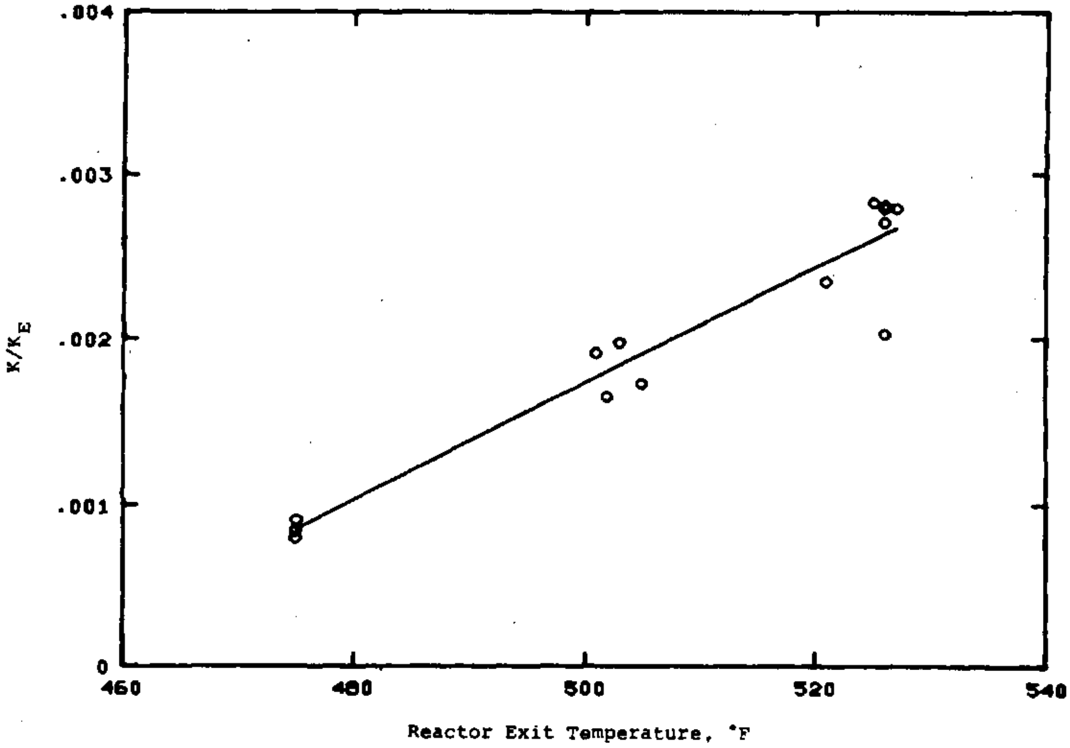
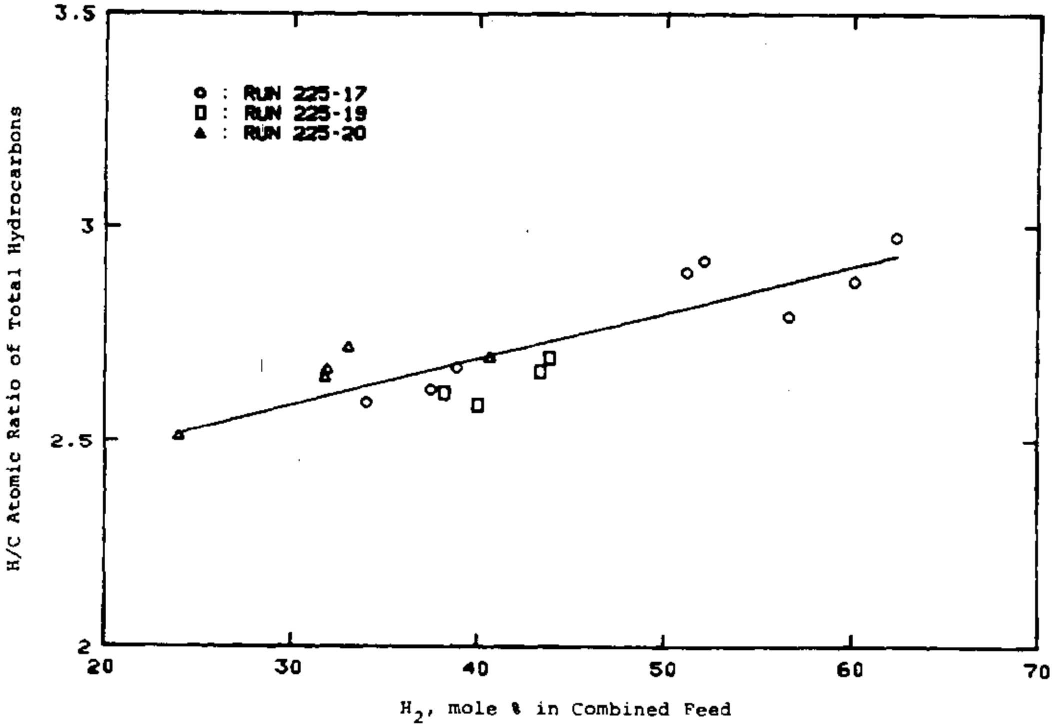


FIGURE 73

H/C ATOMIC RATIO OF TOTAL HYDROCARBONS VS. H_2 CONCENTRATION (CATALYST SGF-B-1)



hence, were operated at the same process conditions as Run 20. Table 76 summarizes the results obtained on analyzing these three runs. Note that Runs 17, 20, and part of the balances of Run 19 were operated around 500°F reactor temperature. The remaining balances of Run 19 were operated at two temperatures, i.e., 475°F and 525°F.

To show the effect of feed composition on product selectivity, the H/C atomic ratios for the hydrocarbons produced for those balances made around 500°F are plotted in Figure 73 against the mole % H_2 in the combined feed. Corresponding to a change of H_2 concentration from about 20% to 60%, the H/C increases considerably from 2.5 to 2.9. Accompanying this change is the shift of methane selectivity from 20 to 40 weight % of the total hydrocarbon yield, as shown in Figure 74. Excluding C_1 and C_2, the H/C's in the C_3+ hydrocarbons are plotted in Figure 75, which shows only a slight increase from 2.14 to 2.16. This indicates that the increase of H/C atomic ratio of the hydrocarbons produced with hydrogen partial pressure is mainly due to the higher production of light gas, particularly methane.

The temperature effect on product selectivity is demonstrated in Figure 76, in which the methane selectivity is plotted with the H_2 concentration in the combined feed at three temperatures, 475, 500, 525°F. The straight line representing 500°F is reproduced from Figure 74. From this figure one can immediately conclude that raising temperature promotes methane formation. Figure 77 shows the H/C ratios in the C_3^+ hydrocarbons of the same data versus the H_2 concentration. Again the straight line representing 500°F is reproduced from Figure 75. The points corresponding to 475°F and 525°F fall right along the 500°F line. It can be concluded that the temperature has little effect on the H/C ratio of the C_3^+ hydrocarbons.

TABLE 76

PRODUCT SELECTIVITY OF SGF-B-1

Balance No.	Reactor Temperature, °F	Mole % H_2 in Combined Feed	H/C Ratio	CH_4 Yield (wt %)	H/C for C_3^+
225-17-1	501	34.1	2.59	24.4	2.15
2	502	37.5	2.62	26.6	2.14
3	501	38.9	2.67	29.5	2.13
4	505	56.6	2.79	35.6	2.14
5	504	62.3	2.97	44.4	2.16
6	503	60.1	2.87	39.1	2.16
7	505	51.1	2.89	39.9	2.17
8	504	52.0	2.92	41.4	2.17
225-19-1	503	38.2	2.61	25.5	2.15
2	501	40.0	2.59	24.5	2.14
3	475	50.3	2.64	26.8	2.16
4	475	50.1	2.63	26.4	2.15
5	475	50.3	2.65	27.7	2.15
6	502	43.3	2.66	28.7	2.13
7	502	43.8	2.69	30.5	2.13
8	526	38.6	2.87	39.8	2.14
9	525	39.2	2.89	40.7	2.14
10	526	41.0	2.91	41.9	2.14
11	526	42.2	2.92	42.6	2.14
12	526	43.1	2.91	42.3	2.13
13	521	43.3	2.97	45.4	2.13
14	527	42.6	3.06	49.5	2.15
225-20-1	500	24.0	2.51	19.9	2.16
5	500	31.8	2.65	28.3	2.14
6	498	32.0	2.67	29.2	2.14
7	498	40.6	2.70	30.4	2.15
8	497	33.1	2.72	31.6	2.15

FIGURE 74

METHANE SELECTIVITY VS. H_2 CONCENTRATION
(CATALYST SGF-B-1)

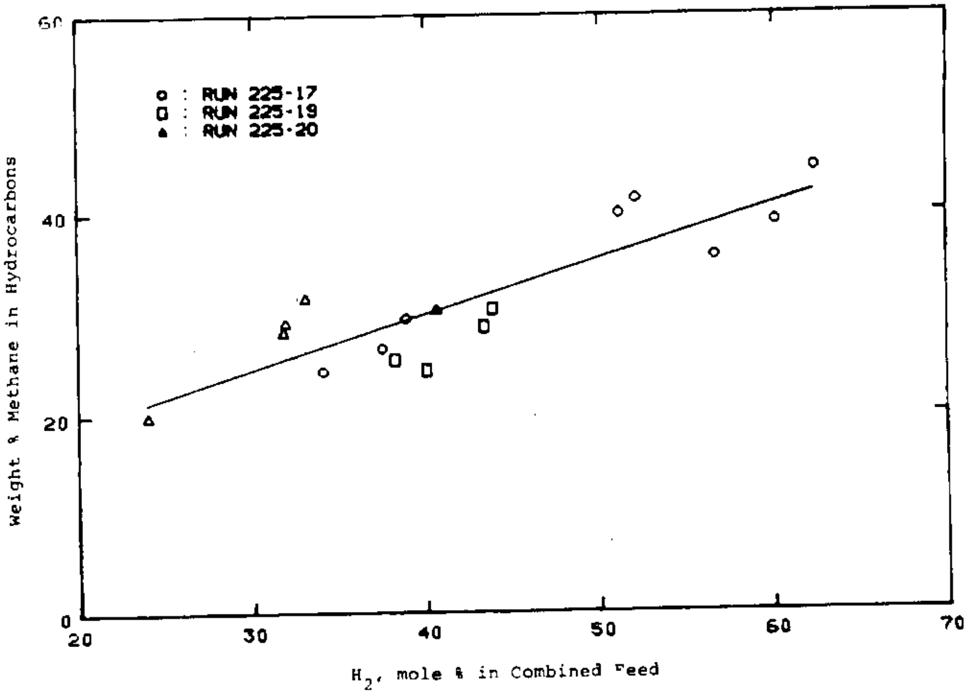


FIGURE 75

H/C ATOMIC RATIO OF C_3^+ HYDROCARBONS VS. H_2 CONCENTRATION
(CATALYST SGF-B-1)

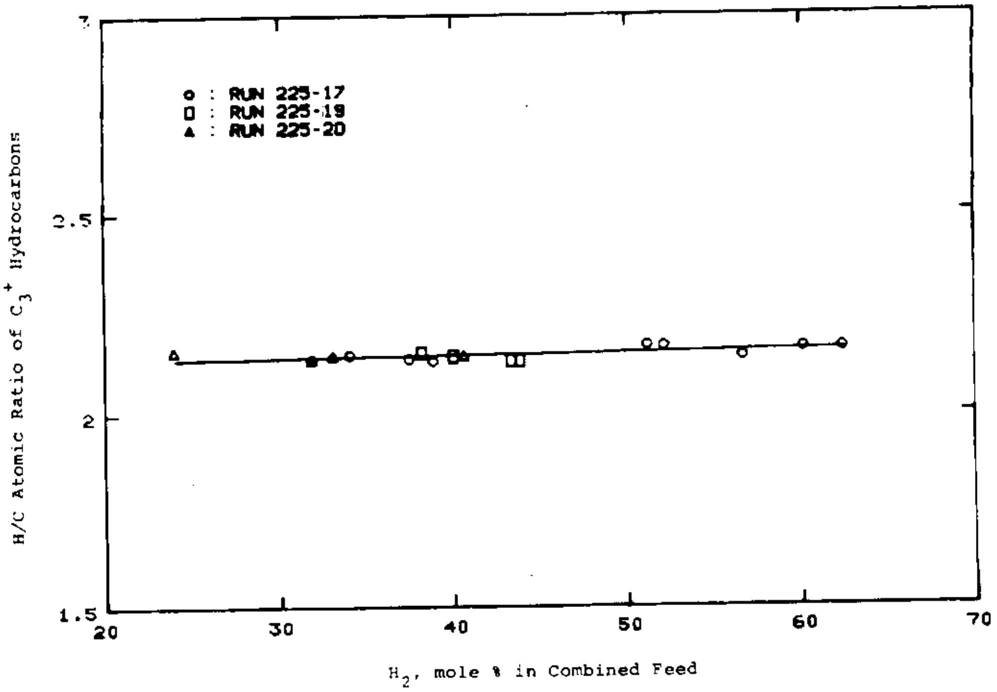


FIGURE 76

EFFECT OF TEMPERATURE ON METHANE SELECTIVITY
(CATALYST SGF-B-1)

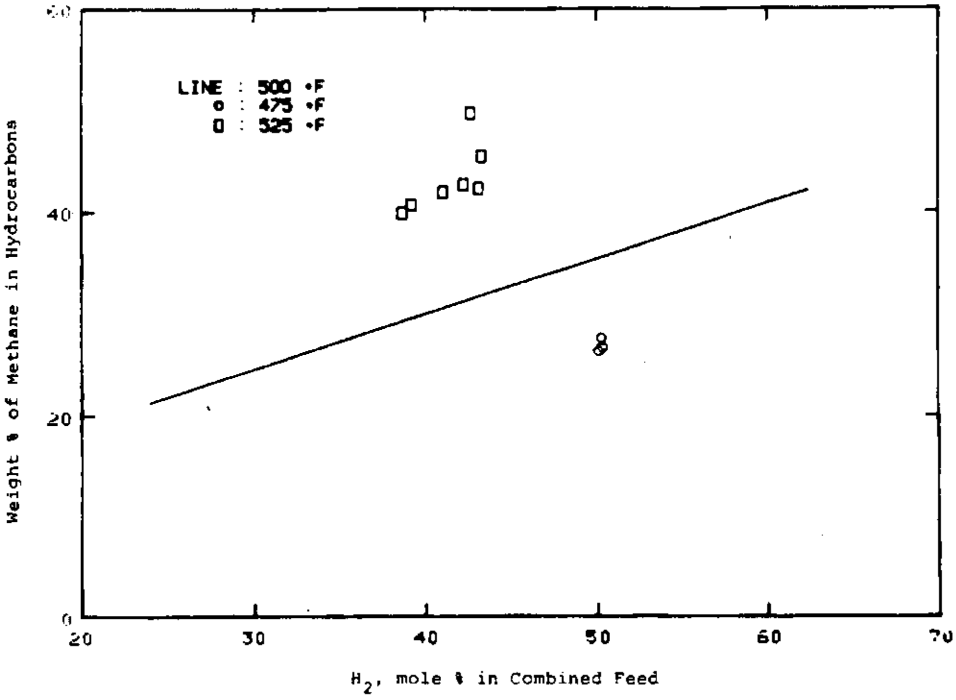


FIGURE 77

EFFECT OF TEMPERATURE ON H/C ATOMIC RATIO OF C_3^+ HYDROCARBONS
(CATALYST SGF-B-1)