FINAL REPORT - PART I

CONTRACT NAS9-1782

Integrated Carbon Dioxide Reduction System
Feasibility Study

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April 16, 1964

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I. INTRODUCTION

This feasibility study was initiated under contract to NASA for a study of a new method for the physical recovery of carbon dioxide from the atmosphere of a space cabin and the chemical recovery of metabolic oxygen from that carbon dioxide and metabolic water. A condition was that the effluent from the reduction system have the minimum possible H/C ratio--preferably the 0.7 corresponding to perfect H/C/O balance with no cabin leakage and a diet RQ of 0.8 or higher.

Since the contract was started a report has been published[1] offering an extensive comparison of various life-support systems. The following quotation from that report is pertinent to the work reported here.

"For space vehicle applications, the Fischer-Tropsch synthesis has the following advantages over the Sabatier process:

1) Lower loss of hydrogen due to formation of hydro-
   carbons with lower hydrogen content.

2) Nature of product is less dependent on maintaining
   a definite stoichiometric H_2/CO_2 ratio."

However, "The Fischer-Tropsch synthesis requires more make up hydrogen. By operating to produce a higher fraction of olefins or aromatics, with a special catalyst or a second catalytic reactor in series, hydrogen losses can be limited and the Fischer-Tropsch synthesis yields a more readily handled product than methane pyrolysis.

It is necessary that the Fischer-Tropsch synthesis be adapted to conversion of carbon dioxide, for use in space vehicles".

II. SUMMARY

The design study and experimental program were based on a preliminary study outlined in our proposal to NASA. The more thorough design study confirmed the original estimates for the carbon dioxide recovery system. It was found that the critical mechanical components-- a turbo-expander and turbo-compressor of very small size--were not state-of-the-art. It was also found as the work progressed that United Aircraft Corp. has been assigned two patents [2] covering a very similar system for carbon dioxide recovery from air.

The experimental program was started with studies of the reaction kinetics of the carbon dioxide reduction and Fischer-Tropsch subsystems. The original dehydration and dehydrocyclization subsystems estimates were based on quite firm Houdry proprietary data which we planned to incorporate in the preliminary design study. In the program investigating the very important carbon dioxide to saturated hydrocarbon conversion it soon became apparent that two stages were necessary in the present state-of-the-art. A single stage would have represented a great simplification of process equipment and saving in energy input. The investigation has also shown that the assumption of an 80% liquid hydrocarbon yield (atom percent carbon based on carbon dioxide feed) giving a recycle ratio of 1.25 was optimistic. The best yield at present indicates a recycle ratio of 3.4 moles of carbon dioxide

per mole of fresh carbon dioxide feed. These experiments did confirm that operation at elevated pressure was favorable to minimization of reactor size and catalyst requirements.

A single extended run of the Fischer-Tropsch subsystem, during which a factorial experimental design was imposed to determine the effects of several process variables, gave check results indicating slow catalyst deactivation over a one week period. This observed deactivation makes it mandatory to provide for in-situ regeneration of the F-T catalyst.

III. BACKGROUND

The present study is the outgrowth of much reflection on the state-of-the-art and the requirements for life support of man in space. Many have carried out parametric studies which show when oxygen storage, potassium super oxide, chemical regenerative and biological systems over laps or successively become the practical system for life support as stay-time, with and without resupply, increases. As chemists and chemical engineers with catalyst and process experience, questions which we asked ourselves included:

1) What chemical processing system promises to most nearly maintain cabin waste H/C balance in a liquid effluent?

2) What physical or chemical systems for carbon dioxide recovery promises to most nearly approach the ideal isothermal permeation separation?

3) What is the chance of successfully designing and operating such systems?

4) What are the critical parameters for life (reliability in aero-space language) of a catalytic process?

5) What are the critical components for the mechanical design necessary to accomplish the physical and chemical processes? What is the state-of-the-art with respect to these components?

6)   What must we do to achieve minimum volume, weight, and power consumption of the resulting system without violating our commercial instincts of minimum practicable cost and maximum on-stream periods (utilization factor)?

The answer to the first question is straightforward. It is the system on which this feasibility study is based--carbon dioxide conversion to largely saturated liquid hydrocarbons followed by dehydrogenation and dehydrocyclization to olefins and/or aromatics. In theory one can adjust the effluent hydrogen to carbon ratio in such a process to almost any value, even the 0.7 for theoretical waste from diet of RQ = 0.8, if one changes the restriction that the product be liquid to that it have a high volatility at moderate temperatures. Fortunately this restriction is partly eased by the fact that make-up oxygen and nitrogen must be supplied to the cabin atmosphere to replace that lost by leakage. Since the food carries excess water it appears most reasonable to make up the oxygen loss by electrolyzing part of this excess water. To further minimize the chemical process system size one should consider the balance between rejecting some unreduced carbon monoxide, making up the oxygen loss by water electrolysis, and conserving water as an emergency oxygen source.

The ideal separation process for carbon dioxide would be a perfect membrane with its attendant Maxwellian demon. This separation would require work of RT ln p_2/p_1 (the isothermal compression energy) per mole of carbon dioxide separated from the dilute to the pure dioxide phase. This is only 3.5 watts per gram mole of carbon dioxide recovered from a 0.6% carbon dioxide feed. Unfortunately practical membranes require high driving forces and large areas to accomplish the desired separation. The low temperature freezeout process of this study is smaller and lighter. It is highly efficient in its use of power.

The answer to the third question is unity, if one chooses systems which have been employed in industrial practice. The carbon dioxide recovery system is modeled after the pretreatment systems of liquid air plants. The Fischer-Tropsch dehydration and dehydrocyclization processes have been employed in commercial operations for many years. Conversion of carbon dioxide to carbon monoxide is not practiced commercially but the reverse reaction is. Catalysts for this reaction are known to be stable.

The critical parameters for catalyst life are generally determined experimentally. Those catalysts to be employed in the process scheme of this study have been used for many years. In general, experience with them has shown that they may be counted on to perform at high efficiency for many years provided they are cleaned of deposits, usually by careful combustion, at suitable intervals.

The critical components for mechanical design, the state-of-the art in these and the methods of minimizing volume, weight and power demand for the processes are areas which require further investigation.

A. Discussion

A flow sheet of the chemical process scheme originally chosen is shown in Figure 1. This scheme was selected after considering the waste product carbon-hydrogen balance. In Figure 2 this balance is shown as a function of food composition (represented by the Respiratory Quotient) and cabin oxygen loss through leakage and air lock depressurization. The Figure clearly shows that at presently attainable oxygen losses, and within the range of normal diets, that H/C ratios in the cabin waste are likely to be greater than one, but are unlikely to exceed two. It is possible to balance the system in another way. In the original design not all the water introduced into the recovery system from the food is utilized for oxygen supply.

When the total water from the "dry-food" is collected and utilized in the carbon-dioxide reduction system one finds that about one mole of water is available per mole of carbon dioxide. This allows the recovery of 1.5 moles of oxygen per mole of carbon dioxide treated and the discharge of CH_2 in a total recovery operation. This is more oxygen than is needed for normal operation, even with rather major leakage. It would cause an enriched atmosphere and increase in pressure. In a better balanced (chemically) operation one would recover all the oxygen possible by

CO_2 REDUCTION
150 PSIA

1550°F

CO, H_2, CO_2

TC

PC

CYCLONE

100°F

LC

HP RECYCLE

LC   LC

LP RECYCLE

H_2 150 PSIA

Two-Stage
Compressor

PROPORT.
FEED
CONTROL

CO_2 32 PSIA
100°F

H_2O
TO STORAGE

H_2O
(CONTAMINATED WITH HOAC, ALCOHOLS)

8-1

R-2

R-3

FISCHER-TROPSCH
< 150 PSIA

DEHYDRATION
15 PSIA

450°F

572°F

400°F

572+

400°F

500°F

100°F

200°F

100°F

200°F

100°F

CYCLONE

OIL

SURGE

FC

PC

CYCLONE

LC

8-2

R-4

1022+°F.

Dehydrocyclization
3 PSIA

+
−

°F

TC   1022°F

Cyclone

Aromatics
to
Storage

LC

Two-stage
Compressor

INTEGRATED
CO_2 REDUCTION SYSTEM
FIGURE-1

-8-3

FIGURE 2

HYDROGEN TO CARBON RATIOS
IN
ENVIRONMENTAL CONTROL SYSTEM EFFLUENT
AS A FUNCTION OF
OXYGEN LEAK RATE TO METABOLIC OXYGEN RATIO

RQ = 0.8

RQ = 0.85

DESIGN-RC = 0.86, 20% LOSS

RQ = 0.9

$$H/C = 4 \left(\frac{1-RQ + F}{RQ} \right)$$

EFFLUENT H/C RATIO

$$F = \frac{\text{OXYGEN LEAK RATE}}{\text{METABOLIC OXYGEN}}$$
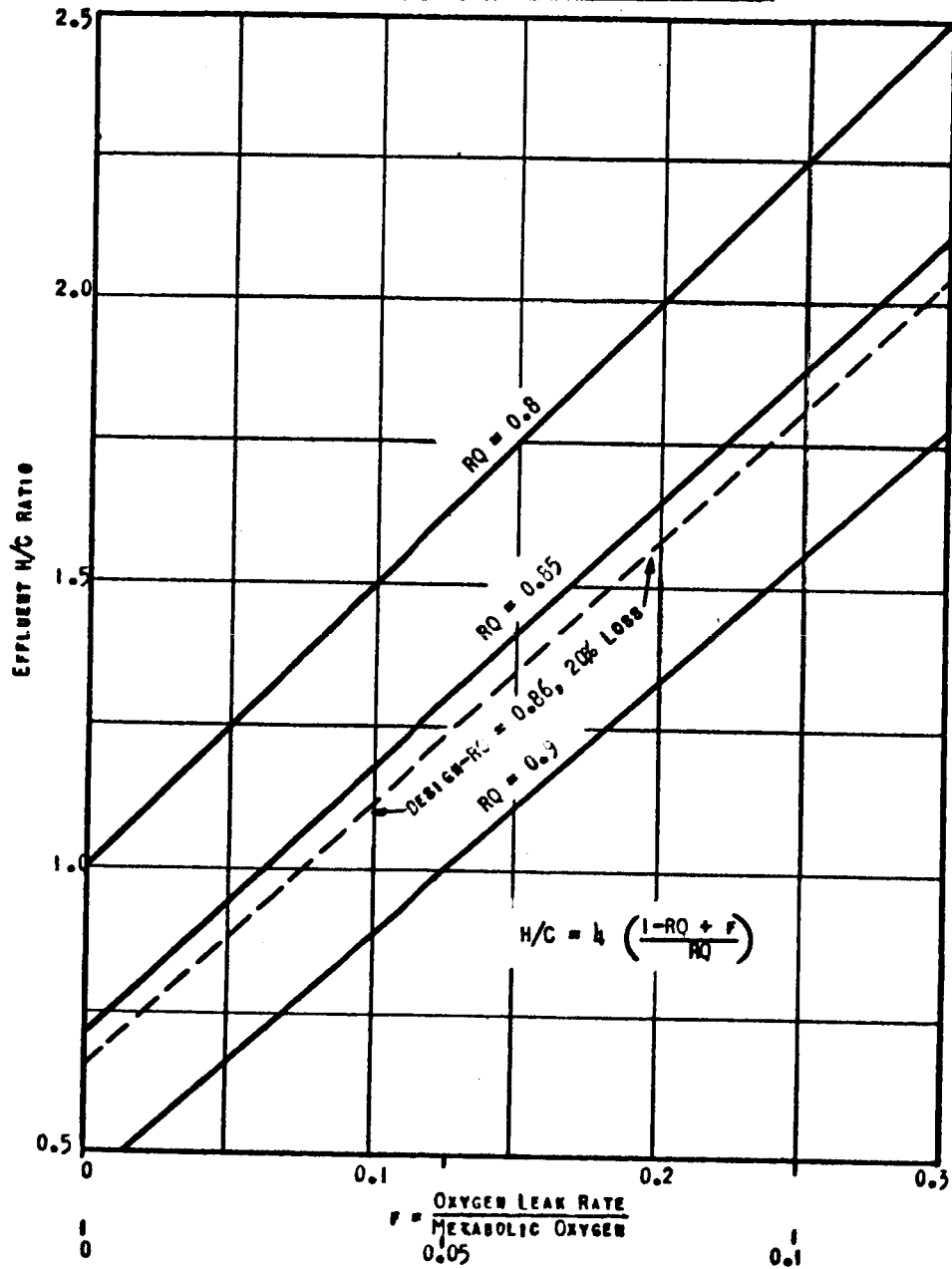
EQUIVALENT SCALE, O_2 LOSS BASIS, 40:60=O_2/N_2

N_2H_4 - NITROGEN SOURCE.

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electrolysis of this metabolic water, then adjust the carbon dioxide reduction system to waste at a H/C ratio greater than 2 and vent unreacted CO_2 and/or CO. The consequences of this have not been fully explored.

In the dual gas atmosphere cabin nitrogen must also be supplied to make up leakage. One means of supplying nitrogen is the decomposition of stored hydrazine. The resulting excess hydrogen is vented or used in the carbon dioxide reduction system. For example:

    Diet RQ = 0.86
    CO_2 burden $\sim$ 1 g mol/hr man
    O_2 req'd = 1.163 mols
    O_2 loss   = 0.163 mols (10% of metabolic requirement)
    N_2 loss   = 0.245 mols (40:60 = O_2/N_2)

<u>To compensate losses</u>

   0.163 mols O_2 $\doteq$ H_2 by electrolysis 0.326 mols H_2O = 0.326 mols

   0.245 mols N_2 $\cong$ H_2 by decomposition 0.245 mols N_2H_4 = <u>0.490 mols</u>

                                        Sub Total   = 0.816 mols

<u>For O_2 (0.163 mols) in excess of that from CO_2 at total recovery</u>

                     H_2 by electrolysis 0.326 mols H_2O = <u>0.326 mols</u>

                                        Total   1.142 mols H_2
                                                 or 2.28 atoms H

                     $\therefore$ H/C = 2.28 in Waste

    Metabolic H_2O = 1.000 mol
    Water used   = <u>0.652 mol</u>
                       0.338 mol to H_2O storage, in addition to moisture in food

The excess metabolic water of the example will support a leak rate just over twice that assumed before drawing on the main supply in the water management system. The resulting hydrogen, with that from the required hydrazine to maintain balance, will permit discharge of H/C = 3.97 as waste at 100% efficiency of carbon dioxide reduction.

Possible emergency conditions require that the ecology be managed as carefully as possible. It is, however, reasonable to inquire what advantages will result from so managing carbon dioxide recovery as to absolutely minimize the waste H/C ratio. The primary advantage is that the reserve supply of oxygen in the form of water is continually added to under normal conditions. In thecase of the illustrative example 0.32 lb H_2O/day would accumulate in a tight, but not leak free, cabin. This is equivalent to one metabolic day per 7.8 days mission time. With no leakage and perfect oxygen recovery 4 days mission time would accumulate one metabolic day of reserve oxygen.

The disadvantage is increased system complexity and servicing problems. The originally proposed system had four parts. The last, dehydrocyclization, it now appears must be a swing reactor system with high temperature automatic valving. Such valving is not available in miniature sizes. In large sizes even with years of development constant service attention is required.

It is our belief that the best compromise is the system depicted in Figure 3. Detailed discussion of the operating experience obtained in testing the first two stages of this system and recommendations for future work are presented in the next section of this report.

R-1

CO_2 Reduction
150 PSIA

TC

1550°F

CO_2 H_2,

CYCLONE

100°F

H_2
150 PSIA

LC

PROPORT.
FEED
CONTROL

HP. RECYCLE

2 STAGE
COMPRESSOR

CO_2 FEED
100°F
32 PSIA

H_2O TO
STORAGE

13-1

R-2

FISCHER-TROPSCH

< 150 PSIA

450°F

TC

CO₂

PC

100°F

CYCLONE

OIL

STORAGE
OR
VENT

LC   LC

H₂O
(CONTAMINATED)
(ACETIC ACID ALCOHOL)
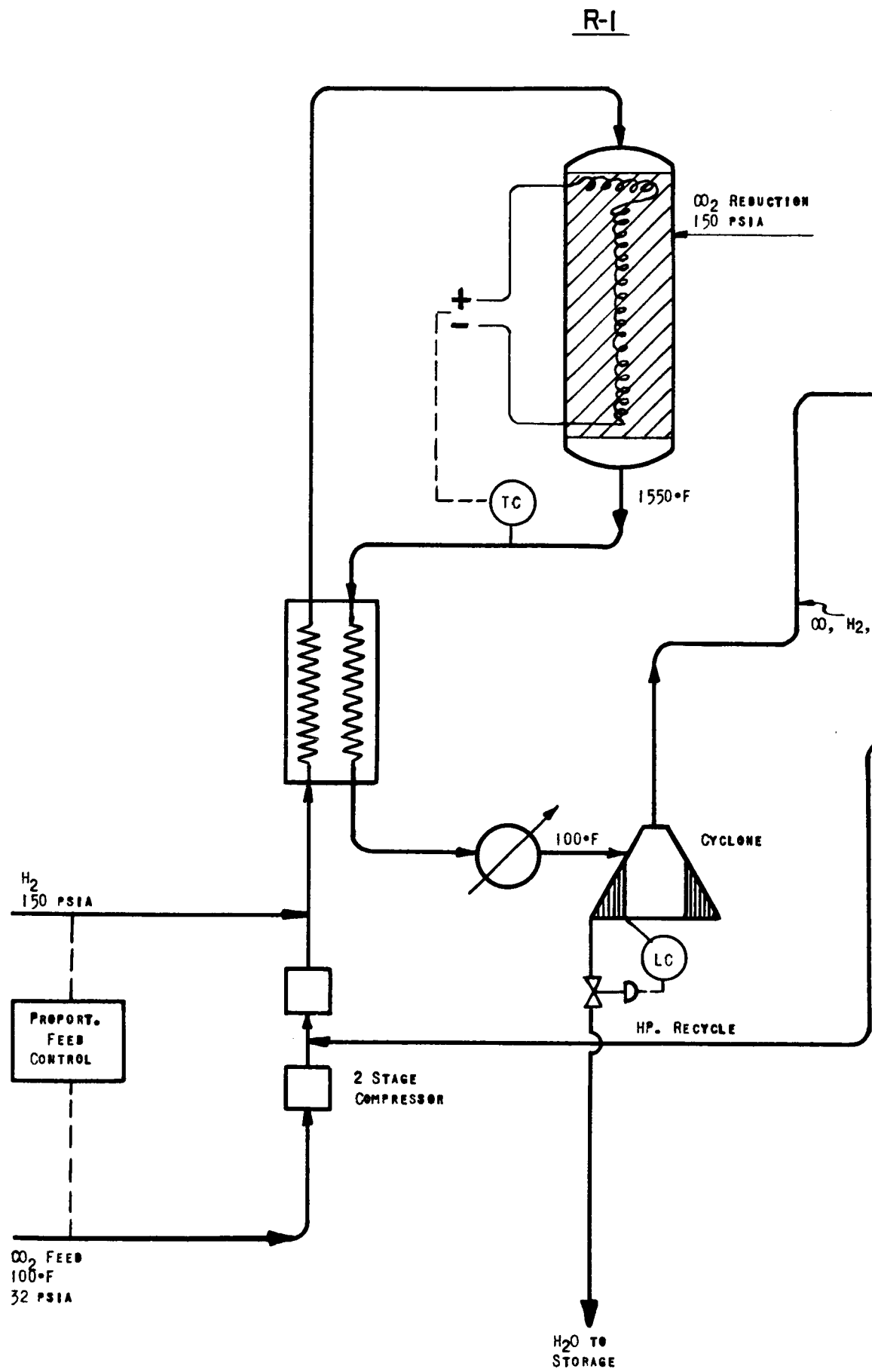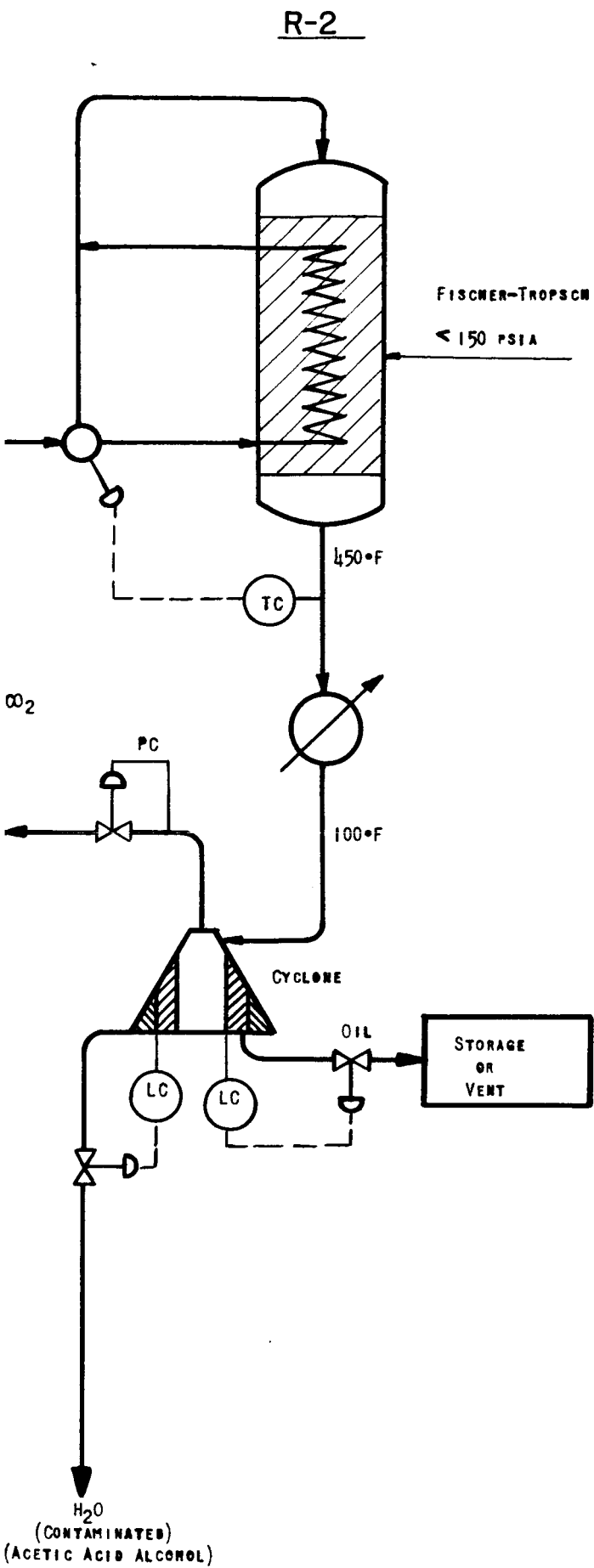
INTEGRATED
CO₂ REDUCTION SYSTEM
FIGURE-3

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IV. EXPERIMENTAL

The experimental program was separated into five parts as follows:

a) assembly of a catalyst testing pilot unit;

b) study of the direct conversion of carbon dioxide and hydrogen to a mixture of paraffins, olefins, alcohols, and water;

c) study of the reverse water gas shift conversion of carbon dioxide and hydrogen to carbon monoxide and water;

d) study of the Fischer-Tropsch reaction (carbon monoxide and hydrogen to water and hydrocarbons).

e) study of a simulated recycle type Fischer-Tropsch reaction using a mixed feed of carbon monoxide-carbon dioxide and hydrogen.

A. Materials and Apparatus

The carbon monoxide and carbon dioxide gases were obtained in No. 1A cylinders from Air Products and Chemicals, Inc. The hydrogen used was also obtained from Air Products in cylinder racks but was purified prior to use in order to remove any oil and water contaminants. All the catalysts used were commercially available (Girdler or Houdry) or were custom prepared in the Houdry catalyst laboratory from commercially available components (kieselguhr base, macroporous silica base, cobalt nitrate, ruthenium chloride, etc.).

The experimental apparatus consisted of a high pressure (1000 psig), high temperature (1500°F) catalytic reactor adapted for operation in the gas phase. Rapid changes in the gas feed rates were accomplished by using calibrated rotameters. A flow diagram of the equipment is given in Figure 4. The experimental equipment and procedure are discussed in the following sections.

1. Experimental Procedure and Equipment

   a. General Description of the Process

In general, all the experimental work using pure gas feeds was performed in a similar fashion. The metered mixed gas feed was directed through a catalytic reactor and the effluent gas-liquid product was separated and analyzed. It was possible to study the feasibility of the reduction reactions and Fischer-Tropsch synthesis reaction consecutively merely by changing the unit operating conditions and the catalyst used.

Known constant flows of the pure gas feeds were maintained by using calibrated rotameters operating at a constant back pressure. The gases were mixed immediately after being metered and then flowed into the reactor. The liquid-gas effluent from the reactor passed first into a hot condenser and then into a cold condenser to remove water and liquid hydrocarbons. The residual gas was discharged thru a pressure-control valve, metered, and vented.

   b. Experimental Procedure

A Matheson two-stage gas regulator was placed on each pure gas cylinder (carbon monoxide, carbon dioxide, and hydrogen) in order

FIGURE 4

CATALYST TESTING PILOT UNIT

CARBON DIOXIDE REDUCTION AND FISCHER-TROPSCH REACTION
NAS9-1782
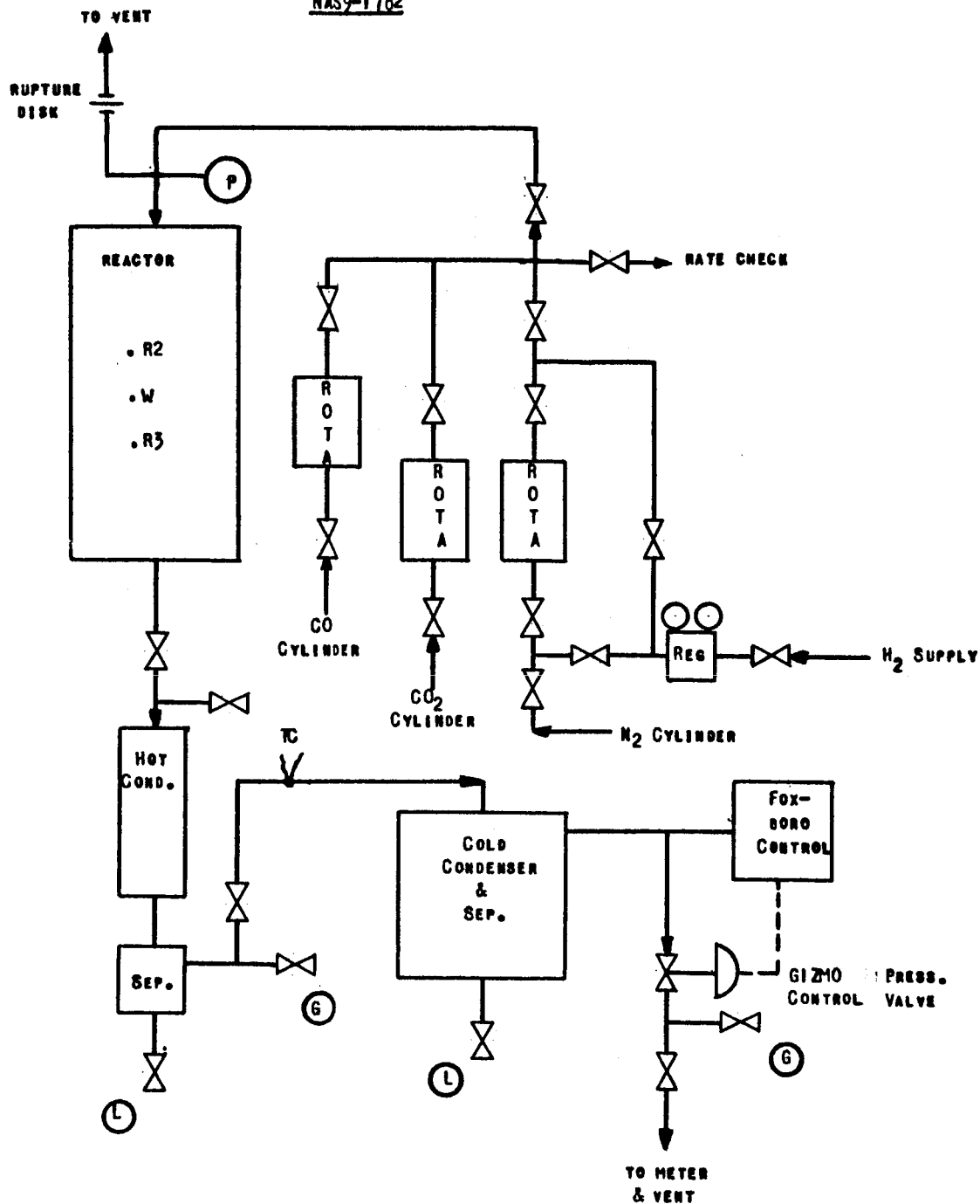
L = LIQUID PRODUCT DRAIN
G = GAS PRODUCT TAP

to provide a constant 200 psig back pressure on the Brooks rotameter tubes (sizes No. 1 and 1A). The pressure drop between 200 psig and unit pressure was taken across the Hoke metering valve used to set the gas flow rate through each rotameter. This insured a constant, measured gas flow into the reactor at any unit pressure from 0 psig to 150 psig.

The metered, mixed feed gases entered the top of the vertical catalytic reactor, passed downward through the catalyst bed, and were discharged into the hot condenser through a heated transfer line (approx. 220°F). The reactor operating conditions were varied within the following limits:

Pressure	- 0 psig to 150 psig
Temperature	- Ambient to 1500°F
H_2/CO_2 Mole Ratio	- 1.2 to 6.6
H_2/CO_2 Mole Ratio	- Approx. 2.0
CO/CO_2 Mole Ratio	- 0.8 to 3.8 (recycle type operation only)

The hot condenser was maintained at a temperature of approximately 220°F so that the majority of the water and light hydrocarbons would be vaporized into the cold condenser. The cold condenser was cooled with chilled water to approximately 50°F. The light hydrocarbons (through C_5) and unreacted feed gases were removed through a Gizmo pneumatic pressure control valve operated by a Foxboro pressure controller. The gases were metered through a wet test meter and vented.

The liquid products from the hot and cold condensers were weighed into calibrated burettes in order to obtain a total weight of liquid and an oil-water volumetric split. The oil layer was analyzed for normal paraffins, iso-paraffins and olefins in order of ascending carbon number by conventional vapor fractometer techniques. The effluent gas stream was analyzed in a mass spectrometer for residual feed components and hydrocarbons through carbon number 6.

c. Experimental Equipment

The catalytic reactor consisted of two separable parts--a heavy walled jacket flanged at the top and a thin walled liner, also flanged at the top, containing 400 cc of catalyst. The liner was dropped into the jacket and a pressure-tight seal was made between the flanges by using a V-grooved copper gasket. A perforated screen at the bottom of the liner supported the catalyst within the liner. The assembled jacket and liner were immersed in a lead bath used for heating purposes. The lead bath was wound with an upper and lower electric circuit; the upper circuit was automatically controlled and the bottom circuit was manually controlled by a Variac.

B. Results and Discussion

The laboratory experimental work was concerned primarily with determining the feasibility of sub-system 2, "Carbon Dioxide Reduction" and sub-system 3, "Fischer-Tropsch Synthesis" presented in the Houdry Proposal, March 7, 1963. Chronologically considered, a small exploratory program was set up to investigate the direct conversion of carbon dioxide and hydrogen to a mixture of paraffins,

olefins, alcohols, and water by means of a Fischer-Tropsch type synthesis. This direct approach, if successful, would eliminate the need for the carbon dioxide reduction sub-system (number 2) as postulated in the proposal. This experimentation was not successful and the investigation of the conversion of carbon dioxide to carbon monoxide (reverse water gas shift) was initiated. The results of this portion of the study indicated that the conversion of carbon dioxide to carbon monoxide was feasible as a recycle type operation within the conditions specified in the Houdry Proposal.

The Fischer-Tropsch synthesis reaction was investigated using (a) carbon monoxide and hydrogen feed gases only and (b) a carbon monoxide-carbon dioxide-hydrogen feed gas blend in a simulated recycle type operation.

1. Study of the Direct Conversion of Carbon Dioxide
   and Hydrogen to Hydrocarbons and Water

A detailed summary of the results of an investigation for the direct conversion of carbon dioxide and hydrogen by means of a Fischer-Tropsch type synthesis are presented in Table 1.

Several conventional Fischer-Tropsch type catalysts were prepared by impregnating cobalt or ruthenium metal (or metal plus alkali) on Houdry high-area macroporous silica base. The experience of other catalytic investigators at HPCC indicated that the use of a high-area silica base rather than a kieselguhr support would provide the high activity believed to be required for the direct conversion of carbon dioxide to higher (C_6+) hydrocarbons with hydrogen. A cobalt

TABLE 1

SUMMARY DATA
DIRECT CONVERSION OF CARBON DIOXIDE BY FISCHER-TROPSCH SYNTHESIS

CATALYST TYPE	COBALT FORMATE 61e-100 cc	COBALT FORMATE + ALK. (107CX1-1 + ALK.) 26.4e-50 cc				RuCl3 + NaOH 27.2e-47 cc				RuCl3 24.0e-50 cc						RuCl3 + K2CO3 24.0e-50 cc					
CATALYST NO.	107CX1-1	249CX1-1				260CX1-1				260CX2-1						260CX3-1					
RUN NO.	3001 SR	3002 SR			3003 SR			3004 SR					3005 SR							3006 SR		
BALANCE	010	010	011	021	033	009	013	018	020	007	009	015	018	022	025	007	0111	018	023	028	036
CONTROL TEMP. (°F)	1160	1160	1090	905	915	868	1058	742	985	840	990	880	820	739	939	705	915	725	915	1480*	1460*
PRESSURE (Psie)	150	150	150	150	150	150	150	150	150	150	150	25	25	25	25	150	150	25	25	150	150
H2/CO2 MOLE RATIO	4.0	4.1	4.1	4.2	5.3	8.0	8.0	4.2	4.2	3.8	3.8	4.0	2.1	2.3	2.3	7.5	7.5	9.2	9.2	8.9	3.1
CO2 FEED (Ft3/Hour)	1.8	2.7	1.7	1.7	0.3	0.2	0.2	1.7	1.7	1.8	1.8	1.7	1.7	1.6	1.6	0.26	0.26	0.28	0.28	0.28	0.23
H2 FEED (Ft3/Hour)	7.2	11.0	7.0	7.1	1.6	1.6	1.6	7.2	7.2	6.9	6.9	6.8	3.5	3.6	3.7	1.94	1.91	2.57	2.57	2.49	0.71
PRODUCT GAS (Ft3/Hour)	3.27	4.58	3.79	4.65	0.89	0.73	0.71	2.22	2.94	2.05	2.23	2.37	2.01	1.86	1.85	0.86	1.07	1.61	1.14	2.06	0.57
LIQ. PRODUCT, HOT COND. (G/Hr.)	0.7	0	0	0	0	2.5	1.2	0.5	2.5	5.0	2.3	0.4	0.4	1.0	0.8	2.8	0.9	0	0	0.2	0
LIQ. PRODUCT, COLD COND. (G/Hr.)	63.6	86.3	48.4	39.9	9.7	6.8	10.3	64.4	56.1	62.5	59.8	99.0	45.9	35.8	1.1(2)	0	9.1	10.8	14.2	9.7	1.6
CONVERSION, %	75	72.3	66.5	56.3	94.7	97.6	81.6	89.4	75.9	94.3	88.9	93.1	43.6	40.2	52.9	97.8	98.5	95.4	96.1	90.4	58.1
PRODUCT GAS ANALYSIS, MOL % CO2	11.7	15.0	11.8	13.8	1.2	0.4	5.2	7.4	12.0	4.3	7.9	4.5	48.1	50.2	42.1	0.3	0.2	0.6	0.6	1.3	14.4
CO	2.0	1.7	3.2	2.6	0.2	0.4	1.2	0.6	1.6	0.7	1.1	0.5	0.6			0.3	0.2	0.2	0.3	7.0	24.3
H2	41.9	35.7	54.0	61.7	67.7	59.7	59.1	18.3	39.9	16.9	20.9	26.5	7.5	4.0	10.2	62.5	71.3	79.2	68.8	85.6	57.5
CH4	44.4	47.6	31.0	21.9	30.9	39.5	34.5	73.7	46.5	78.1	70.1	68.5	43.8	45.8	47.7	36.9	28.3	20.0	30.3	6.1	3.8

* HIGH TEMPERATURE FOR $CO_2 \rightarrow CO$

catalyst was used as it was well known that alkali promoted cobalt catalysts gave good hydrocarbon yields at high conversion of carbon monoxide when operated at moderate pressures (<15 atmospheres). Ruthenium catalysts produce high molecular weight hydrocarbons at high pressures (300+ atmospheres) but it was hoped the use of a highly active, high area base would promote the activity of ruthenium at moderate pressures. This did not happen.

The analytical results showed carbon dioxide conversion predominantly to methane and water in every instance. The operating conditions were varied within the following limits.

Pressure   - 0 psig to 150 psig

Temperature   - Ambient to 1000°F

H_2/CO_2 Mole Ratio - 2.1 to 9.2

There was very little carbon monoxide formation. Conversions in excess of 95% and hydrocarbon selectivities (methane) of 100% were readily obtained (3006 SR, $RuCl_3$ x H_2O + K_2CO_3).

Table 2 presents a summary of the catalysts used in the experiments concerned with the direct conversion of carbon dioxide with hydrogen to Fischer-Tropsch type products. Conventional catalyst preparation techniques were used such as no-excess solution, multiple dip, excess solution, etc. as required by the catalyst composition.

2. Study of the Reverse Water Gas Shift Conversion

of Carbon Dioxide to Carbon Monoxide

Before discharging the ruthenium/alkali catalyst from run 3006 SR, a preliminary attempt was made to reduce carbon dioxide to

TABLE 2

SUMMARY DATA
CATALYST PREPARATION

DIRECT CONVERSION

RUN NO.	3001-SR	3002-SR	3003-SR	3004-SR	3005-SR	3006-SR
CATALYST NO.	107CX1-1	107CX1-1	249CX1-1	260CX1-1	260CX2-1	260CX3-1
CATALYST BASE	HOUDRY POWDER-INCLUDED MACROPOROUS SILICA					
METAL	COBALT	COBALT	COBALT	RUTHENIUM	RUTHENIUM	RUTHENIUM
WT.% METAL (NOMINAL)	15	15	15	5	5	5
ALKALI	-	-	K_2CO_3	NAOH	-	K_2CO_3
WT.% ALKALI (NOMINAL)	-	-	2	5	-	2

BEFORE USE, ALL CATALYSTS REDUCED WITH HYDROGEN 2 HOURS/900-1000°F/0 PSIG/10 FT^3/HR.

carbon monoxide at 1500°F and 150 psig. A detailed summary of the data is presented in Table 1, 3006 SR, balances 028,036. At a H_2/CO_2 ratio of 8.9 (3006 SR-028), the results indicated a 90.4 percent conversion of carbon dioxide and a selectivity for carbon monoxide of 49.2 percent. At a H_2/CO_2 ratio of 3.1 (3006 SR-036), the conversion decreased to 58.1 percent, but the selectivity for carbon monoxide increased to 85.9 percent.

Two commercially available conventional water gas shift catalysts (Girdler G-13 and G-66) and one Houdry experimental catalyst (nickel-copper on macroporous silica base) were also used for the reverse water gas shift conversion of carbon dioxide and hydrogen to carbon monoxide and water (Table 3). The Girdler G-13 type catalyst provided a moderate conversion of 62.8 weight percent and a selectivity for carbon monoxide of 68.4 percent. The operating conditions for this catalyst were 1500°F, 100 psig, and 2.1 H_2/CO_2 mole ratio inlet gas (Run 3012 SR). The other catalysts tested provided similar conversions and selectivities, varying in degree only.

The above results indicated that the conversion of carbon dioxide to carbon monoxide was feasible as a recycle type operation within the conditions specified in the Houdry proposal.

3. Study of the Fischer-Tropsch Reaction

Several Fischer-Tropsch catalysts were prepared by impregnating cobalt or ruthenium metal (or metal plus alkali) on

TABLE 3

SUMMARY DATA
REVERSE UNDER GAS SHIFT CONVERSION OF CARBON DIOXIDE TO CARBON MONOXIDE

CATALYST TYPE	GIRDLER G-66 147.6a-100 cc				NI-Cu ON MACROPOROUS SILICA 48.1a-100 cc			GIRDLER G-13 152.2a-100 cc		
CATALYST NO.	519X1-1				261CX1-1			448X1-1		
		3008 SR				3010 SR			3012 SR	
RUN NO. BALANCE	004	009	014	024	009	016	024	010	021	028
CONTROL TEMP. (°F)	315	525	318	1440	1425	1285	1275	1440	1440	1445
PRESSURE (PSIG)	0	0	100	100	0	140**	100	0	100	100
H2/CO2 MOLE RATIO	1.2	1.2	1.4	1.6	1.2	1.0	1.0	1.1	1.2	2.1
CO2 FEED (FT3/HR.)	1.94	1.94	1.83	1.91	2.07	1.97	1.97	2.02	1.94	0.89
H2 FEED (FT3/HR.)	2.31	2.31	2.48	2.99	2.51	1.97	1.97	2.26	2.30	1.85
PRODUCT GAS (FT3/HR.)	4.23*	4.39*	4.13*	3.60	3.57	2.84	2.96	3.26	3.21	2.13
LIQ. PRODUCT, HOT COND. (G/HR.)	0	0	0	0.3	0	0	0	0	0	0
LIQ. PRODUCT, COLD COND. (G/HR.)	0	0	0	21.2	19.1	16.2	16.6	21.0	20.7	14.5
CONVERSION, %				55.6	57.5	43.5	41.3	50.8	46.2	62.8
PRODUCT GAS ANALYSIS, MOL %										
CO2	45.7	46.6	42.8	23.7	24.7	39.1	39.2	30.4	32.5	15.5
CO		0.2	0.2	32.1	31.7	27.4	28.5	33.3	33.0	30.3
H2	54.3	53.2	57.0	44.2	43.6	31.4	31.4	36.0	34.5	54.2
CH4						2.1	0.8	0.3		
O2							0.1			
CO SELECTIVITY, %				69.9	58.5	55.0	62.2	64.4	70.9	68.4
CH4 SELECTIVITY, %						2.4	0.8	0.3		
O2 + GAS SELECTIVITY, %							0.2			
TOTAL LIQUID SELECTIVITY, %				30.1	41.5	42.6	36.8	35.3	29.1	31.6

* NO APPRECIABLE CONTRACTION
** UNIT PARTIALLY PLUGGED

Houdry high area macroporous silica base. The historical develop-
ment of the Fischer-Tropsch catalysts indicated that the incorporation
of K_2CO_3 and ThO_2 into a cobalt-metal catalyst provided a significant
improvement in the production of higher molecular weight products.
A detailed summary of the data is presented in Table 4, and Table
5 presents a summary of the catalyst preparation. The analytical
results through Run 3015 SR indicate carbon monoxide conversion to
predominantly methane, water, and carbon dioxide.

The operating conditions were varied within the following
limits:

Pressure — 0 psig to 150 psig

Temperature — Ambient to 1000°F

H_2/CO Mole Ratio — 1.2 to 6.6

No combination of the above operating conditions provided a liquid
product containing more than trace quantities of C_5+ hydrocarbons.
This was verified by making a carbon balance around an equilibrium
set of data. In each instance, the carbon content was in balance
when the liquid product was assumed to be water only. A possible
reason for the presence of C_5+ liquid hydrocarbons could be attributed
to the temperature programming where the temperatures were raised
from ambient to 1000°F in approximately six hours. Subsequent data
has indicated that the best C_5+-yield occurs within a relatively
narrow temperature range for any particular set of operating conditions.
The programmed temperatures could have increased so rapidly through

CATALYST TYPE	COBALT-FORMATE + K_2CO_3 59.2g-100 CC				$RuCl_3$ + K_2CO_3 24.8g-50 CC		COBALT-FORMATE + K_2CO_3 29.9g-50 CC			
CATALYST NO.	249CX2-1				260CX4-1		249CX2-1			
RUN NO.	3011 SR				3007 SR		3009 SR			
BALANCE	004	006	009	011	006	015	005	013	017	023
CONTROL TEMP. (°F)	850	1005	812	975	433	533	320	790	1005	760
PRESSURE (PSIG)	100	100	100	100	150	150	0	0	0	100
H_2/CO MOLE RATIO	1.3	1.3	3.1	3.1	1.6	2.3	2.3	2.4	2.4	2.5
CO FEED (FT^3/HOUR)	0.90	0.90	0.19	0.19	0.61	0.47	0.55	0.51	0.51	0.51
H_2 FEED (FT^3/HOUR)	1.17	1.17	0.59	0.59	1.00	1.10	1.28	1.21	1.21	1.30
PRODUCT GAS (FT^3/HOUR)	0.96	0.93	0.28	0.28	1.54	1.55	1.68	1.17	0.87	0.77
LIQ. PRODUCT, HOT COND. (G/HR.)	0	0	0	2.6	0	0	0	0	0	0.2
LIQ. PRODUCT, COLD COND. (G/HR.)	0	0	0	0	0	0	0	0	3.1	TRACE
CONVERSION, %	98.4	98.4	91.1	97.7	•	•	•	91.0	93.7	93.6
CO_2 SELECTIVITY, %	64.7	63.7	17.7	23.4	–	–	–	60.9	50.1	31.9
CH_4 SELECTIVITY, %	28.4	27.5	32.9	43.5	–	–	–	35.4	38.2	35.6
C_2 + GAS SELECTIVITY, %	0.2	0.1	0.9	0.3	–	–	–	0.9	–	0.4
TOTAL LIQUID SELECTIVITY, %**	6.7	8.7	48.5	32.8	–	–	–	2.8	11.7	32.1

• NO CONTRACTION
•• OBTAINED BY DIFFERENCE FROM ST. BALANCE CALCULATION

26-1

TABLE 4

MARY DATA
ROPSCH REACTION

	COBALT-FORMATE + K₂CO₃ 175.0g-300 CC 249CX2-2						Co(NO₃)₂+ Th(NO₃)₄+ K₂CO₃ (THRU 10 ON 20) 60.2g-100 CC 296CX1-1			COBALT-FORMATE + K₂CO₃ (THRU 10 ON 20 MESH) 170.6g-300 CC 249CX2-2				
	3013 SR						3014 SR			3015 SR				
027	007	011	021	028	031	039	009	017	024	005	012	016	018	024
990	625	1000	1035	800	900	795	1005	500	490	632	555	620	770	710
100	100	100	100	100	100	100	150	150	150	100	100	100	100	100
2.5	2.8	2.8	3.6	2.8	2.8	2.3	4.1	5.2	2.6	2.7	2.5	2.4	2.4	3.1
0.51	0.20	0.20	0.39	0.44	0.44	0.40	0.15	0.15	0.60	0.37	0.39	0.40	0.40	0.21
1.30	0.56	0.56	1.40	1.21	1.21	0.93	0.63	0.81	1.55	1.00	0.98	0.96	0.96	0.65
0.48	0.35	0.26	0.88	0.99	0.76	0.81	0.40	0.82	2.14	0.67	0.63	0.59	0.51	0.31
4.4	0	3.4	8.8	2.7	6.9	1.2	0	0	0	1.5	1.9	0	2.1	1.8
2.2	0	0	0	1.1	1.9	0.3	0	0	0	0	7.5	1.8	2.0	0.3
99.1	85.2	99.2	96.9	98.9	99.5	73.2	95.7	•	•	99.8	99.0	95.8	98.5	99.1
4.7	17.8	13.8	-	8.3	1.2	17.5	11.8	-	-	37.2	38.0	36.1	30.6	35.2
8.7	37.2	41.9	51.5	48.8	46.5	46.7	43.8	-	-	33.5	31.4	26.1	37.4	43.0
0.1	1.1	0.3	-	0.6	-	-	0.7	-	-	3.3	7.1	6.5	0.7	1.4
6.5	43.9	44.0	48.5	42.3	52.3	35.8	43.7	•	•	26.0	23.5	31.3	31.3	20.4

TABLE 5

SUMMARY DATA
CATALYST PREPARATION

FISCHER-TROPSCH

RUN NO.	3007-SR	3008-SR	3009-SR	3010-SR	3011-SR	3012-SR	3013-SR	3014-SR	3015-SR
CATALYST NO.	260CX4-1	519X1-1	249CX2-1	261GX1-1	249CX2-1	448X1-1	249CX2-2	296CX1-1	249CX2-2
CATALYST BASE	HPCC PI MPS*	GIRDLER G-66	HPCC PI MPS	HPCC PI MPS	HPCC PI MPS	GIRDLER G-13	HPCC PI MPS	HPCC PI MPS**	HPCC PI MPS**
METAL	RUTHENIUM	-	COBALT	NICKEL-COPPER	COBALT	-	COBALT	COBALT-THORIA	COBALT
WT.% METAL (NOMINAL)	5	-	15	5	15	-	15	100-18	15
ALKALI	K_2CO_3	-	K_2CO_3	-	K_2CO_3	-	K_2CO_3	K_2CO_3	K_2CO_3
WT.% ALKALI (NOMINAL)	2	-	2	-	2	-	2	2	2
REACTION	$CO \longrightarrow HC$	$CO_2 \longrightarrow CO$	$CO \longrightarrow HC$	$CO_2 \longrightarrow CO$	$CO \longrightarrow HC$	$CO_2 \longrightarrow CO$	$CO \longrightarrow HC$	$CO \longrightarrow HC$	$CO \longrightarrow HC$
UNIT	8B1	8B4	8B1	8B4	8B1	8B4	8B1	8B4	8B1

NOTE

ALL HPCC MPS CATALYSTS APPROX. 4 MM BEAD PARTICLE SIZE.

* HOUDRY POWDER INCLUDED MACROPOROUS SILICA BASE.

** THRU 10 ON 20 MESH.

this optimum temperature range as to inhibit the formation of measureable amounts of liquid hydrocarbons.

However, at the time the above data was analyzed (through Run 3015 SR), the results indicated that experiments on the Fischer-Tropsch synthesis using radically different catalyst types (cobalt, nickel, Ruthenium on high area macroporous silica) should be discontinued and a more classical approach should be taken. A cobalt-thoria-kieselguhr catalyst was prepared employing the method of the U.S. Bureau of Mines[3]. Table 6 presents a summary of the catalyst preparation.

The initial studies using the cobalt-thoria-kieselguhr catalyst were made with only 100 cc of active catalyst (Table 7). Once again the analytical results of this run indicated carbon monoxide conversion to predominantly methane, water, and carbon dioxide. However, trace odors of a hydrocarbon were detected in the liquid product. This was most noticeable when the liquid receivers were drained after standing overnight. To minimize the effect of liquid product hold-up, subsequent studies were made with 400 cc active catalyst bed volume.

Table 7 presents the data from the first run using 400 cc of active catalyst. After approximately 35 hours operation (balance 035), a 50-50 oil-water volumetric split was obtained in the cold receiver liquid product. A detailed analysis of the two liquid layers is presented in Table 8.

TABLE 6

298CXI-I

CATALYST PREPARATION SUMMARY
COBALT-THORIA-KIESELGUHR CATALYST

NOMINAL COMPOSITION

    100 COBALT - 18 ThO_2 - 100 KIESELGUHR

ACTUAL COMPOSITION

    73.2 COLBALT - 16.3 ThO_2 - 100 KIESELGUHR

PARTICLE SIZE

    THRU 7 ON 14 MESH

PREPARATION

    TO A SOLUTION OF COLBALT AND THORIUM NITRATES ADD KIESELGUHR AND COLD
    POTASSIUM CARBONATE, SLIGHTLY IN EXCESS OF STOICHIOMETRIC EQUIVALENT,
    WHILE STIRRING. HEAT QUICKLY TO BOILING. FILTER, WASH WITH DISTILLED
    WATER UNTIL THE WASH WATER IS NITRATE FREE (NEGATIVE TEST WITH
    DIPHENYLAMINE—SULFURIC ACID REAGENT). DRY IN THRU CIRCULATION AIR
    AT 250°F FOR 3 HOURS. GRIND TO SIZE.

REDUCTION

    NITROGEN PURGE FOR ONE-HALF HOURS.
    HYDROGEN REDUCTION
        2 HOURS - 900/1000°F - 0PSIG - 10 FT^3/HOUR

TABLE 7

SUMMARY DATA
FISCHER-TROPSCH REACTION

CATALYST TYPE	COBALT-THO2 ON KIESELGUHR (100 Co - 18 ThO2 - 100 KIESEL BY WT.) (40.8e-100 cc (THRU 7 ON 14 MESH)						COBALT-THO ON KIESELGUHR (100 Co - 18 ThO2 - 100 KIESEL BY WT.) (100e-150 cc (1-2MM PELLETS)					
CATALYST NO.	3016 SR 298CXI-I						3017 SR 298CXI-I					
RUN NO.	008	015	021	025	038	045	008	013	017	024	031	035
BALANCE												
CONTROL TEMP. (°F)	500	565	685	715(1)	615	475	500	590	480	470	730	445
PRESSURE (PSIG)	150	150	150	25	25.40	25	150	150	25	0	25	25
H2/CO MOLE RATIO	2.0	2.0	2.0	2.0	2.0	1.5	2.0	2.0	2.0	1.5	1.5	1.5
CO FEED (FT3/HR.)	0.33	0.67	0.67	0.67	2.7	0.4	0.33	0.33	0.33	0.4	0.4	0.4
H2 FEED (FT3/HR.)	0.67	1.33	1.33	1.33	5.3	0.6	0.67	0.67	0.67	0.6	0.6	0.6
PRODUCT GAS (FT3/HR.)	0.40	0.55(2)	0.88	0.98	5.63	0.68	0.24	0.30	0.29	0.43	0.22	0.57
LIQ. PRODUCT, HOT COND. (G/HR.)	0	0	0	0	0	0	3.3	4.7	1.2	TRACE	0	1.7
LIQ. PRODUCT, COLD COND. (G/HR.)	0	0	11.8	5.8	10.7	2.8	0.3	0.9	4.1	3.1	0.3	(4)
CONVERSION, %	95	99.5	99.1	100	44.2	60.7	98.7	100	99.4	67.0	94.3	81.3
CO2 SELECTIVITY, %	27.9	13.8	28.3	36.6	31.3	44.5	25.2	35.2	28.2	35.9	23.0	26.6
CH4 SELECTIVITY, %	24.1	17.9	42.4	28.2	28.7	43.9	21.0	40.9	11.2	49.2	11.4	6.6
C2 + GAS SELECTIVITY, %	4.9	1.5	0.7	0.9	0.9	8.2	3.7	4.3	12.6	14.4	8.2	13.8
TOTAL LIQUID SELECTIVITY, % (3)	43.1	55.8	28.6	34.3	39.1	3.4	50.1	19.6	48.0	0.5	65.4	53.8

(1) ERRATIC TEMPERATURES
(2) NOT STABLE; CONTRACTION INCREASING
(3) OBTAINED BY DIFFERENCE FROM WT. BALANCE CALCULATION
(4) WATER 1.4 cc   2.3e
    OIL   1.4 cc

TABLE 8

ANALYTICAL RESULTS - LIQUID PRODUCT DISTRIBUTION
RUN 3017SR-035

OIL LAYER		WATER LAYER	
COMPONENT	WT.%	COMPONENT	VOL.%
N-C4	0.16	ACETIC ACID	1.8
N-C5	0.54	ETHANOL	3.2
I-C6	0.82	METHANOL	9.5
N-C6	1.80	FORMIC ACID	0.2
I-C7	2.52	WATER	81.0
N-C7	4.50	HYDROCARBONS	4.3
I-C8	4.79	(INCL. C6+)	
N-C8	6.89		
I-C9	4.22	NOTE	
N-C9	6.62	WATER LAYER COMPONENT	
I-C10	3.72	ANALYSIS IS ONLY APPROXIMATE	
N-C10	5.94		
I-C11	3.10		
N-C11	6.78		
I-C12	2.98		
N-C12	6.08		
I-C13	2.05		
N-C13	5.40		
I-C14	1.64		
N-C14	4.89		
I-C15	1.45		
N-C15	4.28		
I-C16	1.59		
N-C16	3.59		
I-C17	1.71		
N-C17	2.91		
I-C18	1.55		
N-C18	2.11		
I-C19	0.61		
N-C19	1.52		
I-C20	0.18		
N-C20	1.08		
I-C21	0.73		
N-C21	0.69		
I-C22	0.19		
N-C22	0.37		

ISO - PARAFFINS	33.85
NORMAL - PARAFFINS	66.15

Following a catalyst change, run 3018 SR was initiated. Table 9 presents a summary of the process conditions and product compositions for this run. Stabilized yield data will accompany this report in a separate appendix section.

From this data, several qualitative observations can be made. The first and most important is that a Fischer-Tropsch type reaction system is capable of converting approximately 95+ percent of the carbon monoxide charge into carbon dioxide, water, and hydrocarbons (C_1-C_5 gas and C_6+ liquid). Temperature is very critical in obtaining the maximum carbon monoxide conversion and maximum liquid hydrocarbon yield (Table 9, balances 006/013 and 029). Atmospheric pressure operation gives much lower conversions (75 percent vs 95+ percent) than 25 psig operation (balances 060 and 013) and pressures above 25 psig do not appear to yield an appreciable advantage (Table 9, balances 034/055 and 013). A two-fold increase in the gaseous hourly space velocity gives a lower conversion with a loss in hydrocarbon oil yield (Table 9, balances 049 and 013).

It can be deduced from the foregoing analysis that precise control of the operating conditions is necessary. At this point in the study, a 24-hour weekly pilot plant study was useful in minimizing mechanical problems which are exaggerated in runs of short duration. This led to the study of a recycle type of Fischer-Tropsch synthesis. It is also more practical to study recycle type operation as the carbon dioxide reduction sub-system is not a 100% conversion-100% selectivity operation.

TABLE 2

FISCHER-TROPSCH SUMMARY DATA
COBALT-ThO₂ ON KIESELGUHR (100Co-18ThO₂-100 KIESEL BY WT.)
102.9g 298CXL-3 + 90.1g 298CXL-1 (THRU 7 ON 14 MESH)

RUN NO. 5018SR

BALANCE	006	013	020	025	029	034	042	049	055	060
CONTROL TEMPERATURE (°F)	438	458	360	395	410	430	480	460	430	450
H₂/CO MOLE RATIO	2.0	2.0	2.0	2.0	2.0	2.0	2.0	1.9	2.0	2.0
CO FEED (FT³/H)	0.67	0.67	0.67	0.67	0.67	0.67	0.34	1.34	0.67	0.67
H₂ FEED (FT³/H)	1.33	1.33	1.33	1.33	1.33	1.33	0.67	2.6	1.33	1.33
PRODUCT GAS (FT³/H)	0.26	0.27	0.74	0.76	0.72	0.71	0.24	1.20	0.70	0.49
HOT PRODUCT (g-cc)										
WATER	5.4 {5.0	5.2 {4.8	7.7 {7.2	4.4 {4.5	1.8 {1.5	4.6 {4.8	3.1 {3.5	6.9 {5.2	0.3 {0.4	0.3 {0.6
OIL	1.0	1.2	1.2	0.3	0.5	-	0.3	2.6	-	-
COLD PRODUCT (g-cc)										
WATER	9.1 {5.8	10.6 {8.0	3.2 {2.7	6.6 {5.7	8.2 {7.3	2.7 {2.5	4.1 {2.4	18.0 {15.0	1.2 {1.3	10.2 {8.4
OIL	4.8	4.0	0.5	1.3	1.5	0.5	2.6	5.0	0.2	3.1
PRESSURE (PSIG)	25	25	25	25	25	100	25	25	50	0
CONVERSION %	92.6	96.3	98.6	83.8	56.0	99.6	99.6	74.2	98.7	75.6
CO₂ SELECTIVITY %	13.8	19.3	41.8	38.1	3.5	38.4	13.6	5.7	38.7	9.8
CH₄ SELECTIVITY %	5.9	5.0	20.6	11.4	3.5	3.4	6.8	6.2	31.8	7.3
C2+ GAS SELECTIVITY %	10.5	10.3	2.8	13.1	11.9	0.3	6.5	10.5	0.4	12.7
TOTAL LIQUID SELECTIVITY %	69.8	65.4	34.8	37.4	81.1	57.9	73.1	77.6	29.1	70.2
LIQUID HYDROCARBON SELECTIVITY %	20.0	15.3	-	4.0	11.9	5.8	19.7	17.1	-	14.4
LIQUID, OIL LAYER, HOT										
AVG. C-NO. ± 1%	C₁₄	C₁₅	C₁₂	C₁₅	C₁₅	C₁₆	C₁₅	C₁₇		
n-HYDROCARBONS, WT.%	66.92	71.97	73.87	80.67	78.63	81.44	80.91	73.55	-	-
i-HYDROCARBONS, WT.%	27.48	25.95	15.26	12.59	14.39	14.62	18.65	20.97	-	-
OLEFINS, WT.%	5.60	2.08	10.87	6.74	6.98	3.94	0.44	5.48	-	-
LIQUID, OIL LAYER, COLD										
AVG. C-NO. ± 1%	C₁₁	C₁₀		C₁₂	C₁₁	C₁₄	C₁₂	C₁₀		C₁₂
n-HYDROCARBONS, WT.%	61.48	66.78	-	70.22	70.56	77.20	79.33	58.20	-	58.95
i-HYDROCARBONS, WT.%	22.35	22.43	-	10.20	11.62	13.31	19.02	18.52	-	17.26
OLEFINS, WT.%	16.17	10.79	-	19.58	17.82	9.49	1.65	23.28	-	23.79

4. Study of a Simulated Recycle Type Fischer-Tropsch
    Reaction Using a Mixed Carbon Dioxide-Carbon Monoxide Feed

    a. Paper Study on Integrated Carbon Dioxide Reduction-
        Fischer-Tropsch Synthesis Unit

Despite the fact that hydrogenation of carbon dioxide is possible under most conditions of the Fischer-Tropsch synthesis, sizeable amounts of carbon dioxide are produced during the hydrogenation of carbon monoxide. This characteristic of the synthesis should be accompanied by a recycle type operation. The production of carbon dioxide may be decreased by increasing the space velocity. Also when the carbon monoxide has been almost completely consumed, the carbon dioxide could be hydrogenated. This observation is based on the experiments of Fischer and Pichler[4] and Anderson, Krieg, Friedel, and Mason[5] in which carbon dioxide was not hydrogenated in the presence of carbon monoxide.

Therefore the presence of carbon dioxide in the feed gases to the Fischer-Tropsch sub-system should inhibit the formation of additional carbon dioxide and provide the maximum conversion of carbon monoxide to hydrocarbons. At this point a paper study was made presenting a typical weight balance and energy balance around an integrated carbon dioxide reduction-Fischer-Tropsch synthesis unit. This paper study assumed that the equilibrium product from the carbon dioxide reduction sub-system would be the feed to the Fischer-Tropsch sub-system.

As a starting point, data for the conversion of carbon
dioxide to carbon monoxide were taken from run no. 3012-SR-028,
Table 3 of this report. Data for the conversion of carbon monoxide
by the Fischer-Tropsch synthesis were taken from run no. 3018-SR-025
presented in Table 9 of this report. The weight balance over the
completely integrated system was calculated by matching the carbon
dioxide in the product of the carbon dioxide reduction sub-system
to the carbon dioxide remaining in the Fischer-Tropsch synthesis
product. A description of the calculation method follows.

An assumption was made that all carbon dioxide in the
Fischer-Tropsch reactor effluent would be the equilibrium amount
necessary to suppress the carbon monoxide to carbon dioxide reaction
completely. Since, in run 3018-SR-025 no carbon dioxide was present
in the Fischer-Tropsch reactor feed, the carbon dioxide contained
in the effluent was taken to be the equilibrium amount. If this
equilibrium amount of carbon dioxide were present in the Fischer-Tropsch
reactor feed, the $CO \longrightarrow CO_2$ reaction could be assumed to be
completely suppressed and all the carbon dioxide would pass through
the system unreacted. Thus, the weight balance of run 3018-SR-025
was adjusted to include in the feed the equilibrium amount of carbon
dioxide necessary to completely suppress the $CO \longrightarrow CO_2$ reaction.
In the actual run the feed consisted only of carbon monoxide and
hydrogen. This adjusted weight balance around the Fischer-Tropsch
system is presented in Table 10.

TABLE 10

INTEGRATED CO REDUCTION SUB SYSTEM - FISHCHER-TROPSCH SYSTHESIS - WEIGHT BALANCE
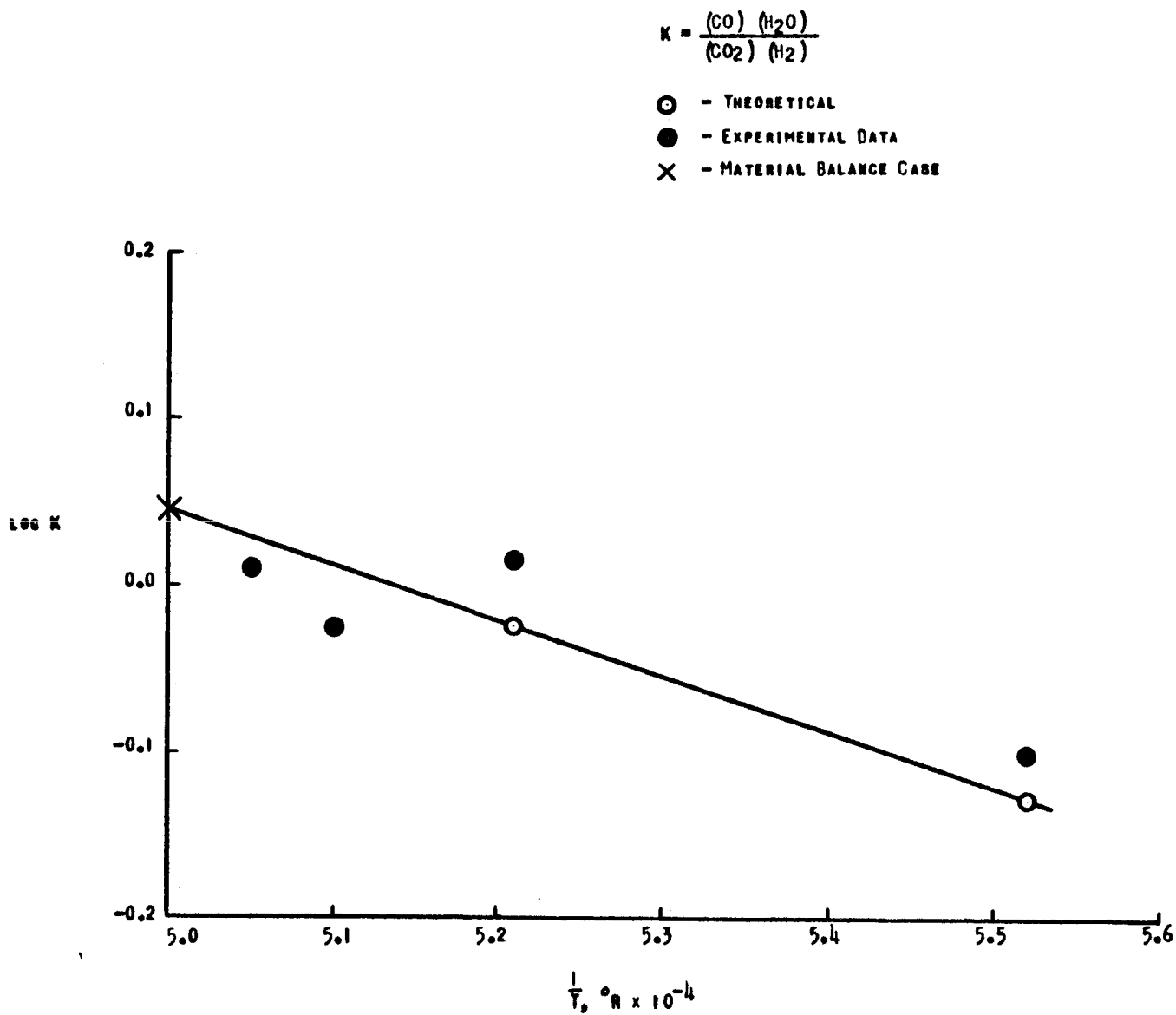
BASIS: 100 GMS. TOTAL FEED

| COMPOUND | CO_2 REDUCTION | | | | FISCHER-TROPSCH SYNTHESIS | | | |
| | FEED | | PRODUCT | | FEED | | PRODUCT | |
	WT.%	GM.	WT.%	GM.	WT.%	GM.	WT.%	GM.
CO_2	88.6	88.6	21.9	21.9	30.1	21.9	30.1	21.9
CO			42.5	42.5	58.4	42.5	14.4	10.5
H_2	11.4	11.4	8.4	8.4	11.5	8.4	6.9	5.0
CH_4							8.9	6.5
$C_2 \longrightarrow C_6$ (C_4 ave.)							10.3	7.5
LIQ. HC (C_7 ave.)							2.2	1.6
H_2O	____	____	27.3	27.3	____	____	27.2	19.8
TOTAL	100.0	100.0	100.0	100.0	100.0	72.8	100.0	72.8

It now was necessary to calculate the proper weight balance around the carbon dioxide reduction sub-system so that the effluent composition from this system was identical to the feed composition to the Fischer-Tropsch sub-system, previously established. The approach to equilibrium in the carbon dioxide-reduction sub-system was ascertained for several runs reported in Table 3 of this report (runs 3010-SR-024, 3012-SR-010, 3012-SR-021, and 3012-SR-028). A plot of log K versus reciprocal absolute temperature is given in Figure 5 where K is the equilibrium constant for the reaction $CO_2 + H_2 \rightarrow CO + H_2O$. Also plotted in Figure 5 are logs of the theoretical equilibrium constants at 1460°F and 1350°F. Points calculated from the experimental data scatter closely around the line drawn through the two theoretical points. Having shown that near equilibrium did exist in the experimental runs it was now possible to choose one run whose effluent composition most nearly matched the desired Fischer-Tropsch reactor feed composition. Since a greater carbon dioxide conversion than had actually been obtained from any experimental run was desired, an operating temperature of 1550°F was chosen as a first approximation of the operating severity necessary to achieve the desired product distribution (pressure of 100 psig was assumed constant throughout). Using this temperature the K value was obtained from Figure 5 from which the complete product distribution from the carbon dioxide-reduction sub-system could be calculated. A stoichiometric calculation then related these data to the proper feed composition. The complete weight

FIGURE 5

INTEGRATED CO_2 REDUCTION SUBSYSTEM — FISCHER-TROPSCH SYNTHESIS

REVERSE SHIFT REACTION EQUILIBRIUM

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

$\odot$ — THEORETICAL

● — EXPERIMENTAL DATA

✕ — MATERIAL BALANCE CASE

balance around the entire integrated unit is presented in Table
10 on the basis of 100 gms. total feed. To correspond more closely
to the actual average human carbon dioxide respiration rate of
approximately 1.0 gm-mole carbon dioxide per hour, the data in
Table 10 was recalculated on the bases at 1.0 gm-mol CO_2 feed. These
data are presented in Table 11.

In Table 12 is presented an energy balance around the
integrated unit. Values are given in Kcal. and KW and are based
on the material balance of Table 11; namely, 1.0 gm-mole carbon
dioxide in the carbon-dioxide-reduction sub-system feed. Assuming
the entire system operating at 100 psig, basis for the energy balance
calculations were as follows:

(a) CO_2-reduction feed from 70°F to 1550°F;

(b) CO_2-reduction effluent from 1550°F to 70°F except
water vapor which went from 1550°F to saturation
temperature at 100 psig (338°F), condensing at
338°F, and then as liquid from 338°F to 70°F;

(c) Fischer-Tropsch sub-system feed from 70°F to
450°F;

(d) Fischer-Tropsch reactor effluent from 450°F to
70°F except water vapor and C_7+ hydrocarbons;

(e) Water vapor and C_7+ hydrocarbons from 450°F to
338°F (assuming the same condensing temperature for
hydrocarbon as for water vapor), condensed at 338°F,
and cooled as liquid from 338°F to 70°F.

TABLE II

INTEGRATED CO₂ REDUCTION SUB SYSTEM – FISCHER-TROPSCH SYNTHESIS – MATERIAL BALANCE

BASIS: 1 GM.-MOLE CO₂ FEED

COMPOUND	CO$_2$ REDUCTION				FISCHER-TROPSCH SYNTHESIS			
	FEED		PRODUCT		FEED		PRODUCT	
	MOLE%	GM.-MOLE	MOLE%	GM.-MOLE	MOLE%	GM.-MOLE	MOLE%	GM.-MOLE
CO$_2$	26.1	1.00	6.5	0.25	8.1	0.25	10.0	0.25
CO			19.6	0.75	24.4	0.75	7.6	0.19
H$_2$	73.9	2.83	54.3	2.08	67.5	2.08	49.6	1.24
CH$_4$							8.0	0.20
C$_2$ $\longrightarrow$ C$_6$ (C$_4$ ave.)							2.4	0.06
LIQ. HC (C$_7$ ave.)							0.4	0.01
H$_2$O	___	___	19.6	0.75	___	___	22.0	0.55
TOTAL	100.0	3.83	100.0	3.83	100.0	3.08	100.0	2.50

TABLE 12

INTEGRATED CO_2 REDUCTION SUB SYSTEM - FISCHER-TROPSCH SYNTHESIS - ENERGY BALANCE

BASIS: KCAL GM.-MOLE CO_2 FEED AND

KW GM.-MOLE CO_2

COMPOUND	CO_2 REDUCTION				FISCHER-TROPSCH SYNTHESIS			
	FEED		PRODUCT		FEED		PRODUCT	
	KCAL	KW (x 10^{-3})	KCAL	KW (x 10^{-3})	KCAL	KW (x 10^{-3})	KCAL	KW (x 10^{-3})
CO_2	0.00972	0.01130	0.00243	0.00265	0.00052	0.00060	0.00052	0.00060
CO			0.00449	0.00522	0.00113	0.00131	0.00029	0.00034
H_2	0.01680	0.01952	0.01230	0.01430	0.00309	0.00359	0.00185	0.00215
CH_4							0.00041	0.00048
$C_2 \longrightarrow C_6$ (C_4 AVG.)							0.00038	0.00044
LIQ. HC. (C_7 AVG.)							0.00016	0.00019
H_2O			9.49465	11.05000			6.31529	7.34000
TOTAL	0.02652	0.03082	9.51387	11.07217	0.00474	0.00550	6.31890	7.34220

HEAT OF REACTION•   7.9 KCAL   -18.15 KCAL

• NEGATIVE HEAT INDICATES AN EXOTHERM

Heats of reaction in the carbon dioxide-reduction sub-system at 1550°F and the Fischer-Tropsch synthesis sub-system at 450°F were calculated from thermodynamic data presented in American Petroleum Institute Research Project 44. The heats of reaction are included in Table 12.

b. <u>Experimental Study of Simulated Recycle Operation</u>

No adverse effects were predicted from the paper study just described and an experimental program was devised to investigate the effect of carbon dioxide as a feed component in the Fischer-Tropsch synthesis sub-system. The nominal operating conditions for this study are presented in Table 13. A detailed summary of the actual operating conditions and product properties is presented in Table 14.

The following qualitative observations concerning the Fischer-Tropsch sub-system can be obtained from this study.

(a) A deactivation comparison at 25 psig pressure (all other operating conditions being constant) indicated a decrease in conversion and liquid hydrocarbon selectivity with time (Table 14, balances A27, D38, H65, Q109).

(b) Through 72 hours on stream, an increased CO/CO_2 mole ratio in the feed showed an increase in both conversion and liquid hydrocarbon selectivity at both 25 and 75 psig (Table 14, balances A27, B30, C33 and E48, FS4, G60). No definitive trend was obtained in repeat runs

TABLE 13

NOMINAL OPERATING CONDITIONS

SIMULATED RECYCLE OPERATION - FISCHER-TROPSCH SYNTHESIS

CATALYST NOS: 298CXI-1 + 298CXI-3 (88.1g EX 3018SR)

298CXI-1 (26.1g FRESH)

CATALYST TYPE: COBALT - ThO_2 ON KIESELGUHR
(100 Co - 18 ThO_2 - 100 KIESEL BY WT.)

CODE	PRESSURE (PSIG)	TEMPERATURE (°F)	FT³/HOUR H_2	CO	CO_2
A	25	475	0.77	0.38	0.38
B	↓				0.19
C					0.095
D	↓				0.38
E	75				0.38
F	↓				0.19
G	↓				0.095
H	25	↓			0.38
I	75	440			0.19
J		510			0.19
K		510			0.095
L (G)		475			0.095
M (F)					0.19
N (E)	↓				0.38
O (B)	25				0.19
P (C)					0.095
Q (A)	↓	↓	↓	↓	0.38

	EFFECT OF TIME				25 PSI(		
BALANCE	A 27	D 38	H 65	Q 109	A 27	B 30	C 33
HOURS ON STREAM	32	48	77	141	32	37	41
CONTROL TEMPERATURE (°F)	470	475	468	472	470	473	468
PRESSURE (PSIG)	25	25	25	25	25	25	25
H_2/CO MOLE RATIO INLET	2.06	2.06	2.25	2.22	2.06	2.00	2.03
CO/CO_2 MOLE RATIO INLET	0.81	0.81	0.77	0.90	0.81	1.98	3.22
INLET GAS (FT^3/HR.)	1.53	1.53	1.53	1.53	1.53	1.34	1.25
OUTLET GAS (FT^3/HR.)	0.80	0.72	1.00	1.05	0.80	0.57	0.44
HOT LIQUID PRODUCT (e–CC)							
WATER	0.3 {0.3	1.0 {0.8	0.2 {0.4	0.1 {0.1	0.3 {0.3	2.0 {1.7	2.7 {1.8
OIL	{–	{0.3	{0.1	{–	{–	{0.5	{1.0
COLD LIQUID PRODUCT							
WATER	3.7 {3.5	4.0 {3.5	4.5 {4.8	2.7 {2.7	3.7 {3.5	4.1 {3.6	3.0 {2.1
OIL	{0.7	{0.5	{0.4	{0.3	{0.7	{1.3	{1.5
CO CONVERSION (%)	66.35	63.07	34.91	59.42	66.35	72.43	70.78
CO_2 SELECTIVITY (%)	11.70	15.73	– *	29.58	11.70	7.71	14.18
CH_4 SELECTIVITY (%)	10.89	8.80	17.03	10.86	10.89	7.71	9.49
C_{2+} GAS SELECTIVITY (%)	20.16	17.96	32.60	18.72	20.16	17.09	18.47
TOTAL LIQUID SELECTIVITY (%)	57.25	57.51	50.37	40.84	57.25	67.49	57.86
LIQUID HYDROCARBON SELECTIVITY (%)	8.29	6.70	5.99	3.10	8.29	13.7	18.8
LIQUID, OIL LAYER, HOT							
AVG. C–NO., ± 1	17	18	16	–	17	17	15
N–HYDROCARBONS, WT.%	71.58	72.88	79.61	–	71.58	73.68	71.32
I–HYDROCARBONS, WT.%	15.58	14.66	10.51	–	15.58	14.33	11.85
OLEFINS, WT.%	12.84	12.46	9.88	–	12.84	11.99	16.83
LIQUID, OIL LAYER, COLD							
AVG. C–NO., ± 1	11	11	11	12	11	11	10
N–HYDROCARBONS, WT.%	56.22	58.32	62.00	54.82	56.22	55.29	54.47
I–HYDROCARBONS, WT.%	15.34	12.21	10.39	10.88	15.34	12.29	11.62
OLEFINS, WT.%	28.14	29.47	27.61	34.30	28.14	32.42	33.91

• 2.46 % CO_2 CONSUMP.
  VERY POOR WT. BALANCE

44-1

ATA
FISCHER-TROPSCH SYNTHESIS

OPERATION				75 PSIG OPERATION				
Q 109 141	O 102 128	P 106 133	E 48 60	F 54 65	G 60 72	N 97 121	M 89 113	L 83 104
472	472	471	468	465	480	475	477	468
25	25	25	75	75	75	75	75	75
2.22	1.74	2.23	2.06	2.00	2.03	2.16	2.00	2.03
0.90	2.36	3.76	0.81	1.98	3.22	0.88	1.98	3.22
1.53	1.34	1.25	1.53	1.34	1.25	1.53	1.34	1.25
1.05	0.58	0.56	0.68	0.37	0.32	0.61	0.32	0.36
$0.1\begin{cases}0.1\\-\end{cases}$	$1.6\begin{cases}1.5\\0.4\end{cases}$	$3.2\begin{cases}3.3\\1.2\end{cases}$	$4.3\begin{cases}4.0\\0.6\end{cases}$	$4.9\begin{cases}4.2\\1.2\end{cases}$	$5.9\begin{cases}4.6\\1.8\end{cases}$	$5.0\begin{cases}4.2\\1.4\end{cases}$	$4.6\begin{cases}3.9\\1.2\end{cases}$	$3.7\begin{cases}3.8\\0.8\end{cases}$
$2.7\begin{cases}2.7\\0.3\end{cases}$	$3.1\begin{cases}2.3\\1.4\end{cases}$	$2.2\begin{cases}2.0\\0.4\end{cases}$	$2.3\begin{cases}1.6\\0.7\end{cases}$	$2.7\begin{cases}1.8\\1.5\end{cases}$	$0.7\begin{cases}0.2\\1.0\end{cases}$	$2.2\begin{cases}1.5\\1.5\end{cases}$	$2.9\begin{cases}2.8\\0.3\end{cases}$	$0.7\begin{cases}0.6\\0.5\end{cases}$
59.42	78.09	73.00	82.03	88.73	100.00	84.22	100.00	92.26
29.58	16.01	4.37	14.09	17.77	18.12	-	-	14.11
10.86	11.33	10.82	13.90	10.25	11.32	8.17	14.36	11.77
18.72	17.55	15.92	19.21	11.77	14.61	13.64	12.28	16.05
40.84	55.11	68.89	52.80	60.21	55.95	78.19	73.36	58.07
3.10	14.40	11.65	7.85	15.20	17.02	21.65	10.55	10.56
-	17	17	15	13	13	15	15	14
-	71.45	77.00	84.31	79.51	86.88	66.04	82.81	79.42
-	13.71	9.86	11.64	9.09	10.05	10.16	11.22	11.39
-	14.84	13.14	4.05	11.40	3.07	23.80	5.97	9.19
12	10	11	9	7	8	9	9	9
54.82	57.39	58.71	74.09	66.79	74.74	61.96	76.64	68.09
10.88	8.78	11.17	11.00	6.81	8.43	6.46	9.32	9.05
34.30	33.83	30.12	14.91	26.40	16.83	31.58	14.04	22.86

between hours 104 and 141 (Table 14, balances Q109, 0102, P106 and N97, M89, L83).

(c) Operation at higher pressure (increased residence time) gave a higher conversion and carbon dioxide selectivity at essentially the same liquid hydrocarbon selectivity (Table 14, balances A27, B30, C33 and E48, FS4, G60).

With the data thus described for the Fischer-Tropsch subsystem, it was possible to construct a yield picture of the integrated carbon dioxide reduction-Fischer-Tropsch synthesis unit on a carbon atom basis. The assumption was made that the feed to the Fischer-Tropsch sub-system was the equilibrium product from the carbon dioxide reduction sub-system. A back-calculation through the carbon dioxide reduction sub-system provided the amount of carbon dioxide feed to this unit. It was thus possible to determine the yield of carbon atoms in the oil product from the Fischer-Tropsch sub-system as a percentage of the total number of carbon atoms charged to the carbon dioxide reduction sub-system as carbon dioxide. Table 15 summarizes this data.

It will be observed that the highest yield of carbon atoms in the liquid hydrocarbon oil occurred at the highest CO/CO_2 mole ratio (Table 15, balances C33, G60). At these conditions an internal recycle ratio of approximately 4 is required to convert all the carbon atoms fed into the integrated unit into liquid hydrocarbons.

TABLE 15

SUMMARY DATA
O-ATOM YIELDS, SIMULATED RECYCLE OPERATION – FISCHER TROPSCH SYNTHESIS

BALANCE	PRESS	FEED TO CO_2 REO'N (MOLES CO_2)	CO/CO_2 RATIO IN FISCHER-TROPSCH	O-ATOMS IN FT PRODUCT (MOLES)	YIELD (%)	RECYCLE TO CONVERT ALL O-ATOMS IN FEED
A 27	25	2.59	0.81	0.143	5.5	18.2
B 30	25	2.77	1.98	0.419	15.1	6.6
C 33	25	2.86	3.22	0.656	22.9	4.4
D 38	25	2.58	0.81	0.050	1.9	52.7
E 48	75	2.59	0.81	0.169	6.5	15.4
F 54	75	2.77	1.98	0.562	20.3	4.9
G 60	75	2.86	3.22	0.839	29.4	3.4
H 65	25	2.56	0.77	0.067	2.62	38.2
L 83	75	2.86	3.22	0.472	16.5	6.1
M 89	75	2.77	1.98	0.437	15.8	6.3
N 97	75	2.59	0.88	0.575	22.2	4.5
O 102	25	2.84	2.36	0.487	17.1	5.8
P 106	25	2.86	3.76	0.439	15.4	6.5
Q 109	25	2.59	0.90	0.051	1.9	52.7

Qualitatively, it seems that there is a stabilizing tendency in time with respect to the yield of liquid hydrocarbons àt 75 psig (Table 15, balances E48, F54, G60 and N97, M89, L83).

The data thus presented for the integrated unit prove that the conversion of carbon dioxide into disposable (or convertible) liquid hydrocarbons is quite feasible. No attempt was made in the work thus described to optimize the operating conditions or finalize on a choice of catalyst.

C. Recommendations for Future Work

The feasibility of an integrated carbon dioxide reduction-Fischer-Tropsch synthesis unit has been clearly demonstrated. Future work should be directed towards optimizing the process conditions for the maximum conversion of the carbon dioxide obtained from the air conditioning sub-system into disposable CH_2 type paraffinic hydrocarbons. This study would entail not only the construction of boiler-plate equipment for a final demonstration but also the construction of a small bench scale pilot unit which would be highly versatile and readily adaptable to changes in process conditions. With a smaller scale unit it would also be much easier to investigate additional catalysts before finalizing the catalyst selection.

For the reasons indicated in the beginning of this report, no studies will have to be made in the dehydrocyclization sub-system. However, it would be necessary to investigate the removal of the trace contaminants which are present in the water effluent from the Fischer-Tropsch synthesis (Table 8) and also to investigate the regeneration of the Fischer-Tropsch synthesis catalyst.

V. PROCESS DESIGN

The basic objectives desired for this system are:

(1) operability,

(2) minimum weight and power requirements,

(3) reliable operation for one year,

(4) little or no attention required to operate or maintain the unit.

Without a thorough analysis of the unit components, it appears that the major problem will be control. Four distinct chemical operations are involved which, in a commercial plant, would roughly require 80 instruments including process stream analyzers for the Fischer-Tropsch feed gas and aromatics product. In addition, stream purification facilities between operations would normally be provided which may be impractical or even impossible to include in this system. It will be necessary to determine the effects of undesirable components in the feed streams. These include coking rates in the CO_2 reduction unit, R-1, from recycle C_2-C_5 hydrocarbons and the effect on the dehydrocyclization catalyst of water and oxygenated compounds in the feed to R-4.

A flow diagram, Figure 1, has been prepared incorporating many of the points developed below. It does not include facilities for regeneration of catalysts and starting and stopping the units which are major considerations in themselves.

The working assumptions used in studying the scheme were:

(1) hydrogen would be supplied "as produced" from the electrolysis unit since the oxygen requirement is primary and CO_2 supply can be varied within the time limits of the CO_2 filters in the CO_2 separation unit.

(2) Surge capacity for liquids is preferable to that for gases.

(3) Long catalyst lives for the CO_2 and Fischer-Tropsch units compared to the dehydration and dehydrogenation units.

The following comments are offered for the individual units:

CO_2 Reduction, R-1 -- Internal heating of R-1 would be preferred since heat is required for the reactions involved. Even without the requirement to reform the light hydrocarbons, supplying of the heat requirement by superheating the feed gases will probably be impractical. Although CO_2 in the feed to the F-T is probably desirable, it may be thermodynamically more efficient to obtain maximum conversion in R-1 by higher temperatures and by-pass CO_2 from the feed or recycle F-T residue gas.

Rapid cooling of the reaction products will be necessary to avoid reversal to CO_2 and methane. Industrially this is accomplished

by quenching with steam or condensate. The feed-product exchanger should be designed to accomplish this with minimum reversal, for best heat economy and simplicity.

The original sketches do not show water removal before the F-T unit. This would be desirable not only because water is one of the products of the F-T reaction but the water produced here should be pure enough for drinking or direct feeding to the electrolysis unit.

Synthesis gas composition control will be difficult if it must be held within narrow limits. Proportional control of feed H_2 and CO_2 is shown. Thermal conductivity of the product gas may possibly be used to reset the feed proportion. With varying feed rates, compressor control must be considered. Recycle gas streams fed to each of the stages will further complicate this problem.

Fischer-Tropsch Reaction, R-2 -- This reaction is a heat producer and is understood to be sensitive to temperature both for product distribution and catalyst life. Decreasing catalyst activity normally requires continuously rising temperatures controlled within very narrow limits. Primary temperature control is shown by having the feed gas cool the reactor. This type of control is poor; more precise control would involve injection of cold synthesis gas along the reactor and blending of hot R-1 effluent into the feed. The latter would be used to heat R-2 for starting up.

The hydraulic cyclone shown attempts to separate in one unit the three phases that are produced; this should be possible in zero gravity if sufficient centrifugal force is imported. Capacitance probe level controllers can be used.

Surge volume for the oil produced is provided after the cyclone since R-1 and R-2 must be operated together and have the longest on stream cycle. This surge could be incorporated into the cyclone volume using hi-lo level switches on the oil layer. Stagnant surge, such as shown on the diagram, would be a problem since it would normally be kept almost empty and there will be no gravity to direct the oil to the outlet.

Control of the extent of reaction in R-2 should be considered. Excessive consumption of synthesis gas will decrease the system pressure. Low consumption of synthesis gas or formation of excessive amounts of light hydrocarbons will tend to raise the system pressure. A flow meter on the F-T recycle gas which resets the R-2 temperature control, will be a means of control. Appreciable fluctuation of F-T feed and residue gas rates will impose flow restrictions on the H_2 and CO_2 feed streams.

A major problem will be the water produced from the F-T reaction. Sufficient amounts of water soluble organics will be carried out with the water to render it unsuitable for direct use

as drinking water or electrolysis feed. Vapor-liquid fractionation appears unfeasible. Catalytic oxidation to metabolic organics is a possibility as is absorption on active carbon followed by hot vapor stripping and recycle to R-1.

Dehydration and Dehydrocyclization, R-3 and R-4 -- These two units were considered together to reduce the number of heaters required to only one. It was assumed that higher than normal temperatures would not be detrimental to the dehydration catalyst and would avoid the necessity for a carrier gas to dehydration. No aftercooler on the R-3 product is shown in the anticipation that water formed in the dehydration reaction could be separated as steam along with the light gases and thus avoid an additional stream of contaminated water. This should be a small amount of water compared to that produced in R-1 and R-2.

Although external heating is shown on the feed to R-4, the comments made previously about internal heaters apply here also.

An alternate design of cyclone is shown on the R-4 product which should be operable both with and without gravity.

General -- Advantage can be taken of the fact that multistage compression is probably required for both the feed gases and R-4 off gas. Thus, the R-3 off gas is recompressed in the second stage of the R-4 compressor and the F-T residue gas recompressed in the second stage of the feed gas compressor. Running of R-1 at 15 PSIA would not only be better for equilibrium and reduce high pressure equipment, but could reduce overall compressor

requirements by eliminating the need to repressure the R-3 vent gas. Since the water product from the CO_2 reduction reaction is removed before compression, at least the hydrogen used in this reaction does not have to be compressed.

Start-up, shutdown, stand by and safety requirements are necessary considerations. Start-up or heating of units can be accomplished by suitable valving and piping which will use the existing compressors and reactor electric heaters to bring the system up to temperature. Synthesis gas (R-1 product) can be used for R-1 and R-2 and hydrogen with the R-4 compressor for R-3 and R-4. Shutdown, or cool down if required, can use the same circuit as start up with the electric heaters shut off. Standby will probably involve shutting down the compressors and heaters. Safety items would be pressure relief, excess temperature cut off, and CO and H_2 leak detection.

Regeneration techniques and requirements should be better defined. If a nickel based catalyst is used in R-1, industrial practice for coke removal is reduction with super-heated steam. CO_2 might be used here. New catalysts developed for naphtha-cracking processes for hydrogen production are reputed to be able to operate very close to the coking ratios of steam-hydrocarbon. Regeneration of R-3 and R-4 may be possible with R-1 and R-2 operating by circulating CO_2 through these reactors and injecting oxygen. This could reduce the load on the CO_2 separation unit if

cabin air is used and minimize the amount of additional piping and

valves required.

VI. LOW TEMPERATURE CARBON DIOXIDE REMOVAL SUB-SYSTEM

The complete report on this study is being issued by
the Research and Development Department of Air Products and Chemicals,
Inc., as Part II of this Final Report.

In summary:

The results of the design study show that the low-
temperature carbon dioxide removal sub-system is feasible if the
compressor discharge pressure is greater than 70 psia. At this
pressure level power consumption is a minimum and amounts to 550
watts for a four-man capacity Life Support System. The sub-system
has a volume of 7 cubic feet and will weigh approximately 200
pounds.

The compressor and turbo-expander required for this sub-
system are presently unavailable. All other components are
conventional.

VII. CONCLUSIONS

The conclusions from this initial study are:

(1) The carbon dioxide recovery scheme postulated in the Houdry proposal will work if compressors and expanders having the necessary characteristics can be obtained.

(2) At present the chemical efficiency of the carbon dioxide reduction process is about one-fourth that necessary to make good the postulated sizes and power demands of the proposal flow sheet.

(3) The mechanical design studies have shown the need for developing small high-temperature (1000°F working) control valves for the chemical process.

(4) A further program of study is required to advance the state-of-the-art to a position where the proposed system can clearly demonstrate its superiority to the present, more fully investigated and developed systems.

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