SECTION 15

EXPERIMENTAL DATA BASIS FOR KEY CONVERSION PROCESS

15.1. FISCHER-TROPSCH SYNTHESIS

15.1.1 INTRODUCTION

The design for the conceptual U.S. Fischer-Tropsch plant is based on
a review and analysis of published research and development results, discussions with R&D personnel, and published commercial experience.

The yields and reaction conditions used in the design are based on the
results of work of the Pittsburg Energy Research Center (PERC) over the past
15 years. The reactor design selected was based on the PERC-developed flame
sprayed catalyst (FSC) reactor concept, where catalyst is thermally deposited
on steel by flame spraying. This catalyst system has been demonstrated by
PERC to be capable of efficiently producing liquids from syngas. A summary of
key elements of the PERC experimental program considered pertinent to the
support of the Fischer-Tropsch design is presented here.

Data from experimental systems using other catalyst forms, notably steel
lathe turnings catalyst (SLTC), were used to extend the limited data base of
the flame sprayed catalyst system after comparison of the performance of the
systems. These comparisons will be described.

A number of reactor types were analyzed and compared prior to selection
of the flame sprayed option. The analyses made are summarized in this report.

15.1.2 EXPERIMENTAL EQUIPMENT

A sketch of the experimental equipment used by PERC is shown in Figure
15.1-1[6]. The system included facilities for mixing fresh feed gas with hot
and cold recycle gas, preheating the mixed gases, converting them to liquids
condensing the liquids, separating the liquids from unconverted syngas, cooling
a portion of the recycle gas to control the moisture content of the feed gas
to the reactor, contacting a portion of the recycle gas with amine solution
to control the carbon dioxide content of the reactor feed gas, and combining
fresh feed with recycled syngas as feed to the reactor.

The fresh syngas feed rate to the reactor was varied from 165 to
1,214 scfh and liquid product rates obtained were from 1.2 to 13.7 pounds
per hour (pph). The pressure was approximately 400 psig, while the tempera-
ture range studied was 515 to 615°F [6,7,8].

The system permitted testing a number of reactor types. The plate reactor system used in Experiments HGR 33 and HGR 34 consisted of a 3-inch Schedule 80 steel pipe 12 feet long with catalyst coated plate grid inserts. The plates were 5-3/4 inches long, 1/32 to 1/16 inch thick, made of steel, and spray coated with Alan Wood Magnetite (AWM) melted with oxyhydrogen or oxyacetylene flame. The coated catalyst thickness was 0.02 to 0.04 inch and the distance between plates was 1/8 inch. Figure 15.1-2 shows the plates and their assembly and Figure 15.1-3 illustrates the method of catalyst application[6].

The syngas passed through the inside of the pipe in contact with the catalyst surfaces. The linear superficial velocity of the syngas in the pipe was in the range of 2.0 to 3.5 feet per second and the gas rate was varied from 5.3 to 17.7 scfh/square foot of catalyst area. The heat of reaction was removed by recycling the reaction mixture through an external heat exchanger.

15.1.3 PROCEDURE

The catalyst plates, coated with the flame sprayed magnetite, were dipped into a 6% aqueous solution of potassium carbonate, dried, and placed in the 3-inch pipe. The catalyst was reduced in a hydrogen atmosphere at 715 to 750°F and reaction then begun with syngas composition in the range of 1.4 parts of hydrogen to 1.0 part carbon monoxide.

Carbon dioxide was scrubbed from a portion of the cooled recycle gas to control the carbon dioxide and moisture content of the feed gas to the reactor. The total recycle ratio, recycle gas to fresh feed gas, was about 18 with the cold recycle ratio in the range of 1.5 to 2.0.

Quantities and compositions of feed, product, and intermediate streams, as well as reaction conditions, were measured to provide data for calculation of syngas conversion, catalyst activity, space velocities, product rates, product compositions, and other pertinent design factors.

15.1.4 DATA

The data presented originates in published PERC reports. For consistency in presentation in this report some minor changes were made to column and figure captions, and descriptive additions in the form of line items were inserted; also, temperatures were changed from Centigrade to Fahrenheit scale and in some cases data items were rounded. These same procedures were also used in the section on the methanation design.

Data were generated for two experimental series. Data for four of the runs from these series are presented in Table 15.1-1. Experiment 34 was voluntarily interrupted after 540 hours of operation following Run 2. Hourly space velocities of 2,000 were successfully tested. Experiment 33 ran 1,500 hours.

15.1.5 ANALYSIS

The data in Table 15.1-1 show hydrogen and carbon monoxide conversions of the order of 90% were achieved, indicating good catalyst activity. Gasoline production, in the range of 45 to 55% of the total hydrocarbons recovered, was achieved. Very little wax was produced.

A careful consideration of the potential for use of this catalyst type directed us to analyze the preferred geometry for sprayed catalyst. We concluded that application of the catalyst to the outside surface of an extended surface heat exchanger would have significant advantages; these advantages exist in the adjoining process sections as well as in the reactor itself. However, it was necessary to recognize the limited data base which exists for the flame sprayed catalyst system. The next step, therefore, was to evaluate the data available from related catalyst systems and determine their applicability to extend the data base. Of particular import was the effect of process parameters such as temperature, pressure, space velocity, and feed gas composition on conversion and product yields/compositions. A brief summary of alternate data sources is given in the following sections.

15.1.6 ALTERNATE DATA SOURCES

PERC has reported Fischer-Tropsch data for the following catalyst systems:

- Packed beds of steel lathe turnings catalyst (SLTC) with active iron oxide surfaces.

- Flame sprayed magnetite on an external tube surface.

15.1.6.1 EXPERIMENTAL EQUIPMENT

15.1.6.1.1 Steel Turning Beds

The experimental unit shown in Figure 15.1-1 was used. Characteristics of the reactor are shown in Figure 15.1-4.[8] The reactor tube was 3 inches in diameter by 12 feet long. The catalyst bed was varied from 6 to 10 feet in depth.[8] A 12-inch diameter reactor tube containing a 3-foot catalyst bed was also used.

15.1.6.1.2 Flame Sprayed Tube Surface

These were bench scale experiments. Figure 15.1-5 presents a sketch of the reactor assembly and Figure 15.1-6 is a photograph of a 3/4-inch sprayed catalyst tube.[9]

15.1.6.2 PROCEDURES

15.1.6.2.1 Steel Lathe Turnings Catalyst (SLTC) Beds)

The SLTC, with a void volume of 84 to 87%, was oxidized by steam, impregnated with potassium carbonate, and dried to give a catalyst containing 0.04 to 0.36% potassium oxide equivalent. The catalyst was then

reduced with hydrogen in the reactor. Usual reduction conditions were 2,000 cfh of hydrogen flow rate, 100 psig, and 750°F for 40 to 60 hours. The water formed was removed. The active catalyst surface consists primarily of the alpha form of iron; the procedure produces a porous, high surface area catalyst.

The reduced catalyst was inducted in the reactor for 10 days at an hourly space velocity of 200 to 250, temperature of 500 to 518°F, a pressure of 400 psig, and a feed gas H_2:CO ratio of about 1.0. Then the bed temperature was raised to 570 to 610°F and the feed H_2:CO ratio raised to 1.3 to 1.5. The tests were then ready to begin using procedures similar to those earlier described for the FSC experiments.[6, 7]

15.1.6.2.2 Flame Sprayed Tube Surface

The catalyst application procedure was similar to that used for the flat plates previously described. The experimental procedures were also similar.[6]

15.1.6.3 DATA

15.1.6.3.1 Steel Lathe Turnings Catalyst (SLTC)

Fifteen experimental runs, spanning approximately 14,000 operating hours, were completed for this phase of the program. This represents the largest Fischer-Tropsch data source from the PERC work.

Representative data are presented in Table 15.1-2.[7] Conclusions drawn from the data are:

(1) The conversion of H_2 + CO, and therefore the catalyst activity, was lower than obtained with the FSC.

(2) Product distribution was lower in gas and higher in liquid fractions than that obtained in the FSC experiments. The gasoline fraction was reported to be almost 60% by weight of the hydrocarbons recovered.

(3) A higher percentage of oxygenates than in the FSC experiments was in the synthesized hydrocarbons.

15.1.6.3.2 Flame Sprayed Catalyst on Tube Wall Reactor (TWR)

Six runs of short operating duration were completed. Representative data, shown in Table 15.1-3,[9] indicate that:

(1) The H_2 + CO conversion was of the order of 50%.

(2) The high gas rate per unit catalyst surface area favored the formation of light hydrocarbons.

(3) The quantity of C_1 to C_4 alcohols produced increased with increase in pressure.

15.1.7 COMPARISON OF RESULTS FROM ALTERNATE CATALYST SYSTEMS

Representative results from tests using the FSC, SLTC, and TWR catalyst systems are compared in Table 15.1-4. The results indicate a number of common trends. From this comparison, it is concluded that:

(1) The syngas compositions and hydrocarbon recovery, expressed as lb/1,000 scf fresh gas, were approximately the same in the FSC and SLTC runs.

(2) The highest H_2 + CO conversion (approximately 90%) and catalyst activity were obtained in the FSC experiments.

(3) The highest gasoline yield (approximately 60% of recovered hydrocarbons) was obtained in the SLTC experiments.

15.1.8 DATA SELECTION

Based on the results of data analyses summarized above, plus an analysis of preferred reactor geometry and process efficiency, it was decided:

(1) To use an FSC iron oxide catalyst coated on the outside of an extended heat exchanger tube surface.

The geometry was selected for reasons of predicted performance in the converter as well as effect on the interfacing process sections and plant thermal efficiency.

(2) Data from the SLTC runs have sufficient commonality with the flame sprayed plate runs to permit use of the lathe turnings data to establish elements of the product distribution.

● Run No. 26C was selected by analysis to be representative of the PERC SLTC data; the results of this run were used to establish the point design basis.

● The conceptual design product mix was set to be identical to that obtained in Run 26C.

15.1.9 CATALYST LIFE

The design was based on a catalyst life of one stream year, or 8,000 operating hours. The reasons for selection of this projected life are:

(1) The flame sprayed catalyst performed well for 540 hours in PERC Run HGR 34; total operation using this catalyst form exceeded 2,000 hours.

(2) Extensive syngas cleanup and desulfurization facilities are provided in the design. The specification for syngas feed to the Fischer-Tropsch reactors set at 0.001 grain/100 scf particulates and 0.05 ppm sulfur, maximum. Prior reported experience indicates that high purity feed gases result in extended catalyst life.

(3) The expectation that future research and development work will produce improved catalyst stability.

PERC work published to date had not set itself to experimentally determine the best procedure for catalyst preparation or effective catalyst life. It is anticipated that such a program will define ways to produce a long-lived catalyst system.

15.1.10 CATALYST ACTIVITY

Representative catalyst activities for steel lathe turnings and flame sprayed catalyst are shown in Table 15.1-5. Data for the design basis Run 26C SLTC and FSC Run 34 catalyst runs are included. Here the catalyst activity factor is defined as by PERC Av/G, where:[10]

$$Av = 1.241 \times 10^{-8} \times S \times 10^{4130/T} \times \log_{10} \frac{1}{1-C}$$

where:

C = Fractional Conversion of $(CO + H_2)$

G = Geometric surface area of catalyst per unit volume of catalyst bed, sq ft/cf

= 400 for steel turnings

= 113 for flame sprayed catalyst plates

S = Hourly space velocity (stp) of fresh feed gas

T = Average catalyst temperature (degrees Kelvin)

Table 15.1-5 indicates that the FSC activity can be significantly higher than the SLTC activity. The selection of an activity in the lower FSC range therefore represents a conservative design criterion based on information available at this time.

A space velocity indicator proposed by PERC, which relates to catalyst surface area, is termed "J" factor and is defined as:

$$J = \frac{\text{Volumes (stp) of fresh syngas per hour}}{\text{square foot of catalyst surface}}$$

Comparisons of catalyst activity based on "J" are also included in Table 15.1-5. Here we see that the FS catalyst has shown activities 5 to 10 times greater than the SLC type.

15.1.11 DESIGN BASIS

The key design basis elements selected for the Fischer-Tropsch reaction system are summarized below; reasons for their selection have been discussed in the preceding sections.

Key Reactor Design Basis Elements

Capacity, Btu/day total products HHV, billion	500
Pressure, psig	400
Temperature (average), °F	606
Space Velocity Factors	
J, scf/hr/sq ft of catalyst area	10
S_v, scf/hr/cu ft of reaction zone volume	1,330
Catalyst Activity	1.33
Syngas Composition	
Fresh Feed H_2:CO ratio	1.45
CO + H_2 Conversion, percent	80
Reactor Recycle Ratio	
Volume Recycle Gas ÷ Volume (CO + H_2) in Fresh Syngas Feed	1.5
Heat of Reaction at Reactor Conditions	
Btu/scf of (CO + H_2) Converted	72.8

Reactor Product Composition

	Weight Percent	Appears in Product Listed Below
C_1, C_2, C_2^-	19.3	SNG
C_3, C_3^-	4.5	SNG
C_4, C_4^-	11.9	Butane
C_5, C_5^-, C_6	13.6	Light Naphtha
C_7, C_8, C_9	19.2	Heavy Naphtha
C_{10}, C_{11} to 640°F B.P.	18.8	Diesel Fuel
640 to 940°F B.P.	7.3	Fuel Oil
Alcohols and Ketones	4.9	Oxygenates
Acids	0.5	
Total	100.0	

For reference, a comparison of the design basis elements listed above and representative values from the flame sprayed plates (FSP), steel lathe turnings (SLT), and tube wall (TW) test runs are presented in Table 15.1-6.

15.1.12 DISCUSSION

15.1.12.1 KINETICS

A limited number of kinetic studies have been made on the Fischer-Tropsch synthesis using iron catalysts.[10] The data have been correlated by a simple empirical equation, similar to that for a first-order reaction, relating the fraction of (CO_2 + H_2) converted c, to the space velocity S (at stp), and a reaction rate constant, K.

$$- \ln (1 - c) = \frac{K}{S}$$

The catalyst reaction rate constant K is of the form $K = A\, e^{-E/RT}$ in which A is a constant, E the apparent overall activation energy of the synthesis, T the absolute synthesis temperature, and R is the universal gas constant.

Arrhenius plots of the logarithm of the catalyst space time yield versus the reciprocal of the absolute temperature are presented in Figure 15.1-7 for both sprayed plate catalyst and oxidized steel turnings catalyst, at 400 psig.

The apparent overall activation energy of the synthesis, E, is 12.1 Kcal/mole for both the SLTC and the FSC. The activity constant A is 2.46×10^7 scfh/cf for the SLTC, and 5.12×10^7 scfh/cf for the FSC.

This correlation indicates that the conceptual Fischer-Tropsch plant synthesis results could be obtained with a FSC space velocity of 2,800 scfh/cf, or a "J" factor of 25 scfh/sf (total reactor feed).

The conceptual plant reactor has been designed for a "J" factor (total reactor feed) of 24 scfh/sf, or a fresh gas "J" factor of 10 scfh/sf. The equality of activation energies for the two types of catalyst further indicates that the steel lathe turnings and flame sprayed catalysts are sufficiently similar to permit use of the lathe turnings data in setting product distribution. This projection further indicates that the design basis "J" factor is realistic to conservative.

PERC studies with fused iron catalyst showed that the catalyst activity constant A was proportional to the first power of the operating pressure, over the range of 0 to 250 psia. Bench scale test results for the TWR[9] at 300, 650, and 1,000 psig show no change of catalyst activity with changing pressure.

15.1.12.2 SULFUR CONTENT OF SYNGAS

Poisoning of the Fischer-Tropsch iron catalysts can be caused by the presence of impurities in the syngas; examples include dust, tar, resin formers, sulfur compounds, organic compounds, and halogens.[11, 12] In the conceptual plant design extensive gas cleaning facilities prior to the acid gas removal plant remove essentially all gas particulates, tars, and halogens.

During gasification, sulfur in the coal is converted to hydrogen sulfide, together with small amounts of sulfur dioxide, carbonyl sulfide, and organic sulfur compounds. These sulfur compounds are removed by an acid gas removal unit, and by zinc oxide/cobalt-molybdenum guard reactors. The efficiency of this removal system is determined by the sensitivity of the Fischer-Tropsch catalyst to sulfur.

The PERC Fischer-Tropsch studies maintained the sulfur content of the syngas below 0.1 grain (gr) per 100 cu ft by passing the gas through activated carbon. Usually the sulfur content was less then 0.02 gr per 100 cu ft.[2] These sulfur contents are equivalent to 1.7 and 0.34 ppm (vol), respectively.

The South African Coal, Oil and Gas Corporation (SASOL) reported that they obtained an average syngas sulfur content of 0.3 ppm (vol) up to 1964.[13] Improved operating techniques after this date have reduced the sulfur content to about 0.015 ppm (vol).[13] The SASOL plant expansion, SASOL II, is designed for a syngas sulfur content of 0.03 ppm (vol).[14]

The conceptual Fischer-Tropsch sulfur removal system is designed to obtain 0.1 ppm (vol) after the acid gas removal unit, and 0.05 ppm after the zinc oxide/cobalt-molybdenum guard reactors.

15.1.12.3 CARBON FORMATION

PERC experiments with the large diameter (12-inch) Fischer-Tropsch reactor[7] demonstrated that carbon deposition could be avoided in these experiments by maintaining the maximum bed temperature below 340°C (644°F), if good heat transfer rates from the catalyst to the circulating gas also existed. Adequate heat transfer rates were obtained by careful packing of the catalyst to avoid uneven distribution of the gas. The desired linear gas velocity for a commercial reactor using the hot-gas-recycle process was estimated to be 3 to 4 feet per second.

The conceptual reactor design permits close control of the heat transfer rates from the gas to the catalyst surface, and from the catalyst surface to the coolant. The close control of heat transfer rates, heat transfer surface, and the good gas distribution inherent in the conceptual design, avoid the formation of catalyst hot spots or excessive catalyst face temperatures that might result in carbon formation.

The conceptual reactor is designed for an average catalyst face temperature of 606°F with a bulk gas phase temperature of 601°F.

The triangular coordinate carbon phase diagram, Figure 15.1-8, shows the equilibrium isotherm for the (H_2), (CH_4), (CO), (CO_2), and (H_2O) system.[15] Points for the PERC experimental reactor Run 26C (steel turnings catalyst) and the conceptual reactor are shown as being outside the theoretical carbon forming region. The Fischer-Tropsch synthesis gases contain hydrocarbons other than methane, and so are not at thermodynamic equilibrium. All hydrocarbons except methane are thermodynamically unstable with respect to carbon and hydrogen above 200°C.[16] However, the carbon phase diagram is useful in that it shows the conceptual reactor gas composition to be closer towards the H-O axis and farther away from the carbon formation region than the Experiment 26C gas.

The partial equilibrium isotherm for the system (H_2), (CO), (CO_2) and (H_2O), shows that both the conceptual reactor and the PERC reactor lie in the carbon formation region for this system. However, kinetic effects are also responsible for the suppression of carbon formation and since carbon deposition was not a problem in Experiment 26C, the conceptual reactor is not expected to experience carbon deposition. In addition, the consequence of carbon laydown in the plate reactor is not as great as with a fixed bed reactor where the bed may plug.

The composition of the active catalyst surface is determined by the chemical reactions which occur between the catalyst and the gas. The carbon content of the catalyst can be increased (carbiding) or decreased by these reactions. As made, the steel turnings catalyst is mainly iron oxide Fe_3O_4 promoted by potassium salts, but under operating conditions the catalyst is reduced to Fe, Fe_3O_4 or Fe_2C (Hägg carbide). All these forms of the catalyst have been found to be equally active for the Fischer-Tropsch synthesis[7] so that catalyst carbiding will not reduce the catalyst activity.

X-ray analysis of catalyst samples from Experiment 26 show the active surface to be entirely composed of Hägg Fe_2C. Consideration of carbon dioxide/carbon monoxide partial pressures indicates that the active form of the conceptual reactor catalyst will also be that of Hägg Fe_2C.

Table 15.1-1 - Example Experimental Results
Flame Sprayed Catalyst (FSC) Fischer-Tropsch Runs[6]

Item	Experiment No. HGR 33		Experiment No. HGR 34	
Catalyst type	Coated Plates	Coated Plates	Coated Plates	Coated Plates
Fresh gas space velocity, vol/vol/hr	600	1000	1000	2000
Fresh feed rate, scfh	165	275	275	550
Recycle ratio: Total recycle ÷ fresh feed, vol/vol	52	15.9	20.4	14.4
Reactor pressure, psig	400	400	400	400
Catalyst temperature, °F				
Average	516	617	608	617
Differential	36	90	72	90
H_2 conversion, %	73.4	90.9	90.1	83
CO conversion, %	80.6	98.8	98.2	94.4
H_2 + CO conversion, %	76.4	94.4	93.4	87.5
Overall weight balance, %	93.6	90.8	87.8	96.6
Hydrocarbons recovered, lb/1,000 scf fresh gas	7.4	9.5	10.3	11.6
Hydrocarbons recovered, wt%				
C_1 + C_2	59.7	36.5	33.9	29.5
C_3	6.6	14.1	13.3	12.8
Gasoline (C_3 = <400°F)	31.8	43.7	48.5	53.0
Diesel fuel (400 to 600°F)	1.9	5.0	4.0	3.8
Fuel oil (600 to 842°F)	0	0.4	0.2	0.5
Wax (>842°F)	0	0.3	0.1	0.4

Table 15.1-2 – Example Experimental Results
Steel Lathe Turnings Catalyst (SLTC) Fischer-Tropsch Runs[7]

Item	Experiment 26 Period C
Catalyst type	SLTC
Synthesis, hours	416 – 488
Reactor conditions:	
Fresh feed rate, scfh	1,214
Space velocity, vol/vol/hr	607
Reactor pressure, psig	405
Recycle to fresh feed ratios:	
Total	27
Hot	25.5
Cold	1.5
CO_2 scrubbed	1.5
Reactor temperature, °F	
In gas	552
Out gas	610
Increment	58
Average catalyst temperature, °F	586
Maximum catalyst temperature, °F	622
Catalyst pressure drop, inches of H_2O/foot	6
H_2:CO ratio, fresh gas	1.45
Results:	
CO_2 free contraction, %	74.6
H_2 conversion, %	73.7
CO conversion, %	88.7
H_2 + CO conversion, %	79.8
H_2: CO ratio:	3.35
Recycle gas	1.21
Usage	
Water vapor in recycle gas, vol %	7.0
Heating value of tail gas, [a] Btu/ft^3	536
Tail gas composition, vol %: [b]	
H_2	55.2
CO	16.5
N_2	1.2
CO_2	9.6

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Table 15.1-2 (Contd)

Item	Experiment 26 Period C
Tail gas composition, vol %:[b]	
C_1	9.8
$C_2=$	0.7
C_2	2.3
$C_3=$	0.3
C_3	1.0
$C_4=$	0.6
C_4	1.8
$C_5=$	0.2
C_5	0.8
$C_6=$	0
C_6	0
Yield, g/m^3 (H$_2$ + CO) converted:	
C_1	24
$C_2=$	3
C_2	12
$C_3=$	2
C_3	7
$C_4=$	6
C_4	18
$C_5=$	2
C_5	9
$C_6=$	0
C_6	0
Oil	0.97
Aqueous	130
$C_1 - C_3OH$[c]	8
Other oxygenates[c]	3
Water	119
CO_2	307
Hydrocarbon recovery, g/m^3	191
Theoretical recovery, g/m^3	201
Hydrocarbon recovery, wt %	
$C_1 + C_2$	19.4
C_3	3.5
Gasoline (C_3 = <400°F)	59.0
Diesel oil (400 to 600°F)	9.1
Fuel oil (600 to 842°F)	6.2
Wax (<842°F)	2.8

[a] Cubic foot corrected to 60°F and 30 inches of mercury (dry).

[b] Dry basis.

[c] Calculated as hydrocarbons.

Table 15.1-3 - Example Experimental Results
Flame Sprayed Catalyst on Tube-Wall Reactor (TWR) Fischer-Tropsch Runs[9]

Item	Experiment Number FT-TW-1		
Fresh gas, $\dfrac{\text{vol. gas, ft}^3\text{ (stp)/hr}}{\text{Ft}^2\text{ catalyst surface}}$	30	30	30
Fresh gas feed rate, scfh	4.37	4.37	4.37
H_2:CO ratio in feed gas	3:1	3:1	3:1
Reactor pressure, psig	300	650	1,000
Catalyst temperature, average, °F/°C	615.2/324	602.6/317	609.9/318
H_2 conversion,%	40.32	43.67	45.12
CO conversion, %	78.30	78.46	76.21
H_2 + CO conversion, %	49.38	52.02	52.70
Heating value tail gas Btu/ft^3			
With CO_2	383	383	418
Without CO_2	419		453
Overall weight balance, %	93.96	97.05	95.72
Hydrocarbons recovery, lb/1,000 scf fresh gas[a]	4.148	5.139	5.714
Theoretical hydrocarbons, g/m^3(H_2 + CO) conversion	188.65	184.13	166.98
Recovery, %	71.33	82.76	108.09
Hydrocarbon recovery, wt%			
C_1 + C_2	71.26	67.01	69.56
C_3	17.70	19.92	11.75
Gasoline (C_3= + <400°F)[a]	9.18	12.14	18.32
Diesel fuel (400 to 600°F)	1.60	.83	.32
Fuel oil (600 to 842°F)	.25	.10	.06
Wax (>842°F)	0.0	0.00	0.00

Item	Period					
	1st	2nd	1st	2nd	1st	2nd
Aqueous layer, g/m^3(H_2 + CO) conversion						
C_1 – C_4OH	3.16	4.34	7.70	17.14	30.34	42.33
Other oxygenates	.19	.13	.13	.18	0.0	0.0
H_2O	126.7	124.9	140.6	135.2	125.6	113.7
Percent CO in tail gas	8.09		8.0		8.3	

[a] Includes alcohols and oxygenates.

Table 15.1-4 - Comparison of Example FSC, SLTC, and TWR
Fischer-Tropsch Experimental Results

Item	FSC Experiment HGR 34[9]		SLTC Experiment 26 C[7]	TWR Experiment[9]
Fresh gas, $\dfrac{\text{vol gas, ft}^3 \text{ (stp)/hr}}{\text{ft}^2 \text{ catalyst surface}}$	8.85	17.7	(a)	30
Fresh gas feed rate, scfh	275	550	1214	4.37
H_2:CO ratio in feed gas	1.4:1	1.4:1	1:45	3:1
Reactor pressure, psig	400	400	405	300
Catalyst temp. average °F/°C	608/320	617/325	586/308	615.2/324
$\quad$ H_2 conversion, %	90.1	83	73.7	40.32
$\quad$ CO conversion, %	98.2	94.4	88.7	78.30
$\quad$ H_2 + CO conversion, %	93.4	87.5	79.8	49.38
Heating value tail gas Btu/ft³				
$\quad$ With CO_2	930	785	536	383
$\quad$ Without CO_2	1000	852	593	419
Overall weight balance, %	87.8	96.6	---	93.96
Hydrocarbons recovery, lb/1,000 scf fresh gas [b]	10.3	11.6	9.5	4.15
Theoretical hydrocarbons, g/m³ (H_2 + CO) conversion	190.28	197.0	201	188.65
$\quad$ Recovery %	119.53	97.39	95	71.33
Hydrocarbon recovery, wt%				
$\quad$ $C_1 + C_2$	38.00	32.71	19.4	71.26
$\quad$ C_3	13.58	12.07	3.5	17.70
$\quad$ Gasoline (C_3= + <400°F) [b]	48.11	50.01	59.0	9.18
$\quad$ Diesel fuel (400 to 600°F)	4.46	4.27	9.1	1.60
$\quad$ Fuel oil (600 to 842°F)	.18	.52	6.2	.25
$\quad$ Wax (>842°F)	.11	.42	2.8	0.0

				Period	
				1st	2nd
Aqueous layer, g/m³ (H_2 + CO) conversion					
$\quad$ $C_1 - C_4OH$	4.34	6.11	8 [c]	3.16	4.34
Other oxygenates	.32	.36	3	.19	.13
$\quad$ H_2O	97.54	108.32	130	126.7	124.9
Percent CO in tail gas	4.21	9.67	16.5	8.09	

(a) Lathe turning bed reactor with hot gas recycle. Total recycle to feed ratio of 27 to 1, 607 scfh/cf catalyst.

(b) Includes alcohols and other oxygenates.

(c) $C_1 - C_3OH$.

Table 15.1-5 - Catalyst Activity (A_s) and "J" Factor Comparisons

Experiment No.	Catalyst Type	Range of Activity Factor A_s	"J" Factor Cu Ft Gas/ft^2 Catalyst Area
5871/7[1]	Steel Lathe Turnings	0.08 to 0.20	1.0 to 1.5
5871/8	Steel Lathe Turnings	0.10 to 0.54	0.5 to 3.5
5871/9	Steel Lathe Turnings	0.10 to 0.34	0.5 to 2.5
5871/15	Steel Lathe Turnings	0.18 to 0.30	0.63 to 2.5
5871/16	Steel Lathe Turnings	0.20 to 0.66	0.63 to 2.5
5871/17	Steel Lathe Turnings	0.12 to 0.20	2.5 to 3.75
6126/26[7]	Steel Lathe Turnings	0.12 to 0.20	1.5 to 2.0
HGR 33[8]	Flame Sprayed Plates	1.1 to 1.7	5.3 to 8.85
HGR 34	Flame Sprayed Plates	1.2 to 1.6	8.85 to 17.7
TW - 1[9]	Flame Sprayed Tube Wall	0.9 to 0.93	30
Conceptual Plant Flame Sprayed Fintube		0.9	10

Table 15.1-6 - Conceptual Fischer-Tropsch Reactor Design
Compared with PERC Experimental Data

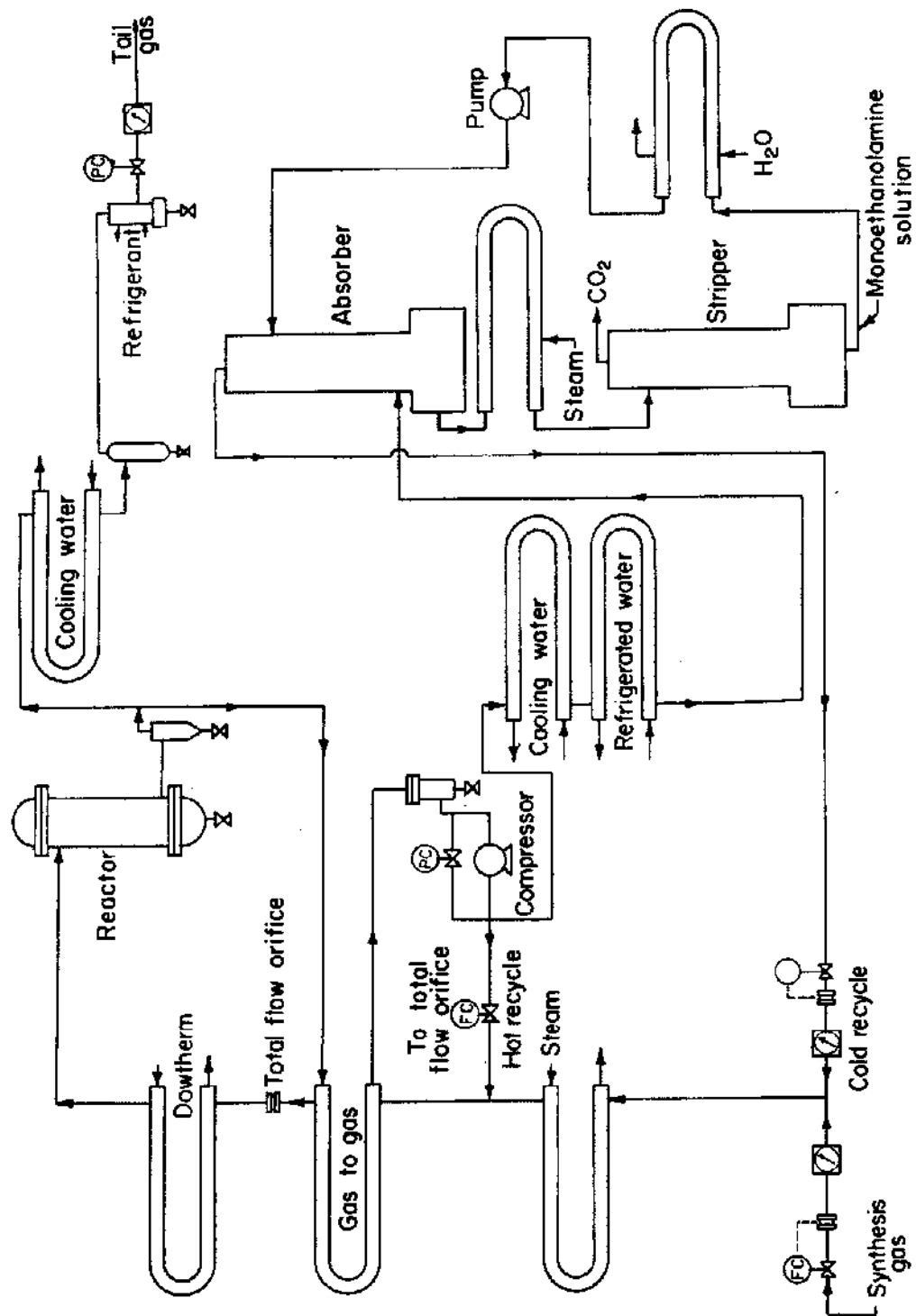| Item	Experiment HGR 34[9]		SLTC[7] Experiment 26 C	TWR Experiment FT-TW-1[9]	Conceptual Design Basis
"J," scfh/sf catalyst surface	8.85	17.7	1.5	30	10.0
H_2:CO ratio in feed	1.41	1.41	1.45	3	1.45
Recycle ratio	20.4	14.4	27.0	-	1.5
(CO + H_2) conversion %	93.4	87.5	80.0	52.0	80.0
Total Reaction Heat Calculated Btu/sf/hr	583.0	1092.0	84.0	1100.0	563.0

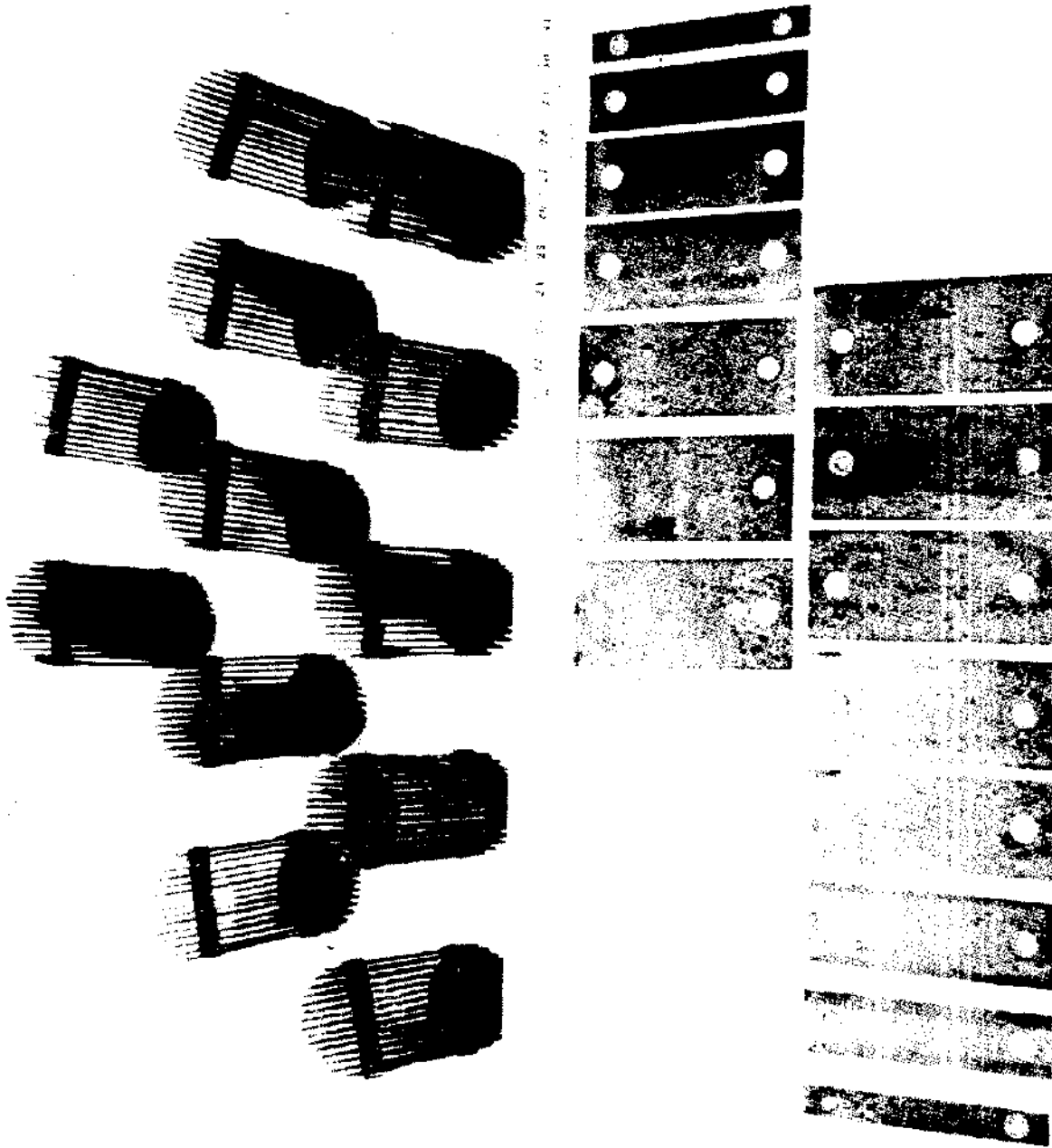Figure 15.1-1 - Sketch: Experimental Equipment Used for Fischer-Tropsch Reaction Runs[6]

Figure 15.1-2 · Plates and Grid Assemblies Used in FSC Fischer-Tropsch Experiments[6]

Figure 15.1-3 - Apparatus Used in Preparing FSC Plates for
Fischer-Tropsch Experiments[6]
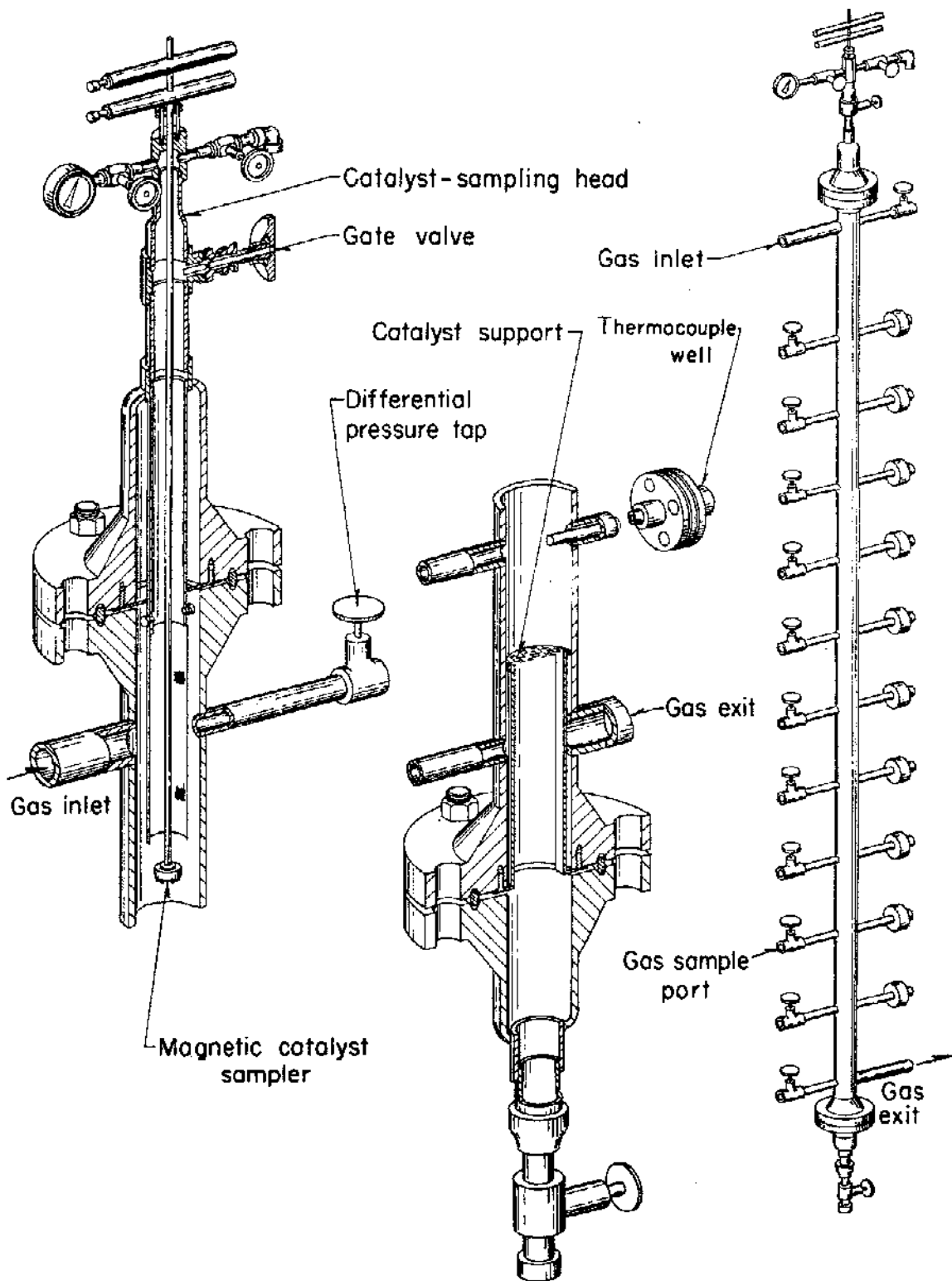
Figure 15.1-4 - Reactor Sketch: Steel Lathe Turnings
Catalyst (SLTC) Experiments[8]

Well for sliding thermocouple $\frac{1}{8}$-inch stainless steel tubing

Coolant thermocouple

Gas inlet

$\frac{3}{4}$-inch od cooling tube

$\frac{3}{4}$-inch pipe coated with catalyst

$1\frac{1}{2}$-inch sch 80 stainless steel pipe

Outlet
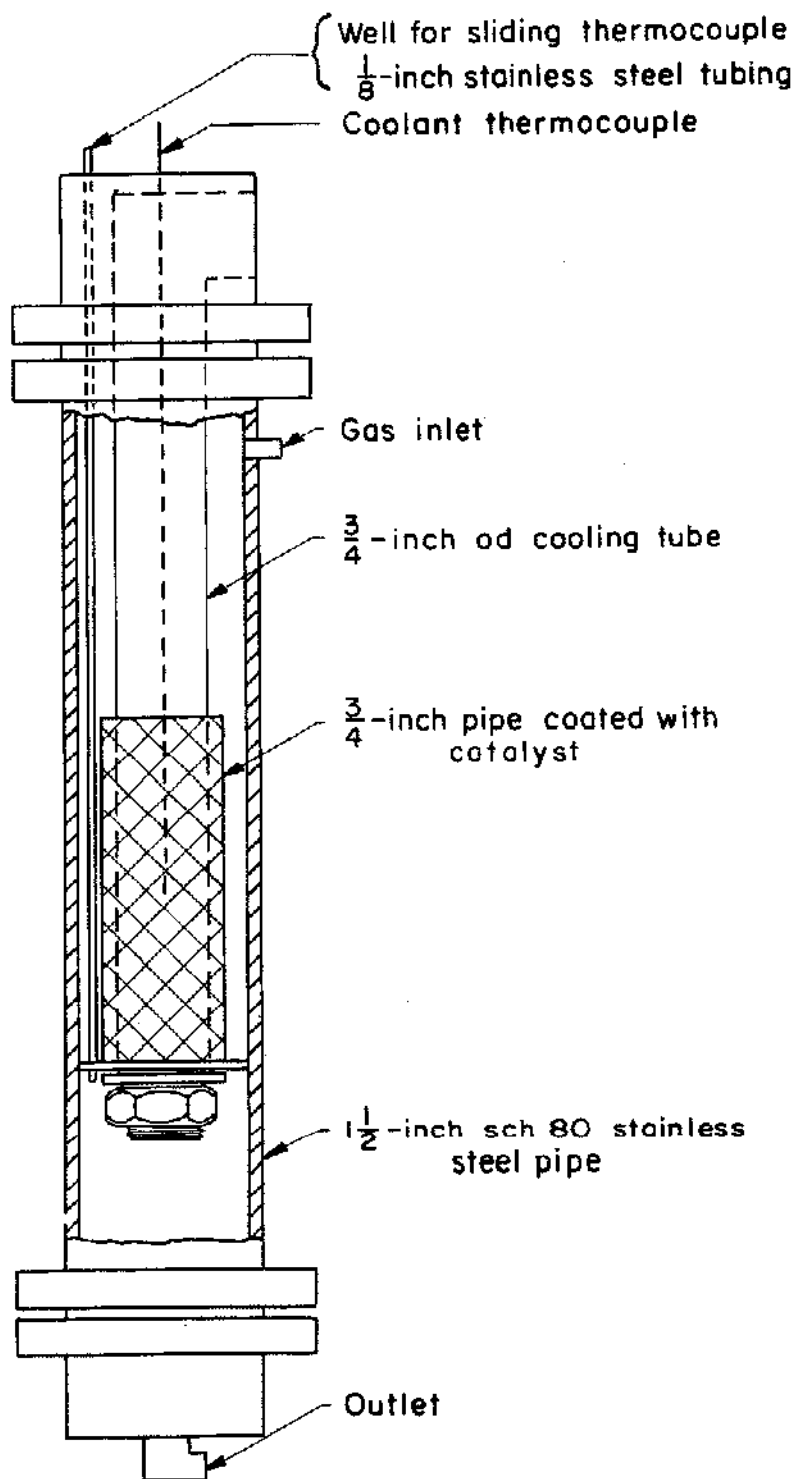
Figure 15.1-5 · Reactor for Testing AMW Iron Catalyst-Coated Tubes[9]

Figure 15.1-6 - Catalyst Sprayed on 3/4-in. Diameter Tube[9]

Figure 15.1-7 - Arrhenius Plots of Space-time Yield vs Reciprocal of Absolute Temperature at 400 psig

PLATE CATALYST EXPERIMENT 33B AND EXPERIMENT 34
E = 12.1 Kcal/mole

STEEL TURNINGS CATALYST
EXPERIMENT 26[7]
E = 12.1 Kcal/mole

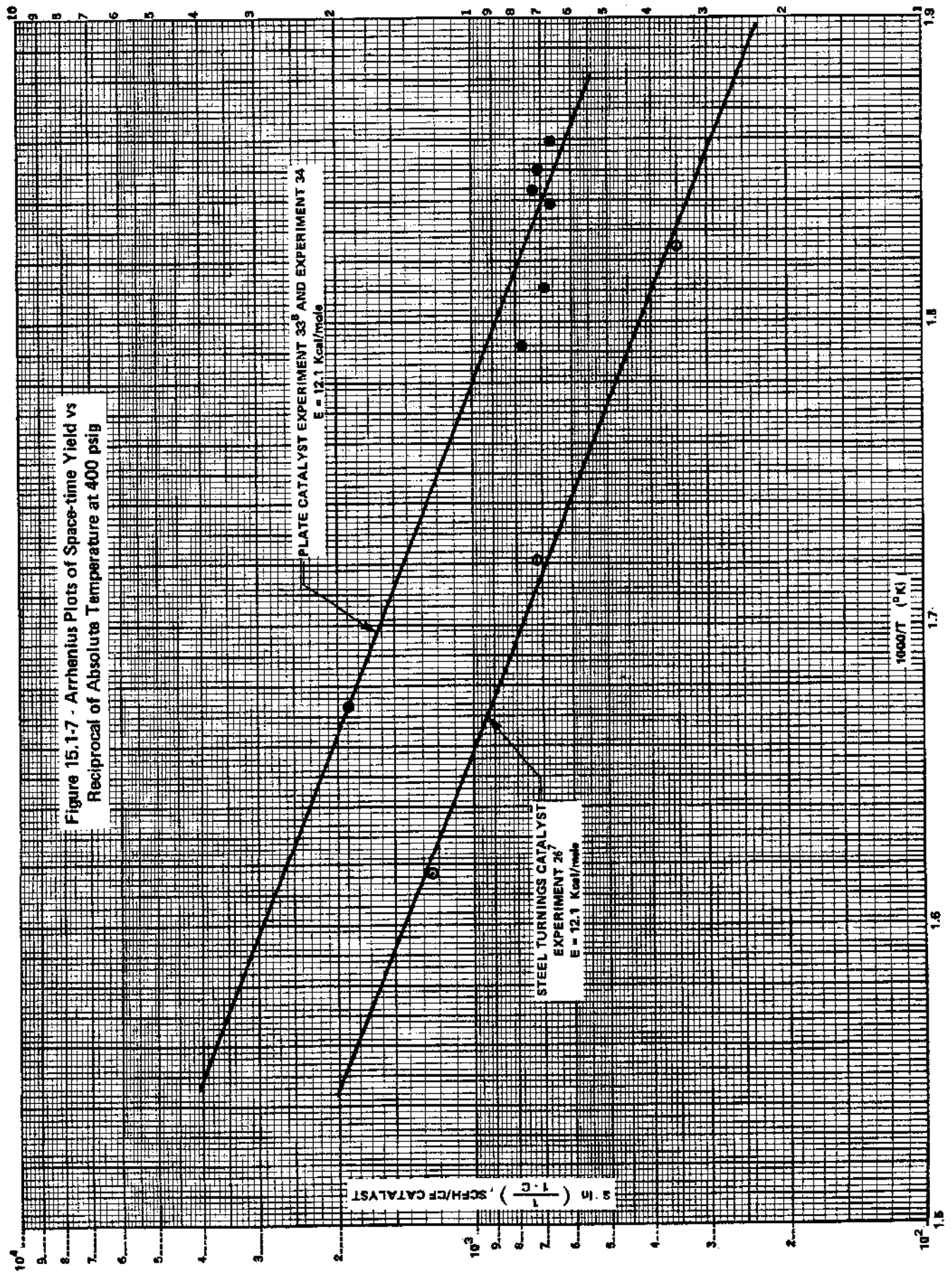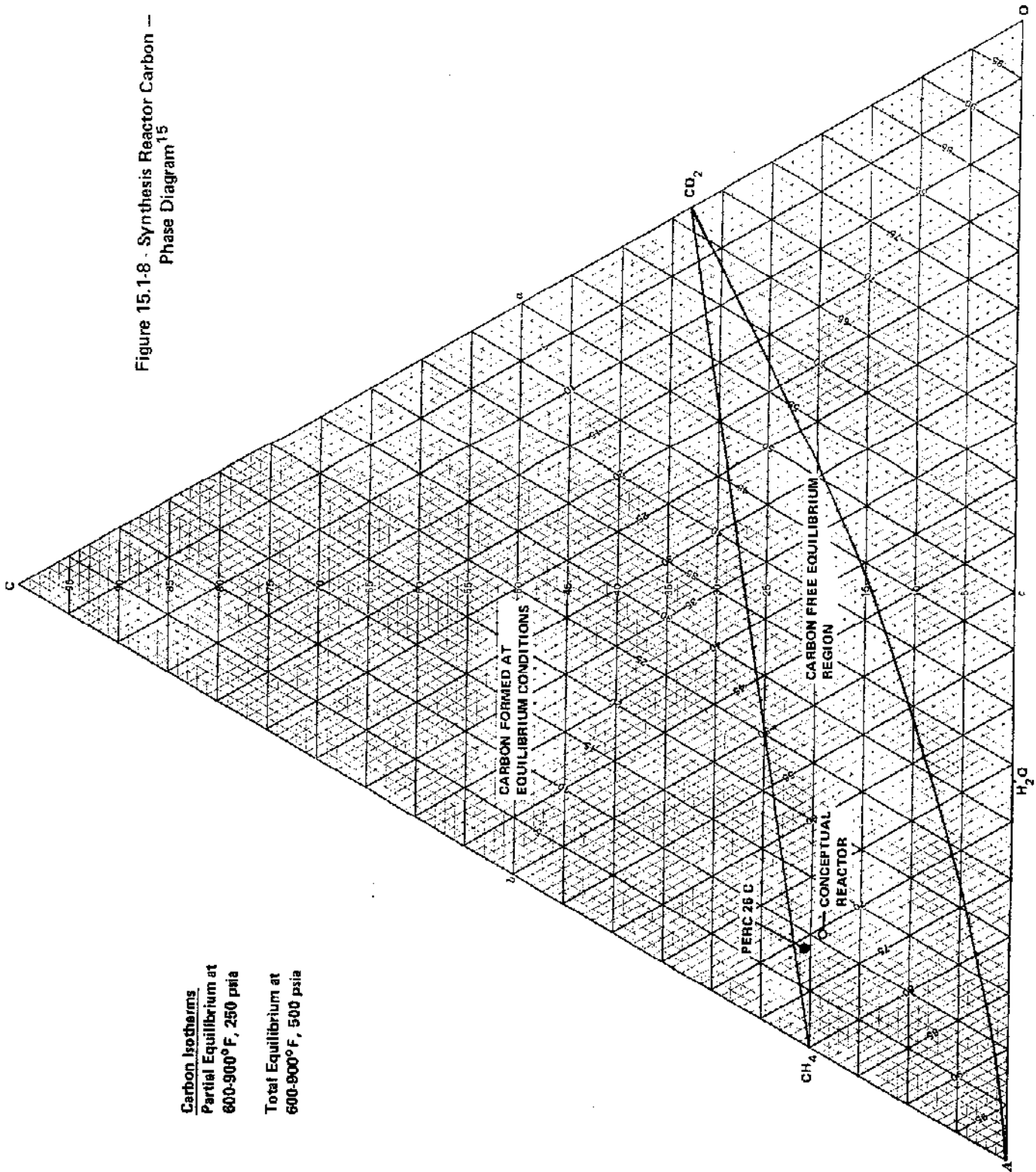$S_T \ln \left(\frac{1}{1-C} \right)$, SCFH/CF CATALYST

$1000/T$ (°K)

Figure 15.1-8 - Synthesis Reactor Carbon — Phase Diagram[15]

Carbon Isotherms
Partial Equilibrium at
600-900°F, 250 psia

Total Equilibrium at
600-900°F, 500 psia

CARBON FORMED AT
EQUILIBRIUM CONDITIONS

CARBON FREE EQUILIBRIUM
REGION

CONCEPTUAL
REACTOR

PERC 26 C

CO_2

CH_4

H_2O

C

H

O

SECTION 15

BASIS OF FISCHER-TROPSCH REACTOR DESIGNS

15.2. METHANATION REACTOR

15.2.1 INTRODUCTION

PERC has conducted an extensive methanation research and development program using flame sprayed Raney nickel coated plate catalytic reactors.[17] The basic principle is identical to that of the FSC described in the Fischer-Tropsch reaction experiments. Fresh gas mixtures of hydrogen and carbon monoxide were fed to the reactor with the product gas stream containing the reaction heat being cooled in an external heat exchanger. A major portion of the product gas was mixed with the fresh feed gas stream and recycled to the reactor.

The conceptual Fischer-Tropsch plant uses a modified version of the PERC coated catalyst plate reactor for its primary methanation process; it also uses a "final" methanator with granular catalyst to assure essentially complete conversion of carbon monoxide. The primary reactor is an extended surface heat exchanger with flame sprayed Raney nickel catalyst coated on external spiral fins connected to the heat exchanger tubes. The configuration is identical to the Fischer-Tropsch synthesis reactor described in the previous section. The coolant is Dowtherm liquid within the tubes. This type of reactor was selected for reasons similar to those which dominated in the Fischer-Tropsch converter selection decision--direct efficient reaction heat recovery allowing a reduced recycle rate and use of the heat of reaction to generate 1,200 psig steam.

This section will present basic data and experimental results developed by PERC which served as the basis for the conceptual plant methanation reactor design.

15.2.2 EXPERIMENTAL EQUIPMENT AND PROCEDURE

A sketch of the experimental equipment used by PERC is shown in Figure 15.2-1. The system included facilities for mixing fresh feed gas with hot and cold recycle gas, preheating the mixed gases, a primary reactor and a secondary reactor system, removal of water formed in the reaction by cooling the recycle gas, and recycling the syngas to the reactors.

Fresh syngas feed rate to the primary reactor was in the range of 411 to 1,412 scfh. Product gas rates obtained were from 104 to 340 scfh. Pressure and temperature ranges were 300 to 400 psig and 350 to 425°F, respectively.

The primary reactor was packed with flame sprayed Raney nickel coated stainless steel plate grids (FSC) and the second reactor with precipitated nickel catalyst (PC).[17]

The FSC reactor system used for Experiments 14 and 15 consisted of a 3-inch, Schedule 40, 304 stainless steel pipe, 10 feet long, with 304 stainless steel plate grid inserts. Each grid assembly was 6 inches long, contained 15 plates, and was shaped to conform to the inside diameter of the reactor, adjacent grids being stacked 90 deg with respect to each other. The coated catalyst thickness was 0.022 inch flame sprayed with Raney nickel alloy powder. The assembled grids formed an 8-foot bed in the reactor pipe.

The syngas flowed through the inside of the pipe, contacting the catalyst surfaces. The linear superficial velocity in the pipe was in the range of 2.3 to 6.0 actual feet per second. The gas rate was varied from 90 to 263 scfh/square foot of catalyst area. Heat of reaction was removed by recycling the reaction gas through an external heat exchanger.

15.2.3 PROCEDURE

The catalyst coated plates, coated with flame sprayed Raney nickel, were placed in the reactor and then activated by passing a 2 weight percent caustic soda solution through the reactor until approximately 70% of the aluminum in the Raney alloy was dissolved as determined by measuring the quantity of hydrogen evolved. Following activation, the catalyst was water-washed until the effluent water reached a pH of 7.2. Reactor startup was initially under hydrogen pressure until synthesis temperature and pressure were reached. Synthesis gas was then gradually fed into the system to commence the run.

The quantities and compositions of feed, intermediate and product streams, along with reaction conditions were measured to provide data for calculation of syngas conversion, catalyst activity, space velocities, product composition, and other design factors.

15.2.4 DATA

Data were generated for three experimental series. To illustrate, data for 7 runs of experimental series HGR 15 are presented in Table 15.2-1. Experiments HGR-14 and HGR-15 ran for 2,300 and 1,300 hours, respectively. Hourly space velocities to 2,000 were successfully tested.

15.2.5 ANALYSIS

The data in Table 15.2-1[17] show:

- High (H_2 + CO) conversions in the range of 98 to 99% of the fresh feed and 50 to 65% of the mixed reactor feed

- Methane content in the product is of the order of 90%

- Product heating value is in the range of 930 to 960 Btu/scf.

The FSC reactor data base for the methanation reactor is more extensive than that for the Fischer-Tropsch synthesis FSC reactor. A similar geometry, using sprayed catalyst for the conceptual plant methanation process reactor, was adopted. The modified design has similar significant advantages.

15.2.6 OTHER DATA SOURCES

PERC has reported methanation data for the catalyst systems:

- Packed beds of steel lathe turnings with active iron oxide surfaces constituting the main reactor of the system

- Packed beds of granular Raney nickel as the second reactor.

15.2.6.1 DISCUSSION

This work had the objective of synthesizing high Btu gas. A 12-inch diameter main reactor was operated, covering Experiments 22 through 25.[7] Table 15.2-2 lists typical data for Run C of Experiment 23. These data were included in the data base because of the low 0.1 volume percent CO content in the final product gas stream (tail gas).

15.2.6.2 ANALYSIS

The experimental data covered in Table 15.2-2 indicate the following:

(1) An overall conversion for (H_2 + CO) of 99.5% for the two reactors in the series

(2) A tail gas product heating value of 985 Btu/cu ft

(3) A tail gas product composition of 94.3% methane

(4) Recycle ratios were 27:1 for the main reactor and 7:1 for the second reactor.

15.2.7 DATA SELECTION

Based on the data analyses summarized above, plus analyses of preferred reactor geometry, it was decided:

- To use a flame sprayed Raney nickel catalyst coated on the outside of an extended surface heat exchanger for the primary methanation reactor

  - Data from the FSC Runs HGR-14 and HGR-15 indicated that FSC type reactors could be effectively used as primary methanator reactors

  - The geometry was selected for reasons of predicted performance in the reactor as well as effect on auxiliary process equipment and plant thermal efficiency

- To use a "final" methanation reactor consisting of a granular nickel catalyst bed

  - The purpose is to ensure essentially complete carbon monoxide conversion.

15.2.8 CATALYST LIFE AND ACTIVITY

The conceptual plant methanation design is based on a catalyst life of one stream year, or approximately 8,000 operating hours. The reasons for selecting this projected life are:

- The flame sprayed catalyst in PERC Experiments HGR-14 and -15 ran well for 2,300 and 1,300 hours, respectively

- The conceptual design includes extensive syngas cleanup and desulfurization facilities

- The abbreviated active catalyst lives obtained by the FSC were attributed to sulfur poisoning and carbon deposition

  - The assurance of low sulfur in the design was considered a basis for projecting the 8,000 hours life

  - The carbon deposition rate is expected to be considerably reduced because of the geometry of the reactor and the rapid direct reaction heat removal feature of the extended surface heat exchanger reactor design. Further discussion of this factor follows.

15.2.9 CARBON DEPOSITION

Figure 15.2-2 presents a carbon formation equilibrium isotherm for 500 psig operation.[15] Points representing conditions for the PERC experimental methanation reactor and the conceptual methanation reactor are shown. In all cases, the reactor gas compositions are outside the theoretical carbon forming region. However, carbon deposition and also some catalyst carbiding at the reactor inlet have been observed in the PERC experiments possibly due to trace amounts of iron carbonyl in the reactor feed.[11] The amount of carbon deposition during the life of the conceptual methanator catalyst is expected to be appreciably less because of the reactor geometry plus better temperature control through direct heat conductance.

15.2.10 DESIGN BASIS

Key design basis elements selected for the methanation reaction system are summarized below; reasons for their selection have been discussed in the preceding sections.

Key Reactor Design Basis Elements

Capacity, scf/day SNG, billion	263
Pressure, psig	380
Temperature (average), °F	585
Linear Velocity, actual ft/sec average	2.3
Space Velocity Factors	
J, scf/hr/sq ft of catalyst area	15
S_v, scf/hr/cu ft of shell volume	6,100
Syngas Composition	
Fresh Feed H_2/CO ratio	3.35
Conversion	
Primary reactor (CO + H_2) Conversion, %	89.2
Overall (CO + H_2) Conversion, %	99.25
Reactor Recycle Ratio	
Volume Recycle Gas ÷ Volume Fresh Syngas Feed	1.7
Heat of Reaction at Reactor Conditions	
Btu/scf of methane formed	192
Product Methane Content	
Main Reactor Product, volume percent	77.8
Final SNG Product, volume percent	83.8

Table 15.2-3 compares the conceptual design methanation reactor with PERC FSC and granular catalyst experimental data.

Table 15.2-1 - Example Experimental Data
Methanation Runs
Experiment HGR 15[17]

Item	Period Number					
	2	33	34	41	42	44	45
Catalyst type	The primary reactor was packed with flame sprayed Raney nickel-coated plate grids. The second reactor was packed with a precipitated nickel catalyst. Results for the primary reactor operation only are given.						
Hours on stream	91	955	979	1147	1171	1219	1243
Fresh gas:							
Rate, scfh	810	821	820	822	823	617	411
H_2, vol pct	75.1	75.3	74.6	75.1	75.3	74.7	75.5
CO, vol pct	24.5	23.8	24.5	24.5	24.3	24.2	23.7
CO_2, vol pct	0.1	0.1	0.1	0.2	0.1	0.2	0.2
N_2, vol pct	0.3	0.7	0.7	0.2	0.3	0.8	0.5
CH_4, vol pct	0	0.1	0.1	0	0.1	0.1	0.1
H_2:CO	3.1	3.2	3.0	3.1	3.1	3.1	3.2
Exposure vel., $scfh/ft^2$	17.8	18.0	18.0	18.0	18.0	13.5	9.0
Space vel., hr^{-1}	1990	1986	2013	2015	2017	1512	1008
Mixed feed gas (wet):							
Rate, scfh	12000	9750	7600	8700	10150	6780	4470
H_2, vol pct	8.5	13.5	14.0	13.4	13.7	13.0	12.5
CO, vol pct	1.7	2.5	3.0	3.0	2.7	2.8	2.4
CO_2, vol pct	1.0	0.5	0.5	0.7	0.7	0.6	0.5
N_2, vol pct	3.5	0.9	0.8	1.1	0.8	0.9	0.3
CH_4, vol pct	79.2	78.0	77.7	77.6	77.5	78.4	79.9
H_2O, vol pct	6.1	4.6	4.0	4.2	4.6	4.3	4.4
H_2:CO	5.1	5.4	4.7	4.5	4.9	4.6	5.1
Inlet superficial vel., f/s	6.4	5.2	4.0	4.6	5.4	3.6	2.4
Inlet Reynolds No.	5660	4400	3440	3920	4580	3960	2040
Exposure vel., $scfh/ft^2$	263	214	166	190	222	149	98
Space vel., hr^{-1}	29400	23900	18600	21250	24900	16620	10950
Vol total recycle/vol fresh gas	14.0	11.1	8.5	0.0	11.6	10.2	10.1
Vol cold recycle/vol fresh gas	2.5	3.0	3.0	3.0	3.0	3.0	3.1
Temperatures:							
Gas inlet, °F	576	574	576	574	572	572	576
Maximum catalyst, °F	743	752	793	797	752	750	752
Pressure, psig	300	300	300	300	300	300	300
Product gas:							
Rate, scfh	206.0	212.3	208.6	210.9	211.7	156.4	103.8
H_2, vol pct	4.0	8.2	6.9	7.2	8.6	7.1	6.4
CO, vol pct	.03	0.6	0.4	0.7	0.9	0.7	0.3
CO_2, vol pct	1.17	0.5	0.6	0.3	0.8	0.6	0.5
N_2, vol pct	3.9	1.0	0.9	1.2	0.9	1.0	0.3
CH_4, vol pct	90.7	89.5	91.0	89.9	88.6	90.4	92.3
H_2O, vol pct	0.2	0.2	0.2	0.2	0.2	0.2	0.2
H_2:CO	133.0	13.7	16.9	9.6	9.3	10.4	21.4
Conversion:							
H_2, pct fresh feed	98.7	97.6	98.0	98.0	97.6	98.3	98.8
CO, pct fresh feed	100	99.5	99.7	99.4	99.2	99.5	99.8
(H_2+ CO), pct fresh feed	99.0	98.1	98.4	98.5	97.9	98.6	99.0
H_2, pct mixed feed	38.4	45.6	56.3	52.0	43.4	51.2	54.4
CO, pct mixed feed	98.4	78.8	88.0	77.6	70.0	78.3	89.1
(H_2+ CO), pct mixed feed	65.0	50.8	61.8	56.7	47.9	56.0	60.1
Usage ratio, H_2:CO	3.0	3.1	3.0	3.0	3.0	3.0	3.1
Heating value, Btu/scf	934	937	947	937	931	943	959
Carbon recovery, pct	95.0	100	96.7	97.8	97.3	96.0	96.5

Table 15.2-2 - Experimental Data
Methanation Experiment 23 C[7]

Item		Experiment 23 Period C
Catalyst Type	Primary Reactor:	Steel Turnings
	Second Reactor:	Granular Raney Ni
Synthesis, hours		475-571
Primary reactor conditions:		
Fresh feed rate, scfh		1,412
Space velocity, vol/vol/hr		706
Reactor pressure, psig		398
Recycle to fresh feed ratios:		
Total		27
Hot		25
Cold		2
Reactor temperature, °F:		
In gas		570
Out gas		628
Increment		58
Average catalyst temperature, °F		603
Maximum catalyst temperature, °F		653
Catalyst pressure drop, in. of H_2O/ft		6
Water vapor in recycle gas, vol %		7.6
H_2O:CO ratio,		
Fresh gas		2.85
Recycle gas		31.7
Second reactor conditions:		
Fresh feed rate, scfh (from primary reactor)		419
Space velocity, vol/vol/hr		9,100
Space velocity (based on fresh feed), vol/vol/hr		26,000
Recycle to fresh feed ratio		7
Reactor temperature, °F		
In gas		556
Out gas		662
Average catalyst temperature, °F		608
Maximum catalyst temperature, °F		662
Water vapor in recycle gas, vol %		2.9
Overall results:		
Reactors in service		2
CO_2-free contraction, %		76.1
H_2 conversion, %		99.3

Table 15.2-2 (Contd)

Item	Experiment 23 Period C
Overall results: (contd)	
CO conversion, %	99.9
H_2 + CO conversion, %	99.5
H_2:CO ratio, usage	2.83
Heating value of tail gas,[a] Btu/ft^3	985
Tail gas composition, vol %:[b]	
H_2	2.1
CO	0.1
N_2	1.1
CO_2	1.3
C_1	94.3
$C_2=$	0
C_2	0.7
$C_3=$	0.1
C_3	0.3
$C_4=$	0
C_4	0
$C_5=$	0
C_5	0
Feed gas ft^3 tail gas 0 ft^3	4.13
Tail gas[c] ft^3 tail gas 0 ft^3	342
Yield, 9/m^3 (H_2 + CO) converted:	
C_1	163
$C_2=$	0
C_2	2
$C_3=$	0
C_3	2
$C_4=$	0
C_4	0
$C_5=$	0
C_5	0
Oil	4
Aqueous	192
C_1 - C_3OH[d]	11
Other oxygenates[d]	0
Water	181
CO_2	6
Hydrocarbon recovery, g/m^3	171
Theoretical recovery, g/m^3	181

[a] Cubic feet corrected to 60°F and 30 inches of mercury (dry).

[b] Dry basis.

[c] Corrected to °C and 760 mm of mercury.

[d] Calculated as hydrocarbons.

Table 15.2-3 - Comparison of Granular and
Spray Coated Plate Catalyst Systems

	Granular Catalyst Exp. 7	Sprayed Plates Catalyst		
		PERC[17] Exp. HGR 15 (91 hours)	PERC[17] Exp. HGR 15 (1171 hours)	F-T Conceptual Design Fin Tube Reactor
Number of stages	1	1	1	1
Stage Number	1	1	1	1
Pressure, psig	398	300	300	382
Temperature out, °F	662	743	752	600
Temperature in, °F	556	576	572	571
Temperature, avg., °F	609	660	662	586
Overall				
CO Methanated, %	95.46	100	99.2	98.98
CO_2 Methanated, %	88.08	-197.6	-105.8	-1.9
CO Methanated, %	95.46	100	99.2	98.98
T_e-T_{out},[b] °F	+116	-184	+234	+185
CO_2 Methanated	88.08	197.6	-105.8	-1.9
T_e-T_{out},[b] °F	+97	+41	+160	+135
S_v, scfh/cf(a)	9,100	1,900 (J=17.6)	2,017 (J=17.9)	(J=15.0)
Product (Dry) Mol %				
H_2	2.1	4.0	8.6	4.89
CO	0.1	0.0	0.90	0.10
CO_2	1.3	1.2	0.80	1.82
CH_4	94.3	90.80	88.8	85.52
N_2	1.1	3.9	0.9	6.99
C_{2+}	1.1	0.1	1.0	0.68
Feed (Dry) Mol %				
CO	1.54	24.5	24.2	16.97
CO_2	7.65	0.1	0.1	.83
H_2	49.04	75.1	75.3	57.25
C_1	30.63	0.0	0.1	18.22
N_2	0.78	0.3	0.3	3.4
C_{2+}	10.36	0.0	0.0	3.33

(a)Based on fresh feed gas
(b)T_e is equilibrium temperature corresponding to gas composition and
    pressure.
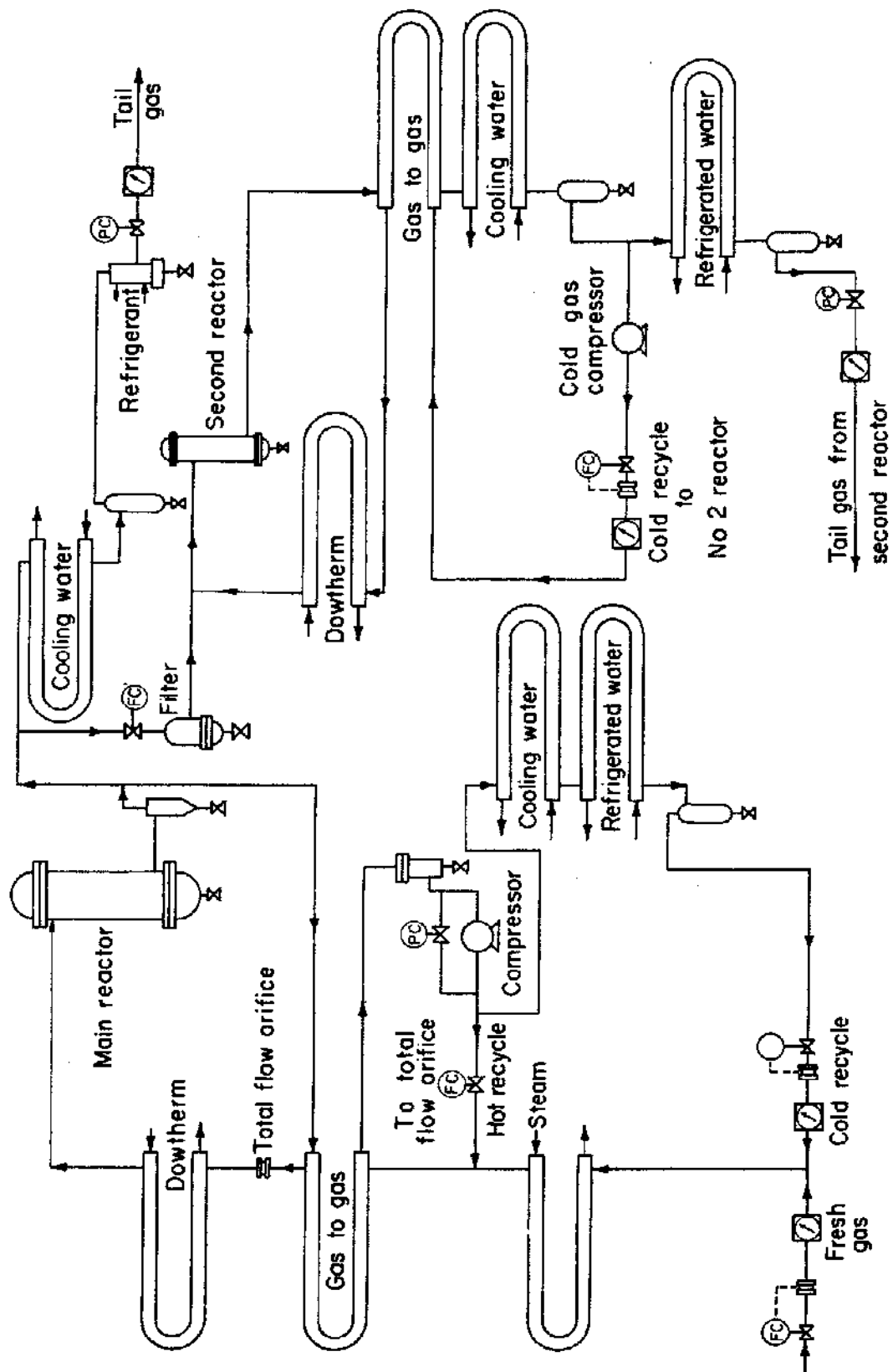
Figure 15.2-1 - Sketch: Experimental Equipment Used for
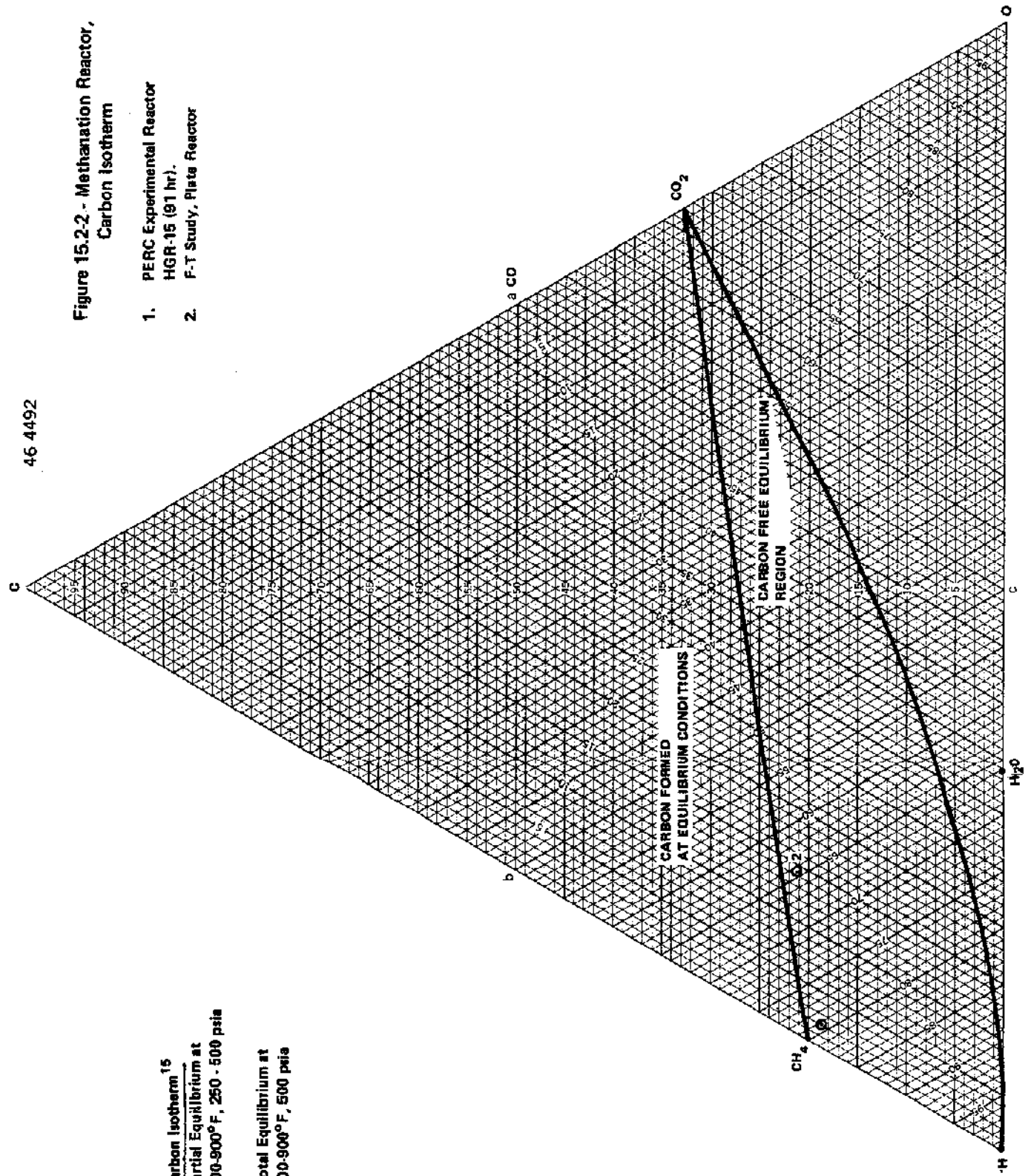Fischer-Tropsch Reactions Runs[7]

Figure 15.2-2 – Methanation Reactor, Carbon Isotherm

1. PERC Experimental Reactor HGR-15 (91 hr).
2. F-T Study, Plate Reactor

46 4492

Carbon Isotherm[15]
Partial Equilibrium at
600-900°F, 250 - 500 psia

Total Equilibrium at
600-900°F, 500 psia

CARBON FORMED
AT EQUILIBRIUM CONDITIONS

CARBON FREE EQUILIBRIUM
REGION

C

a CO

b

CO_2

CH_4

H_2O

H

O

SECTION 15

BASIS OF FISCHER-TROPSCH REACTOR DESIGNS

15.3. SHIFT REACTOR

15.3.1 INTRODUCTION

The design for the Fischer-Tropsch sour shift reactor is based upon an isothermal design using flame sprayed catalyst deposited on an extended surface heat exchanger. This is the same basic reactor design concept used for the Fischer-Tropsch and the methanation reactors.

It was hypothesized that the FSC-type reactor, with advantages described earlier in this report for the Fischer-Tropsch synthesis and methanation reactions, could be favorably adapted to the shift conversion operation. The selection of this reactor design concept was based on the analyses that are summarized in the following paragraphs.

15.3.2 REACTOR PARAMETERS

Steam is added to the gas feed to the shift reactor both to provide reaction steam for increasing the H_2 to CO molar ratio and to suppress the formation of carbon on the catalyst.

15.3.2.1 SHIFT REACTOR SELECTION

This reaction is exothermic, but to a lesser degree than the Fischer-Tropsch synthesis and methanation reactions.

Heats of reaction for these processes are:

(Btu/lb mol CO converted)

Shift	16,600
Fischer-Tropsch	60,900
Methanator	100,500

The shift conversion cobalt-molybdenum metallic catalysts are amenable to successful flame spraying. The simplified FSC reactor installation, along with its predicted beneficial heat recovery performance, which contributes to a high process thermal efficiency, were key factors in selection of this reactor design.

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15.3.2.2 CARBON DEPOSITION

Carbon may be formed by any one of the following reactions:

$$2CO \rightleftharpoons C + CO_2$$

$$CO + H_2 \rightleftharpoons C + H_2O$$

$$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O$$
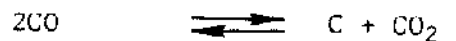
The triangular coordinate carbon phase diagram, Figure 15.3.1,[15] shows that both commercial sour and sweet shift granular catalysts operate in a region where carbon laydown is theoretically possible. However, sour shift catalysts appear to be able to operate at lower steam-to-dry gas ratios than sweet shift catalysts - as indicated by the two lines drawn parallel to the carbon isotherm.

The design case is represented by point 7P and corresponds to a steam-to-total dry gas molar ratio of 0.63.

While carbon formation can be avoided by correct selection of thermodynamic conditions, kinetic effects are also responsible for the suppression of carbon formation. In addition, carbon formation will only occur when a certain limiting driving force for the carbon forming reaction is exceeded.[18] This limiting value is a specific parameter for each catalyst, and can be determined experimentally.

The possibility of carbon laydown in the extended surface heat exchanger is reduced by the short gas residence time and good temperature control obtained with this type of reactor design. The consequence of carbon laydown in the plate reactor is not as great as with a fixed bed reactor where the bed may plug due to segregated hot spots with attendant carbonizing at the catalyst surfaces.

Conventional COMOX shift catalyst can be regenerated by the controlled burning of any deposited carbon. Catalyst regeneration facilities in the form of connected steam, compressed air, and vent gas lines have been provided.

15.3.3 CATALYST COMPOSITION

Commercial granular sour shift catalyst is a cobalt oxide-molybdenum oxide-alumina catalyst, containing more cobalt and molybdenum than a typical COMOX hydrodesulfurization catalyst.

Chemical Analysis:[19,20]

	Sour Shift	COMOX
Wt% CoO*	4.1	3.5
MoO_3	13.8	10.0

*Co and Mo calculated as the oxide.

Sour shift catalyst must be maintained in the sulfided state, and cannot be used on a sulfur-free stream. The chemical analysis of used catalyst is reported to be:

Wt% CoC*	4.1
MoO_3	13.8
S	7.3
C	0.61

The molecular proportions of Co, Mo, and S are 1, 1.75, and 4.15, respectively. These proportions would correspond to the Co and Mo existing entirely as their sulfides, Co_3S_2 and MoS_2. Hydrotreating catalysts are also sulfided in situ with the sulfur consumed closely approaching that required to convert the metals to their sulfides.[21]

The alumina functions as a carrier for the active elements, increasing the active catalyst surface and prolonging the life of the catalyst by retarding or preventing crystal growth. It is not known if the alumina also has an active role in the shift reaction. However, it is interesting to note that unsupported metal sulfides have been used as hydrotreating catalysts[21,22] and that most hydrotreating catalysts will also function as sour shift catalysts.[22]

In the proposed isothermal reactor design, a 40-mil layer of cobalt/ molybdenum alloy is flame sprayed onto steel extended surface heat exchanger tubes. Dowtherm circulation through the tubes is used to remove the heat of reaction, and to maintain the gas temperature constant. The catalyst is reduced and presulfided in situ using the process gas stream.

15.3.4 REACTOR DESIGN

The reactor is designed to operate isothermally at 650°F, and to obtain 95% of the theoretical CO conversion.

Table 15.3-1 compares the design values for the proposed El Paso SNG plant and reported performance results for tests made at Westfield, Scotland and the Girdler data.

The proposed plate reactor is designed to operate at a "J" factor of 32 scfh/sf. This provides almost twice the amount of active catalyst required by the granular catalyst design. The average catalyst surface heat release rate is 315 Btu/hr/ft^2.

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*Co and Mo calculated as the oxide.

Used sour shift catalyst is characterized by small pore diameters, generally less than 8°A, and a surface area of about 65 m^2/gm.[20] The proportion of the granular catalyst surface area available is dependent upon the relative rates of diffusion of carbon monoxide and carbon dioxide within the pores as compared to the rate of reaction. If diffusion is fast enough as compared to the rate of reaction, all of the pellet surface area is available. Sweet shift unsupported iron oxide catalysts are generally about 75% surface area effective.

The flame sprayed catalysts are generally characterized by large pore diameters, generally greater than 30°A, and an active surface area of about 25 m^2/gm. Consideration of the relative active surface areas of flame sprayed and granular catalysts indicates that at the design "J" factor of 32 and 40 mil film thickness, the granular catalyst would have about 6 times the active surface area of the plate catalyst. Thus, the activity of the plate catalyst must be some 6 times greater than that of the granular catalyst, on a surface basis, for equal reactor performance. Experiments are required for verification.

Key Design Basis Elements

Capacity, mols per hour	30,000
Pressure, psig	450
Temperature, °F	650
Conversion: (CO + H_2) Conversion, %	79
Space Velocity Factors	
J, scf/hr/sq ft of catalyst area	32
S_v, scf/hr/cu ft	5,800
Heat of Reaction at Reactor Conditions, Btu/scf of CO Converted	43.7

Syngas Composition	Shift Reactor Feed mol %	Shifted Syngas mol %
H_2	24.1	46.6
CO	28.3	5.8
CO_2	6.6	29.1
CH_4	1.2	1.2
H_2S	0.7	0.7
N_2	0.5	0.5
H_2O	38.6	16.1
NH_3, COS, SO_2	Trace	Trace
Total	100.0	100.0

Table 15.3.1 - Process Performance Comparison Sour-Shift Conversions

Item	Lurgi El Paso (FPC)	Westfield [22,23]		Girdler [19] G-93	I-T Conceptual Design
Number of Stages	2	2		1	1
Stage Number	1 and 2 (overall)	1	2	1	1
Pressure, psig	400	350		425	450
Temp. Out, °F	–	891	745	870	650
Temp. In, °F	–	734	733	850	650
Temp. Avg., °F	–	814	739	860	650
Net % CO converted	77	64		47	79
S_v, scfh/cf	–	1,656	2,426	14,783	5,800
CO converted, %	–	64	36	47	79
Equilibrium, %	–	83	83	63	95
T_e(a)$-T_{out}$, °F	–	58	38	437	50
Dry Gas Composition, mol%					
C	23.8		24.5	28.0	28.0
H	38.2		38.2	38.7	37.7
O	38.0		37.3	33.3	33.3
	100.0		100.0	100.0	100.0
H_2O/Dry Gas mol/mol	0.7		0.42	0.80	0.65
H_2O/C Mol/mol	1.5		0.85	1.41	1.1
Wet Gas Composition, mol%					
C	11.5		15.1	12.8	14.5
H	52.9		49.1	53.9	52.2
O	35.6		35.8	33.3	33.3
	100.0		100.0	100.0	100.0

(a) T_e is equilibrium temperature corresponding to product gas composition and pressure.

(b) CO, CO_2, H_2, and H_2O only.

Figure 15.3-1 - Carbon Phase Diagram, Shift Reactor

Carbon Isotherm[15]
Partial Equilibrium
at 600-900°F, 250 psia

Dry gas = $CO + CO_2 + H_2$
(0.6526) = H_2O:Dry gas
Moler Ratio

CO_2

GRAPHITE ISOTHERM

CARBON FREE EQUILIBRIUM REGION

CARBON FORMED AT EQUILIBRIUM CONDITIONS

H_2O

H

O
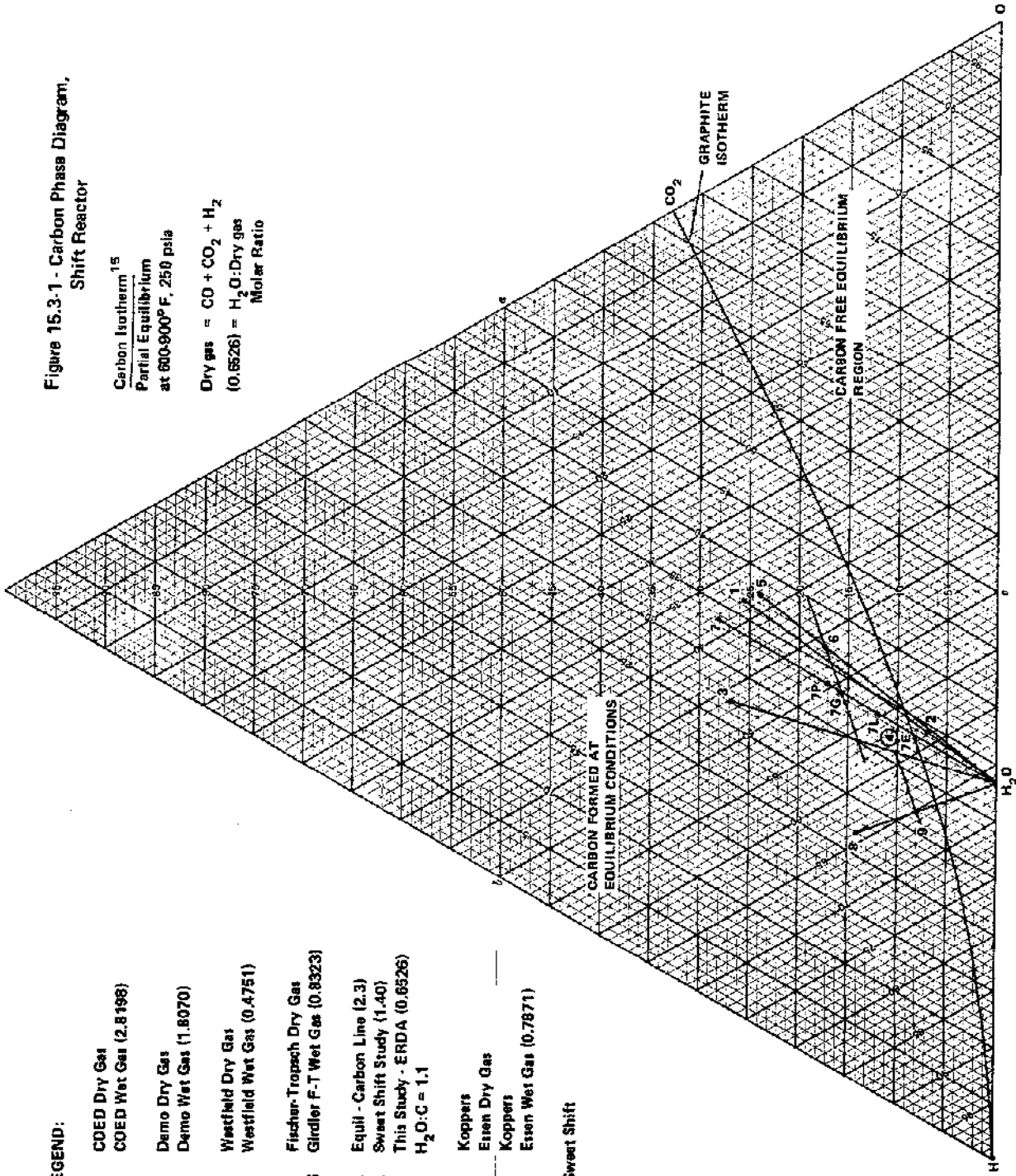
LEGEND:

| 1 | COED Dry Gas |
| 2 | COED Wet Gas (2.8198) |

| 3 | Demo Dry Gas |
| 4 | Demo Wet Gas (1.8070) |

| 5 | Westfield Dry Gas |
| 6 | Westfield Wet Gas (0.4751) |

| 7 | Fischer-Tropsch Dry Gas |
| 7G | Girdler F-T Wet Gas (0.8323) |

7E	Equil - Carbon Line (2.3)
7L	Sweet Shift Study (1.40)
7P	This Study : ERDA (0.6526)
	H_2O:C = 1.1

8	Koppers
	Essen Dry Gas
9	Koppers
	Essen Wet Gas (0.7871)

* Sweet Shift