B. Coal to Gasoline - Mobil Direct Conversion Process

A conceptual design for an integrated coal to gasoline plant using Mobil's direct conversion technology is illustrated by the block flow diagram in Figure 7. Various types of gasifiers may be used. Tables 1 and 2 list many of the gasifiers currently being studied, along with the composition of the synthesis gases produced. Note, most of these gasifiers yield synthesis gas with a H_2/CO ratio of about one or less. A direct conversion catalyst without water-gas shift activity, requires synthesis gas having a high H_2/CO ratio. For this type catalyst, if the candidate gasifier yields low H_2/CO synthesis gas, a shift converter is necessary.

For a direct conversion catalyst with water-gas shift activity, the shift will occur in the direct conversion reactor. The steam obtained on carbon monoxide reduction is used to produce the needed hydrogen. For this type of catalyst, a synthesis gas with a H_2/CO ratio of about one is preferred for the following:

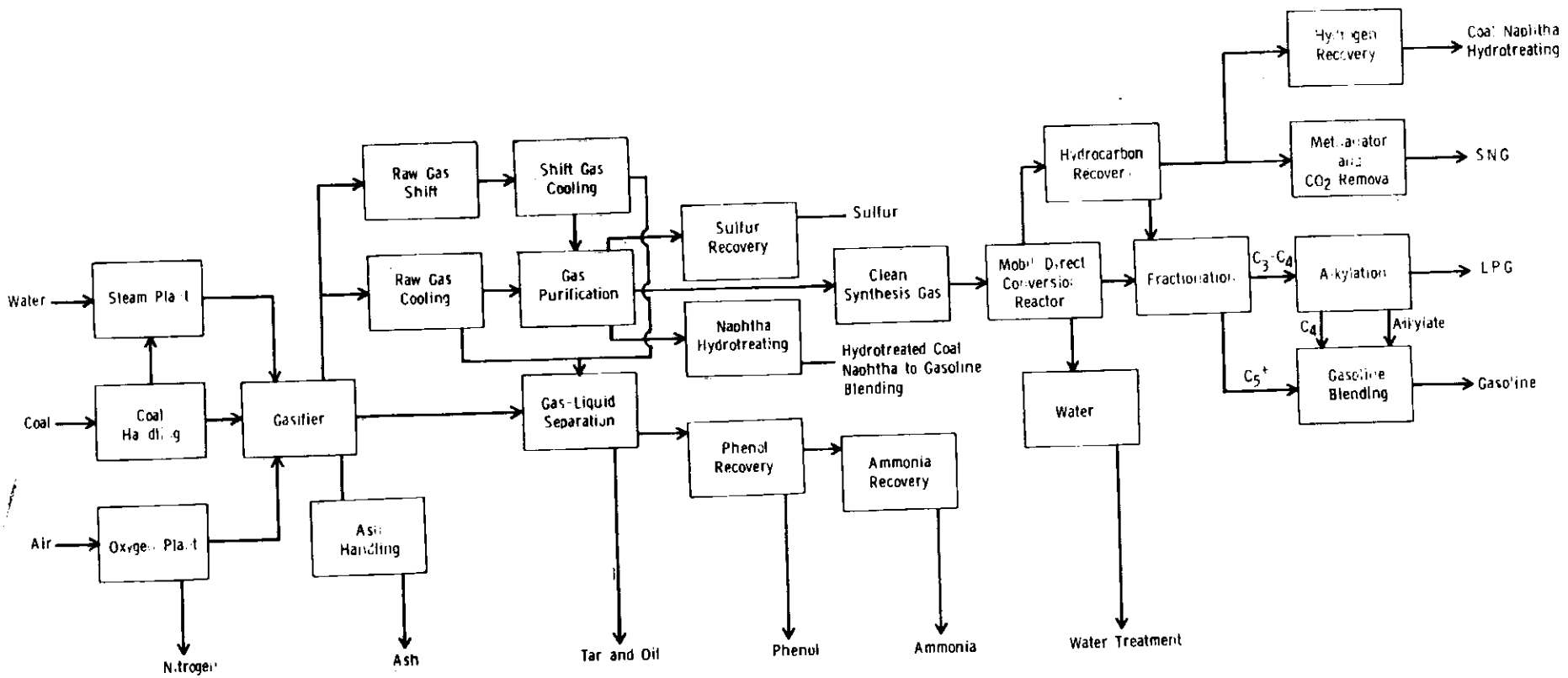
- Many of the potentially cheaper gasifiers produce low H_2/CO gas.
- Small or no shift reactor required, resulting in large savings on steam consumption and capital investment.

The portion of Figure 7 downstream of the clean synthesis gas represents the Mobil technology. The synthesis gas is converted to a product low in oxygenates and in which essentially all of the hydrocarbons are C_{11} or less. That is, nothing boiling higher than gasoline is produced. The hydrocarbon product is separated in a conventional gas plant. Three fractions are obtained, a light gas (H_2, CO, CO_2 and C_2^- hydrocarbons), a C_3-C_4 fraction, and C_5^+ gasoline. The light gas may be used directly as fuel gas or upgraded to SNG (synthetic natural gas) after methanation and carbon dioxide removal. The C_3 and C_4 olefins and the isobutane, produced in the direct conversion unit, are upgraded in a conventional alkylation unit to high quality C_5^+ gasoline. The unreactive propane and butane go to LPG (liquified petroleum gas). The excellent selectivity and quality of the product from the direct conversion unit make downstream processing extremely simple.

The Mobil direct conversion reactor is envisioned as a fluid bed reactor using low gas recycle for heat removal and excellent gas-solid phase mixing.

Figure 7

CONCEPTUAL INTEGRATED COAL TO GASOLINE PLANT USING MOBIL DIRECT CONVERSION TECHNOLOGY



C. Comparison of Mobil Direct Conversion and Fischer-Tropsch Processes

1. Comparison of Products Made Over Fischer-Tropsch and Mobil Developmental Catalysts

Mobil has discovered a series of catalysts capable of converting synthesis gas directly into high octane gasoline. Unlike a conventional Fischer-Tropsch catalyst, which yields a low octane number gasoline in low yield, the Mobil catalysts make only trace amounts of fuel oil and undesirable oxygenates. The comparison in Table 4A clearly distinguishes between a Fischer-Tropsch product and those obtained over three Mobil proprietary catalysts. The Fischer-Tropsch product is typical of that obtained from a commercial Synthol unit as operated by SASOL in South Africa(24); the Mobil products were made in a laboratory reactor. Note the improved gasoline yield. The Mobil catalyst, by limiting the size of the hydrocarbons produced to about C_{11}, and by eliminating the oxygenates, markedly improves the selectivity to gasoline.

Note also the higher quality of the Mobil products as measured by their octane numbers, 92 and 87 clear research octane number (R+0), versus only 55 for the Fischer-Tropsch product. This octane increase is due primarily to molecular structure differences of the gasoline components. In general at high carbon monoxide conversion, for either Fischer-Tropsch or Mobil derived products from catalysts SG-A-1 and SG-B-2, there is an increase in olefin content with increasing carbon numbers two through five. Detailed compound analyses of the C_6^+ fraction from Fischer-Tropsch, SG-A-1 or SG-B-2, are extremely complicated because of the large number of isomeric olefins present. At carbon numbers greater than five, Synthol naphtha, a Fischer-Tropsch product, shows a constant acyclic olefin content of about 70-75 weight percent(25). The remaining product is mostly paraffinic with aromatics accounting for only about five weight percent at carbon numbers 7 and 8. In contrast a typical C_6^+ naphtha fraction, from a SG-A-1 catalyzed synthesis gas converion contains cyclic olefins and 15-20% alkybenzenes.

Detailed analyses, however, of the total naphtha fractions are not needed to distinguish the products nor rationalize the difference in octane number between Fischer-Tropsch and Mobil products. Inspection of the C_5 fraction shows both products contain about 70 percent total olefin. The Fischer-Tropsch olefins are largely 1- and 2-pentenes while those from catalysts SG-A-1 and SG-B-2 are about 80 percent methylbutenes (Table 4B). It is assumed these same structural differences persist at higher carbon numbers along with the formation of aromatics and cyclo-olefins as SG-A-1 and SG-B-2 products. Thus, analysis of the C_5 fraction and measurement of the 90% overhead boiling point are the only tests required for an excellent indication of product quality.

TABLE 4A

SELECTIVITIES OVER FISCHER-TROPSCH AND MOBIL CATALYSTS

Selectivity, wt %	Fischer-Tropsch[24]	Mobil Catalysts		
		SG-A-1	SG-B-2	SG-C-1
Light Gas (C_1+C_2)	23	29	18	7
LPG (C_3+C_4)	29	16	12	12
Gasoline (C_5-400°F)	34	56	70	76
Fuel Oil	5	Nil	Nil	<5
Oxygenates	9	<1	<1	<1
Gasoline R+0	55*	92	87	**

*Estimated from composition.
**Selectivities to aromatics in the C_5^+ naphtha are as high as 85%.

TABLE 4B

SELECTIVITIES IN THE C_5 FRACTION

C_5 Selectivity, wt %	Synthol	Mobil Catalysts	
		SG-A-1	SG-B-2
Paraffin	27	31	29
Olefin	73	69	71
Iso C_5 Olefins			
1-Pentene	27	3	2
2-Pentene	35	18	17
Methylbutenes	18	79	81

2. Process and Economic Comparison

A process and economic comparison indicates that the Mobil Direct Conversion is potentially 20% cheaper than Fischer-Tropsch technology for making gasoline from coal. The study was made under DOE Contract No. EF-76-C-01-2447, "Research Guidance Studies to Assess Gasoline from Coal by Methanol to Gasoline and SASOL Type Fischer-Tropsch Technologies." All of the processes used in the study are commercially proven with the exception of Mobil's Direct Conversion and Methanol to Gasoline.

The Lurgi Dry Ash Gasifier was adopted for the comparison. It yields, and Fischer-Tropsch requires, a synthesis gas with a high H_2/CO ratio. A SGF-A type catalyst in the Mobil Direct Conversion can utilize synthesis gas of low H_2/CO ratio (about one). The potential advantage of the Mobil route over Fischer-Tropsch would be greater than 20% had a low H_2/CO ratio producing gasifier been used. High H_2/CO ratio gas is more expensive to produce than low H_2/CO ratio gas. High H_2/CO ratio gas requires more water-gas shift with the accompanying larger steam consumption and larger capital investment.

A schematic for the preparation of clean synthesis gas from coal is shown as part of Figure 7. For convenience in comparing Mobil's Direct Conversion with Fischer-Tropsch, the upstream processing and the amount of coal processed are identical for both cases. The conversion of synthesis gas to gasoline using Fischer-Tropsch is shown as Figure 8A. Nine upgrading steps are required to improve the yield of gasoline and to provide the quality needed to satisfy U.S. market specifications. In contrast to this complex upgrading scheme, the product from the Mobil Direct Conversion reactor requires only two upgrading steps (Figure 8B).

The product yield data for the Fischer-Tropsch process are from the literature(26). Target yield data for the Mobil Direct Conversion were based on micro reactor unit experiments which were later closely confirmed in the fluid, bench-scale unit (Run 225-42-3) using catalyst SGF-A-3. The final product yield comparison for the two processes are shown in Table 5. The Mobil route has a 32% higher gasoline yield and about a 4% higher thermal efficiency. The higher thermal efficiency is mainly due to processing simplicity.

The capital investments for both processes are given in Table 6. The Mobil route shows substantially lower investment for gasoline production, again attributable to processing simplicity. The potential saving on total investment is $150MM. The economic basis for the comparison is October, 1977 with the plant located at a Wyoming mine. Table 7 summarizes the gross and net operating costs for both processes. The gasoline production costs at the plant gate based on both equity financing (12% discounted cash flow) and utility financing (75/25 Debt/Equity Split, 9% interest on debt) are:

Financing	Cents/Gallon	
	Fischer-Tropsch	Mobil Direct Conversion
Equity	134	106
Utility	97	76

Figure 8A

FISCHER-TROPSCH ROUTE

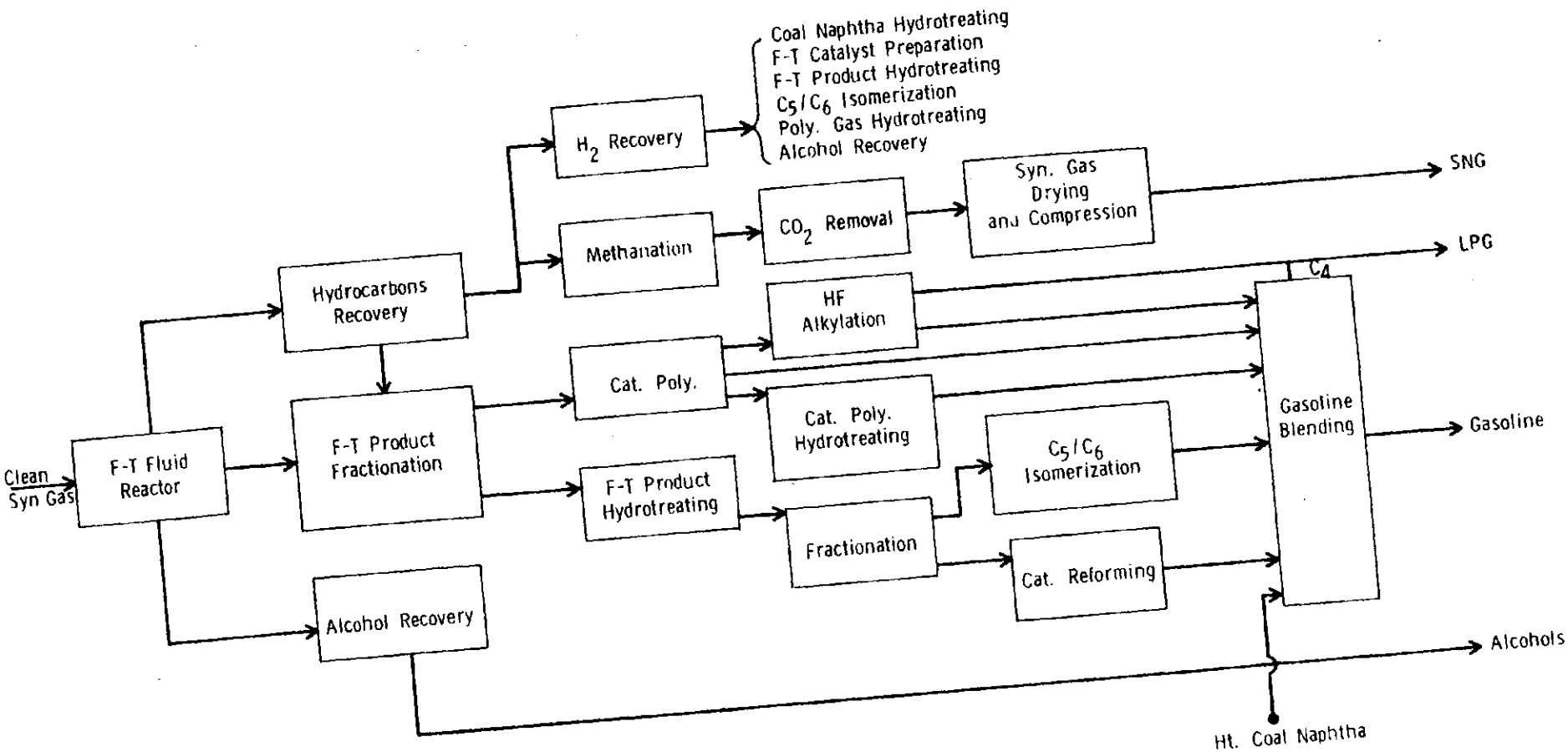


Figure 8B

MOBIL DIRECT ROUTE

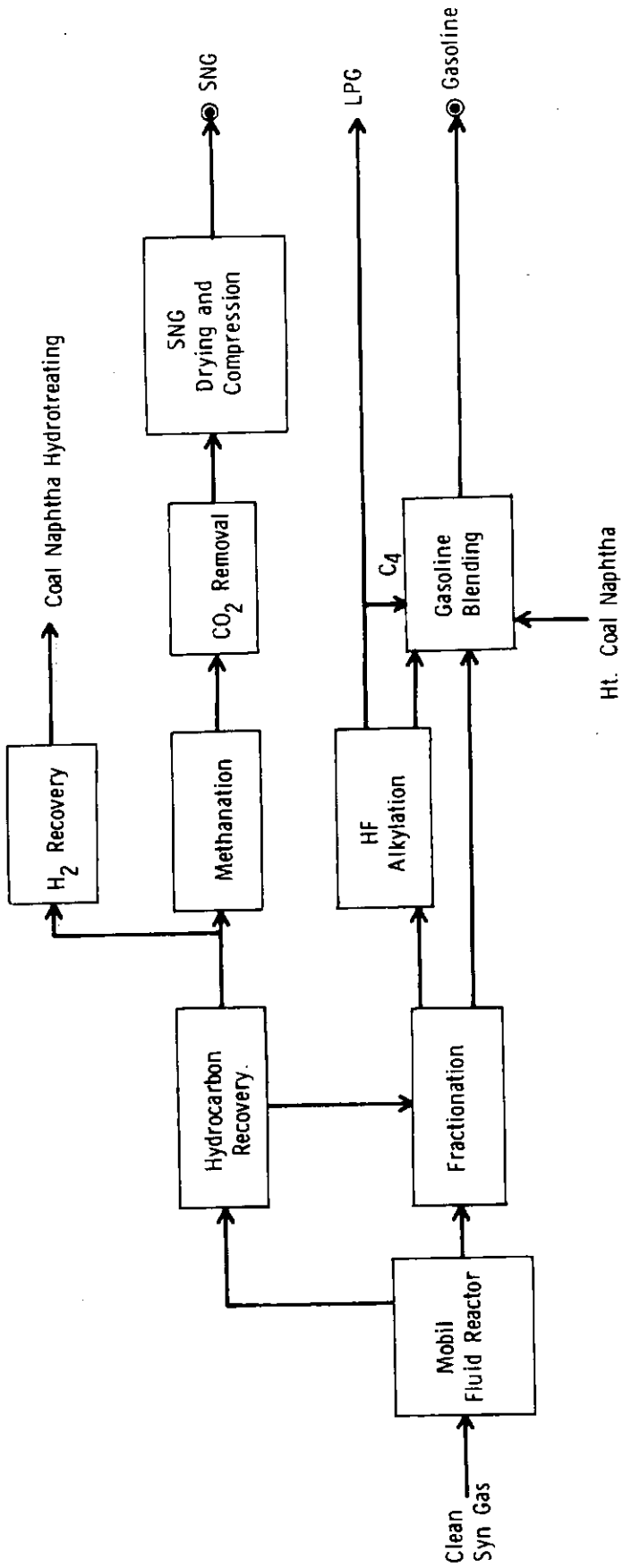


TABLE 5

PRODUCT YIELD COMPARISON

(Basis: One standard ton of dry ash free coal)

	Fischer-Tropsch Route	Mobil Route
Gasoline, bbl	0.733	0.968
Diesel, bbl	0.125	-
Heavy Fuel Oil, bbl	0.034	-
SNG, MSCF	9.352	10.265
C_4, bbl	0.008	-
C_3, bbl	0.060	0.093
Alcohols, ST	0.014	-
Sulfur, ST	0.003	0.003
Anhydrous NH_3, ST	0.006	0.006
Electricity, KW	0.378	-0.056
Process Thermal Efficiency (HHV)	57.8	61.8

TABLE 6

INVESTMENT COMPARISON

(October, 1977, Wyoming)

Basis: MM$

	Fischer-Tropsch Route	Mobil Route
Depreciable Capital		
Process Units		
Gasification, et al	430	430
Gasoline Production	180	119
SNG Production	26	26
Subtotal	636	575
Offsite Units		
Oxygen Facilities	110	110
Steam Facilities	148	139
Water Facilities	73	73
Catalyst Preparation	28	0
Other	145	148
Subtotal	504	470
Infrastructure	46	46
Field Construction	1,186	1,091
Engineering & Design	152	139
Other Project Costs	270	248
Estimating Allowance	242	222
Miscellaneous	15	15
Total	1,865	1,715
Expense Capital		
Total	22	19

TABLE 7

COMPARISON OF GROSS AND NET OPERATING COSTS

(October, 1977, Wyoming)

Basis: MM$/Year

	Fischer-Tropsch Route	Mobil Route
Raw Materials	65	64
Catalysts and Chemicals	6	4
Purchased Water	1	1
Labor		
Process Operating Labor	10	8
Maintenance Labor	33	30
Administration and General Overhead	26	23
Supplies		
Operating	3	2
Maintenance	22	20
Local Taxes & Insurance	50	46
Total Yearly Gross Operating Cost	216	198
Byproduct Credits	-6	-6
Total Net Yearly Operating Cost	210	192

D. Fixed Bed Studies with Developmental Catalyst SG-A-1

1. Task 1 - Exploratory Process Research

Micro reactor process variable studies with developmental catalyst SG-A-1 were made using three different feed compositions:

- $2H_2/CO$
- $3H_2/CO/2CO_2$
- H_2/CO

The first, $2H_2/CO$, is the stoichiometric composition for the reaction,

$$CO + 2H_2 \longrightarrow (CH_2) + H_2O$$

The second, $3H_2/CO/2CO_2$, is typical of that obtained on combining $2H_2/CO$ as fresh feed with recycle gas (no hydrocarbons) from the synthesis gas conversion unit. The H_2/CO feed approximates the synthesis gas composition (without shift) available from many of the gasifiers currently being studied (Tables 1 and 2). Studies with synthesis gas of H_2/CO composition were limited by the decision, made while this work was in progress, to concentrate on fluid catalysts. Data for the process variable studies are summarized in Appendix B (Tables B1 through B10). Check experiments made during the studies indicate some catalyst aging occurred during runs at the more severe conditions. However, this aging was not felt to affect the trends or the conclusions drawn from the experiments. Aging and regeneration studies on developmental catalyst SG-A-1 are summarized in Tables B11 - B14 of Appendix B.

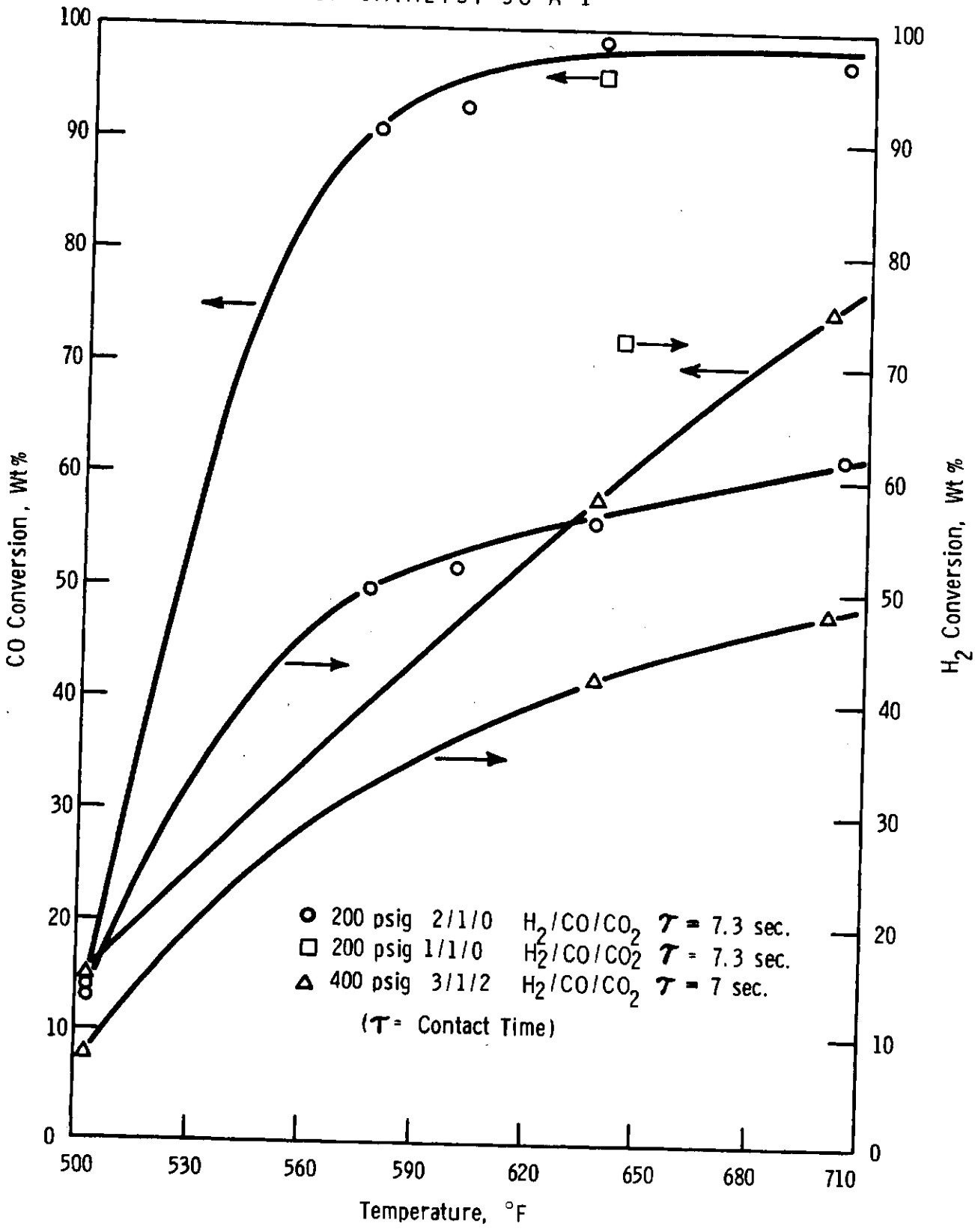
The contact time, as defined for these and all ensuing studies, is the reciprocal space velocity calculated at system temperature and pressure. Volumetric gas hourly space velocities (GHSV) were calculated at standard conditions of one atmosphere and 60°F.

a. Activity of Catalyst SG-A-1

The effects of temperature on the activity of catalyst SG-A-1 were determined at similar contact times and carbon monoxide GHSV using all three charge stocks (Tables B1 and B2). The results are plotted in Figure 9 and show excellent activity for converting both $2H_2/CO$ and H_2/CO. The conversion of carbon monoxide with these charge stocks is greater than 90% at 575°F and exceeds 95% at temperatures of 600°F or higher. The catalyst is apparently less active for converting either hydrogen or carbon monoxide when $3H_2/CO/2CO_2$ is used. As shown below, the activity approached 90% CO conversion with this charge stock at more optimum conditions.

Figure 9

EFFECT OF TEMPERATURE ON ACTIVITY
OF CATALYST SG-A-1



The effect of reaction pressure (Tables B3 - B6) is depicted in Figure 10. Comparisons at each pressure are made at the same carbon monoxide GHSV using a peak temperature of 635°F. Thus, the shorter contact time accounts for the lower CO and H_2 conversions when charging $3H_2/CO/2CO_2$. With $2H_2/CO$ and H_2/CO as feed this catalyst converts over 95% of the CO.

A more detailed look at the effect of pressure as well as contact time while charging $3H_2/CO/2CO_2$ is given in Tables B7 - B9 and plotted in Figure 11. At 50 and 100 psig the activity is quite low, but could be improved by operation at undesirably low feed rates. Increasing the contact times at 200, 300 and 400 psig gave CO conversions approaching 90%. The activity at 300 psig was lower (constant contact time) than at 200 psig. This lower activity with higher pressure can be illustrated by,

Time Needed for 80% CO Conversion

psig	200	300	400
Contact Time, sec.	4.8	10.6	17.6

These are real losses in activity (at equal contact times) as the extent of the water gas shift reaction is essentially constant at these pressures.

The activity of SG-A-1 can, thus, be maximized by adjusting pressure toward 200 psig and increasing contact time and temperature.

b. Selectivity

In addition to high activity, process conditions were selected such that catalyst SG-A-1 would produce a good yield of high olefinic C_5^+ gasoline. Secondary reactions such as cracking and hydrogenation were undesirable.

In Figure 12 is shown the effect of temperature on hydrocarbon selectivity for the $3H_2/CO/2CO_2$ charge. At temperatures of 600°F or higher, the $3H_2/CO/2CO_2$ charge yields more C_5^+ and C_3+C_4 hydrocarbons and less C_1+C_2 than the $2H_2/CO$ charge (Table 8). Selectivities at 700°F are still sufficiently high to permit processing at this temperature level, although, the C_5^+ content is a maximum between 630-640°F. This also happens to be the temperature level needed to get good conversion of the $3H_2/CO/2CO_2$ charge.

Variation of selectivity with pressure is given in Figure 13 for the $3H_2/CO/2CO_2$ charge at 635°F. Again as shown in Table 9, 200 psig is the optimum pressure for the $2H_2/CO$ charge, whereas $3H_2/CO/2CO_2$ gave little change in selectivities at 200 and 400 psig.

Figure 10

EFFECT OF REACTION PRESSURE ON ACTIVITY
OF CATALYST SG-A-1 AT 635°F

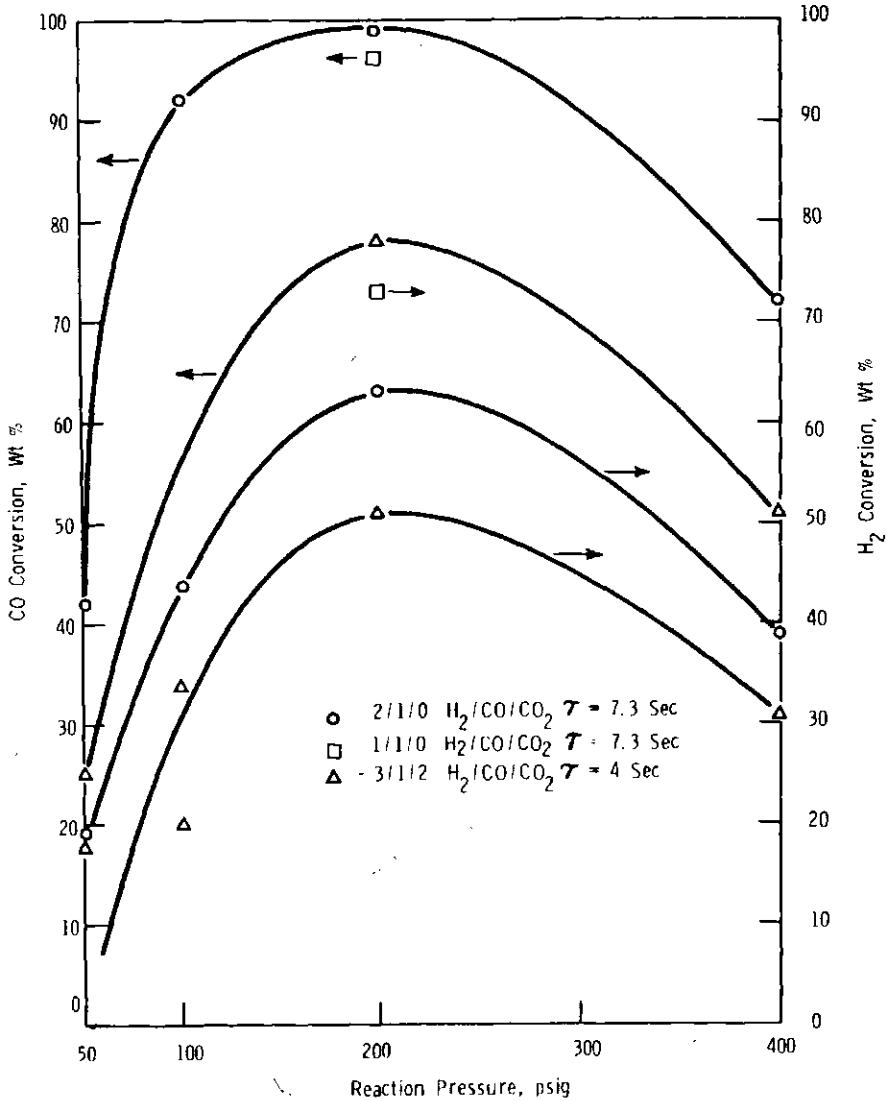


Figure 11

EFFECT OF CONTACT TIME ON ACTIVITY AT 635°F
WITH 3/1/2 $H_2/CO/CO_2$

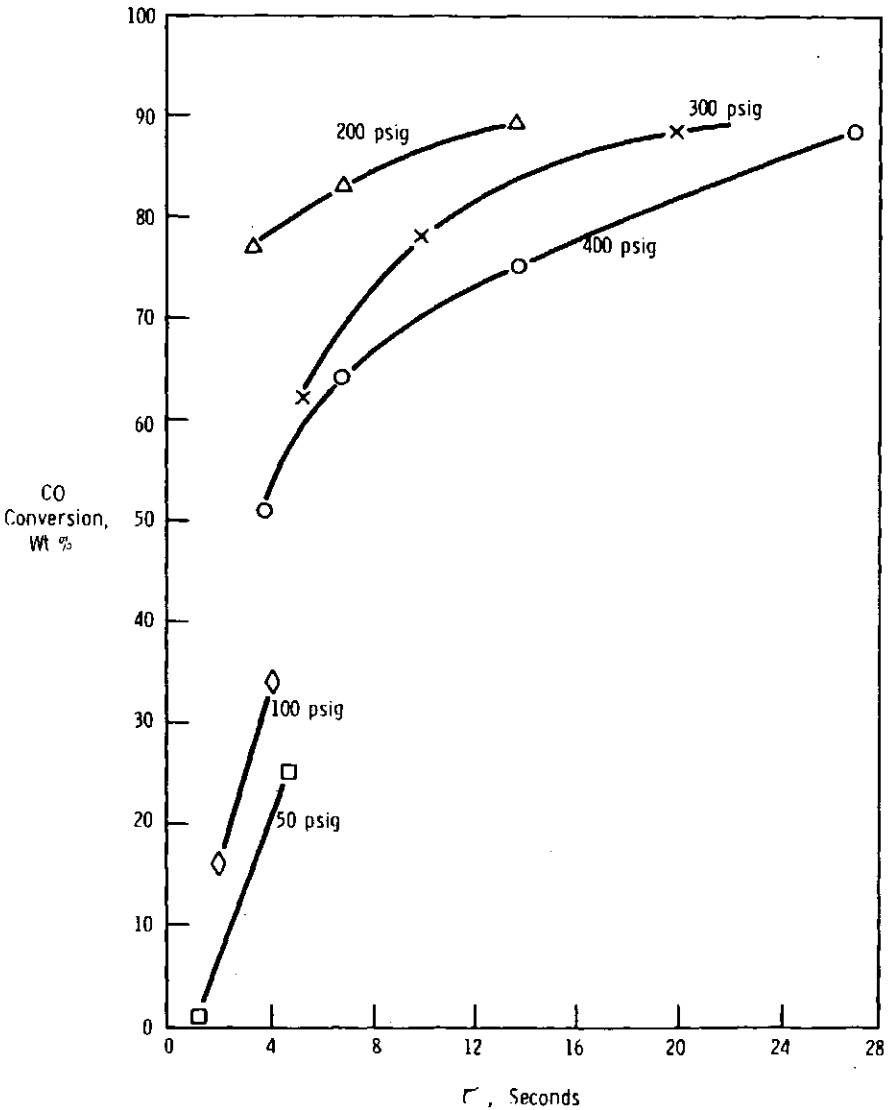


Figure 12

EFFECT OF TEMPERATURE ON HYDROCARBON SELECTIVITY
FOR CATALYST SG-A-1

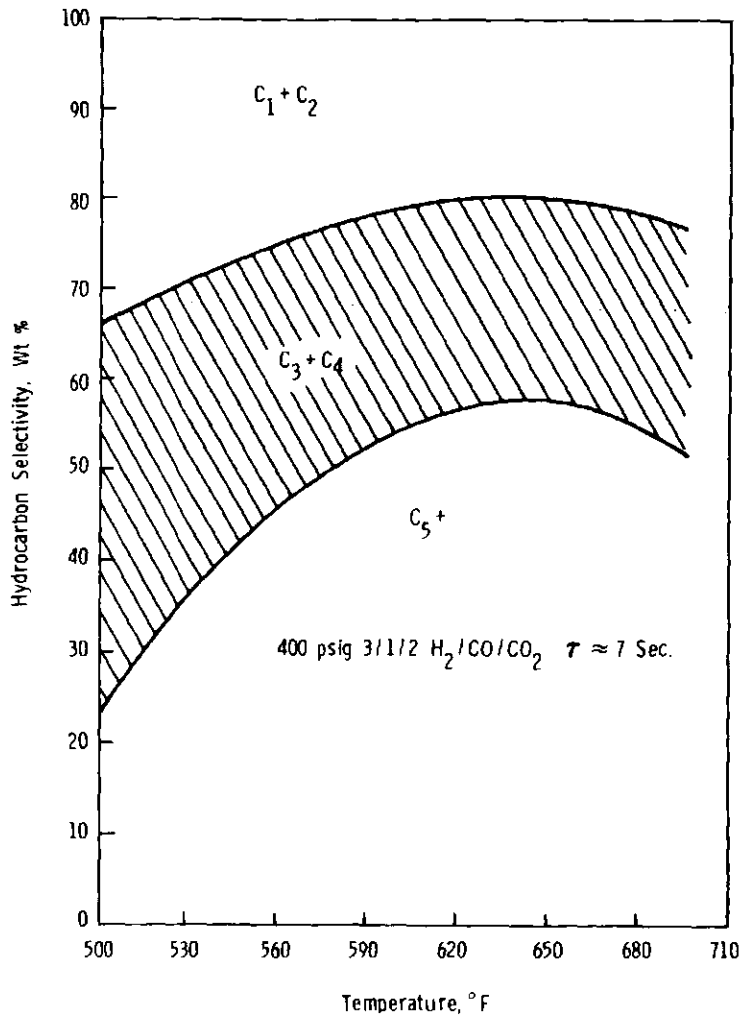


Figure 13

EFFECT OF REACTION PRESSURE ON HYDROCARBON SELECTIVITY
FOR CATALYST SG-A-1 AT 635°F

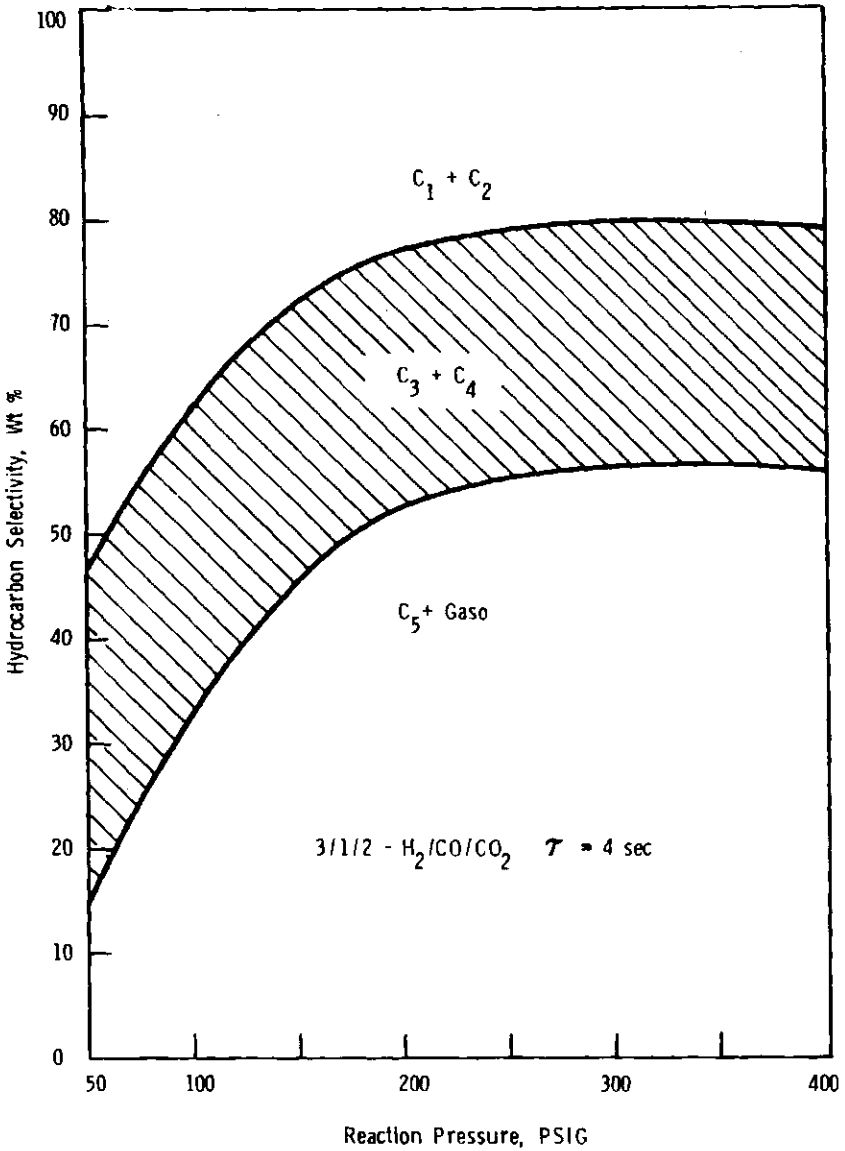


TABLE 8

EFFECT OF TEMPERATURE ON CATALYST SG-A-1 SELECTIVITY

Temperature, °F	Charge $H_2/CO/CO_2$	Selectivity, wt % C_1+C_2	C_3+C_4	C_5^+
635	3/1/2	20	22	58
	2/1/0	30	15	55
700	3/1/2	24	25	51
	2/1/0	33	18	49

TABLE 9

EFFECT OF PRESSURE ON CATALYST SG-A-1 SELECTIVITY (635°F)

Pressure, psig	Charge $H_2/CO/CO_2$	Selectivity, wt % C_1+C_2	C_3+C_4	C_5^+
200	3/1/2	23	24	53
	2/1/0	27	16	57
400	3/1/2	21	23	56
	2/1/0	31	26	43

TABLE 10

SELECTIVITY VERSUS CONTACT TIME FOR $3H_2/CO/2CO_2$ OVER SG-A-1

Selectivity, wt % at		Contact Time, sec. 3.8	6.9	13.7
200 psig,	C_1+C_2	23	23	25
	C_3+C_4	24	22	21
	C_5^+	53	55	54
300 psig,	C_1+C_2	24	21	20
	C_3+C_4	29	25	20
	C_5^+	47	54	60
400 psig,	C_1+C_2	21	23	24
	C_3+C_4	23	20	17
	C_5^+	56	57	59

Likewise for the $3H_2/CO/2CO_2$ charge, contact time had little effect on hydrocarbon selectivity in the 200-400 psig range (Table 10). At contact times of about seven seconds, selectivities are quite similar. Selectivities at 300 and 400 psig are equivalent and somewhat better than those for 200 psig. Higher conversion at 200 psig (Figure 11), however, will offset this advantage, and hydrocarbon production should be essentially the same at all three pressure levels. For shorter contact times it was observed that C_5^+ yields dropped rapidly with high light gas make. These results point out that the C_5^+ gasoline, once produced from "lighter hydrocarbons," did not undergo secondary cracking reactions at these conditions.

However, the olefins in the C_5^+ can undergo further reaction to paraffins and aromatics. The former sacrifices octane while the latter is undersirable since an olefinic gasoline and long catalyst cycles are desired. The effect of contact time is illustrated in Table 11. Since increased contact time results in aromatic formation with loss of olefins, the upper limit on contact time becomes defined by the aromatic/olefin balance in the hydrocarbon product.

In summary, the optimum operating conditions for a fixed bed, synthesis gas conversion process with catalyst SG-A-1 as determined in the micro reactor unit experiments using three feed compositions are shown in Table 12.

c. Aging and Regeneration of Catalyst SG-A-1

Proprietary work done with a prototype of catalyst SG-A-1 prior to this contract indicated good activity even after 50 days of processing a $2H_2/CO$ synthesis gas composition at 635°F and 200 psig. That study is summarized in Figure 14 and shows that both activity and selectivity were recovered by regenerating in situ with hydrogen at 950°F and process pressure.

For a fixed bed, adiabatic reactor with recycle, charging $2H_2/CO$ as fresh feed the catalyst will see a synthesis gas approximating $3H_2/CO/2CO_2$ in composition. Thus, aging and regeneration studies were initially carried out on catalyst SG-A-1 with $3H_2/CO/2CO_2$ at two pressures -- 200 psig for maximum activity, as discussed above, and 350 psig to match the conditions used with the prototype catalyst. The data are presented in Appendix B (Tables B10-11) and plotted as Figures 15 and 16. Aging at both conditions is significantly faster than anticipated, although the rate did decline somewhat after regeneration.

An aging run with $2H_2/CO$ over catalyst SG-A-1 attempted to elucidate the discrepancy between the recent and earlier results.

TABLE 11

EFFECT OF CONTACT TIME ON COMPOUND TYPE

	Contact Time, sec.			
Selectivity, wt % at	4	6	14	27
200 psig				
Olefin in C_5	83	70	49	-
Aromatics in C_6^+	15	19	32	-
400 psig				
Olefin in C_5	82	76	65	45
Aromatics in C_6^+	-	15	17	29

TABLE 12

OPTIMUM CONDITIONS FOR FIXED BED PROCESS WITH CATALYST SG-A-1

Charge ($H_2/CO/CO_2$)	1/1/0	2/1/0	3/1/2
Temperature, °F	635	635	635
PSIG	200	200	200
GHSV (CO)	1800	1300	600
Contact Time, sec.	7	7	8
Conversion, wt %			
CO	95	95	85
H_2	72	63	52
g HC/m^3 CO	321	423	441
Selectivity, %			
CH_4	19	19	19
C_5^+	56	57	55
Octane No. C_5^+ (R+0)	93	93	93
90% OH, °F	<400	<400	<400

Figure 14

AGING OVER PROTOTYPE CATALYST SG-A-1

Pressure, 200 psig
Temperature, 635°F
H_2/CO Ratio 2/1 (Molar)
Space Velocity, 3100 V/Hr/V, 1.5 Lb/Hr/Lb

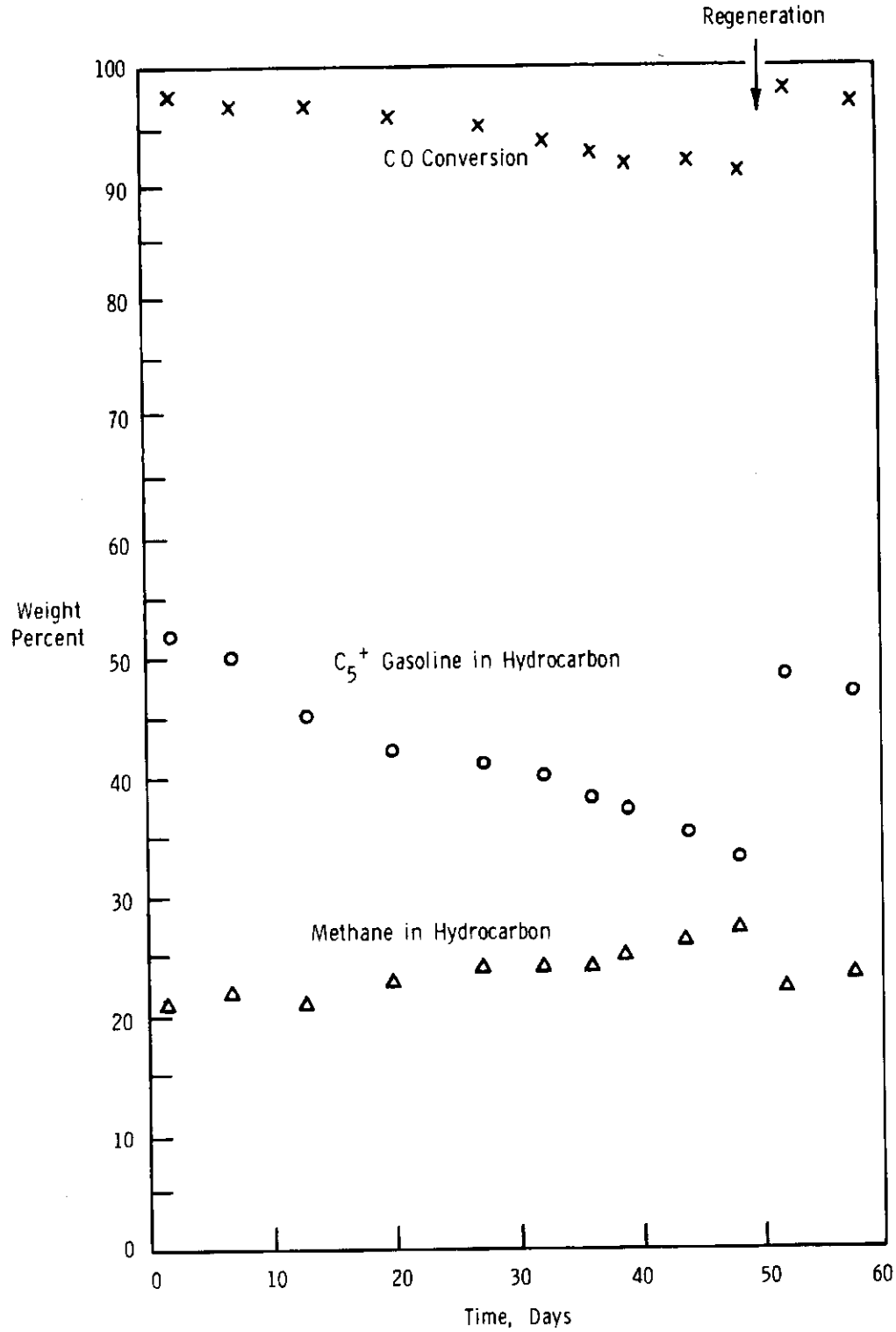


Figure 15

AGING OF SG-A-1 WITH 3 H_2/CO/2 CO_2-200 psig AND 635°F

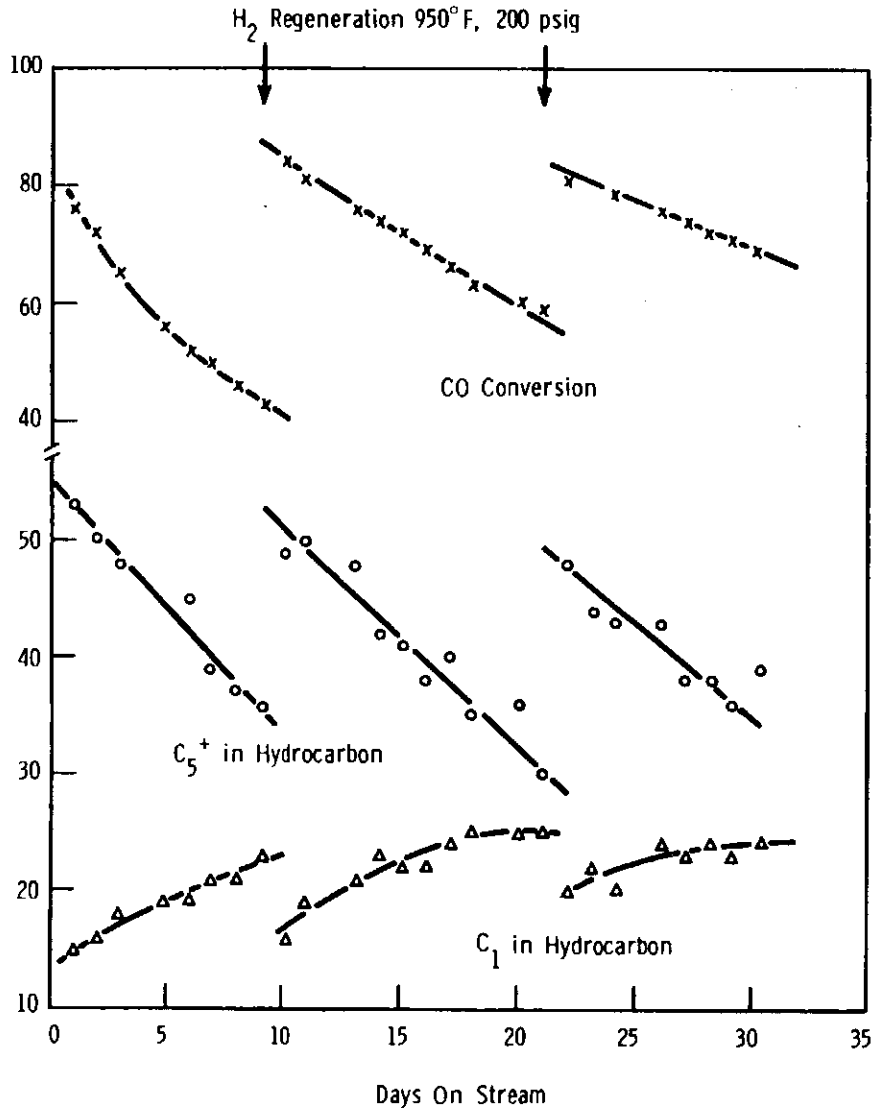


Figure 16

AGING OF SG-A-1 WITH 3 H_2/CO/2 CO_2-350 psig AND 625°F