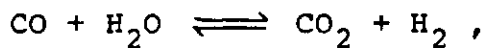


shows all runs using SG-B-2 catalyst were operated at or very near the adiabatic condition. The result from Run 225-14-7 shows that there was a substantial heat input to the reaction stream (36% of the reaction heat). This heat might well be from the heating coils surrounding the reactor (see Figure 5).

The recycle ratio used in the fixed bed adiabatic reactor is too high to be commercially practical. The recycle ratio, however, can be reduced if the temperature operation range of the catalyst is increased. For example, if a catalyst with a 100°F temperature operation range requires a recycle ratio of 14 to control the reactor temperature, a catalyst with a 300°F temperature operation range would require only a recycle ratio of about 4. Unfortunately, the temperature operation range of the current catalysts can not be extended very much beyond 100°F.

3. Water-Gas Shift Reaction

During the synthesis gas conversion, the rejection of oxygen in carbon monoxide as water or carbon dioxide dominates the overall stoichiometry of the synthesis reactions. The extent of water-gas shift reaction,



reflects the mode of oxygen rejection and, hence, affects the feed requirement. It also influences the recycle gas composition, reaction kinetics, product selectivity, and, consequently, the process economics.

The water-gas shift activity of fixed bed catalysts SG-A-1 and SG-B-2 was studied based on both micro reactor data and bench scale unit data. Since the shift reaction is equilibrium-controlled, we choose to express the reaction extent, in the following analyses, by the ratio, K/K_E , where:

$$K \equiv \frac{(\text{H}_2)(\text{CO}_2)}{(\text{H}_2\text{O})(\text{CO})}$$

and $K_E = K$ at equilibrium.

Shift Activity of SG-A-1

The conclusions drawn from these analyses are:

- SG-A-1 has considerable shift activity.
- Water is a primary product from synthesis gas conversion.
- The shift reaction approaches equilibrium with increasing temperature.

The ratios, K/K_E , derived from the micro reactor data show substantial scattering because,

- The shift equilibrium is strongly affected by temperature (Figure 31).
- The temperature varies along the catalyst bed.
- The actual temperature profile inside a catalyst particle is unknown and may be much higher than the measured bulk gas temperature.

The results obtained from micro reactor experiments using $2H_2/CO$ as feed are summarized in Table 32. Since there is temperature variation along the reactor, K/K_E values based on both the minimum and maximum observed temperatures are included. Among the 14 experiments, balances 51-4, 52-1, 53-1 and 53-3 have carbon monoxide conversions $>97\%$ and these results are questionable. At very high conversion levels, a small absolute deviation in the measured carbon monoxide concentration at the reactor exit, translates into a large deviation in the K value. Balance 51-3 is also questionable because of the small amount of water produced. Excluding the questionable balances, the K values of the remaining experiments are plotted against the (H_2+CO) conversion in Figure 32. The data show that, at low conversion, the ratio K/K_E is very small, which strongly suggests that water formed then reacts with carbon monoxide in the shift reaction to form carbon dioxide. Figure 32 also shows an increase of K/K_E with increasing (H_2+CO) conversion. The dashed line suggests a probable relationship between K/K_E and conversion. Note that K/K_E must be <1 in the present case, if the direction of the shift reaction is from water to carbon dioxide.

The results obtained with the $3H_2/CO/2CO_2$ feed are summarized in Table 33. Again, K_E values based on both the minimum and maximum reactor temperature, are used. The K/K_E ratios for all experiments, except that of balance 87-3, are plotted against the (H_2+CO) conversion in Figure 33. Balance 87-3 is excluded because of the low H_2O yield. Also in this figure, the dashed line shows the probable relationship between K/K_E and conversion. Since the feed contains CO_2 but not H_2O , the K/K_E at zero conversion must approach infinity, assuming the direction of the shift reaction is from H_2O to CO_2 . The ratio declines sharply due to the water produced in the carbon monoxide reduction. The K/K_E eventually is lowered to <1 which indicates that, at that time, the rate of water formation is faster than the rate at which water disappears in the shift reaction. As the (H_2+CO) conversion continues to increase, the relative rates of water formation and disappearance will be reversed and the shift reaction will eventually approach equilibrium, i.e. $K/K_E \rightarrow 1.0$, as the (H_2+CO) conversion approaches completion.

Figure 31

WATER GAS EQUILIBRIUM CONSTANT AT VARIOUS TEMPERATURES

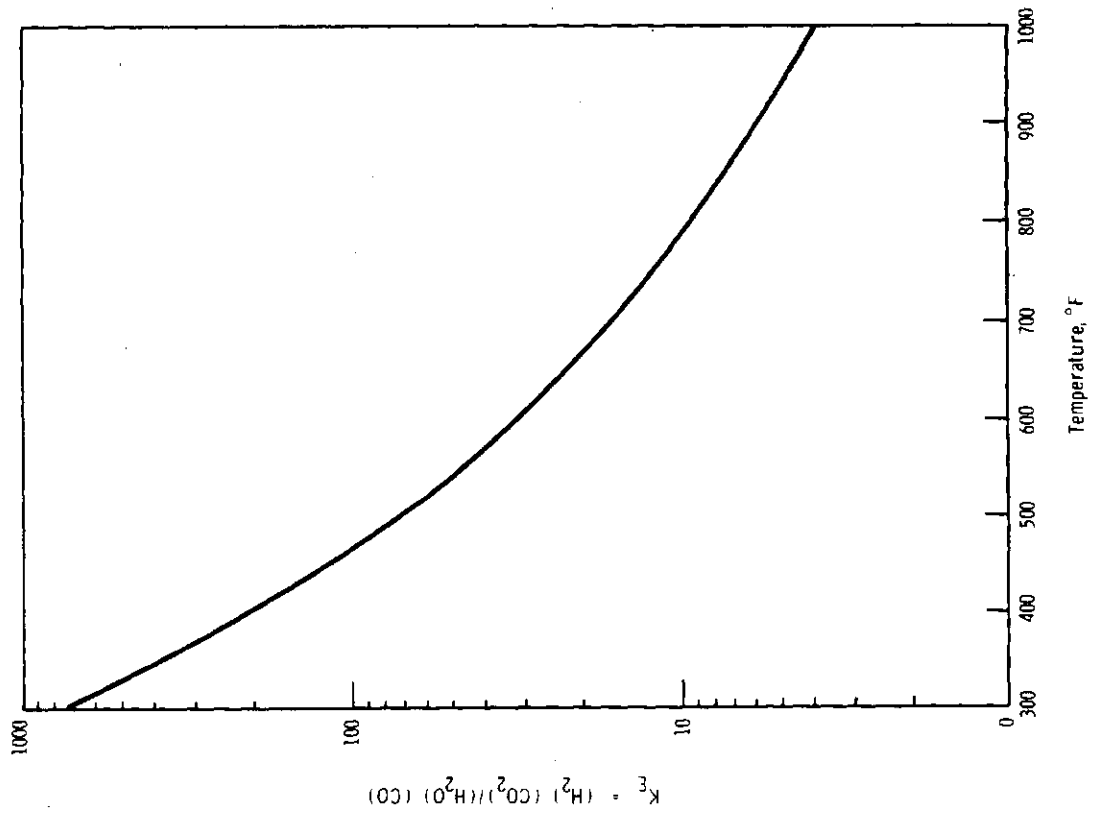


Figure 32

K/K_E VS H_2+CO CONVERSION WITH $H_2/CO = 2/1$ FEED

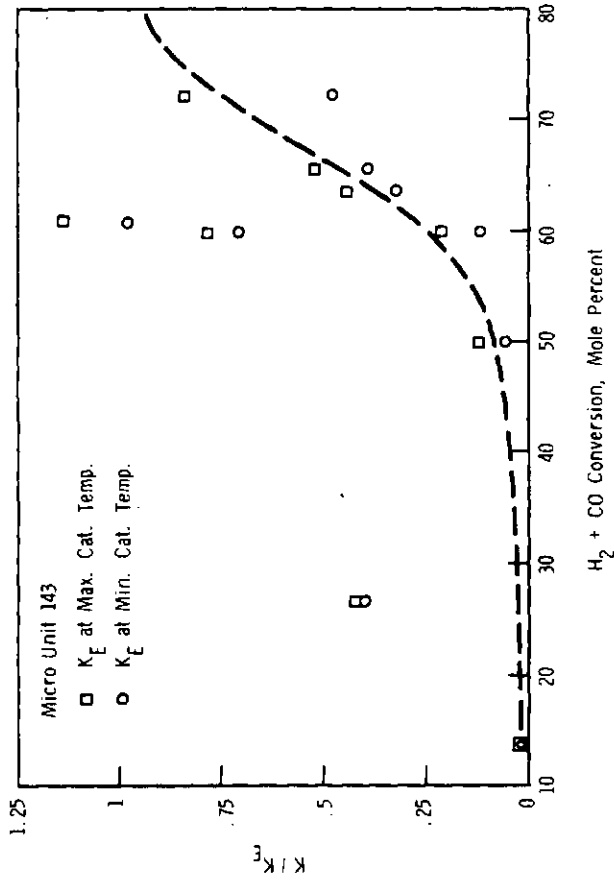


TABLE 32

STUDY OF WATER GAS SHIFT REACTION FROM MICRO-REACTOR
EXPERIMENTS WITH $H_2/CO = 2/1$ AS FEED (UNIT 143)

Balance No.	$H_2 + CO$ Conv. (%)	K (1)	K/K_F (K_F at T Min.)	K/K_F (K_F at T Max.)
51-2	72.3	20.7	0.478	0.838
51-3 (2)	7.33	16.7	0.652	0.705
51-4 (3)	75.0	37.2	1.097	1.563
51-5	61.0	27.6	0.975	1.131
52-1 (3)	71.7	71.8	1.915	2.943
52-2	50.0	3.04	0.055	0.122
52-3	60.0	13.1	0.705	0.780
52-4	26.7	10.1	0.398	0.417
53-1 (3)	70.3	91.8	2.446	3.857
53-2	13.7	1.29	0.016	0.018
53-3 (3)	73.7	26.2	1.224	1.701
54-2	63.7	16.4	0.365	0.441
54-3	65.7	16.2	0.389	0.510
55-2	60.0	5.22	0.118	0.214

(1) $K = (H_2)(CO_2)/(H_2O)(CO)$

(2) K value questionable because of low H_2O made.

(3) K value questionable because of high CO conversion.

TABLE 33

STUDY OF WATER GAS SHIFT REACTION FROM MICRO-REACTOR EXPERIMENTS
WITH $H_2/CO/CO_2 = 3/1/2$ AS FEED (UNITS 158 AND 159)

Balance No.	$H_2 + CO$ Conv. (%)	K (1)	K/K_F (K_F at T Min.)	K/K_F (K_F at T Max.)
CT-158-87-1	56.0	18.0	0.608	0.798
87-3 (2)	6.25	77.8	2.981	3.176
87-4	58.5	21.0	0.781	0.996
87-5	16.0	33.9	1.270	1.380
88-1	51.75	21.1	0.651	0.898
89-1	46.0	14.9	0.457	0.629
89-2	9.75	51.0	0.646	0.730
89-3	54.75	17.0	0.733	1.076
89-4	43.0	19.5	0.540	0.799
90-1	46.0	15.65	0.424	0.702
90-2	53.25	17.2	0.462	0.680
90-3	63.25	25.1	0.794	1.020
90-4	25.5	21.1	0.567	0.872
90-5	34.5	17.9	0.485	0.734
91-1	54.5	20.7	0.629	0.885
91-2	59.75	22.4	0.698	0.918
91-3	65.75	26.9	0.921	1.121
91-4	24.5	24.3	0.757	0.996
91-5	36.0	22.8	0.722	0.916
CT-159-127-2	36.0	20.1	0.472	0.824
127-3	19.75	29.0	1.142	1.209
127-4	52.75	34.0	1.201	1.490
127-5	23.5	25.9	0.887	1.012

(1) $K = (H_2)(CO_2)/(H_2O)(CO)$.

(2) K value questionable because of low H_2O made.

Figure 33

K/K_E VS $H_2 + CO$ CONVERSION WITH $H_2/CO/CO_2 = 3/1/2$ FEED

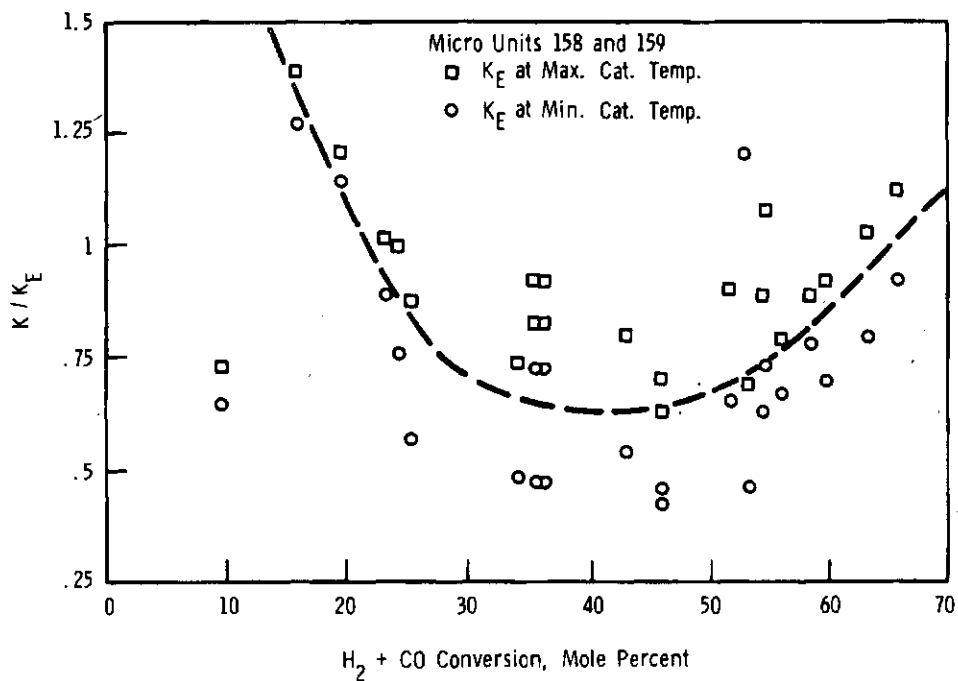
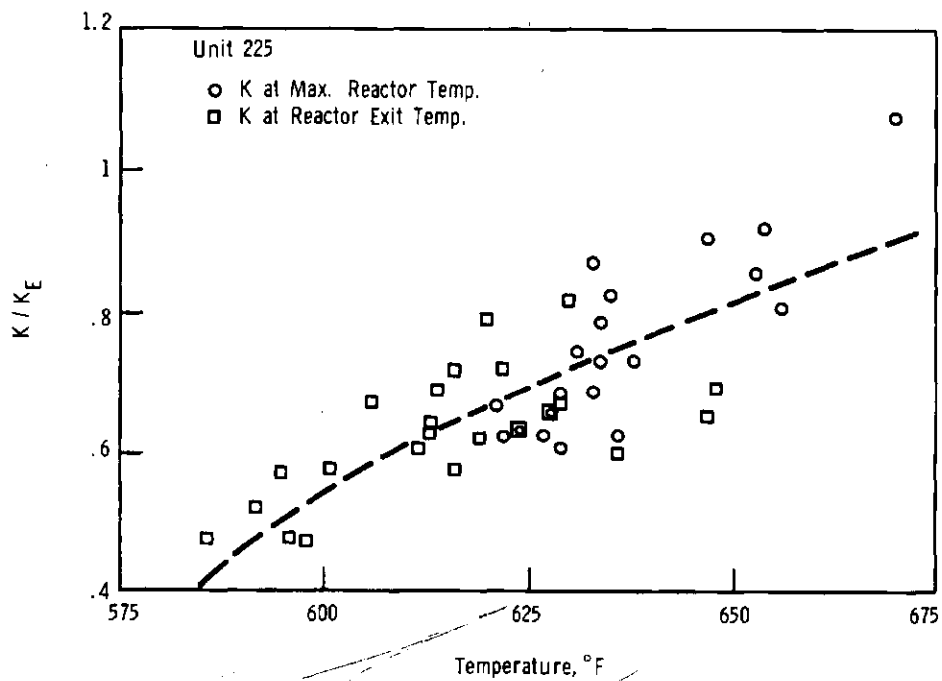


Figure 34

WATER GAS SHIFT REACTION OVER SG-A-1 IN THE BENCH-SCALE UNIT



Analyzing bench-scale unit data is more complicated than analyzing micro reactor data, because the actual exit gas composition must be calculated from the

- Recycle gas composition
- Recycle ratio
- Fresh feed composition
- H_2+CO conversion
- Assumption that the recycle gas is saturated with water at the conditions of the separator.

The result of this type calculation is summarized in Table 34. The experimental data used in this analysis were obtained from run 225-10 with 23 material balances. Since there is usually a small drop in temperature at the exit end of the catalyst bed, there is an uncertainty as to the temperature on which the equilibrium constant (K_E) should be based. This is an important point because K_E is strongly dependent on the temperature (Figure 31). Because of the uncertainty of temperature, it was decided that K_E 's at maximum reactor and at reactor exit temperature would be used in calculating the K/K_E ratios.

Figure 34 shows a correlation between K/K_E 's and the reactor temperature. One can conclude from the fact that all K/K_E 's are less than one, that the water is shifted into carbon dioxide during synthesis gas conversion. At the higher temperatures, this ratio becomes closer to 1. This phenomenon can probably be explained by a higher kinetic rate at higher temperature which drives the shift reaction closer to equilibrium. Since not all of the balances were obtained at the same catalyst contact time, some effects due to this variation should be investigated.

Shift Activity of SG-B-2

Unlike SG-A-1, developmental catalyst SG-B-2 has very little, if any, water-gas shift activity. This conclusion is based on analyses of micro reactor and bench-scale unit data with this catalyst.

Due to temperature variation along the micro reactor, K/K_E values based on both the minimum and maximum reactor temperatures are included in Table 35. Two charge compositions, $0.9 H_2/CO/0.3 CO_2$ and H_2/CO were used and the K/K_E values for $0.9 H_2/CO/0.3 CO_2$ are about 100 times larger than those found for H_2/CO , because of the presence of CO_2 in the former case. In either case, only a small amount of CO_2 is formed. The highest reactor temperature, $602^\circ F$ (balance 58-10), shows the greatest extent of shift activity; however, it is far less than that exhibited by catalyst SG-A-1. There are

TABLE 34

STUDY OF WATER GAS SHIFT REACTION FROM
BENCH-SCALE UNIT EXPERIMENTS (UNIT 225)

Balance No.	K (1) Reactor Exit	K/K _E	
		K _E at T Max.	K _E at T Exit
10-1	16.8	0.662	0.662
2	16.6	0.634	0.634
3	16.9	0.691	0.672
4	14.5	0.645	0.602
5	15.4	0.827	0.695
6	14.6	0.789	0.655
7	20.5	1.072	0.817
8	19.5	0.917	0.692
9	20.1	0.905	0.676
10	18.3	0.856	0.646
11	16.9	0.807	0.623
12	18.6	0.746	0.573
13	17.4	0.688	0.524
14	16.6	0.625	0.478
15	16.0	0.627	0.579
16	17.9	0.671	0.579
17	20.0	0.826	0.721
18	17.8	0.732	0.630
19	17.4	0.734	0.610
20	21.3	0.870	0.793
21	19.2	0.788	0.723
22	15.1	0.627	0.476
23	15.4	0.609	0.478

$$(1) K = (H_2) (CO_2) / (H_2O) (CO).$$

TABLE 35

WATER GAS SHIFT REACTION IN MICRO-REACTOR WITH CATALYST SG-B-2 (UNIT 143)

Balance No.	Max. T (°F)	(H ₂ +CO) Conv.	K _E ⁽¹⁾	K/K _E	
				(K _E at Min. T)	(K _E at Max. T)
Charge: 0.9 H ₂ /CC/0.3 CO ₂ /3.4 CH ₄					
58-1	504	47.4	2.54	3.28 × 10 ⁻²	3.67 × 10 ⁻²
58-2	504	19.2	1.45	1.76 × 10 ⁻²	2.09 × 10 ⁻²
58-3	507	31.8	7.42 × 10 ⁻¹	1.02 × 10 ⁻²	1.10 × 10 ⁻²
Charge: H ₂ /CO					
58-4	506	51.6	8.00 × 10 ⁻³	1.03 × 10 ⁻⁴	1.16 × 10 ⁻⁴
58-5	507	50.4	7.25 × 10 ⁻³	9.62 × 10 ⁻⁵	1.08 × 10 ⁻⁴
6	484	32.7	8.12 × 10 ⁻³	9.07 × 10 ⁻⁵	9.70 × 10 ⁻⁵
7	525	60.8	1.06 × 10 ⁻²	1.60 × 10 ⁻⁴	1.85 × 10 ⁻⁴
8	552	64.6	1.82 × 10 ⁻²	3.26 × 10 ⁻⁴	3.99 × 10 ⁻⁴
9	577	70.3	2.31 × 10 ⁻²	4.90 × 10 ⁻⁴	6.21 × 10 ⁻⁴
10	602	70.9	3.18 × 10 ⁻²	9.44 × 10 ⁻⁴	1.20 × 10 ⁻³
11	510	27.3	1.90 × 10 ⁻²	2.72 × 10 ⁻⁶	2.90 × 10 ⁻⁴

$$(1) K \equiv (H_2) (CO_2) / (H_2O) (CO)$$

three possible sources responsible for the small amounts of CO₂ observed:

- Shift reaction catalyzed by SG-B-2
- Shift reaction catalyzed by the reactor wall
- Disproportionation of CO into CO₂ and carbon.

Disproportionation cannot be the only source for CO₂, since the corresponding amount of carbon made would amount to 200% of the catalyst weight over the catalyst cycle. This is highly unlikely, unless much of the carbon migrates out of the reactor.

Table 36 summarizes the study with bench-scale unit data. The maximum temperature in the bench-scale unit is usually observed at the reactor exit and only the maximum temperature was used to evaluate K_E .

TABLE 36

WATER GAS SHIFT REACTION IN
BENCH-SCALE UNIT WITH CATALYST SG-B-2

<u>Run No.</u>	<u>K⁽¹⁾ Rx. Exit</u>	<u>Max. Rx. T (°F)</u>	<u>K_E At T_E Max.</u>	<u>K/K_E</u>
15-1				
15-2	1.25	531	54.5	2.30 x 10 ⁻²
3	0.640	527	56.4	1.13 x 10 ⁻²
4	0.726	528	55.9	1.30 x 10 ⁻²
5	0.613	531	54.4	1.13 x 10 ⁻²
6	0.579	524	57.9	1.00 x 10 ⁻²
7	0.887	532	54.0	1.64 x 10 ⁻²
8	0.305	524	57.9	5.27 x 10 ⁻³
10	0.342	523	58.4	5.86 x 10 ⁻³
11	0.430	529	55.4	7.76 x 10 ⁻³
13	0.904	518	61.0	1.48 x 10 ⁻²
14	0.908	526	56.9	1.60 x 10 ⁻²
15	0.864	517	61.5	1.40 x 10 ⁻²
16	0.672	524	57.9	1.16 x 10 ⁻²
17	0.687	531	54.4	1.26 x 10 ⁻²
18	1.29	527	56.4	2.29 x 10 ⁻²

(1) $K \equiv (H_2)(CO_2)/(H_2O)(CO)$

G. Fixed Bed Studies with Developmental SG-C Catalysts

1. Task 1 - Exploratory Process Research

Three catalysts in this series were investigated under the codes SG-C-1, SG-C-2, and SG-C-3. While their compositions vary, their chemical nature and catalytic behavior are sufficiently similar to treat the three as one group. The developmental SG-C series materials, while less active than SG-A-1 or SG-B-2, are of interest because the hydrocarbon products synthesized over these catalysts are characterized by a lower selectivity to methane and a significantly higher aromatic component selectivity (Table 37). Further, the SG-C catalysts exhibit high water gas shift at typical operating conditions.

Catalyst SG-C-3 was specifically introduced as a more active alternative for aromatic gasoline production. As illustrated in Figure 35 SG-C-3 has a higher activity, a lower aging rate and a lower selectivity to methane when compared with SG-C-1.

a. Process Variable Studies with SG-C Catalysts

For synthesis gas conversion over SG-C catalysts, process variables have been studied over a wide range of temperatures (740-900°F), pressures (400-1700 psig), contact times (60-240 sec.) - as measured by the reciprocal space velocity (bed volume at reactor conditions) - and hydrogen to carbon monoxide feed ratios (0.5/1 to 5/1 - mole). Because significant decay was found to occur, runs were conducted over periods of at least 90 hours. All runs show aging in selectivity and conversion - as illustrated in Figures 35 and 36.

Initial selectivities to liquid, essentially aromatic hydrocarbon products, were found to be high (60-80%). Low initial selectivities to methane were generally observed. Upon aging, liquid selectivities decreased with an associated increase in methane.

The effects of process variables on hydrocarbon selectivities will be illustrated by considering material balances taken at about 42 hours of operation. Shown in Table 38 with 800°F data, satisfactory selectivities are found at pressures up to around 1200 psig. with light gases increasing and liquids decreasing with pressure. At 1700 psig hydrocarbon selectivities to light gases are significantly higher than at lower pressures.

The effects of temperature on hydrocarbon selectivities are illustrated with data at 800 psig (Table 39). While methane make increases and liquid yield decreases with increasing temperature, selectivities are satisfactory for temperatures up to 900°F. Liquid hydrocarbon production rate did not increase between 800 and 900°F, however.

TABLE 37

COMPARISON OF HYDROCARBON PRODUCTS FROM
VARIOUS SYNTHESIS GAS CONVERSION CATALYSTS

	<u>SG-A-1</u>	<u>SG-B-2</u>	<u>SG-C-1</u>	<u>SG-C-2</u>	<u>SG-C-3</u>
Hydrocarbon Selectivity, wt %					
CH ₄	20	21	7	11	5
C ₂ -C ₄ , P+O	23	13	18	18	27
C ₅ ⁺	57	65	75	71	69
Aromatics	13	11	46	58	58
Run Number	CT-143 41-4	CT-143 58-7	SCO-90 176T2	SCO-11 876T1	SCO-30 277T1

TABLE 38

EFFECTS OF PRESSURE ON HYDROCARBON SELECTIVITIES

800°F, 42 Hours On Stream

Pressure, psig	<u>H₂/CO; τ=150 sec</u>			<u>4H₂/CO; τ=60 sec</u>	
	<u>820</u>	<u>1220</u>	<u>1720</u>	<u>410</u>	<u>1220</u>
Selectivity, wt%					
CH ₄		10	47	7	16
C ₁ +C ₂	15	13	57	12	22
C ₆ -10, Ar	58	60	24	47	52
C ₅ ⁺ PONA ^(a)	71	77	31	59	64

(a) PONA = Paraffins, olefins, naphthenes and aromatics.

TABLE 39

EFFECTS OF TEMPERATURE ON HYDROCARBON SELECTIVITY

42 Hours On Stream

H₂/CO; τ=150 sec; P=800 psig

Temperature, °F	<u>744</u>	<u>796</u>	<u>898</u>
Selectivity, wt %			
CH ₄	3	11	16
C ₁ +C ₂	6	15	23
C ₆ -10, Ar	64	58	47
C ₅ ⁺ PONA	82	71	57
Liq. Space Time Yield			
mg C ₅ ⁺ /g cat/hr	18	32	28

Figure 35

COMPARISON OF CATALYSTS SG-C-3 AND SG-C-1
(H₂/CO; 800°F)

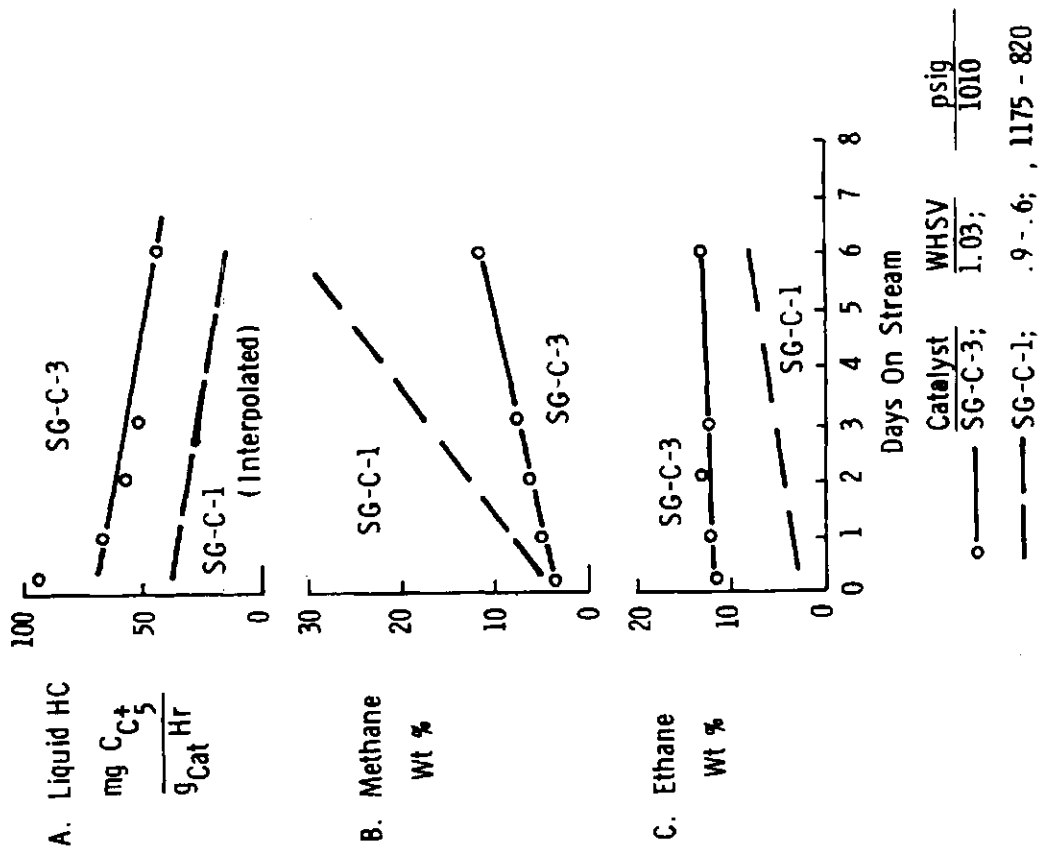
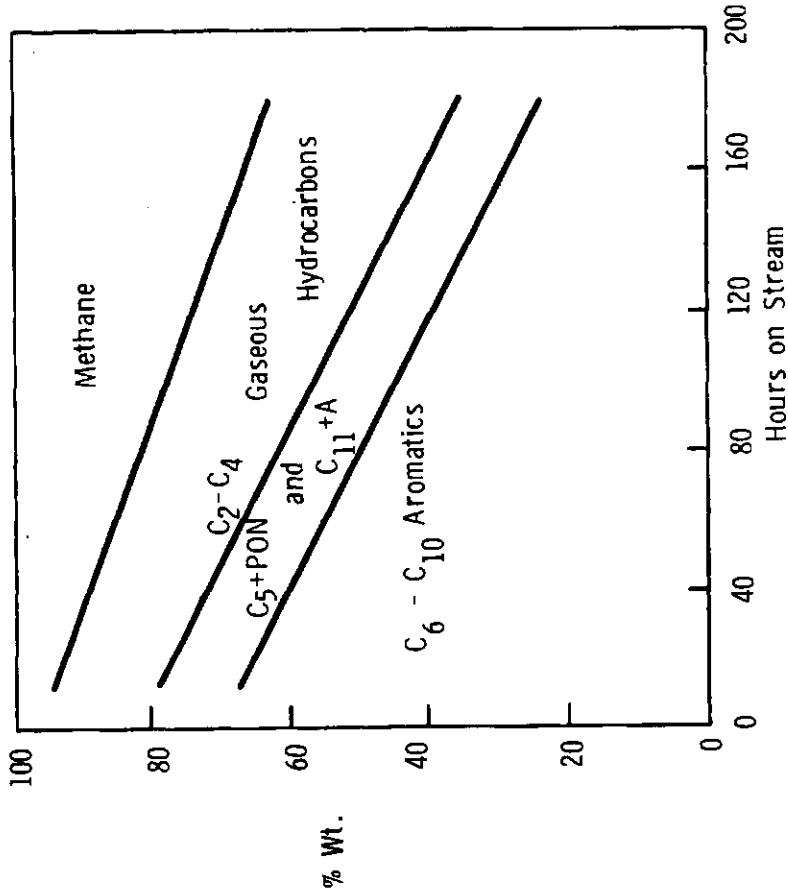


Figure 36

SUMMARY OF HYDROCARBON SELECTIVITIES FOR
SYNGAS CONVERSION OVER CATALYST SG-C-1

Reaction Conditions:

Charge: H₂/CO = 1/1 (Mole)
 Temperature 800°F
 (Sp. Vel.)⁻¹ 150 Sec.
 Pressure 1220 and 820 psig



Over the wide range investigated, contact time had little or no effect on selectivity of hydrocarbons (Table 40).

The effect of co-feeding excess hydrogen was to cause a noticeable increase in light gas selectivities at H_2/CO ratios of about 4/1. However, for over a tenfold increase in H_2/CO ratio (i.e., 0.5/1 to 5/1) hydrocarbon selectivities are acceptable (Table 41).

For synthesis gas conversion over SG-C catalysts, aging is associated with both change in conversion to hydrocarbons and a decrease in the selectivity of hydrocarbons to C_5^+ liquids. Therefore, the Liquid Space Time Yield of C_5^+ was selected to characterize the gasoline production ability of the catalyst as it aged.

In Figures 37-39, Liquid Space Time Yields are presented as a function of time on stream for typical experiments. After the first day of operation these hydrocarbon liquid yields show an apparent, reasonably linear decay with time. For the data presented in Figures 37-39 at constant temperature (800°F) and reciprocal space velocity (150 sec), both base activity and decay rate appear to increase with CO partial pressure. Deviations from this behavior could be associated with temperature and contact time. While increasing temperature to 900°F resulted in little change in activity or aging (Figure 37-B vs 38-A), decreasing temperature to 744°F resulted in reduced activity (Figure 38-C). Decreasing contact time was associated with reduced aging rates (e.g., Figure 37-B vs Figure 38-B and Figure 39-A vs Figure 39-B).

These process variable studies identified wide regions of satisfactory initial catalyst activity and selectivity but severe aging occurs within several weeks. Relatively high operating pressures (above 800 psig) appear to be necessary for higher initial activity.

b. Catalyst SG-C Regeneration

The fixed bed process variable study indicated a relatively short catalyst life. Further inhibition to catalytic aromatic ring formation can be associated with coke formation. The SG-C catalysts are characterized by highly aromatic liquid product and coke was found on spent catalysts. Hence, the ability to withstand oxidative (coke burning) regenerations is a prerequisite for catalyst use. Experiments indicated that the SG-C catalysts were oxidatively regenerable, as illustrated in Figure 40. Spent catalysts were regenerated by slow oxidation in air at a final temperature of 1000°F. Coke levels on spent catalysts were typically around 20 wt %.

TABLE 40

EFFECTS OF CONTACT TIME* ON HYDROCARBON SELECTIVITIES
42 Hours On Stream

τ , sec.	800°F; 1220 psig <u>4-5 H₂/CO</u>			800°F; 800 psig <u>H₂/CO</u>	
	<u>240</u>	<u>160</u>	<u>60</u>	<u>150</u>	<u>92</u>
Selectivity, wt %					
CH ₄	17	15	16	11	6
C ₁ +C ₂	25	23	22	15	10
C ₆₋₁₀ , Ar	54	49	52	58	60
C ₅ + PONA	62	61	64	71	75

*As measured by reciprocal space velocity

TABLE 41

EFFECTS OF H₂/CO RATIO ON
HYDROCARBON SELECTIVITIES

800°F; 1220 psig; τ =150 sec
42 Hours On Stream

H ₂ /CO	<u>1/1</u>	<u>4.7/1</u>
Selectivity, wt %		
CH ₄	10	15
C ₁ +C ₂	13	23
C ₆₋₁₀ , Ar	60	49
C ₅ + PONA	77	61

Figure 37

EFFECTS ON FEED COMPOSITION AND PRESSURE ON
SG-C-1 AGING AT 800° F

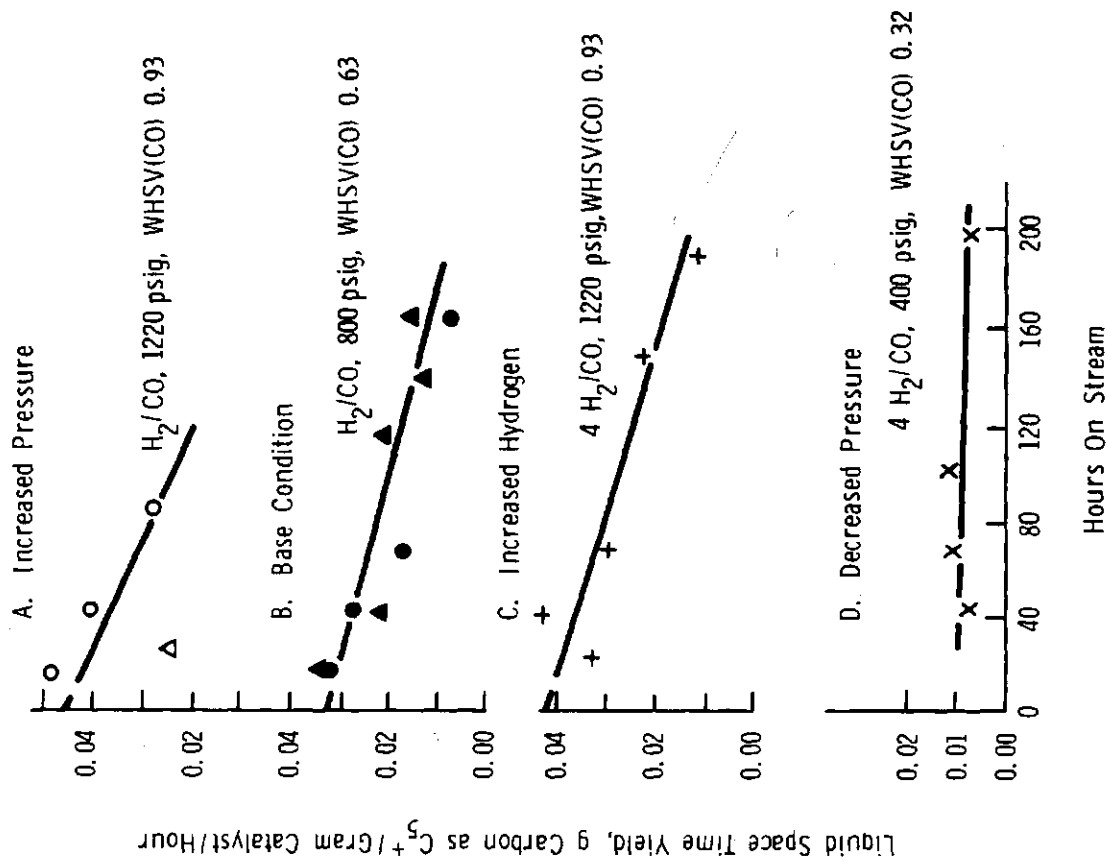


Figure 38

EFFECT OF TEMPERATURE AND CONTACT TIME ON
SG-C-1 AGING
(1.2 H₂/CO, 800 psig)

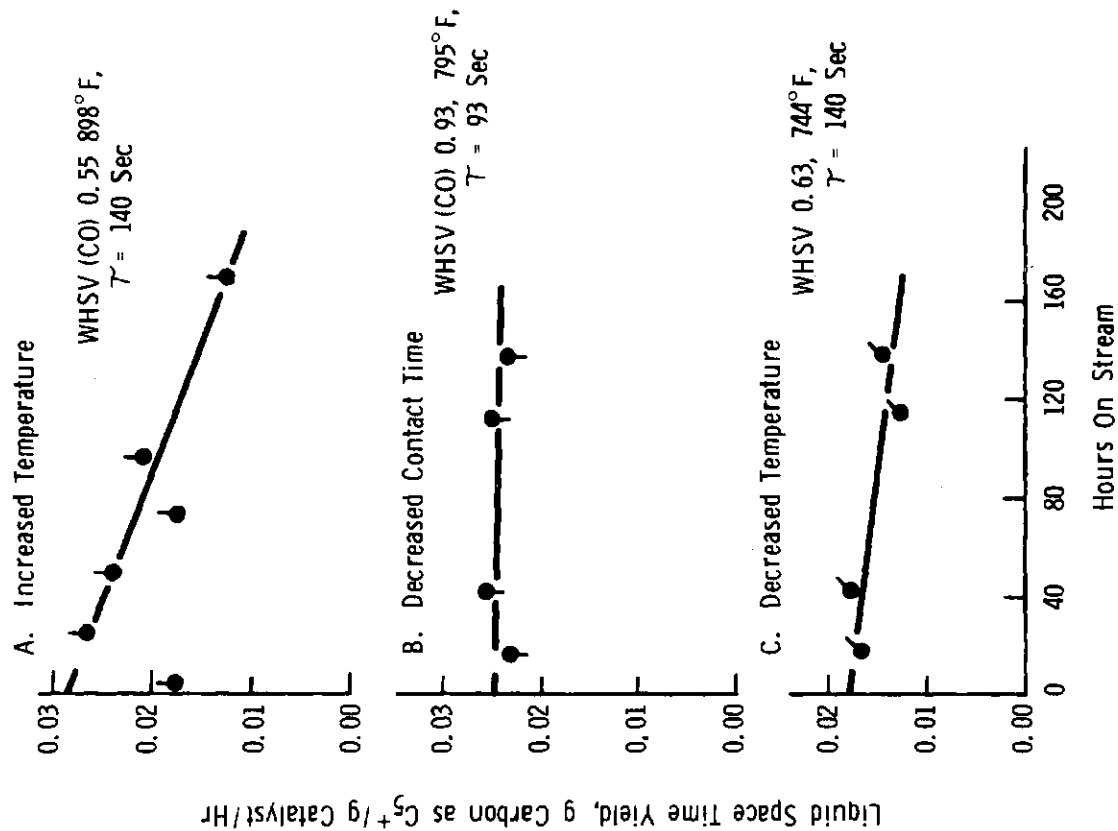


Figure 39

AGING OF CATALYST SG-C-1 AND SG-C-2 AT 790° F

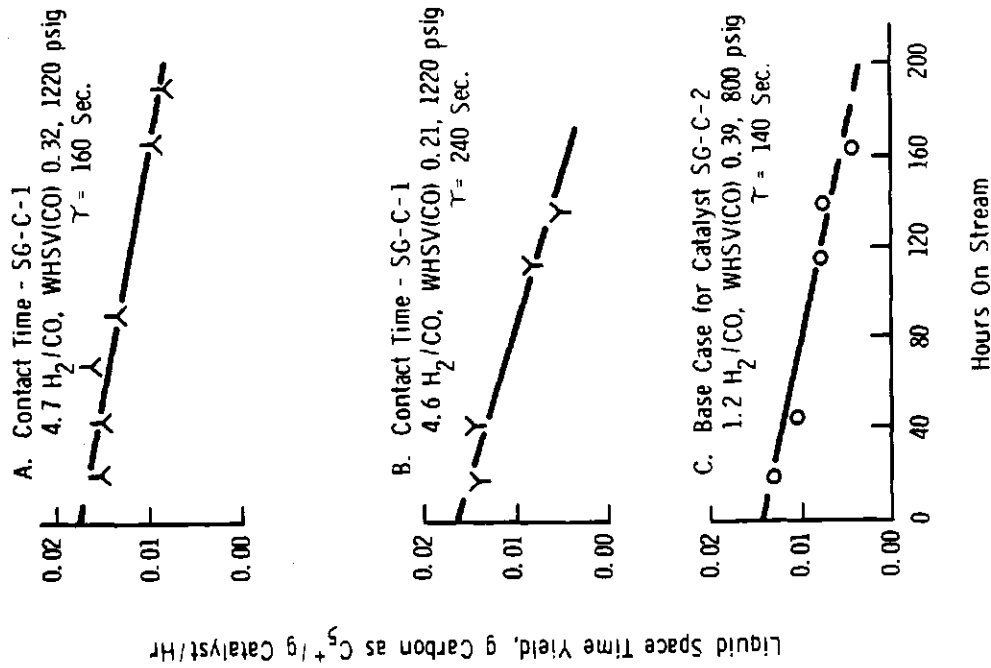
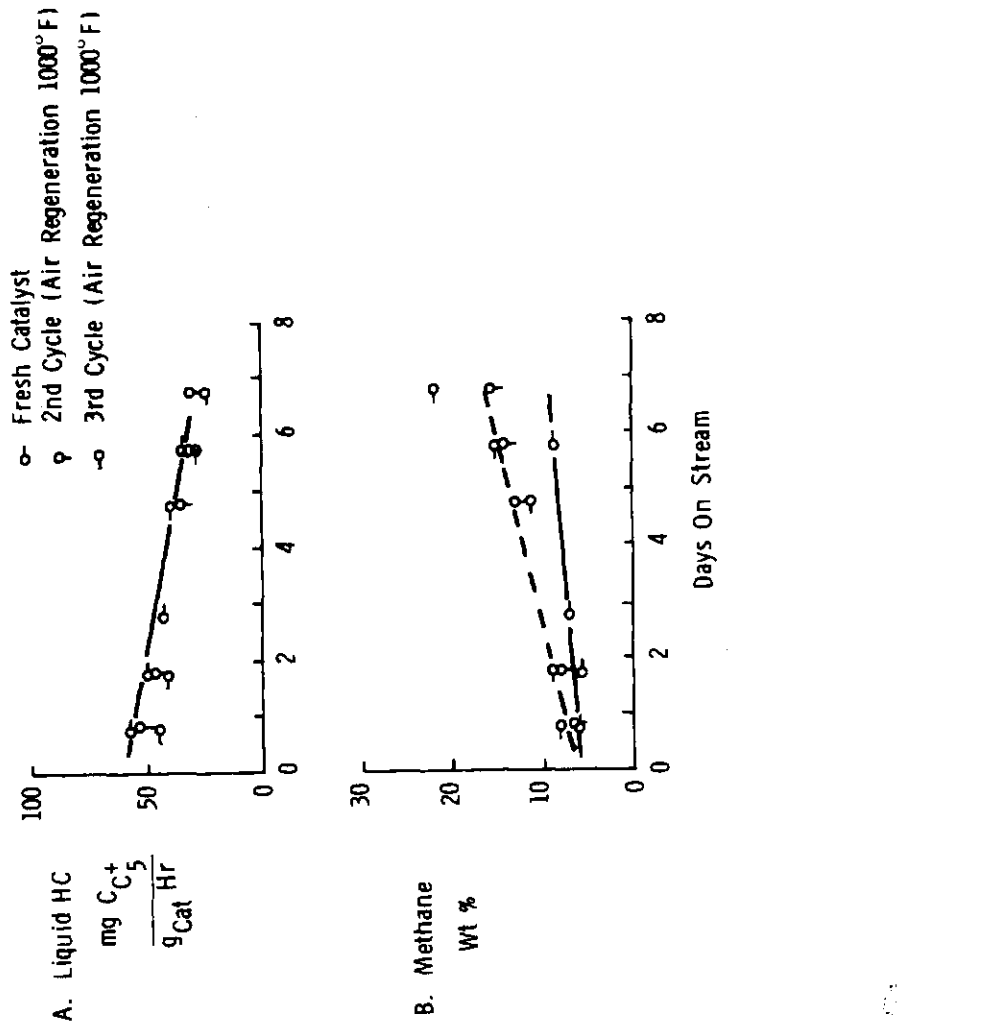


Figure 40

OXIDATIVE REGENERATION OF CATALYST SG-C-3
(H₂/CO; 798° F; 780 psig and 1.02 WHSV)



c. Sulfur Tolerance

Extremely low sulfur tolerance is associated with typical Fischer-Tropsch iron or cobalt based catalysts. For SASOL reactors (iron), design specifications require less than 1.6 ppm sulfur in the feed while improved catalyst performance is reported for feed sulfur levels below 0.016 ppm(39). Emmett associates poisoning of iron catalysts with an accumulated sulfur exposure of 3 mg/g-catalyst and recommends 1 ppm sulfur as the upper limit on feed gas concentrations. In the case of cobalt catalysts, Emmett reports clear poisoning by sulfur fed at 6 ppm levels(40).

Raw syngas is reported to contain from about 1500 to 6000 ppm sulfur (41,42). Typical "gas sweetening" processes remove sulfur from such streams to levels in the range of from 2 to 80 ppm(43). Current SASOL practice is to remove sulfur from syngas to below 0.016 ppm with a Rectisol Process(39).

In Mobil's proprietary catalyst development effort, it was found that catalyst SG-C-3 was reversibly poisoned by sulfur at 8000 ppm, a level potential in raw syngas. The tolerance of SG-C-3 was therefore investigated at a sulfur level typical of gas sweetening processes, i.e., 40 ppm. This sulfur contamination is significantly higher than the Fischer-Tropsch process restrictions (2-0.02 ppm).

A six-day aging run was conducted with 40 ppm H₂S co-fed with syngas [H₂/CO, 1000 psig, 795°F, and 1 WHSV (CO)]. The results of this run are compared with a sulfur-free base run in Figure 41. The activity and selectivities of the sulfur-contaminated run were the same as those for the base case. Further, during the course of the run, 14 mg S/g catalyst was charged. This was five times the exposure level associated with Fischer-Tropsch poisoning.

Catalyst SG-C-1 (and -2) was found to tolerate 3000 ppm sulfur in similar experiments.

d. Catalyst SG-C Deactivation with Water

To test the stability of SG-C catalysts to chemical species anticipated during recycle operation, experiments were conducted with water and carbon dioxide co-feed.

In all cases the presence of water or carbon dioxide in the feed stream was associated with lower catalyst activity, more rapid aging and higher selectivity to methane. Such comparisons for SG-C-3 catalyst are illustrated in Figures 42 and 43. Clearly a relatively small amount of co-fed water (3%) resulted in significantly lowered activity and increased aging. Much larger carbon dioxide co-feed (25 mole %) gave similar deactivation and aging.

Figure 41

EFFECTS OF SULFUR CONTAMINATION AND
AND OXIDATIVE REGENERATION
ON SYNTHESIS GAS CONVERSION OVER CATALYST SG-C-3
(H₂/CO: 792°F; 1000 psig and 1.0 WHSV)

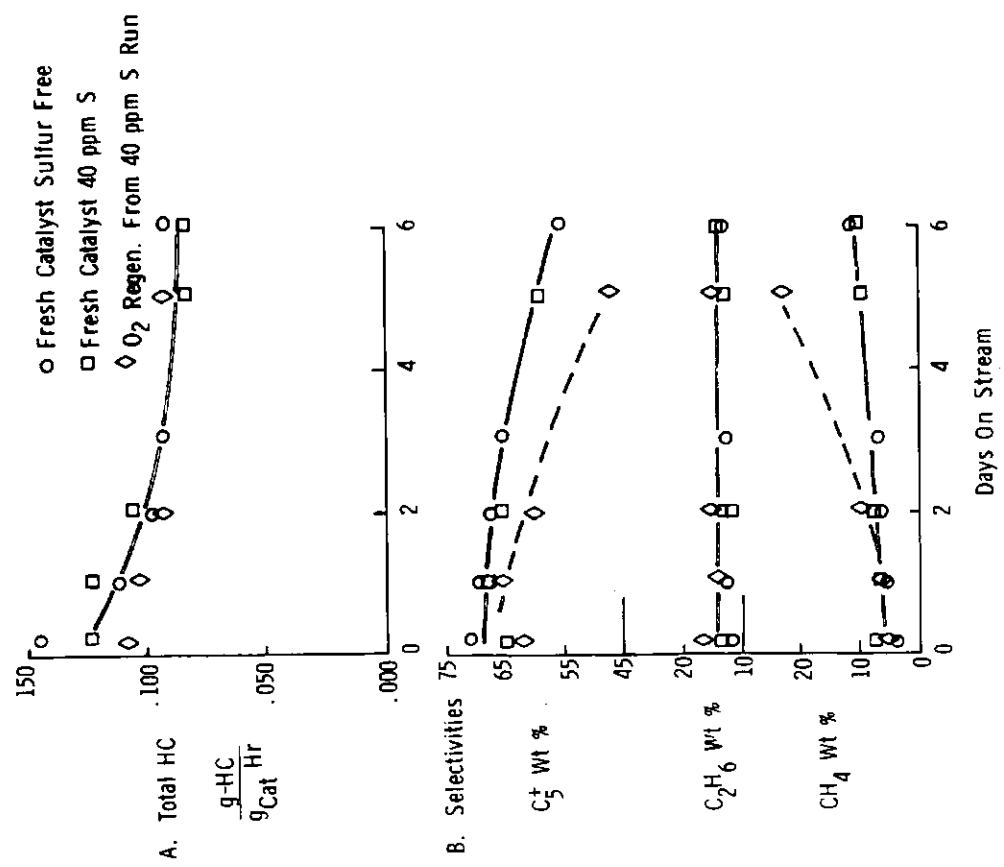


Figure 42

EFFECTS OF WATER CO-FEED OVER CATALYST SG-C-3
(790°F; 1000 psig; dp CO 520 psig)

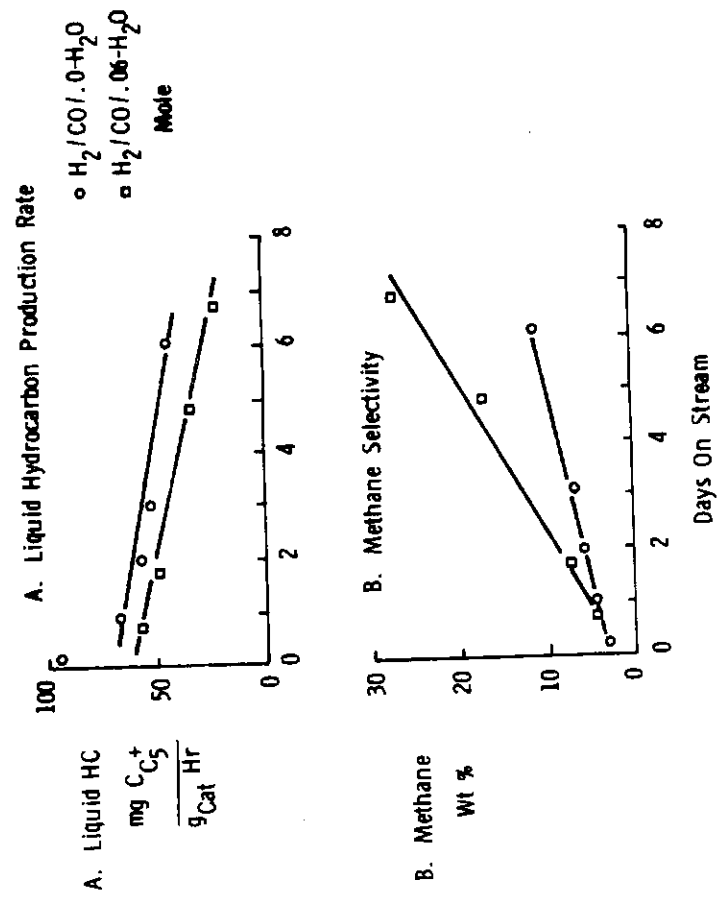


Figure 43

EFFECTS OF CO-FEEDING CO₂ OVER CATALYST SG-C-3
(790° F; pp CO Atm)

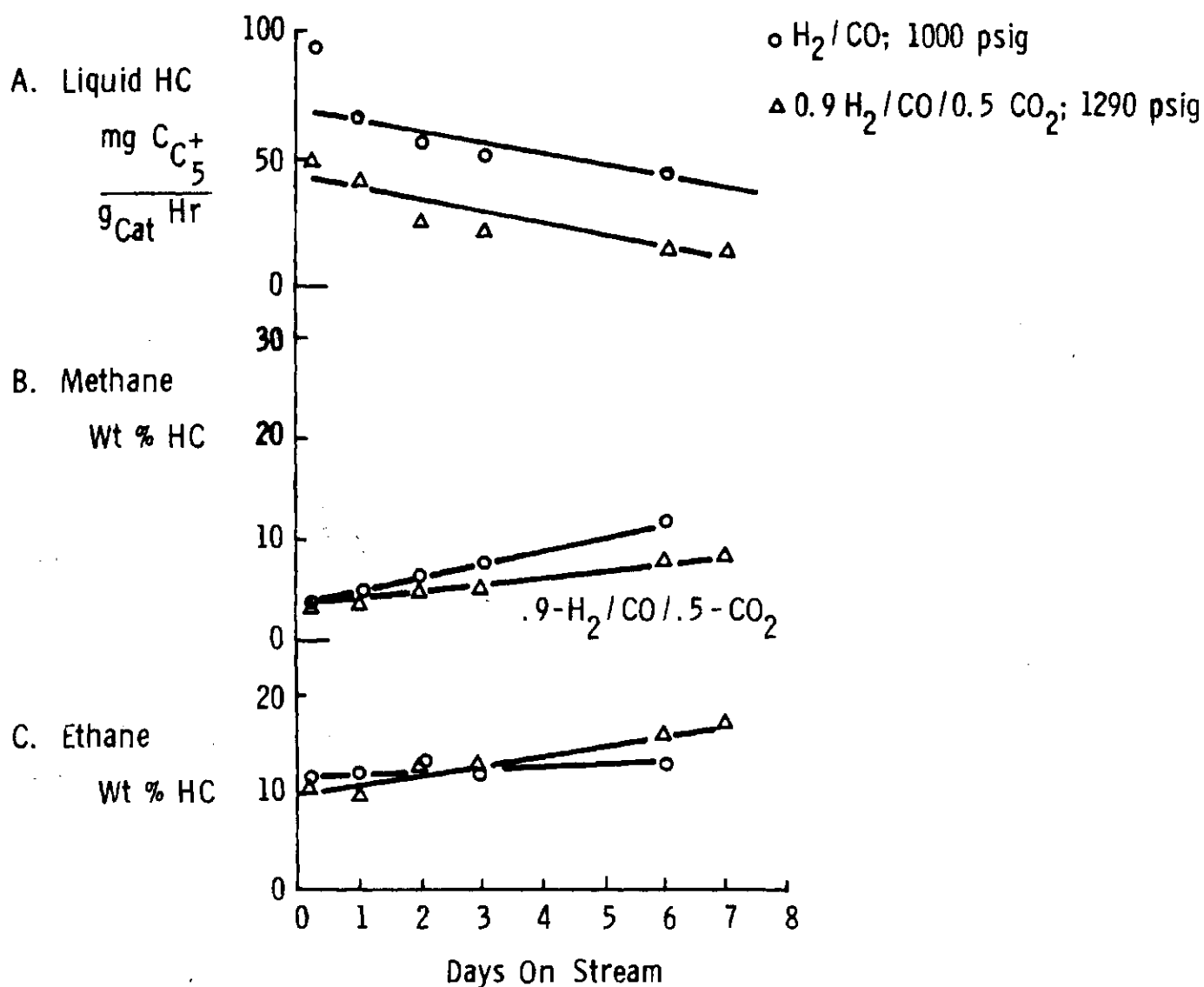
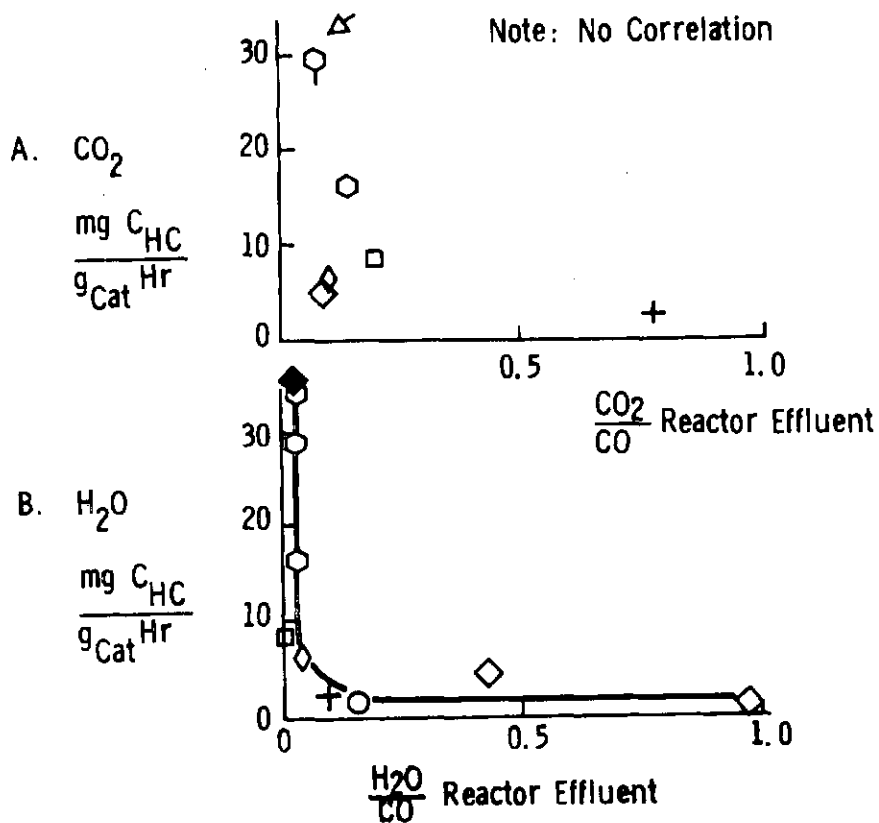


Figure 44

CATALYST SG-C-2 - EFFECT OF CO₂ OR H₂O ON HYDROCARBON PRODUCTION RATE

Synthesis Gas Conversion Over Catalyst SG-C-2
After About 45 Hours on Stream



REACTION CONDITIONS

$\frac{\text{H}_2}{\text{CO}}/\frac{\text{CO}_2}{\text{H}_2\text{O}}$ Feed (Moles)	psig	T (°F)	$\frac{1}{\text{Sp. Vel.}}$ (Sec)	$\frac{\text{H}_2}{\text{CO}}/\frac{\text{CO}_2}{\text{H}_2\text{O}}$ Feed (Moles)	psig	T (°F)	$\frac{1}{\text{Sp. Vel.}}$ (Sec)
◇ 4.2/1/0/0	870	798	160	□ 1./1/.16/0	1175	798	150
◇ 4.2/1/0/.33	1220	802	150	○ 1.2/1/0/0	870	797	45
◆ 4.2/1/0/1.0	1220	799	150	△ 1.2/1/0/0	1720	788	150
○ 1./1/1.9/0	1220	797	200	○ 1.2/1/0/0	800	792	140
+ 1./1/.94/0	1220	802	150				

Because of the high water gas shift capacity of the SG-C catalysts both water and carbon dioxide are present in the reactor. The role of water and carbon dioxide in these systems can be elucidated by correlation of the observed hydrocarbon production rate as a function of the ratio of various reaction components with the product carbon monoxide -- as might be suggested by a Langmuir-Hinshelwood form of the rate expression. Such a technique includes the effects of co-produced water or carbon dioxide in the back mixing reactor effluent stream. This is illustrated in Figure 44 for a large number of runs with catalyst SG-C-2. Hydrogen/carbon monoxide feed ratios varied from 1 to 4, with several levels of co-fed water or carbon monoxide.

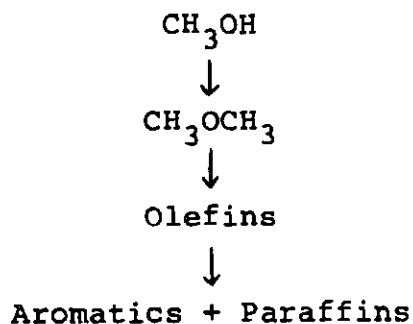
Clearly activity is not correlated well by carbon dioxide presence. But rather activity sharply drops with increased water presence in the reactor effluent.

Thus, the SG-C series catalysts were found to be critically sensitive to water vapor. In spite of the favorable water gas shift characteristics of these systems, water can not be eliminated from the reactor. Further, water presence will increase if carbon dioxide is co-fed as could occur with recycle operation.

H. Fixed Bed Studies with Methanol/Dimethylether Synthesis Catalysts

This contract investigated the direct conversion of synthesis gas to high octane gasoline over Mobil R&D Corporation proprietary catalysts. Both single and two stage processes were considered. An example of a successful two stage process is the preparation of methanol from synthesis gas followed by the conversion of methanol to gasoline. The technology for the conversion of coal derived synthesis gas to methanol is well established and proven commercially. The second step in this sequence, the conversion of methanol to gasoline, has been successfully demonstrated in the laboratory(4,5).

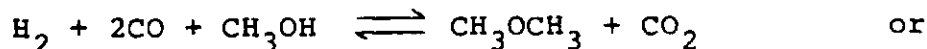
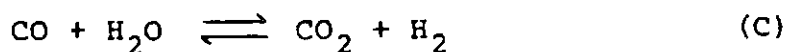
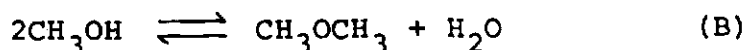
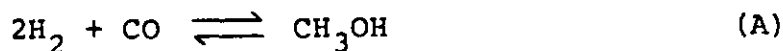
The preparation of gasoline from methanol is explained as:



A key intermediate in the reaction sequence is dimethylether. Consequently, for feedstock in the production of gasoline, dimethylether is as acceptable as methanol.

In methanol manufacture a large part of the cost is associated with the low-per pass conversion, which to some extent is due to thermodynamic constraints. If the methanol is further converted to dimethylether in the methanol reactor, a considerable higher per-pass conversion of synthesis gas to useful oxygenates is possible from equilibrium considerations(44,45).

The important reactions in methanol and dimethylether manufacture are:



Reaction A represents the stoichiometry for methanol production; B is the dehydration of methanol to dimethylether; and C is the water-gas shift equilibrium. On combining A, B and C, reaction D is obtained, which depicts the preparation of dimethylether from synthesis gas with oxygen rejection as carbon dioxide. Inspection of reactions A and D indicates that the stoichiometry for methanol manufacture from synthesis gas requires a H_2/CO mole ratio of two; while dimethylether production may be satisfied by a ratio of one. The lower H_2/CO ratio synthesis gas may present economic advantages when advanced gasifier technology becomes commercial. The improvement in equilibrium conversion for methanol plus dimethylether over methanol alone when using various H_2/CO ratio gases is illustrated in Figure 45. Product gas composition when feeding an equimolar H_2/CO synthesis gas mixture at 1500 psig and 560°F where equation D is at equilibrium is presented in Table 42.

The interrelation of temperature and pressure for equilibrium conversion of equimolar syngas mixtures via Equation D is presented in Figure 46. The effect of increasing pressure is to increase conversion as is the effect of decreasing temperature. Thus dimethylether synthesis can be conducted at reaction conditions similar to "low pressure" methanol synthesis (e.g., 600°F, 1500 psig) and exhibits potential equilibrium conversions higher than methanol (e.g., 80% vs 50%).

Five Mobil R&D Corporation proprietary catalysts were provided for dimethylether process development studies. Key to the initial investigation of these active dimethylether synthesis catalysts is their long term aging. Like methanol synthesis catalysts, these catalysts are not believed to be regenerable. The dimethylether catalysts were evaluated in tubular micro reactors equipped with annular thermowells and described earlier (see Section A - Experimental Equipment). The following conditions were established for the testing of four of the catalysts:

Feed H_2/CO	1.0 (molar)
Temperature (max)	600°F
Pressure	1460 psi
GHSV	~3800

Exclusive of space velocity, these process variables were established consistent with the previous thermodynamic analysis within the pressure limitations of the equipment available (and common practice) and the believed minimum operating temperature of the catalysts. The space velocity selected was high enough to allow initial conversions to fall at or just short of equilibrium conversion.

The performances of these four dimethylether catalysts are summarized in Figure 47. Typical product compositions are presented in Table 43. Clearly for all of these catalysts the product selectivity is quite similar to that for thermodynamic equilibrium.

Figure 46

EFFECT OF TEMPERATURE AND PRESSURE ON
EQUILIBRIUM CONVERSION OF SYNTHESIS GAS

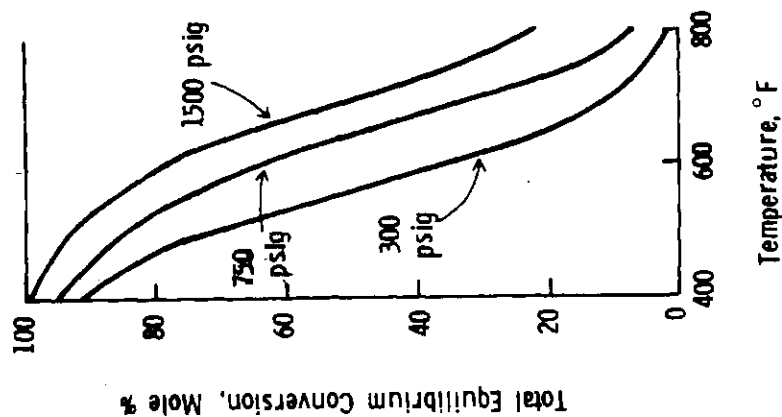
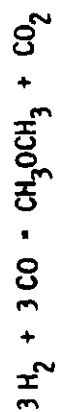


Figure 45

EQUILIBRIUM CONVERSION OF SYNTHESIS GAS

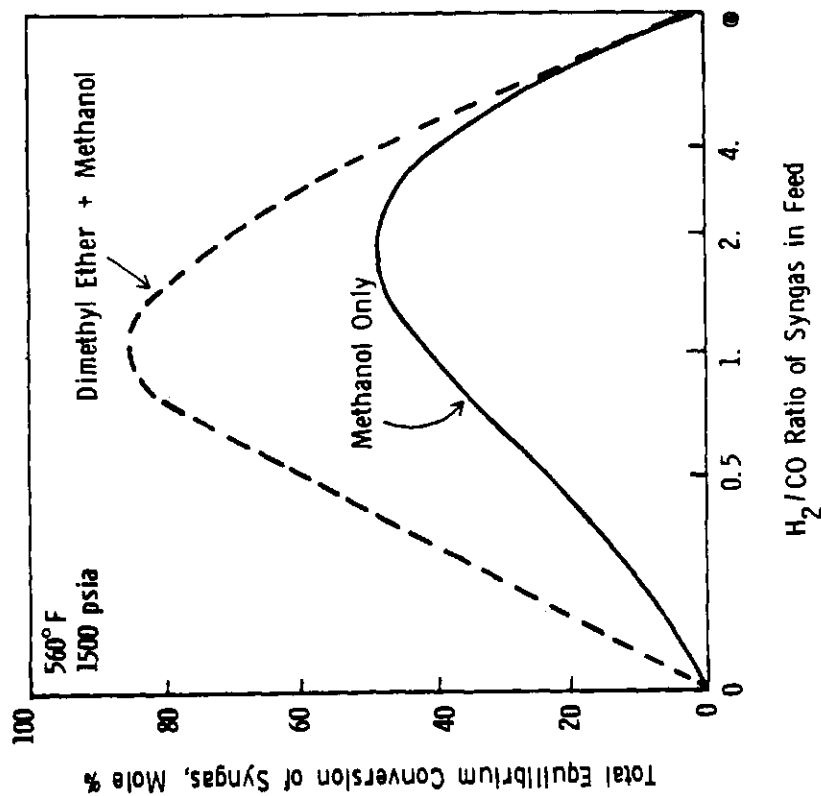


TABLE 42

EQUILIBRIUM CONVERSION OF SYNTHESIS GAS TO DIMETHYLETHER

 $H_2/CO = 1$ molar; P = 1500 psig; T = 560°F

Equilibrium Composition	Wt %
Hydrogen	0.8
Carbon Monoxide	14.5
Carbon Dioxide	39.7
Water	0.3
Dimethylether	42.2
Methanol	2.5
Selectivities	
DME/(DME+M), g/g	0.94
Conversions	Mole %
Hydrogen	84
Carbon Monoxide	88
Total	86

TABLE 43

COMPOSITIONS OF EFFLUENT STREAM FOR
SELECTED DIMETHYLETHER SYNTHESIS RUNS

Catalyst	WHL 518	WHL 525	WHL 526	WB120877
Reaction Conditions				
Time On Stream, days	5	1	0.8	0.8
Temperature, °F	600	601	601	601
Pressure, psig	1500	1500	1500	1500
WHSV	2.9	2.5	3.3	2.9
GHSV	3400	3800	4000	3800
Effluent Compositions, wt %				
Hydrogen	2.9	1.4	0.7	1.7
Carbon Monoxide	42	21	14	30
Carbon Dioxide	31	40	37	32
Water	-	-	2	0.4
Hydrocarbons	0.05	0.1	0.1	0.1
Dimethylether	21	35	43	34
Methanol	1.8	1.8	3.8	1.7
Selectivities				
DME/(DME+M), g/g	0.92	0.93	0.92	0.95
Conversions, mole %				
Hydrogen	55	79	89	74
Carbon Monoxide	56	77	85	68
Total	56	78	87	71

For those sufficiently active catalysts, equilibrium was initially observed, both with respect to the extent of syngas conversion and effluent compositions.

However, as illustrated in Figure 47. Conversion aged markedly during these extended runs. This aging is also apparent for those four catalysts in terms of dimethylether/methanol product rates as illustrated in Figure 48 for the similar space velocity data. Aging rates established by correlation of the last several data points in each of the data sets illustrated in Figure 48 are presented below.

<u>Aging of Selected Dimethylether Synthesis Catalysts</u>	
<u>Catalyst</u>	<u>Estimated Aging Rate Kilogram(DME+MeOH)/ kilogram catalyst/ hour/day</u>
WHL 518	0.01
WHL 525	0.02
WHL 526	0.005
WB120877	0.01

It was possible that this aging could be associated with high temperatures developed within catalyst particles due to poor heat transfer in the experimental reactors. Thus, two additional experiments were conducted: first, a slurry reactor experiment in which catalyst WHL 518 was dispersed in a non-reactive paraffinic oil at a temperature and pressure similar to the previous experiments; and second, an aging experiment with catalyst WHL 528.

The WHL 528 catalyst formulation allowed a lower temperature of operation. Both the slurry system (with poorer contacting efficiency) and the WHL 528 catalyst fixed bed system (lower temperature operation) exhibited lower activity than the previous systems. However, in spite of this lower activity and the improved heat transfer capability of the slurry and the reduced average temperature for WHL 528, aging in both cases was severe. This is illustrated in Figure 49 for the lower temperature experiment. Thus, the aging observed in all these experiments can probably not be attributed to uncontrolled reaction temperature.

While all of these catalysts age at different rates and some more rapidly during the first few days of service, projection of the observed aging indicates an additional 50% drop in production rate in from 1 to 5 months for the various catalysts. These aging rates are not reasonable when compared with those for methanol synthesis catalysts where 14 month catalyst lives are reported. Because of the observed excessive aging for all catalysts investigated, process studies were terminated.

Figure 47

COMPARISON OF SYNGAS CONVERSION OVER
SELECTED CATALYSTS

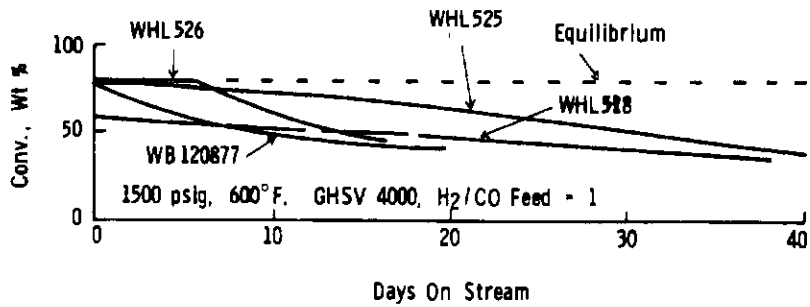


Figure 48

COMPARISON OF DIMETHYLETHER YIELDS FROM
SELECTED CATALYSTS

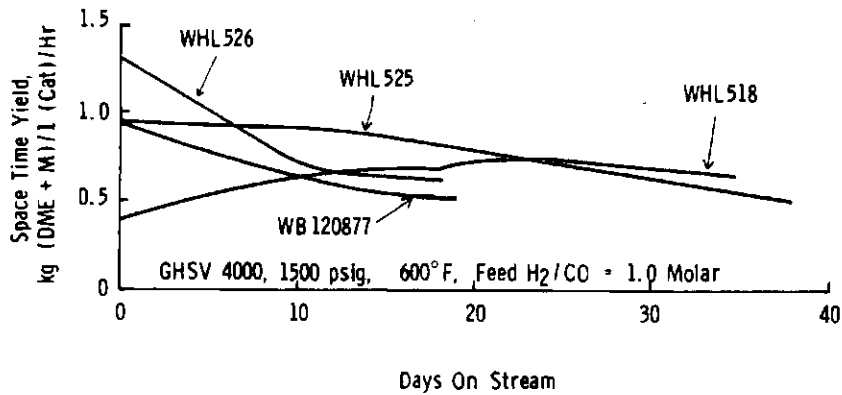
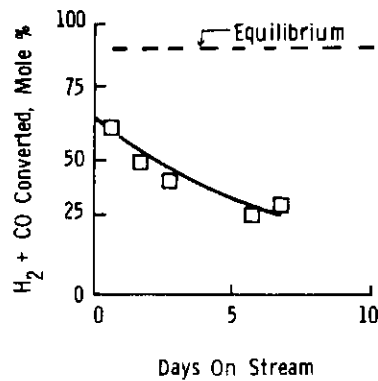


Figure 49

CONVERSION OF SYNTHESIS GAS TO DIMETHYLETHER
WITH CATALYST WHL-528 --
THE EFFECT OF LOWERING TEMPERATURE ON AGING
(GHSV 2000, 1500 psig, 525°F, H₂/CO)



Runs: LPA 339A -- LPA 339E