The data are shown in Figure 17 and in Appendix B (Tables B12 and B13). Aging during the first cycle was rapid. However, performance was much better after regeneration and would be expected to give about a 50 day cycle, as found previously for the prototype catalyst (Table 13 and Figure 14). Longer cycles with $3H_2/CO/2CO_2$ over catalyst SG-A-1 could, thus, be anticipated at the proper conditions. However, this work was not pursued due to plugging problems encountered with catalyst SG-A-1 in the bench-scale unit (below).

2. Task 2 - Process Development

Scale-up from the micro reactor units (10 cc catalyst capacity) to the bench-scale unit (150 cc catalyst capacity) with catalyst SG-A-1 was expected to proceed smoothly. One loading of catalyst SG-A-1 had been run for 50 continuous days in a micro reactor unit and the catalyst was regenerable. However, the micro reactor units are heat-loss units and calculations had shown that high recycle ratios would be needed to maintain adiabatic operation in the bench-scale unit. As it turned out, carbon deposition was the chief problem with catalyst SG-A-1 in the bench-scale unit and was responsible for its removal from the process studies.

Several experiments were made with catalyst SG-A-1 prior to its removal from the program, and these are of interest since a catalyst such as SG-A-1 could probably be used in another type reactor, for example, in a heat-exchange, small-diameter, tubular reactor similar to the Arge reactor used at SASOL in South Africa.

Two incomplete studies, the effect of fresh feed composition and the effect of space rate, were started with catalyst SG-A-1 and these will be discussed.

The results from the exploratory process research (Task 1) had shown that catalyst SG-A-1 performs well at pressures of 200-400 psig and at maximum bed temperatures of about 635°F. Based on this, and a calculation made to determine the amount of recycle needed for adiabatic operation, the following conditions were used:

Catalyst SG-A-1, g	50
Inlet Bed Temperature, °F	450-480
Maximum Bed Temperature, °F	625-645
Pressure, psig	300
GHSV, hr^{-1}	3500
Recycle Ratio	15/1

During the first few days of operation with catalyst SG-A-1, it was found that the recycle ratio could be reduced to about 9/1 without any deleterious effects. The experiment (225-10) ran continuously for 24 days during which material balances were made with two fresh feed compositions and at two space velocities.

Figure 17

AGING OF CATALYST SG-A-1
(635° F, 200 psig and 2 H_2/CO)

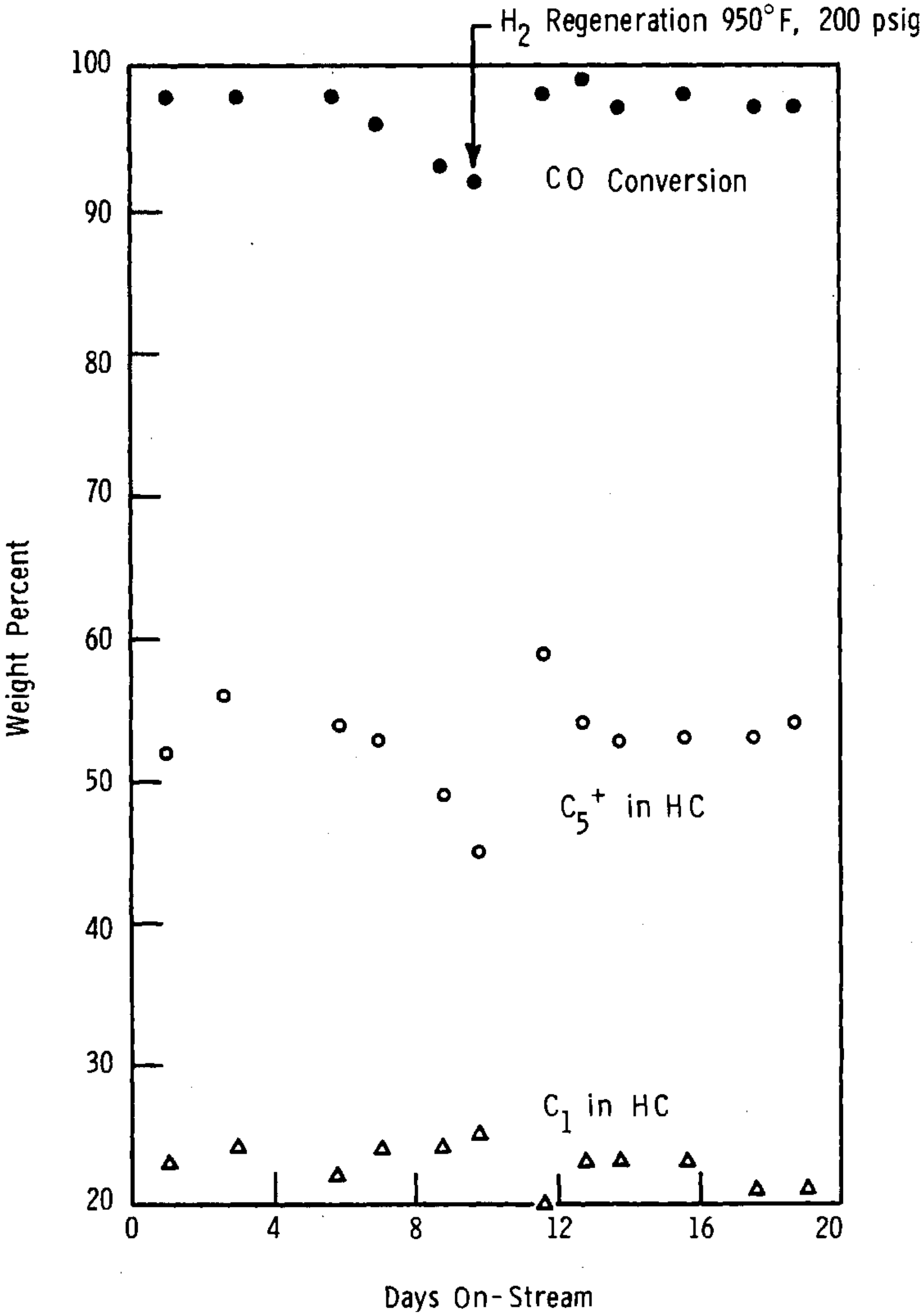


TABLE 13

PERFORMANCE COMPARISON OF CATALYST SG-A-1 WITH ITS PROTOTYPE

	Catalyst					
	Prototype			SG-A-1		
	Fresh		Regen.	Fresh		Regen.
Time, days	1	8	8	1	8	8
Conversion, %						
CO	98	97	97	98	94	97
H_2	57	57	59	56	50	58
Selectivity, %						
C_1	22	21	23	22	24	21
C_2	10	10	10	7	7	9
C_3	5	6	6	5	5	5
C_4	9	15	14	13	13	12
C_5^+	54	48	47	53	51	53

The pressure drop across the reactor bed increased only to about 30 psi by the end of the run from the 10 psi initially. Data for Run 225-10 are shown in Appendix B, Table B15.

a. Effect of Fresh Feed Composition

Selected data (Table 14) show the effect of H_2/CO ratio on conversion and product selectivities. The fresh feed compositions are 2.1 $H_2/CO/0.3$ CH_4 and 3.2 $H_2/CO/0.4$ CH_4 for balances 225-10-13 and -3, respectively. All other conditions are quite similar. The conversions are lower with the 2.1 H_2/CO feed. As expected the H_2O/CO_2 ratio in the product is affected drastically by the H_2/CO ratio in the feed. The total C_1, C_2, C_3, and C_4 selectivities are comparable. For example, the total C_2's are 10.5 and 11.6 weight percent, respectively, in 225-10-13 and 225-10-3. However, the ratios of paraffins to olefins at these carbon numbers are significantly different, probably because more hydrogenation occurs at the higher H_2/CO ratio. The C_5 fraction is 68% olefinic with 2.1/1 and only 39% olefinic with 3.2/1 H_2/CO. Nevertheless, in each case the C_5 olefins are rich in methylbutenes (Table 15).

The composition of the recycle gas is strongly dependent on the H_2/CO ratio of the fresh feed. The H_2/CO molar ratios of the recycle gases in 225-10-13 and -3 are 2.9 and 15.6/1, respectively. At high recycle ratios, such as 9/1, the composition of the gas entering the catalyst bed resembles the recycle gas rather than the fresh feed composition.

Effect of Fresh Feed and Recycle on Combined Gas Composition

Composition	$H_2/CO/CO_2/CH_4$/Other	
	225-10-13	225-10-3
Fresh Feed	2.1/1/0/0.3/0	3.2/1/0/0.4/0
Recycle Gas	3/1/0.4/0.9/0.2	16/1/1/3/1.8
Combined Gas	2.9/1/0.4/0.8/0.2	15/1/1/3/1.8

b. Effect of Space Velocity

The conversion of synthesis gas at three different space velocities, 3500, 2500 and 1500 GHSV, are summarized in Table 16. These experiments were all conducted with fresh feed of about 2 $H_2/1$ $CO/0.3$ CH_4. The other operating conditions were maximum temperature about 630°F, pressure 300 psig, and recycle ratio about 9/1. The four material balances (225-10-13, -17, -21, and -23) were taken at 13, 18, 22, and 24 days on stream, respectively.

TABLE 14

EFFECT OF H_2/CO RATIO ON CONVERSION OF SYNTHESIS GAS

Material Balance	225-10-13	225-10-3
Charge, moles $H_2/CO/CH_4$	2.1/1.0/0.3	3.2/1.0/0.4
GHSV, on Fresh Feed	3512	3563
Pressure, psig	300	300
Maximum Reactor Temperature, °F	629	633
Recycle Ratio, Mole/Mole Fresh Feed	9.4	8.7
CO Conversion, % wt	61.2	95.9
H_2 Conversion, % wt	45.8	77.9
Product Selectivity, % wt		
Hydrocarbons	31	44
H_2O	32	51
CO_2	37	5
Hydrocarbon Selectivity, % wt		
Methane	22	20
Ethane	8	11
Ethene	2	1
Propane	5	6
Propene	5	1
n-Butane	3	5
i-Butane	1	3
Butenes	8	3
C_5^+	46	50

TABLE 15

CHARACTERISTICS OF THE C_5 FRACTION

Balance 225-10	-13	-3
$H_2/CO/CH_4$	2.1/1/0.3	3.2/1/0.4
C_5, % wt		
Paraffin	32	61
Olefin	68	39
Olefin Selectivity, % wt		
1-Pentene	4	3
2-Pentenes	28	22
Methylbutenes	68	75

TABLE 16

EFFECT OF SPACE VELOCITY ON CONVERSION OF SYNTHESIS GAS

Days On Stream	13	18	22	24
Material Balance	225-10-13	225-10-17	225-10-21	225-10-23
Charge, moles $H_2/CO/CH_4$	2.1/1.0/0.3	2.2/1.0/0.3	2.2/1.0/0.3	2.1/1.0/0.3
GHSV, on fresh feed	3512	2339	1490	3478
Pressure, psig	300	300	300	300
Maximum Reactor Temperature, °F	629	640	634	629
Recycle Ratio, mole/mole fresh feed	9	10	10	9
CO Conversion, wt %	61	72	89	52
H_2 Conversion, wt %	46	60	81	40
Yields, wt %				
Hydrocarbons	18	25	33	16
H_2O	19	24	39	16
CO_2	22	21	16	19
Hydrocarbon Selectivity, wt %				
Methane	22	16	14	21
Ethane	8	8	8	9
Ethene	2	2	1	3
Propane	5	4	4	5
Propene	5	3	1	5
n-Butane	3	3	3	3
i-Butane	1	2	2	1
Butenes	8	6	3	9
C_5^+	45	58	65	44

A comparison of material balances 225-10-13 and 225-10-23 provides a measure of catalyst deactivation during eleven days of run 225-10. The hydrogen and carbon monoxide conversions decrease 15 and 13%, respectively. Also, the yields of hydrocarbons, water, and carbon dioxide are slightly lower in run 225-10-23. The hydrocarbon selectivities remain essentially unchanged. As expected, both hydrogen and carbon monoxide conversions increase with decreasing space velocity. The yields of hydrocarbons and water increase; carbon dioxide yield is not significantly changed.

Hydrocarbon selectivity is dependent on space velocity. The C_5^+ product increases about 43% as the space velocity (fresh feed) decreases from 3500 to 1500. Conversely, methane decreases by 39%; the other light paraffins are unaffected by changes in space velocity. Each of the light olefins decreases with decreasing space velocity.

Some further effects of space velocity on olefin selectivity are shown in Table 17. The olefin selectivities of C_2 and C_3 hydrocarbons decrease about 50% as the space velocity is reduced from 3500 to 1500. The corresponding C_4 and C_5 olefin selectivities decrease somewhat less. The pentene selectivities are somewhat dependent on space velocity; more methylbutenes are obtained at the lower space velocity. Comparing the data for material balances 225-10-13 and 225-10-23 in Table 17 further indicates that the olefin selectivities are not significantly changed by catalyst aging (over the eleven-day period).

The molar compositions of the recycle gases for the four material balances are summarized in Table 18. The H_2/CO ratios in the recycle gases at GHSV of 3500 and 1500 are 2.9 and 3.7, respectively. The methane concentration is double at the low space velocity. The compositions of the recycle gas at 13 and 24 days on stream are similar.

The Research octane numbers (R+0) of the raw gasoline products range from 83-87, and the leaded octanes (R+3) are 96-97. The bromine numbers are high (98-110), as expected for olefinic gasolines. The concentrations of oxygenates in the gasoline products are approximately 0.1-0.4 wt %. Simulated distillations (gas chromatography) indicate that gasoline volatility increases (i.e., boiling range distribution decreased) with decreasing space velocity.

c. Carbon Deposition and Reactor Plugging

After completion of run 225-10, a fresh batch of 100 cc of catalyst SG-A-1 (instead of 50 cc) was charged to the fixed bed reactor to achieve a larger catalyst bed (225-11). After only two days of operation, the pressure drop across the reactor

TABLE 17

EFFECT OF SPACE VELOCITY ON OLEFIN SELECTIVITY

Days On Stream	13	18	22	24
Material Balance	225-10-13	225-10-17	225-10-21	225-10-23
GHSV	3512	2339	1490	3478
Olefin Selectivity, wt %				
C_2	20	18	10	23
C_3	49	40	22	52
C_4	65	56	41	69
C_5	67	63	56	71
C_5 Olefin Selectivity, wt %				
1-Pentene	4	3	3	4
2-Pentene	28	23	21	27
Methylbutenes	68	74	76	70

TABLE 18

EFFECT OF SPACE VELOCITY ON RECYCLE GAS

Days On Stream	13	18	22	24
Material Balance	225-10-13	225-10-17	225-10-21	225-10-23
GHSV	3512	2339	1490	3478
Recycle Gas Composition, Mole %				
H_2	54	50	41	56
CO	18	14	11	21
CO_2	8	9	11	6
CH_4	16	22	31	14
Other	4	5	5	3

increased considerably, apparently because of partial plugging. The bench-scale unit was shut down, and the catalyst was removed from the reactor. A coke-like material was found in the last few inches of the catalyst bed.

In run 225-10, the inlet temperature of the reactor was generally maintained at 450-475°F and a recycle rate of about 10/1 was used to keep the maximum bed temperature at 640°F or less. Previous results from exploratory research in the micro units had suggested this was a reasonable maximum temperature. However, under these conditions in a fixed bed bench-scale unit, the temperature increased gradually over most of the catalyst bed, and reached a maximum of about 630°F only near the end of the bed. This type of temperature profile suggests that most of the conversion of synthesis gas was accomplished in the latter part of the catalyst bed.

Based on data on the effect of temperature during synthesis gas conversion in the micro units, it was decided to increase the inlet and maximum temperatures in the fixed bed pilot plant. Thus, another run (225-12) was started with a fresh batch of 100 cc of catalyst SG-A-1 in the pilot plant under the conditions listed below:

Fresh Charge	2 H_2/1 CO/0.3 CH_4
GHSV (of fresh feed)	1500
Pressure	300 psig
Reactor Inlet Temperature	500
Maximum Reactor Temperature	∿700°F
Recycle Ratio	∿10/1

In runs 225-10 and 225-11, a 7/8" ID reactor was employed. A 1-1/4" ID reactor was used in run 225-12. This reactor also plugged during the second day on stream. In contrast to previous runs (i.e., 225-10 and 225-11), the temperature profile of the catalyst bed in run 225-12 was considerably higher. The temperature increased more sharply in the bed from 500°F (inlet temperature) to a maximum of about 700°F. Thus, the conversion of synthesis gas could have occurred over most of the catalyst bed (about 4-1/2" long).

After the reactor plugged in run 225-12, an attempt was made to regenerate the catalyst by treatment with hydrogen at 900°F. The large pressure drop across the reactor (approximately 260 psi) was eliminated by this treatment, and another run (225-13) was started. In this run, the maximum temperature was limited to 650°F; other operating conditions were similar to those in run 225-12. Unfortunately, the reactor plugged again after a day on stream, and no material balances were obtained.

In view of the reactor plugging problems, a catalyst SG-A-2 with larger particles, but chemically identical to SG-A-1, was used in run 225-14, which was started under the following conditions:

Fresh Charge	2 H_2/CO/0.3 CH_4
GHSV (on fresh feed)	500
Pressure	300 psig
Reactor Inlet Temperature	500°F
Maximum Reactor Temperature	625°F
Recycle Ratio	∿10/1

It was hoped that these milder conditions with the larger particle catalyst would eliminate or reduce plugging of the reactor.

After five days on stream, the space velocity (GHSV on fresh feed) was increased to 1000. The pressure drop across the reactor increased during the seventh day indicating the formation of a plug. The run (225-14) was then interrupted, and the catalyst was regenerated in situ with hydrogen at 900°F. The conversion of synthesis gas was then continued with the regenerated catalyst under the same conditions listed above (i.e., fresh feed GHSV of 500). The catalyst did regenerate (Table 19), however, another plug formed after several days.

At this point it was decided to remove catalyst SG-A-1 from the process development studies. The catalyst did run continuously for 24 days (225-10) without plugging due to carbon deposition. However, most of this run was made with a 3 H_2/CO fresh feed using the small diameter reactor. The change to the larger diameter reactor (225-12 through 14), the use of a fresh feed of lower H_2/CO ratio, and achieving an improved reactor temperature profile aggravated the plugging problem.

Catalyst SG-A-1 ran for fifty continuous days in a micro reactor unit with 2H_2/CO synthesis gas and a good reactor temperature profile. However, the micro reactor is a heat loss unit of relatively small diameter. Furthermore, in micro reactor experiments, the catalyst is diluted with quartz which could prevent cementation of catalyst particles.

3. Theoretical Studies in Support of Fixed Bed Process Development

a. Thermodynamics of Carbon Formation

The fixed bed, bench-scale unit encountered operational difficulties with catalyst SG-A-1 due to repeated reactor plugging. A change to a larger sized catalyst of the same chemical composition, designated SG-A-2, resulted in the same problem. Among

TABLE 19

REGENERATED SG-A-2 CATALYST

On-Stream Time (Hr)	173	210	235
Material Balance		225-14-10	225-14-11
Charge ($H_2/CO/CH_4$)	REGENERATION WITH H_2 AT 900°F	2.0/1.0/0.3	1.9/1.0/0.3
GHSV (on fresh feed)		498	493
Pressure (psig)		300	300
Max. Reactor Temp. (°F)		637	638
Recycle Ratio (mole/mole fresh feed)		15.2	17.0
CO Conversion (Wt. %)		98.4	96.4
H_2 Conversion (Wt. %)		95.0	93.9
Yields (Wt. %)			
Hydrocarbons		39.9	36.2
H_2O		50.9	44.0
CO_2		7.2	15.9
Hydrocarbon Selectivity (Wt. %)			
Methane		15.8	13.1
Ethane		4.7	4.2
Ethene		0.2	0.2
Propane		4.5	4.0
Propene		0.2	0.2
n-Butane		3.3	3.1
i-Butane		6.7	6.2
Butenes		0.8	0.8
C_5^+		63.9	68.1
Olefin Selectivity (Wt. %)			
C_2		3.3	4.5
C_3		4.4	5.8
C_4		7.3	7.8
C_5		13.6	18.2
C_5 Olefin Selectivity (Wt. %)			
Pentene-1		1.3	2.1
Pentene-2		17.2	20.1
Methylbutenes		81.5	77.8
Material Balance			
C_5 Selectivity (Wt. %)			
i-Paraffins		61.1	57.9
n-Paraffins		24.3	23.1
Olefins		13.6	18.2
Cyclic C_5		0.9	0.7
C_6^+ Selectivity (Wt. %)			
i-Paraffins		30.2	31.7
n-Paraffins		8.1	8.1
Olefins		15.9	20.9
Cyclic C_5		2.4	1.3
Cyclic C_6		0.8	0.8
Aromatics		42.6	37.1
Recycle Gas Composition (Vol. %)			
H_2		17.1	17.0
CO		3.6	5.7
CO_2		10.8	18.4
CH_4		60.5	52.4
Other		8.0	6.5

the possible causes for plugging, the most prominent is carbon formation, which can be described by the following reaction paths:

$$2\,CO \rightleftharpoons CO_2 + C \qquad (A)$$

$$CO + H_2 \rightleftharpoons H_2O + C \qquad (B)$$

$$CH_4 \rightleftharpoons 2H_2 + C \qquad (C)$$

Equation (A), known as the Boudouard reaction, has been the subject of many investigations. Dry et al.(28) studied this reaction at temperatures between 285 and 338°C using fused magnetite promoted by K_2O. They observed a ten-fold change in the rate of carbon formation over this temperature range (activation energy 27 kcal/mole). Tramm(27) used this information to determine the allowable reactor diameter for a heat-exchanger type, fixed bed reactor similar to the Arge used at SASOL. Too large a diameter will result in a high temperature at the center of the reactor and cause excessive carbon formation.

Equation (B) defines the reaction proposed by Kryukov et al.(29) as an alternative for carbon formation. The reverse reaction in Equation (C), called hydrogasification, is probably responsible for the reactor unplugging by hydrogen as observed in the bench-scale unit with catalyst SG-A-1. This carbon removal reaction suggests that carbon formation could be avoided by increasing the hydrogen content of the feed gas. The work by Pichler and Merkel(30) at about 400°F strongly indicates this possibility (Table 20). Unfortunately no similar study at higher temperatures has been reported.

To assess the possibility of excessive carbon formation during synthesis gas conversion, a thermodynamic study was made to evaluate the potential of carbon formation under equilibrium conditions. Figure 18 shows the temperature dependence of the equilibrium constants for the three carbon formation reactions. The equilibrium constants of the first two reactions (A and B) increase drastically with temperature while that of third reaction (C) decreases. Using these constants, Equations A, B and C can be solved simultaneously to determine whether a reaction mixture will lead to carbon formation when approaching equilibrium. A carbon formation region can thus be defined on a C-H-O atomic composition chart such as Figure 19, in which the two curves represent the boundaries of carbon formation region for 400 and 600°F at 400 psia. Above the boundary, carbon formation is thermodynamically favorable provided all the three reactions are feasible. As can be seen, over the temperature range from 400 to 600°F where synthesis gas conversion with SG-A and -B types of catalysts are usually run, there is only a slight shift of the carbon formation region. The pressure effect is also small as shown in Figure 20 where carbon formation boundaries for 30 and

TABLE 20

FORMATION OF FREE CARBON AS A FUNCTION OF SYN-GAS COMPOSITION[a,b]

Experiment No.	Temperature, °C	Days of Operation	H_2/CO in Syn. Gas	Contraction Percent	Free Carbon g per 10 g Fe
1	190	0	4:1	-	2.21
	200[c]	60	4:1	30	1.88
2	210	0	2:1	-	2.21
	225[c]	151	2:1	35	2.51
3	235	0	2:3	-	1.85
	240[c]	112	2:3	50	3.92

(a) Reproduced from Reference (30).

(b) Alkali promoted Fe catalyst was used.

(c) Temperature required to maintain constant conversion.

Figure 18

EQUILIBRIUM CONSTANTS KP

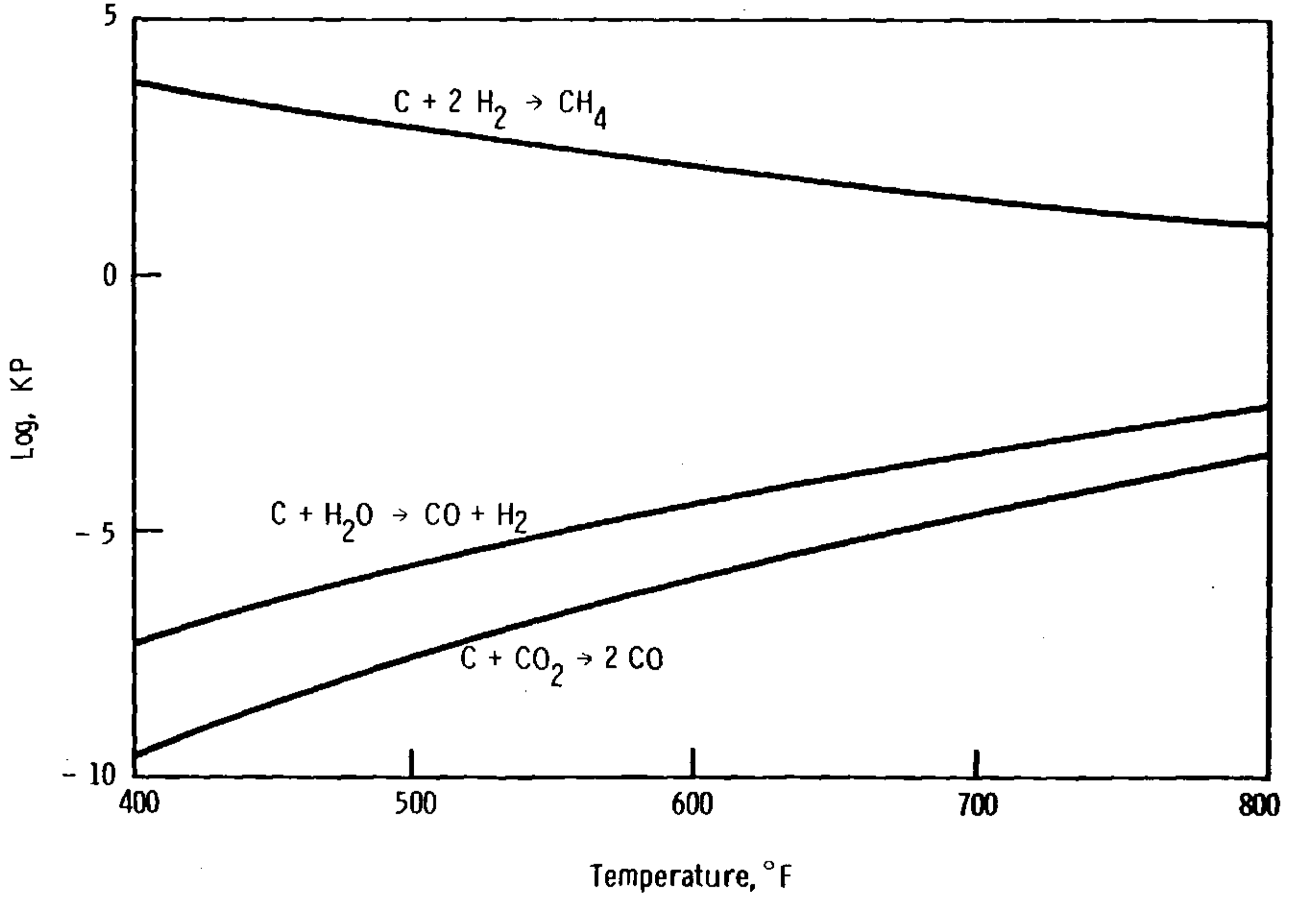


Figure 19

CARBON FORMATION EQUILIBRIUM ISOTHERMS AT 400 psia

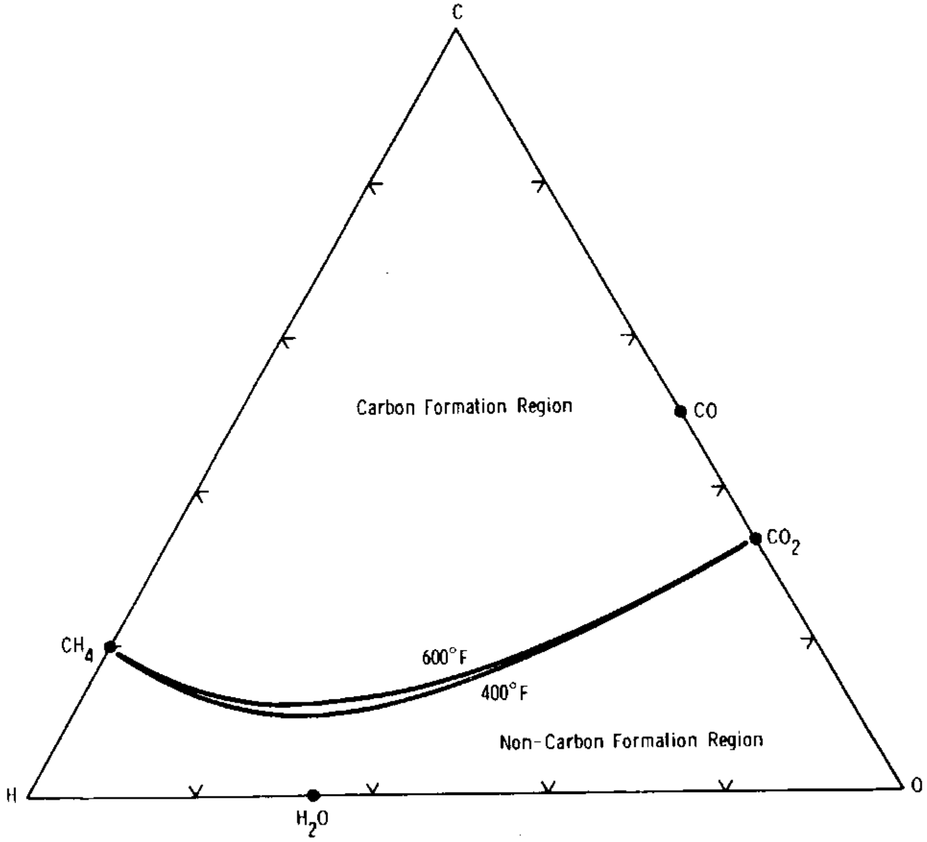
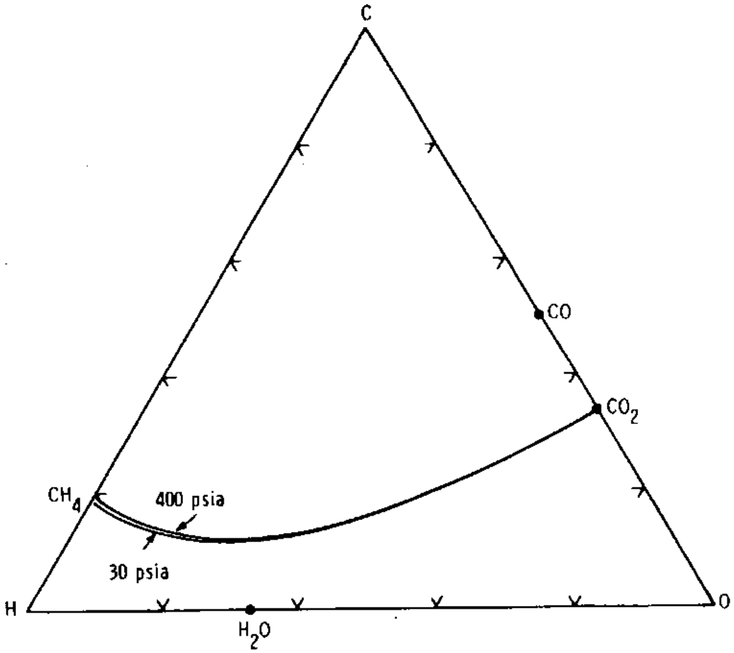


Figure 20

CARBON FORMATION EQUILIBRIUM ISOTHERMS AT 600°F



400 psia at 600°F are compared. The SG-C type catalysts were used at more severe conditions around 800°F and 1200 psia. Carbon formation at these conditions is compared with that at 400°F and 400 psia in Figure 21. The potential carbon formation region is reduced moderately at such high temperature and pressure.

Seven interesting syn gas mixture compositions are noted in Figure 22, together with the equilibrium carbon formation boundaries at 400°F and 600°F and 400 psia. Syn gas compositions of 2 H_2/CO and 3 H_2/CO/2 CO_2 were used in the micro reactor experiments with catalyst SG-A-1. Based on Figure 22, carbon formation is expected to occur with these feed compositions. Probably due to the dilution of catalyst bed with inert particles, these experiments did not result in reactor plugging. A hydrogen rich gas feed was used at the beginning of the bench-scale unit run 225-10 (material balance 1 as shown in Figure 22) and the combined feed composition of that balance was outside of the carbon formation region. No reactor plugging was observed. In a later balance of the same run (material balance 23 in Figure 22), a feed composition change resulted in a shift into the carbon formation region. Near the end of this run, there were indications of reactor plugging. This plugging may be due to carbon formation. The three feed compositions given in Table 18 are also included in Figure 22. The experimental observations are consistent with the thermodynamics. The feed composition for the SASOL Synthol Operation (fluidized bed) is also included. It is within the potential carbon formation region and carbon formation has been observed(10).

Figure 21

THERMODYNAMIC CARBON FORMATION ISOTHERMS

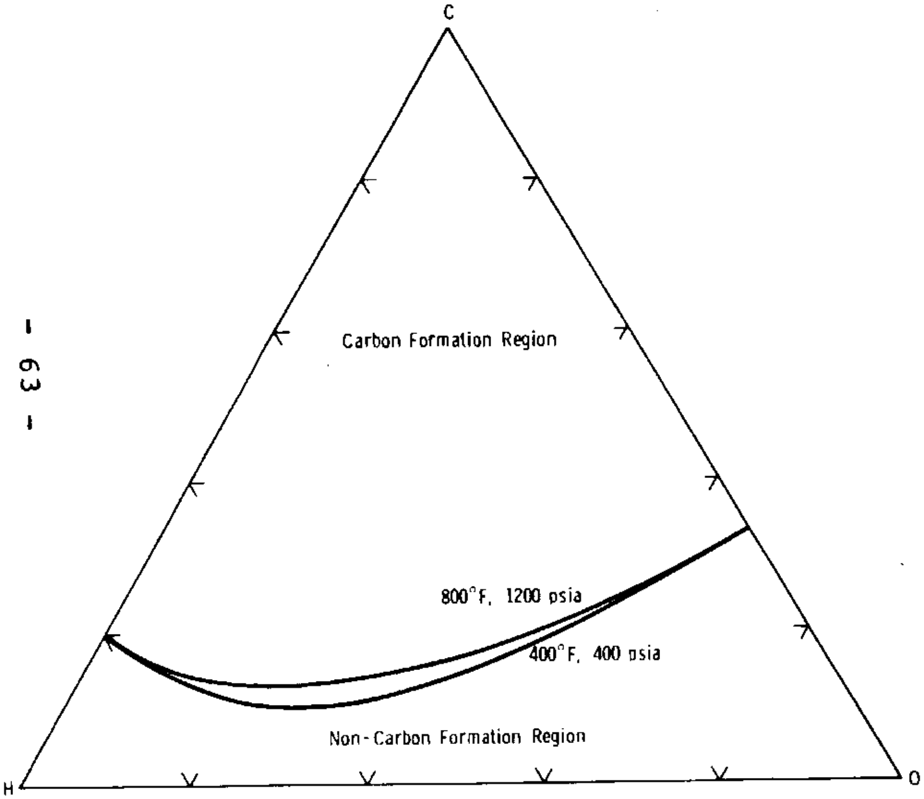


Figure 22

CARBON FORMATION ISOTHERMS (400 psia) AND SOME PERTINENT FEED COMPOSITIONS