

THE CONVERSION OF CARBON MONOXIDE TO CARBON DIOXIDE
OVER IRON CATALYST IN THE FISCHER-TROPSCH PROCESS

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PREFACE

Iron catalysts have important advantages over other commercial Fischer-Tropsch catalysts. The iron catalysts are easily obtained, impart flexibility to the process, and when used in the fluidized-bed have very high space-time yields. A disadvantage of iron catalysts is that they also promote the water-gas-shift reaction and a portion of the carbon monoxide is converted to carbon dioxide instead of to useful products.

Data was obtained in Fischer-Tropsch pilot plant operations with fluidized-iron catalyst to show the effects of space velocity, recycle ratio, carbon dioxide in the reactor feed and hydrogen-to-carbon monoxide ratio in the synthesis gas upon the yield of carbon dioxide. Calculated equilibrium yields are compared with the yields of carbon dioxide obtained in these experiments.

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I. INTRODUCTION

In 1923 Franz Fischer and Hans Tropsch (5,11) of the Kaiser Wilhelm Institute in Germany observed that carbon monoxide and hydrogen would react over alkalized iron turnings at 100-150 atmospheres and 700-800 F to form oxygenated compounds and a minor amount of hydrocarbons. Later Fischer (6,7) observed that at lower pressures the product distribution was reversed and hydrocarbons were the principal product. The first Fischer-Tropsch catalyst was an iron-zinc oxide preparation reported by Fischer in 1925 (11). In the next few years many iron, cobalt and nickel catalysts were tested for the Fischer-Tropsch process. A catalyst prepared in 1931 by precipitation of nickel-thoria on kieselguhr and a corresponding cobalt catalyst prepared in 1932 formed the basis for the development of the Ruhrchemie commercial catalyst (8). However, not until 1937, several years after Fischer-Tropsch processes were in commercial operation with cobalt catalysts, was the development of the iron catalyst successful, and not until the end of World War II were fluidized-catalyst techniques applied and iron catalysts of high mechanical strength developed.

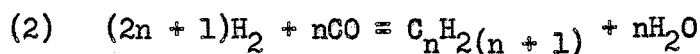
The iron catalysts have two important advantages over the cobalt catalysts in that they are easily available from many sources and they impart flexibility to the Fischer-Tropsch process. In the use of iron catalysts, product distribution may be regulated by variation in catalyst composition, method of preparation, method of reduction, composition of synthesis gas and process conditions. The fluidized-iron catalyst Process is outstanding because of its very high space-time yield.

A disadvantage of iron catalysts is that, in addition to being active in promoting the synthesis of hydrocarbons, they are also active in promoting the water-gas-shift reaction. Thus, a portion of the carbon monoxide is converted to carbon dioxide. It is generally desirable to limit the yield of carbon dioxide so that higher yields of useful products may be obtained.

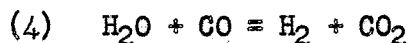
Data have been obtained in Fischer-Tropsch pilot plant operations with fluidized-iron catalyst to show the effects of space velocity, recycle ratio, carbon dioxide in the reactor feed and hydrogen-to-carbon monoxide ratio in the synthesis gas upon the yield of carbon dioxide. Calculated equilibrium yields are compared with the yields of carbon dioxide obtained in these experiments.

II. THEORY

The stoichiometric equations representing the over-all reactions of synthesis gas composed of approximately two parts hydrogen and one part carbon monoxide are:



where olefin, paraffin, alcohol, and water are the products. Similar equations can be written for other oxygenated products. The water vapor formed by the above reactions reacts with carbon monoxide to produce carbon dioxide and hydrogen by reactions equivalent to the water-gas-shift reaction



The equilibrium constant, K_p , for the water-gas-shift reaction,

$$(5) \quad K = \frac{(CO_2)(H_2)}{(H_2O)(CO)},$$

as shown in Figure 1, is large at temperatures below 800 F (2, 9, 10).

Therefore, the formation of carbon dioxide and hydrogen would be favored at practical synthesis conditions, 400-700 F.

Since the water-gas-shift reaction is active over iron catalysts, operating variables and methods of operation that affect the concentration of carbon monoxide, carbon dioxide, or hydrogen in the reactor feed would influence the yield of carbon dioxide. Adding carbon dioxide or removing carbon dioxide from the reactor feed, changing the hydrogen-to-carbon monoxide ratio in the synthesis gas, or changing the recycle ratio are ways of influencing carbon dioxide yields.

III. EXPERIMENTAL EQUIPMENT

A. Flow Diagram

Two pilot plants with batch fluidized reactors were used to obtain the data. A simplified flow diagram of the smaller unit, Pilot Plant One, is shown in Figure 2. The flow diagram of Pilot Plant Two was essentially the same.

Referring to Figure 2, synthesis gas from the high pressure storage cylinders (1) passed through the pressure regulator (2) and through the motor valve (4), which was regulated by the flow controller (3). The synthesis gas mixed with the recycle gas and passed through the preheater (5) into the bottom of the reactor (6). The effluent from the top of the reactor passed through the wax trap (7), through two parallel condensers (8) and into the product separators (9). The liquid product was removed from the bottom of the separators and the gas passed out the top and through a coil, in an ice bath, into another separator (10). A portion of the gas from this separator was vented through the motor valve (11), which was regulated by the pressure controller (12) connected to the top of the reactor. The effluent gas passed through a dry ice trap (13) and was sampled and metered (14). The remainder of the gas from the separator was recycled back to the preheater inlet by the compressor (15).

Two soda lime scrubbers were added to the recycle system for the removal of carbon dioxide from the recycle gas in a special experiment.

B. Description of Equipment

The essential pieces of equipment making up Pilot Plant One are described in this section.

Synthesis Gas Storage Cylinders (1): The storage cylinders for the synthesis gas were standard high pressure gas cylinders connected in two banks of six cylinders each.

Preheater (5): The preheater was constructed from twelve feet of 3/4-inch 18-8 stainless steel pipe. The pipe was bent in an inverted "U" on a four-inch radius and was wound with four 600-watt heating units.

Reactor (6): The reactor was constructed from a four-foot length of two-inch standard seamless pipe. Blind flanges were attached to each end and the reactor was placed in a vertical position. The bottom flange was provided with a gas inlet line, and a catalyst removal port and the top flange with an effluent line, a pressure tap, and a catalyst charge port. A one-fourth-inch thermocouple well (17) extended from the top down the center of the reactor. A perforated cone in the bottom of the reactor distributed the mixed feed and inverted perforated cones attached to the thermocouple well served as baffles. The reactor was jacketed with a four-inch pipe which contained the heat-transfer liquid, tetralin. A 2000-watt heater and a 1000-watt heater were wound on the jacket and the top of the jacket was connected to a condenser. Carbon dioxide was introduced into the jacket to control the pressure of the boiling tetralin, thus controlling the reactor temperature.

Condensers (8): The parallel condensers consisted of three-foot sections of jacketed three-fourths-inch pipe.

Product Separators (9) and (10): Each separator consisted of a one-gallon cylinder immersed in a wet ice bath. The inlet was an induction tube down to the middle of the receiver and the effluent gas line was near the top. Liquid product was withdrawn from the bottom of the receiver.

Recycle Compressor (15): The recycle compressor was a Kelvinator two-cylinder, one-fourth-horsepower refrigerator compressor powered by a

one-half-horsepower, 110 v, 1725 rpm motor.

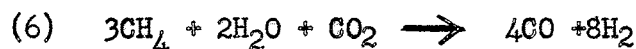
Soda-lime Scrubbers: The soda-lime scrubbers were constructed from three-foot sections of three-inch pipe and were provided with suitable end closures.

Pilot Plant Two equipment was similar, but on a larger scale. The reactor was the same diameter but two and one-half times as high. A gas-fired radiant-type preheater was used in addition to the electric heated pipe. The product separator was a five-gallon vessel. A Norwalk two-cylinder compressor was used for the recycle compressor and a flow controller was used to regulate the recycle rate.

IV. MATERIALS

A. Synthesis Gas

The synthesis gas was prepared by reforming natural gas with steam and carbon dioxide over a supported nickel catalyst at 1400 F and atmospheric pressure.



The excess steam was condensed and most of the unreacted carbon dioxide was removed by caustic scrubbing. The synthesis gas was compressed into high pressure storage cylinders. A typical composition of normal synthesis gas was as follows:

<u>Component</u>	<u>Mol Per Cent</u>
Carbon monoxide	31.0
Hydrogen	66.0
Carbon dioxide	0.2
Methane	1.0
Nitrogen	1.8
Total	100.0

Synthesis gases of different hydrogen-to-carbon monoxide ratios were prepared by changing the natural gas-to-carbon dioxide-to-steam ratio of the feed to the reforming unit. Synthesis gas containing four per cent carbon dioxide was prepared by adding cylinder carbon dioxide to normal synthesis gas.

B. Catalyst

Three catalysts of similar compositions were used in the tests. They were prepared by fusing iron oxide, adding minor amounts of promoters to the molten oxide, cooling, crushing to 100-325 Tyler mesh, and reducing with hydrogen.

The promoters used were:

<u>Promoter</u>	<u>Weight Per Cent</u>
K ₂ O	0.3 - 0.4
Al ₂ O ₃	1.5
CaO	1 - 5

C. Soda Lime

The soda lime used for carbon dioxide scrubbing (Test 1-b) was Fisher, 4-8 mesh material, containing two per cent moisture. It was sprayed with water to increase the moisture content to 15 per cent. Eight and one-half pounds of soda lime was used in each scrubber.

V. PROCEDURES

A. Operating Procedures

The general method of start-up was as follows: The reduced catalyst was charged to the reactor and was treated with synthesis gas at atmospheric pressure, 570 F, and a space velocity of 1000 volume of gas per volume of catalyst per hour until the conversion of the synthesis gas decreased nearly to zero. The system was then pressured with hydrogen to operating pressure, and recycle was started. Synthesis gas was introduced and the rate was gradually increased, while the temperature and other operating variables were adjusted to the specified conditions.

Three catalysts were used in this investigation. Tests 1-a, 1-b, and 1-c were made with the first catalyst. This catalyst was operated at normal conditions for the first twenty hours, and yield data and stream compositions were obtained (Test 1-a). At twenty hours on stream the soda lime scrubbers were pressured up with effluent gas, and recycle gas was passed through the first scrubber until equilibrium conditions were regained in the system. The recycle stream was then switched to the second scrubber, and stream compositions and yield data, including the amount of carbon dioxide removed by the scrubber, were obtained (Test 1-b). After a period of normal operation, data were obtained with synthesis gas containing four per cent carbon dioxide (Test 1-c). The catalyst was then operated at normal conditions to check the change in activity. The change was found to be negligible.

Tests 2-a, 2-b, and 2-c were made with the second catalyst, and the remaining tests, 3-a, 3-b, 3-c, 4-a, 4-b, 4-c, 4-d, and 4-e were

made with the third catalyst. Both of these catalysts were first operated for more than one hundred hours at normal conditions so that any influence of initial catalyst activity would be eliminated.

B. Analytical Procedures

Standard Orsat methods were used to determine the carbon monoxide, hydrogen, and carbon dioxide in the synthesis gas, mixed feed, and effluent gas. Potassium hydroxide was used to absorb the carbon dioxide and copper oxide was used to oxidize the hydrogen and carbon monoxide. Compositions of the reactor effluent and the recycle gas were determined by material balances.

The water was separated from the liquid hydrocarbons by a separatory funnel. The amount of water was determined by weight, with correction for the soluble oxygenated compounds present.

The hydrocarbons were analyzed by mass spectrometer and by fractionation.

The amount of carbon dioxide removed by the soda lime from the recycle stream was determined by treatment of several weighed samples of the soda lime with sulfuric acid and measurement of the volume of carbon dioxide evolved.

VI. DATA

Data for the fourteen tests are presented in Appendix A. These data include process conditions, stream compositions, conversions, and equilibrium calculations. An explanation of the data is also given in Appendix A.

From these data the curves in Figures 3, 4, 5, and 6 were obtained. A discussion of these figures is presented in the following section.

VII. RESULTS AND DISCUSSION

A. Effect of Carbon Dioxide in the Reactor Feed Upon Carbon Dioxide Yield

The concentration of carbon dioxide in the reactor feed has a marked effect on the conversion of carbon monoxide to carbon dioxide. As shown in Figure 3, the carbon dioxide yield decreased as the carbon dioxide in the reactor feed increased. This is in agreement with the water-gas-shift reaction (4) and its equilibrium relationship, equation (5). It is obvious from the equilibrium relationship that any increase in carbon dioxide concentration would tend to limit the shift reaction.

The data at the highest carbon dioxide concentration were obtained with synthesis gas containing four per cent carbon dioxide. In this particular case the conversion of carbon monoxide to carbon dioxide was completely eliminated and the hydrocarbon yield increased five per cent over operation with carbon dioxide free synthesis gas.

Synthesis gases prepared by most methods contain some carbon dioxide, and hydrocarbon yields would be increased at the same natural gas consumption if a portion of the carbon dioxide were left in the synthesis gas. The amount of carbon dioxide to be left in the synthesis gas for optimum hydrocarbon yields will depend upon the catalyst, synthesis conditions, and the hydrogen-to-carbon dioxide ratio of the synthesis gas.

Another method for controlling the carbon dioxide in the feed to the reactor and thus increasing the hydrocarbon yields has been presented by Eastman (3). Carbon dioxide was stripped from the unit effluent and recycled back to the reactor so that the concentration in the reactor was between fifteen and thirty per cent.

B. Effect of Hydrogen-to-Carbon Monoxide Ratio Upon Carbon Dioxide Yield

As shown in Figure 4, the yield of carbon dioxide increased as the ratio of hydrogen-to-carbon monoxide in the synthesis gas decreased. This would be expected from the water-gas-shift equilibrium relationship, for an independent decrease in the hydrogen-to-carbon monoxide ratio would result in an increase in carbon dioxide-to-water ratio.

In most cases the production of carbon dioxide would not be desirable. An exception might be encountered when synthesis gases of hydrogen-to-carbon monoxide ratios lower than two are used. These synthesis gases lack sufficient hydrogen to convert all the carbon monoxide to hydrocarbons, as in equations (1), (2), and (3), and additional hydrogen is needed. A source of this hydrogen is the water-gas-shift reaction. Although hydrogen supplied by the shift reaction increases the carbon dioxide yield, the yield of hydrocarbon per volume of synthesis gas may not be affected.

C. Effect of Space Velocity Upon Carbon Dioxide Yield

The effect of space velocity upon carbon dioxide yield is shown in Figure 5. When the space velocity was increased from 2500 to 5000 volume of gas per volume of catalyst per hour the carbon dioxide yield was almost doubled. This increase in carbon dioxide yield at the higher space velocity can be related to the water-gas-shift reaction. Of the shift-reaction components in the reactor effluent, the greatest change with increasing space velocity is in the concentration of carbon monoxide, as its conversion is decreased. This provides greater driving force for the shift reaction to produce carbon dioxide. The greater production of carbon dioxide at the higher space velocity also indicates that the rate constant

for the shift reaction is greater than that of the hydrocarbon synthesis reaction. The concentration of carbon dioxide in the reactor effluent decreases less with increasing space velocity than that of water, even though water must first be produced by the synthesis reaction to provide a driving force for the shift reaction.

D. Effect of Recycle Ratio Upon Carbon Dioxide Yield

Although the yield of carbon dioxide increased as the synthesis gas space velocity increased, Part C, an opposite effect was obtained when the synthesis gas space velocity was kept constant and the total feed space velocity increased. This is shown in Figure 6 which is a plot of carbon monoxide converted to carbon dioxide versus recycle ratio.

The decrease in carbon dioxide yield was influenced by the increase in ratio of partial pressure of carbon dioxide to that of water vapor at any point in the reactor. This increase in ratio of carbon dioxide partial pressure to that of water vapor was the result of increasing the ratio of recycle gas, which contains considerable carbon dioxide and only traces of water, to that of synthesis gas, which contains only traces of each. Although water was formed rapidly in the synthesis reaction, the partial pressure of water at any point in the reactor decreased as the recycle ratio was increased, thus reducing the tendency toward conversion of carbon monoxide to carbon dioxide by the water-gas-shift reaction. The effect of recycle ratio upon hydrogen and carbon monoxide concentration was in the same direction and largely cancelled out.

E. Comparison of Experimental Data with Water-Gas-Shift Equilibrium

For the eleven runs at 615-620 F in which the space velocity, recycle ratio, and feed composition were varied, the ratios of the product of the mols of carbon dioxide and hydrogen to that of carbon monoxide and water

in the reactor effluent stream ranged from eight to sixteen. The average of these ratios was forty per cent of the equilibrium ratio obtained from the equilibrium constant-temperature curve shown in Figure 1. Although this low percentage indicated the water-gas-shift reaction was far from equilibrium, the actual conversion of carbon monoxide to carbon dioxide was seventy-three to ninety-one per cent of the estimated equilibrium conversion. The method of calculating equilibrium conversion of carbon monoxide to carbon dioxide is presented in Appendix B. This method assumes the yields of other products remain unchanged. The actual and calculated equilibrium conversions of carbon monoxide to carbon dioxide and the ratio of the product of the mols of carbon dioxide and hydrogen to that of carbon monoxide and water are shown with the run data in Appendix A.

VIII. CONCLUSIONS

The data indicate that the production of carbon dioxide was definitely related to the water-gas-shift reaction. Factors that influence the concentration of shift-reaction components in the reactor feed influence the yield of carbon dioxide. Actual carbon dioxide yields were about eighty-five per cent of yields at water-gas-shift equilibrium.

The data show that the production of carbon dioxide can be eliminated entirely and the yield of useful product increased at the same natural gas consumption by leaving carbon dioxide in the synthesis gas. For optimum hydrocarbon yields, the amount of carbon dioxide to be left in the synthesis gas will depend upon the catalyst, synthesis conditions, and the hydrogen to carbon dioxide ratio of the synthesis gas.

This report deals only with carbon dioxide yields. Yields of other products must also be considered in selecting process conditions.

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APPENDIX A

EXPERIMENTAL DATA

A summary of the data obtained in each test is shown on the following pages. An explanation of the data is given below.

Temperature is the average temperature in the catalyst bed to the nearest five degrees Fahrenheit.

Pressure is the average gage pressure in the reactor.

Recycle ratio is ratio of the volume of the recycle gas to the volume of the fresh synthesis gas.

Space velocity is the volume of fresh synthesis gas per hour, measured at 32 F and one atmosphere, per volume of settled catalyst.

Linear velocity is the velocity of the total gas through the reactor, neglecting catalyst volume, non-ideal gas corrections, and contraction due to conversion.

Settled bed depth is the height of the catalyst bed when there is no gas flow and the catalyst has been settled by tapping the reactor.

Synthesis gas is the fresh feed to the reactor.

Recycle gas is the gas that is recycled back from the separator to the reactor.

Mixed feed is the total feed to the reactor, consisting of the synthesis gas plus the recycle gas.

Reactor effluent is the material from the top of the reactor, and is obtained by adding the unit effluent and recycle gas together.

Unit effluent is the gas and liquid removed from the unit.

Carbon monoxide conversion is the disappearance of carbon monoxide.

Hydrogen conversion is the disappearance of hydrogen.

Carbon monoxide converted to carbon dioxide is the difference between the quantity of carbon dioxide in the unit effluent and that in a corresponding volume synthesis gas, divided by the quantity of carbon monoxide in the synthesis gas.

Reactor effluent: $\frac{(H_2) (CO_2)}{(CO) (H_2O)}$ is the ratio of the product of the mols

hydrogen and carbon dioxide to that of carbon monoxide and water in the reactor effluent.

Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium is the difference between the calculated quantity of carbon dioxide in the unit effluent at water-gas-shift equilibrium and that in a corresponding volume of synthesis gas, divided by the amount of carbon monoxide in the synthesis gas.

TEST 1-a

VARIATION OF CARBON DIOXIDE IN THE MIXED FEED: NORMAL OPERATION

Process Conditions

Pilot Plant One

Temperature	565 F	Space Velocity	2500 v/v/hr
Pressure	250 psig	Linear Velocity	0.7 ft/sec
Recycle Ratio	7.5	Settled Bed Depth	1.0 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	31.5	4.6	7.7		
Hydrogen	66.2	26.7	32.5		
Carbon dioxide	0.2	15.9	14.0		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	31.5	34.2	65.7	34.6	0.44
Hydrogen	66.2	200.5	276.7	213.6	3.1
Carbon dioxide	0.2	119.0	119.2	120.8	1.8
Water	0.0	0.0	0.0	27.4	27.4

Conversions

Carbon monoxide	98.6%
Hydrogen	95.3%
Carbon monoxide converted to carbon dioxide	5.1%

Equilibrium Calculations

Reactor Effluent: $\frac{(H_2)(CO_2)}{(CO)(H_2O)}$ 27.2

Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium 5.4%

TEST 1-b

CARBON DIOXIDE SCRUBBED FROM RECYCLE GAS

Process Conditions

Pilot Plant One

Temperature	565 F	Space Velocity	2500 v/v/hr
Pressure	250 psig	Linear Velocity	0.7 ft/sec
Recycle Ratio	7.5	Settled Bed Depth	1.0 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	31.2	2.0	5.5		
Hydrogen	65.9	48.1	50.2		
Carbon dioxide	0.2	0.2	0.2		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	31.2	15.2	46.4	15.4	.22
Hydrogen	65.9	360.8	426.7	369.2	8.4
Carbon dioxide	0.2	1.5	1.7	7.3	5.8
Water	0.0	0.0	0.0	21.1	21.1

Conversions

Carbon monoxide	99.3%
Hydrogen	87.3%
Carbon monoxide converted to carbon dioxide	17.9%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	8.3
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TEST 1-c

VARIATION OF CARBON DIOXIDE IN THE MIXED FEED:

CARBON DIOXIDE ADDED TO SYNTHESIS GAS

Process Conditions

Pilot Plant One

Temperature	565 F	Space Velocity	2500 v/v/hr
Pressure	250 psig	Linear Velocity	0.7 ft/hr
Recycle Ratio	7.5	Settled Bed Depth	1.0 ft

Stream Compositions

	<u>Synthesis</u> <u>Gas</u>	<u>Recycle</u> <u>Gas</u>	<u>Mixed</u> <u>Feed</u>	<u>Reactor</u> <u>Effluent</u>	<u>Unit</u> <u>Effluent</u>
Mol per cent:					
Carbon monoxide	29.4	4.4	7.3		
Hydrogen	64.6	23.8	28.6		
Carbon dioxide	4.0	27.6	24.9		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	29.4	32.9	62.3	33.5	.62
Hydrogen	64.6	178.6	243.2	181.7	3.1
Carbon dioxide	4.0	207.3	211.3	211.2	3.9
Water	0.0	0.0	0.0	27.9	27.9

Conversions

Carbon monoxide	97.9%
Hydrogen	95.2%
Carbon monoxide converted to carbon dioxide	-0.3%

Equilibrium Calculations

$$\text{Reactor Effluent: } \frac{(\text{H}_2)(\text{CO}_2)}{(\text{CO})(\text{H}_2\text{O})} = 41.0$$

Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium	-0.3%
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TEST 2-a

VARIATION OF HYDROGEN-TO-CARBON MONOXIDE RATIO IN THE

SYNTHESIS GAS: 2.3 MOLES HYDROGEN PER MOLE CARBON MONOXIDE

Process Conditions

Pilot Plant Two

Temperature	620 F	Space Velocity	2500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.8	Settled Bed Depth	5.0 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	29.6	2.3	12.0		
Hydrogen	67.7	44.0	52.5		
Carbon dioxide	0.0	8.6	5.5		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	29.6	4.1	33.7	4.4	.27
Hydrogen	67.7	79.2	146.9	85.3	6.1
Carbon dioxide	0.0	15.5	15.5	16.7	1.2
Water	0.0	0.0	0.0	26.4	26.4

Conversions

Carbon monoxide	99.1%
Hydrogen	91.0%
Carbon monoxide converted to carbon dioxide	4.1%

Equilibrium Calculations

Reactor Effluent: $\frac{(H_2) (CO_2)}{(CO) (H_2O)}$ 12.3

Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium 4.6%

TEST 2-b

VARIATION OF HYDROGEN-TO-CARBON MONOXIDE RATIO IN THE SYNTHESIS GAS:

2.0 MOLES HYDROGEN PER MOLE CARBON MONOXIDE

Process Conditions

Pilot Plant Two

Temperature	620 F	Space Velocity	2500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.8	Settled Bed Depth	5.0

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	32.1	4.0	14.0		
Hydrogen	64.3	37.5	47.1		
Carbon dioxide	0.4	19.0	12.4		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	32.1	7.2	39.3	7.8	.60
Hydrogen	64.3	67.5	131.8	73.2	5.7
Carbon dioxide	0.4	34.2	34.6	37.3	3.1
Water	0.0	0.0	0.0	23.8	23.8

Conversions

Carbon monoxide	98.1%
Hydrogen	91.1%
Carbon monoxide converted to carbon dioxide	8.4%

Equilibrium Calculations

$$\text{Reactor Effluent: } \frac{(H_2)(CO_2)}{(CO)(H_2O)} = 14.7$$

Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium 9.4%

TEST 2-c

VARIATION OF HYDROGEN-TO-CARBON MONOXIDE RATIO IN THE SYNTHESIS GAS:

1.7 MOLES HYDROGEN PER MOLE CARBON MONOXIDE

Process Conditions

Pilot Plant Two

Temperature	620 F	Space Velocity	2500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.8	Settled Bed Depth	5.0 ft

Stream Compositions

	<u>Synthesis</u> <u>Gas</u>	<u>Recycle</u> <u>Gas</u>	<u>Mixed</u> <u>Feed</u>	<u>Reactor</u> <u>Effluent</u>	<u>Unit</u> <u>Effluent</u>
Mol per cent:					
Carbon monoxide	36.0	6.2	16.9		
Hydrogen	60.6	30.9	41.5		
Carbon dioxide	0.4	32.0	20.7		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	36.0	11.2	47.2	12.5	1.33
Hydrogen	60.6	55.6	116.2	62.1	6.5
Carbon dioxide	0.4	57.6	58.0	63.7	6.1
Water	0.0	0.0	0.0	19.6	19.6

Conversions

Carbon monoxide	96.3%
Hydrogen	89.3%
Carbon monoxide converted to carbon dioxide	15.8%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	16.1
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		17.3%

TEST 3-a

VARIATION OF SPACE VELOCITY: 2500 SPACE VELOCITY

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	2500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.8	Settled Bed Depth	5.0 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	30.2	2.7	12.5		
Hydrogen	65.8	34.4	45.6		
Carbon dioxide	0.0	13.1	8.4		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	30.2	4.8	35.0	5.1	.33
Hydrogen	65.8	61.9	127.7	66.6	4.7
Carbon dioxide	0.0	23.5	23.5	25.2	1.7
Water	0.0	0.0	0.0	25.9	25.9

Conversions

Carbon monoxide	98.9%
Hydrogen	92.9%
Carbon monoxide converted to carbon dioxide	5.6%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	12.7
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		6.2%

TEST 3-b

VARIATION OF SPACE VELOCITY: 3500 SPACE VELOCITY

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	3500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.8	Settled Bed Depth	3.5 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	30.5	5.6	14.5		
Hydrogen	66.8	42.4	51.1		
Carbon dioxide	0.0	13.2	8.5		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	30.5	10.1	40.6	11.1	.99
Hydrogen	66.8	76.3	143.1	83.5	7.2
Carbon dioxide	0.0	23.8	23.8	26.1	2.3
Water	0.0	0.0	0.0	24.2	24.2

Conversions

Carbon monoxide	96.8%
Hydrogen	89.2%
Carbon monoxide converted to carbon dioxide	7.5%

Equilibrium Calculations

Reactor Effluent: $\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	8.1
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium	9.7%

TEST 3-e

VARIATION OF SPACE VELOCITY: 5000 SPACE VELOCITY

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	5000 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.8	Settled Bed Depth	2.5 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	30.4	8.0	16.0		
Hydrogen	65.8	51.5	56.6		
Carbon dioxide	0.2	13.7	8.9		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	30.4	14.4	44.8	16.1	1.7
Hydrogen	65.8	92.7	158.5	105.6	12.9
Carbon dioxide	0.2	24.7	24.9	28.0	3.3
Water	0.0	0.0	0.0	21.6	21.6

Conversions

Carbon monoxide	94.4%
Hydrogen	80.4%
Carbon monoxide converted to carbon dioxide	10.2%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	8.5
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		13.9%

TEST 4-a

VARIATION OF RECYCLE RATIO: 0.7 RECYCLE RATIO

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	3500 v/v/hr
Pressure	400 psig	Linear Velocity	0.6 ft/sec
Recycle Ratio	0.7	Settled Bed Depth	5.0 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	32.1	6.1	21.4		
Hydrogen	65.2	55.0	61.0		
Carbon dioxide	0.0	17.6	7.2		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	32.1	4.3	36.4	6.2	1.9
Hydrogen	65.2	38.5	103.7	55.8	17.3
Carbon dioxide	0.0	12.3	12.3	17.8	5.5
Water	0.0	0.0	0.0	18.3	18.3

Conversions

Carbon monoxide	94.1%
Hydrogen	73.5%
Carbon monoxide converted to carbon dioxide	17.1%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	8.8
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		21.1%

TEST 4-b

VARIATION OF RECYCLE RATIO: 1.0 RECYCLE RATIO

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	3500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.0	Settled Bed Depth	5.0

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	30.1	5.7	17.9		
Hydrogen	65.0	50.6	57.8		
Carbon dioxide	0.2	16.4	8.3		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	30.1	5.7	35.8	7.0	1.31
Hydrogen	65.0	50.6	115.6	62.1	11.5
Carbon dioxide	0.2	16.4	16.6	20.1	3.7
Water	0.0	0.0	0.0	21.7	21.7

Conversions

Carbon monoxide	96.6%
Hydrogen	82.3%
Carbon monoxide converted to carbon dioxide	11.6%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	8.3
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		15.1%

TEST 4-c

VARIATION OF RECYCLE RATIO: 1.5 RECYCLE RATIO

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	3500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	1.5	Settled Bed Depth	4.0 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	31.3	4.5	15.0		
Hydrogen	65.5	45.5	53.5		
Carbon dioxide	0.2	14.7	8.9		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	31.3	6.2	37.5	7.0	.77
Hydrogen	65.5	68.2	133.7	75.7	7.5
Carbon dioxide	0.2	22.0	22.2	24.6	2.6
Water	0.0	0.0	0.0	24.0	24.0

Conversions

Carbon monoxide	97.5%
Hydrogen	88.5%
Carbon monoxide converted to carbon dioxide	7.7%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	11.1
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		9.2%

TEST 4-d

VARIATION OF RECYCLE RATIO: 2.0 RECYCLE RATIO

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	3500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	2.0	Settled Bed Depth	3.3 ft

Stream Compositions

	<u>Synthesis Gas</u>	<u>Recycle Gas</u>	<u>Mixed Feed</u>	<u>Reactor Effluent</u>	<u>Unit Effluent</u>
Mol per cent:					
Carbon monoxide	30.8	3.8	12.8		
Hydrogen	66.1	33.5	45.7		
Carbon dioxide	0.2	14.0	9.4		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	30.8	7.6	38.4	8.0	.45
Hydrogen	66.1	71.0	137.1	75.2	4.2
Carbon dioxide	0.2	28.0	28.2	29.6	1.6
Water	0.0	0.0	0.0	26.4	26.4

Conversions

Carbon monoxide	98.5%
Hydrogen	93.6%
Carbon monoxide converted to carbon dioxide	4.5%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	10.5
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		5.5%

TEST 4-e

VARIATION OF RECYCLE RATIO: 3.0 RECYCLE RATIO

Process Conditions

Pilot Plant Two

Temperature	615 F	Space Velocity	3500 v/v/hr
Pressure	400 psig	Linear Velocity	0.75 ft/sec
Recycle Ratio	3.0	Settled Bed Depth	2.5 ft

Stream Compositions

	<u>Synthesis</u> <u>Gas</u>	<u>Recycle</u> <u>Gas</u>	<u>Mixed</u> <u>Feed</u>	<u>Reactor</u> <u>Effluent</u>	<u>Unit</u> <u>Effluent</u>
Mol per cent:					
Carbon monoxide	30.3	3.9	10.5		
Hydrogen	66.9	33.7	42.0		
Carbon dioxide	0.4	11.7	8.9		
Water	0.0	0.0	0.0		
Mols per 100 mols synthesis gas:					
Carbon monoxide	30.3	11.7	42.0	12.2	.51
Hydrogen	66.9	101.1	168.0	105.0	3.9
Carbon dioxide	0.4	35.2	35.6	36.7	1.5
Water	0.0	0.0	0.0	26.6	26.6

Conversions

Carbon monoxide	98.3%
Hydrogen	94.2%
Carbon monoxide converted to carbon dioxide	3.6%

Equilibrium Calculations

Reactor Effluent:	$\frac{(H_2)(CO_2)}{(CO)(H_2O)}$	11.9
Carbon monoxide converted to carbon dioxide at water-gas-shift equilibrium		4.2%

APPENDIX B

METHOD OF CALCULATING CONVERSION OF CARBON MONOXIDE TO

CARBON DIOXIDE AT WATER-GAS-SHIFT EQUILIBRIUM

The method of calculating conversion of carbon monoxide to carbon dioxide at water-gas equilibrium is described in this section.

Using the basis of 100 mols synthesis gas and the following symbols:

- a mols carbon monoxide in reactor effluent
- b mols water vapor in reactor effluent
- c mols hydrogen in reactor effluent
- d mols carbon dioxide in reactor effluent
- g mols light hydrocarbons (gases at STP) in reactor effluent
- i mols inert gases in reactor effluent
- p mols heavy hydrocarbons (liquids at STP) in reactor effluent
- t total of the normal gases in reactor effluent,
a + c + d + i + g
- x additional mols carbon monoxide converted to carbon dioxide to obtain equilibrium
- y fraction of the normal gases in reactor effluent that are not recycled
- z per cent carbon monoxide converted to carbon dioxide

the compositions of the reactor effluent, recycle stream and unit effluent are:

<u>Component</u>	<u>Reactor Effluent</u>	<u>Recycle Stream</u>	<u>Unit Effluent</u>	
			<u>Liquid</u>	<u>Gas</u>
CO	a	(1-y)a		ya
H ₂	c	(1-y)c		yc
CO ₂	d	(1-y)d		yd
H ₂ O	b		b	
Inert Gases	i	(1-y)i		yi
Light Hydrocarbons	g	(1-y)g		yg
Heavy Hydrocarbons	p		p	
Total mols	t+b+p	(1-y)t	b+p	yt

The actual conversion of carbon monoxide to carbon dioxide is

$$(7) \quad z = \frac{100(yd-D)}{A}$$

where A and D are mols carbon monoxide and carbon dioxide in the synthesis gas.

The equilibrium relationship for the water-gas reaction is

$$(5) \quad K_p = \frac{(H_2)(CO_2)}{(CO)(H_2O)} .$$

Assuming ideal gases, (H_2) , (CO_2) , (CO) , and (H_2O) are the partial pressures of the products and reactants in the reactor effluent and K_p is the chemical equilibrium constant at the average reactor temperature. Values of K_p are given in Figure 1. Since the ratio of the partial pressures is equivalent to the ratio of the mols and x is the additional mols of carbon monoxide converted to carbon dioxide at equilibrium, the equilibrium relationship may be written as

$$(8) \quad K_p = \frac{(c+x)(d+x)}{(a-x)(b-x)} .$$

Assuming the yields of the other products are not affected, the compositions of the reactor effluent, recycle stream, and unit effluent change to

<u>Component</u>	<u>Reactor Effluent</u>	<u>Recycle Stream</u>	<u>Unit Effluent</u>	
			<u>Liquid</u>	<u>Gas</u>
CO	a-x	$(1-y')(a-x)$		$y'(a-x)$
H ₂	c+x	$(1-y')(c+x)$		$y'(c+x)$
CO ₂	d+x	$(1-y')(d+x)$		$y'(d+x)$
H ₂ O	b-x		b-x	
Inert Gases	i'	$(1-y')i'$		$y'i'$
Light Hydrocarbons	g'	$(1-y')g'$		$y'g'$
Heavy Hydrocarbons	p		p	
Total mols	$t'+b-x-p$	$(1-y')t'$	$b-x+p$	$y't'$

where the "prime" indicates equilibrium values.

The conversion of carbon monoxide to carbon dioxide at water-gas-shift equilibrium equals

$$(9) \quad z' = 100 \frac{y'(d+x) - D}{A} - z \frac{y'(d+x) - D}{yd - D}$$

Values of z , d , and D are given in the run data, Appendix A. The value of x can be calculated from the equilibrium relationship. The value of y is determined from the ratio of the sum of mols of carbon monoxide, hydrogen, and carbon dioxide in the unit effluent to that in the reactor effluent. Values of y determined from individual components will differ slightly because part of the unit effluent gas is removed with the liquid and its composition depends upon vapor-liquid equilibrium. The value of $i+g$ can be determined from the total mols of recycle gas

$$(10) \quad \text{mols recycle gas} = \text{recycle ratio} \times 100 = \\ (1-y)(a+c+d+i+g)$$

and since the mols of inert gas and light hydrocarbon in the unit effluent does not change

$$(11) \quad y(i+g) = y'(i'+g')$$

Equation (11) can be combined with equation

$$(12) \quad \text{recycle ratio} \times 100 = (1-y')(a+c+d+x+i'+g')$$

and $i'+g'$ eliminated. The combined equations rearrange to

$$(13) \quad (a+c+d+x)(y')^2 + \sqrt{\text{recycle ratio} \times 100} y(i+g) - \\ (a+c+d+x)\sqrt{y'} - y(i+g) = 0$$

and the value of y' can be determined. The conversion of carbon monoxide to carbon dioxide at water-gas-shift equilibrium can then be determined.

This method of calculating equilibrium yields assumes the conversion of carbon monoxide increases and that the yields of other products are not affected by the change in composition of the recycle gas.

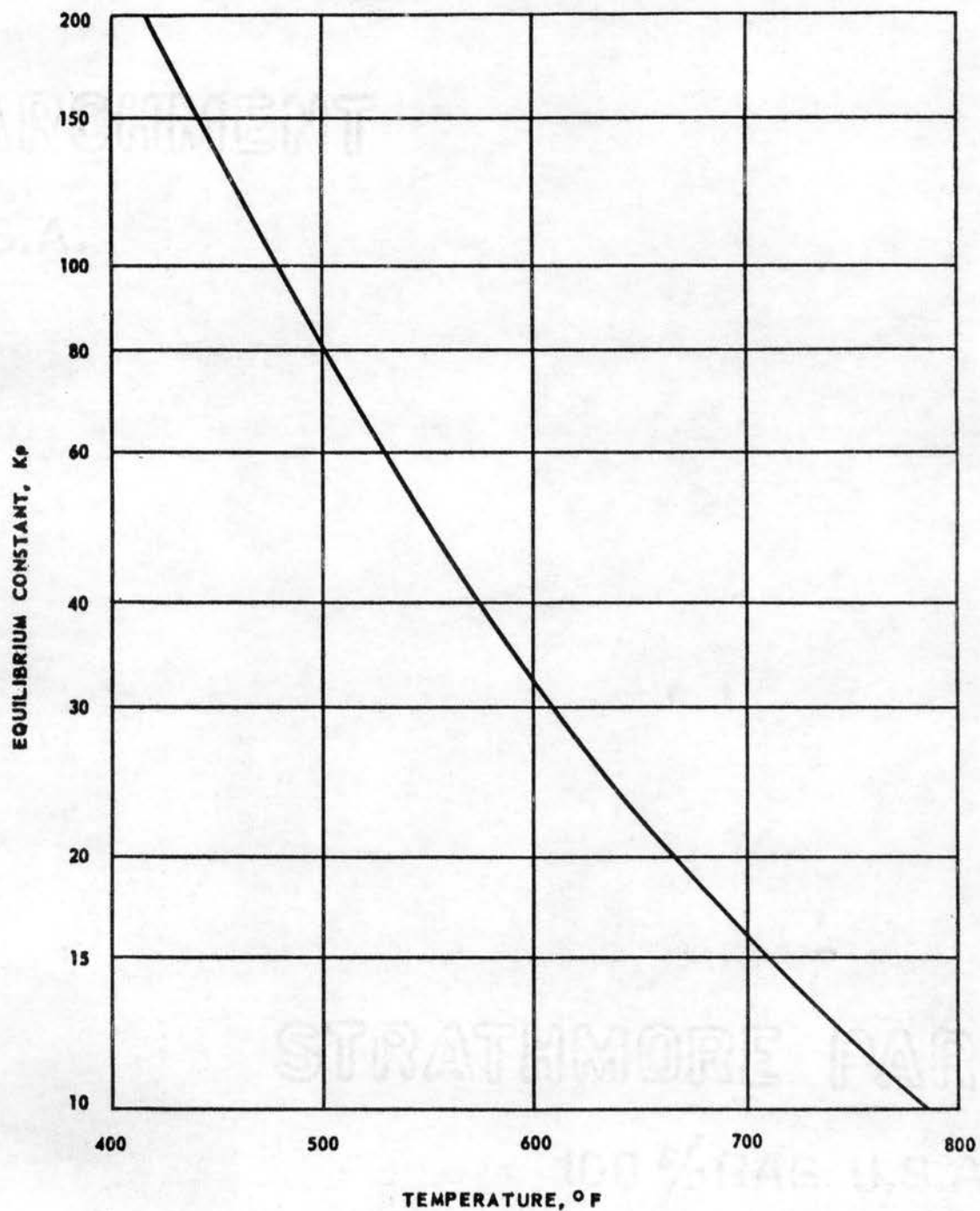
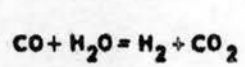


FIGURE 1
EQUILIBRIUM CONSTANT FOR THE WATER-GAS-SHIFT REACTION:



$$K_p = \frac{(\text{H}_2) (\text{CO}_2)}{(\text{CO}) (\text{H}_2\text{O})}$$

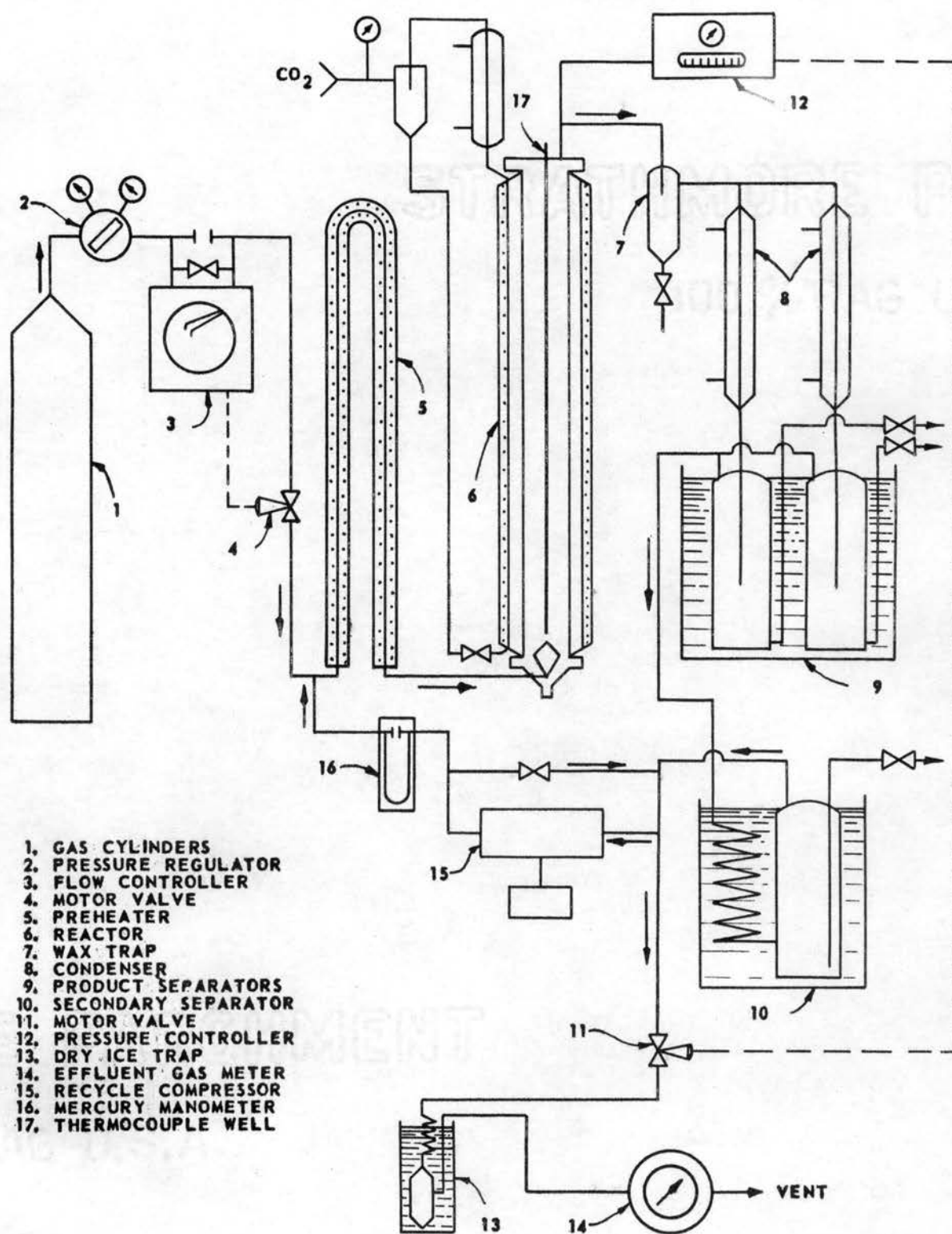


FIGURE 2
 FISCHER-TROPSCH PILOT PLANT

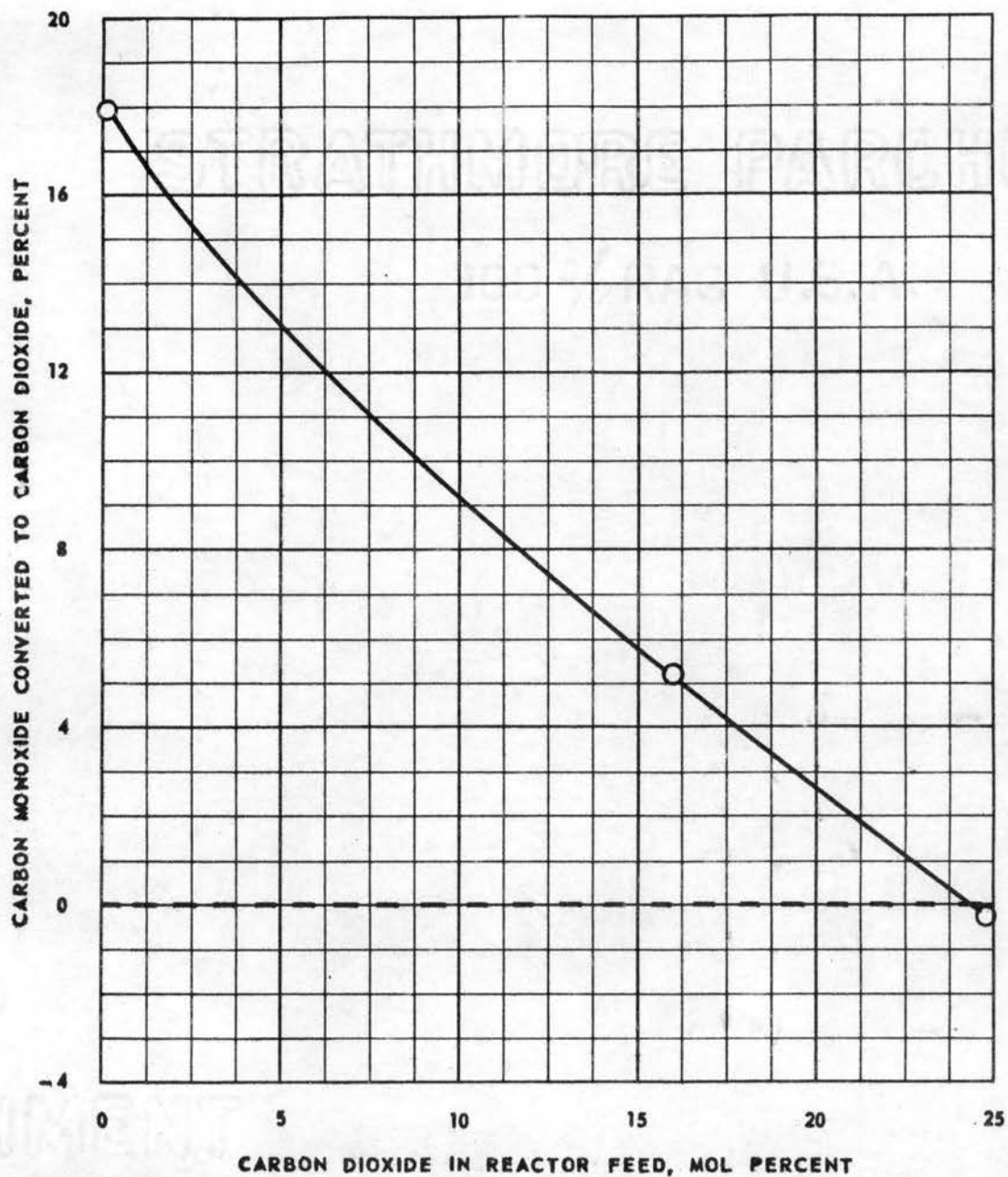


FIGURE 3
EFFECT OF CARBON DIOXIDE IN REACTOR FEED UPON CARBON
DIOXIDE YIELD

OPERATION AT 565 F, 250 psig, 7.5 RECYCLE RATIO,
AND 2500 SPACE VELOCITY (V/V/HR).

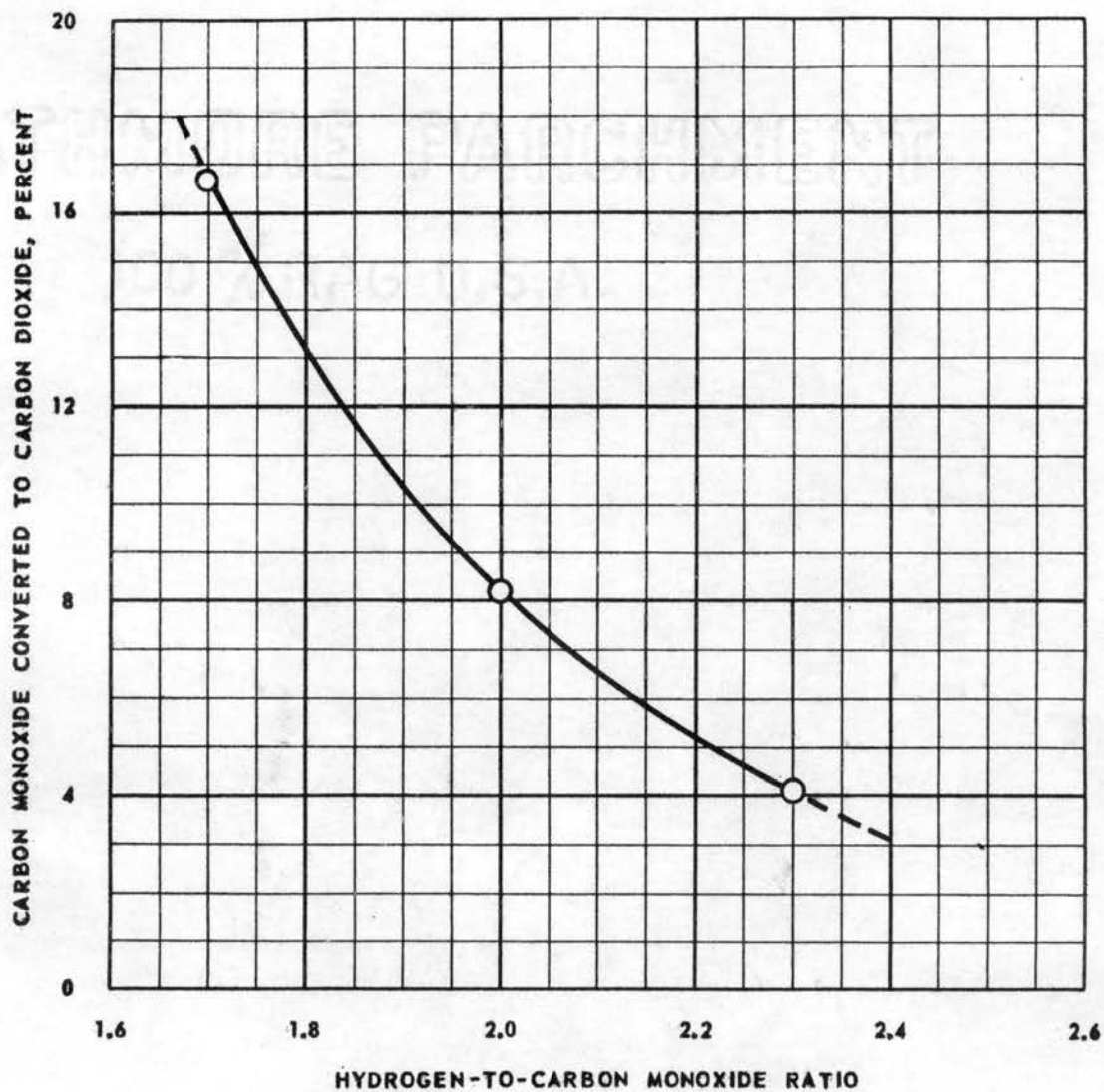


FIGURE 4
EFFECT OF HYDROGEN-TO-CARBON MONOXIDE RATION IN
THE SYNTHESIS GAS UPON CARBON DIOXIDE YIELD

OPERATION AT 620 F, 400 psig, 1.8 RECYCLE RATIO
AND 2500 SPACE VELOCITY (V/V/HR.).

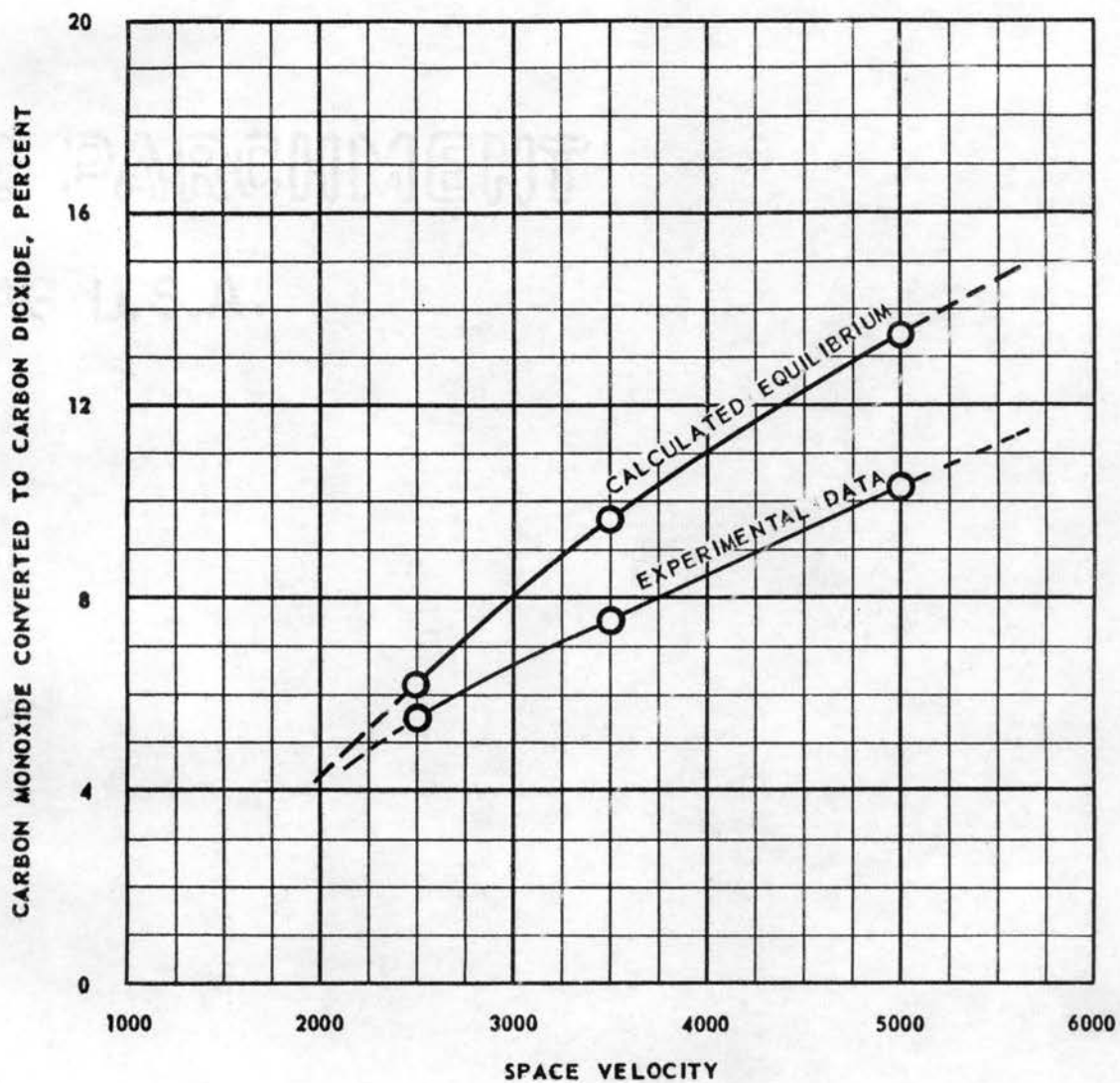


FIGURE 5
EFFECT OF SPACE VELOCITY UPON CARBON DIOXIDE YIELD

OPERATION AT 615 F, 400 psig, AND 1.8 RECYCLE RATIO.

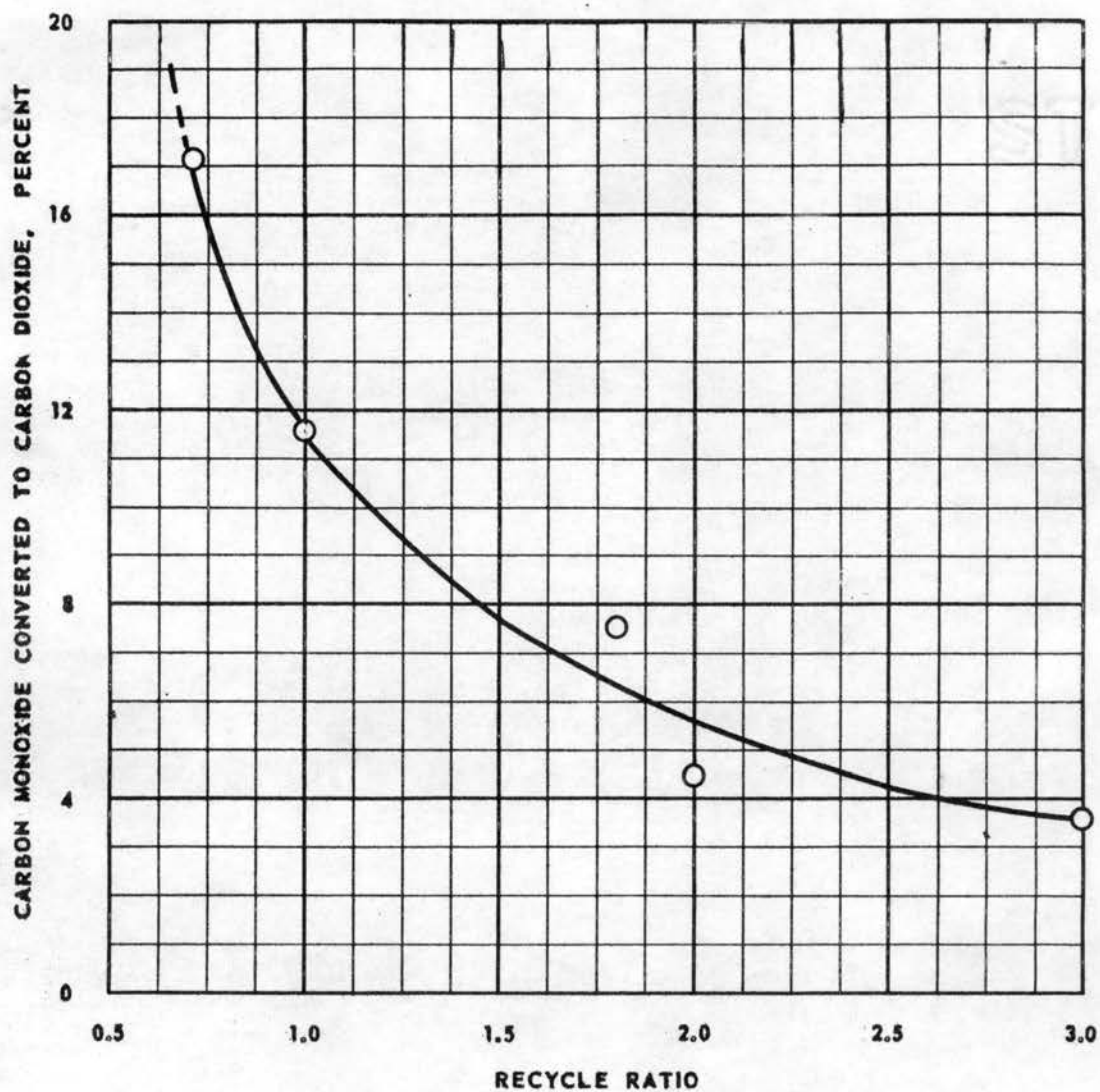


FIGURE 6
EFFECT OF RECYCLE RATIO UPON CARBON DIOXIDE YIELD

OPERATION AT 615 F, 400 psig, AND 3500 SPACE
VELOCITY (V/V/HR.).

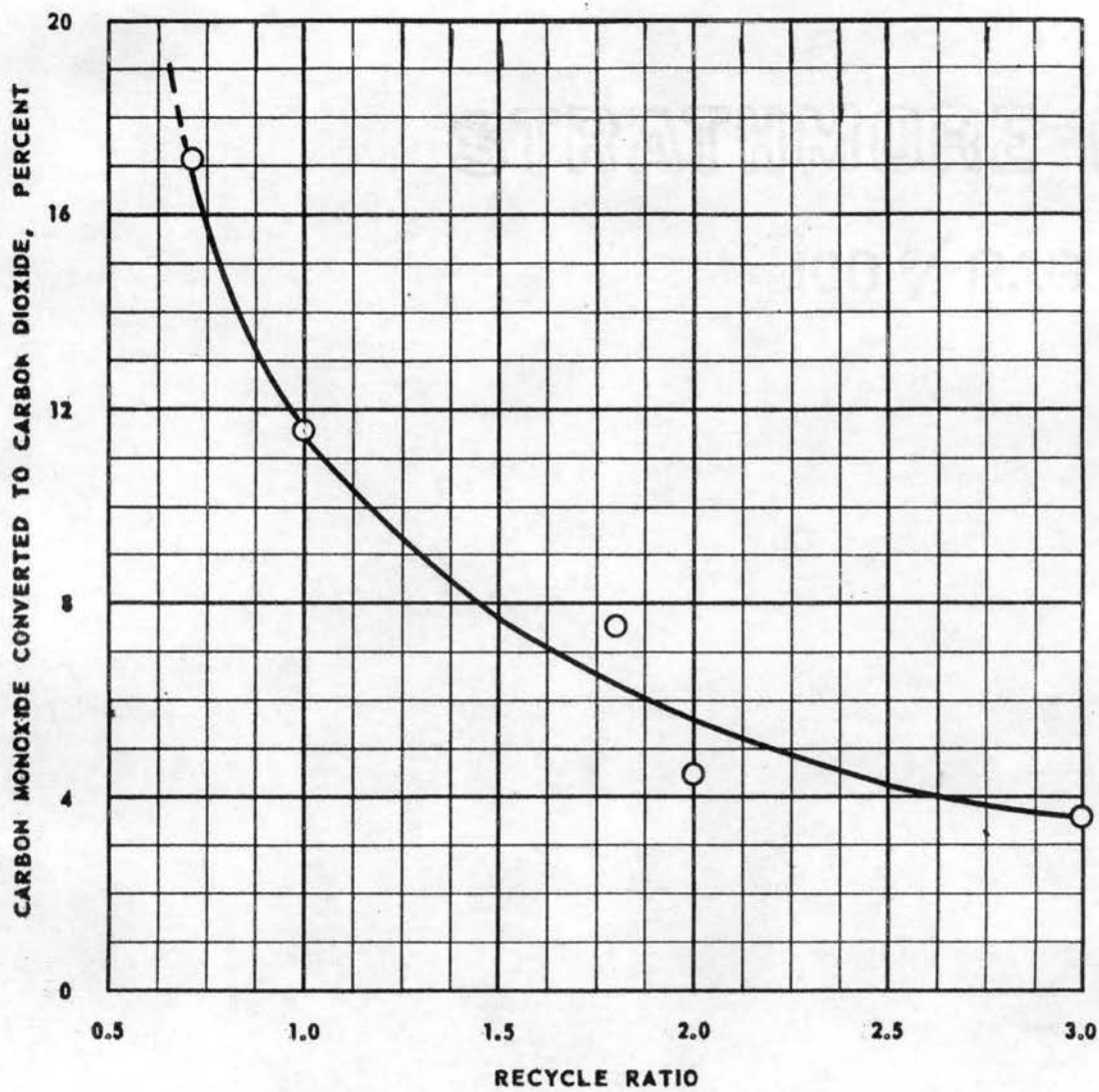


FIGURE 6
EFFECT OF RECYCLE RATIO UPON CARBON DIOXIDE YIELD

OPERATION AT 615 F, 400 psig, AND 3500 SPACE
VELOCITY (V/V/HR.).

VITA

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TYPIST: Kay Smith