N93-27973

ON-SITE MANUFACTURE OF PROPELLANT OXYGEN FROM LUNAR RESOURCES*

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Abstract

The Aerojet Carbothermal Process for the manufacture of oxygen from lunar resources has three essential steps; the reduction of silicate with methane to form carbon monoxide and hydrogen; the reduction of carbon monoxide with hydrogen to form methane and water; and the electrolysis of water to form oxygen and hydrogen. This cyclic process does not depend upon the presence of water or water precursors in the lunar materials; it will produce oxygen from silicates regardless of their precise composition and fine structure.

Research on the first step of the process was initiated by determining some of the operating conditions required to reduce igneous rock with carbon and silicon carbide. The initial phase of research on the second step is completed; quantitative conversion of carbon monoxide and hydrogen to methane and water was achieved with a nickel-on-kieselguhr catalyst. The equipment used in and the results obtained from these process studies are reported in detail.

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*This paper was originally published in 1966. It is republished in this volume so that more recent researchers in the field of lunar resource utilization can have easier access to the results of this research.

S.D. Rosenberg, G.A. Guter and F.E. Miller. *Chemical Engineering Progress Symposium Series.* 62[61] (1966): 228-234.

Background Information

At the present time the Mobile Systems Department of Aerojet-General's Chemical Products Division is carrying out a research program for the Office of Advanced Research and Technology of the National Aeronautics and Space Administration, Washington, D.C. This program is devoted to research on processes for utilization of lunar resources, particularly the manufacture of oxygen from lunar materials. Although the precise composition of the lunar surface and immediate subsurface is unknown at the present time, it is generally agreed that these areas are composed of metallic silicates and that these silicates are widely distributed and are relatively readily available. We have designed a chemical process which will produce oxygen from silicates, regardless of their precise composition and fine structure. We have avoided dependence on the presence of water or water precursors in the lunar materials. However, the process will produce water as by-produce if water, in any form, is present in the lunar materials.

The Aerojet Carbothermal Process for the manufacture of oxygen from lunar materials has three essential steps: the reduction of silicate with methane to form carbon monoxide and hydrogen; the reduction of carbon monoxide with hydrogen to form methane and water; and the electrolysis of water to form oxygen and hydrogen. The process is cyclic in nature and is exemplified by these reactions:

$$MgSiO_3 + 2\,CH_4 \xrightarrow{1{,}625\,C} 2\,CO + 4\,H_2 + Si + MgO \qquad (1)$$

$$2\,CO + 6\,H_2 \xrightarrow{250\,C} 2\,CH_4 + 2\,H_2O \qquad (2)$$

$$2\,H_2O \xrightarrow{75\,C} 2\,H_2 + O_2 \qquad (3)$$

Any water present in the silicate, either as hydrate or hydroxide ion, is obtained as a by-product in the first step.

Equipment Development for Reduction of Silicates

The equipment for the study of the reaction of methane with molten silicates was designed with the following guidelines: induction heating, 450 kc., 10-kw, maximum loading; minimum reaction chamber volume to obtain the best possible material balances using 0.25 lb of rock melt; standard off-the-shelf items, particularly ceramic crucibles and tubes; minimum use of glass for safety of operation; minimum use of metal within the induction current field, except for the tungsten susceptor; and adequate insulation around the reactor to permit the use of thermally sensitive bell jar seals. *Figure 1* is a schematic flow diagram of the silicate rock reduction furnace being used in this program.

Reduction of Igneous Rock with Carbon and Silicon Carbide

A series of reactions of basalt and granite with carbon and silicon carbide was carried out to determine the temperature profile for the reduction reactions which may occur during the reduction of igneous rock with methane. The results of three of these runs are illustrated in *Figure 2*.

In the reaction of basalt (50 g) with carbon (5 g), the initial evolution of carbon monoxide resulted from the reduction of iron oxide. The basalt contained 11.86% of iron oxide (as Fe_2O_3); the reduction of this oxide would require 1.34 g of carbon if present as Fe_2O_3. The carbon monoxide evolved during the first 2.5 hr represented 1.0g of carbon. Other reducible materials

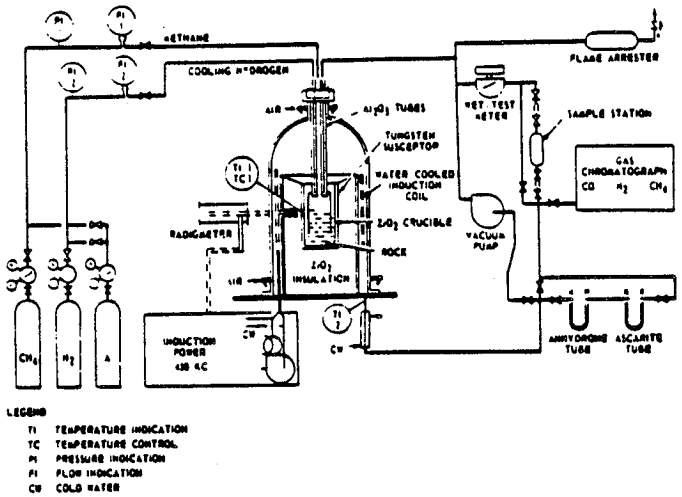

Fig. 1. Schematic flow diagram of silicate reduction furnace.

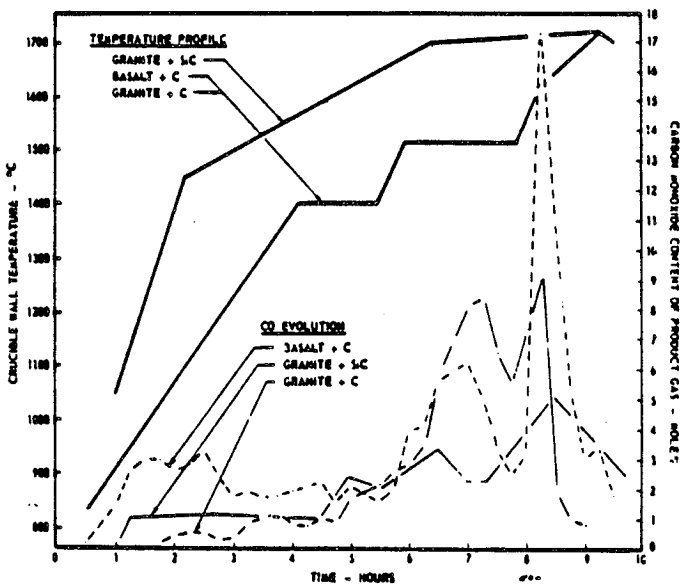

Fig. 2. Reduction of igneous rock with carbon and silicon carbide.

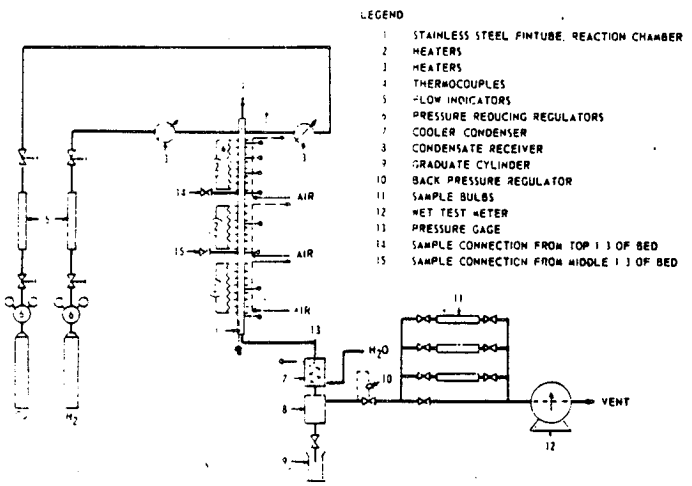

Fig. 3. Schematic flow diagram of hydrogen-carbon monoxide reactor.

present in the basalt were titanium oxide (2.47% as TiO_2) and sodium oxide (3.73% as Na_2O). These oxides would consume 0.43 g of carbon. Consequently, only 35% of the carbon could have been oxidized by materials other than silica. The recovery of 89.1% of the carbon charged as carbon monoxide indicates that a considerable portion of the silica present in the basalt was reduced at temperatures as low as 1,550 C.

Three solid products were obtained; slag and metal remained in the zirconia crucible and sublimate was found at the top of the bell jar. The slag was composed mainly of alumina; the metal contained 82% iron, 13% silicon, and minor amounts of vanadium, titanium, nickel, and copper. The sublimate contained 61% of the highly volatile sodium.

In the reaction of granite (50 g) with carbon (5 g), much less carbon monoxide was produced at low temperature. This is due to the lower percentage of reducible oxides in the granite, that is, iron oxide (2.05% as Fe_2O_3), sodium oxide (3.10%), and potassium oxide (4.90%). These oxides would require 0.85 g (17%) of the carbon charged for complete reduction. A total of 73% of the carbon charged was recovered as carbon monoxide; silica reduction accounts for most of the carbon monoxide evolved at 1,550 C and higher.

The lower carbon balance may be due to reaction of silicon with carbon to form silicon carbide. The slag had nonmagnetic pieces of metal dispersed throughout and contained 2.3% carbon, that is, 20% of the carbon charged.

In the reaction of granite (37.5 g) with silicon carbide (12.5 g), almost no reaction occurred below 1,100 C; about 7% took place between 1,100 and 1,500 C. As the temperature was increased from 1,500 to 1,740 C, the reaction rate gradually increased and then rapidly decreased as most of the carbon was consumed. About 83% of the carbon in the silicon carbide was recovered as carbon oxides. The dark, metallic looking slag contained an additional 10% of the carbon charged. The analysis of the metal recovered from the melt gave 59% iron, 28% silicon, and minor amounts of titanium, vanadium, nickel, and copper; the slag was composed mainly of alumina and silica.

These results indicate that if silicon carbide is formed by reaction of granite and carbon, excess granite will react with the carbide to produce silicon and carbon monoxide. The rate of the granite-silicon carbide reaction at 1,740 C is comparable with that of the graphite-carbon reaction at 1,625 C.

Equipment Development for Reduction of Carbon Monoxide

A schematic flow diagram of the hydrogen-carbon monoxide reactor used in this program is shown in *Figure 3*. The equipment was designed to allow maximum flexibility in operating conditions. Type 316 stainless steel was used as the reaction chamber metal because of its high temperature strength, resistance to corrosion, and nickel content.

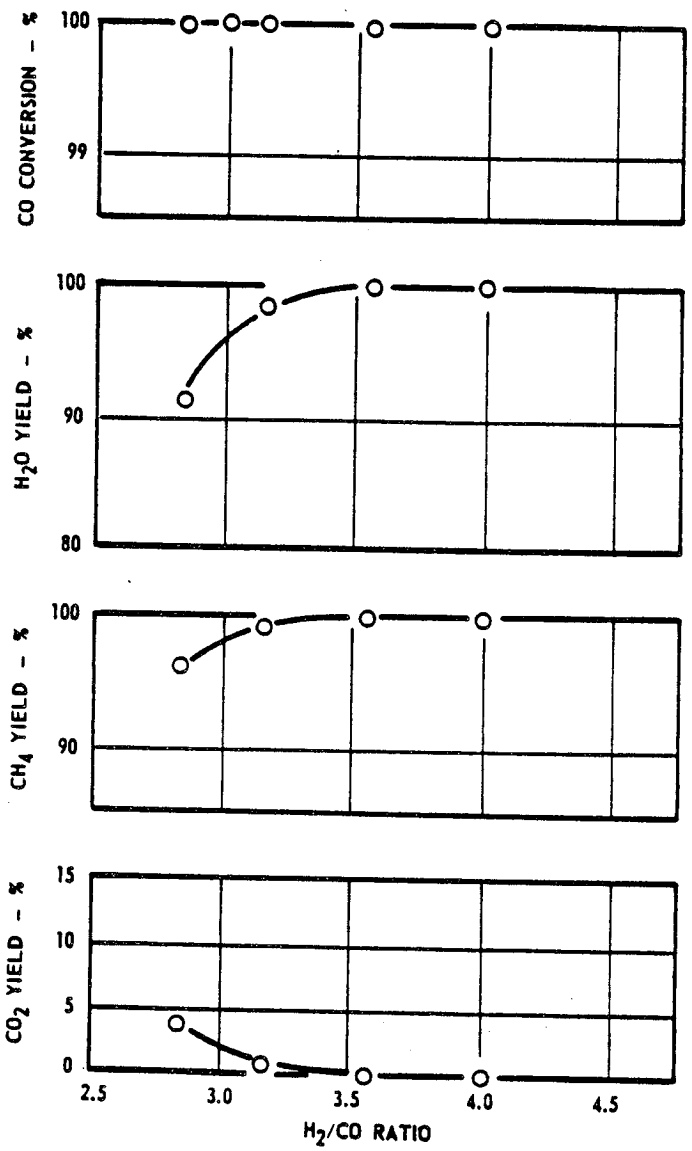

Fig. 4. Carbon monoxide conversion and yields vs. hydrogen-carbon monoxide mole ratio (1,000 hr.$^{-1}$ space velocity; 250° C.; 1.0 atm.).

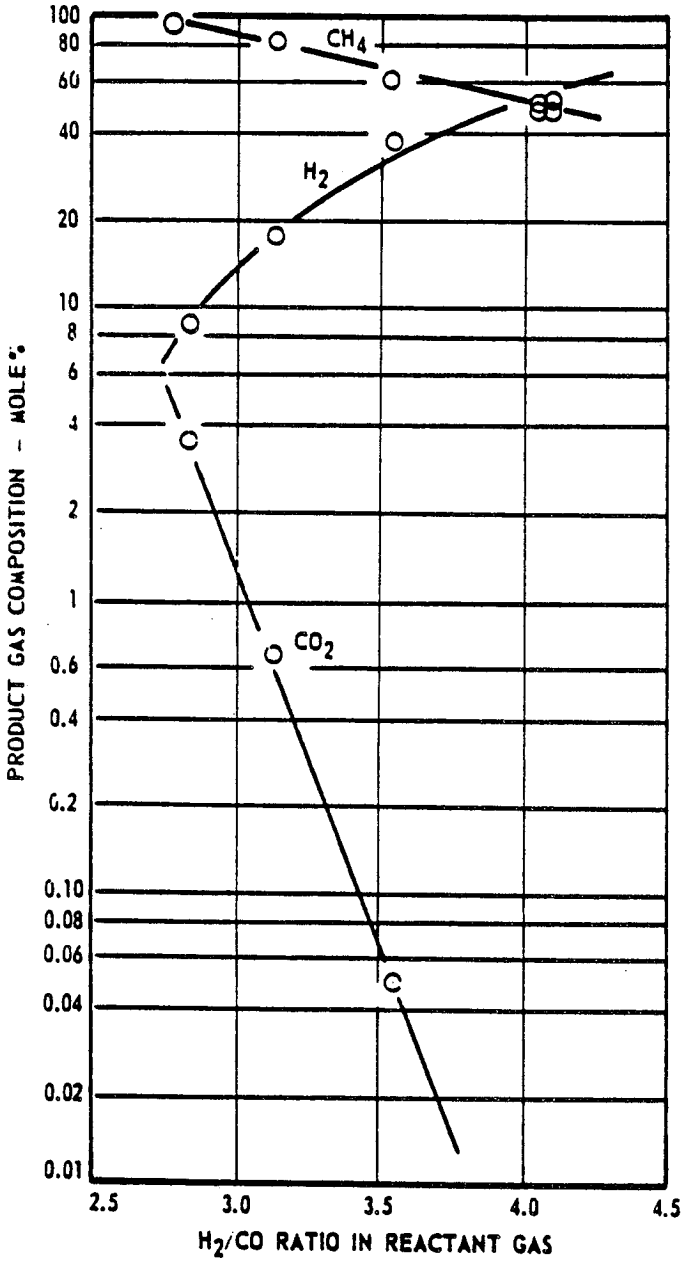

Fig. 5. Product gas composition vs. hydrogen-carbon monoxide mole ratio (1,000 hr.$^{-1}$ space velocity; 250° C.; 1.0 atm.).

TABLE 1. REDUCTION OF CARBON MONOXIDE WITH HYDROGEN (CARBON MONOXIDE CONVERSION AND PRODUCT YIELD)

Run. No.	H_2/CO mole ratio	Space velocity, $hr.^{-1}$	Catalyst bed pressure, atm.	Catalyst bed temp., °C.	Material balance, %	CO conversion, mole %	Normalized product yield, mole %		
							H_2O	CH_4	CO_2
45	4.00	500	1.0	250	101.0	100.0	100.0	100.0	0.0
46	4.00	750	1.0	249	93.3	100.0	100.0	100.0	0.0
47	4.10	1003	1.0	252	99.0	100.0	100.0	100.0	0.0
48	3.96	1481	1.0	253	95.3	100.0	99.8	99.9	0.1
49a	4.06	1000	1.0	251	101.0	100.0	100.0	100.0	0.0
51	4.15	2010	1.0	265	98.6	100.0	100.0	100.0	0.0
52b	2.84	810	1.0	248	98.1	100.0	91.1	96.2	3.7
53	3.56	1000	1.0	254	94.5	100.0	100.0	100.0	0.0
54	3.14	998	1.0	254	95.0	100.0	98.3	99.1	0.8
55	3.03	1000	6.1	253	96.9	100.0	99.2	99.4	0.4
56	3.01	1500	6.1	231	95.4	100.0	97.3	98.5	1.3
57	3.02	1500	6.1	353	94.8	100.0	94.8	97.1	2.5

TABLE 2. REDUCTION OF CARBON MONOXIDE WITH HYDROGEN (PRODUCT GAS ANALYSIS)

Run No.	Composition of product gas, vol.%				
	H_2	H_2O	CO	CH_4	CO_2
45	49.4	1.20	0.0	49.4	0.00
46	49.4	1.15	0.0	49.4	0.00
47	51.5	1.15	0.0	47.3	0.00
48	48.4	1.15	0.0	50.4	0.05
49a	50.8	1.15	0.0	48.1	0.00
51	53.0	1.15	0.0	45.9	0.00
52b	8.9	1.14	0.0	91.5	3.50
53	38.5	1.14	0.0	60.4	0.00
54	17.7	1.14	0.0	80.5	0.65
55	9.3	0.20	0.0	90.2	0.35
56	12.0	0.20	0.0	96.6	1.27
57	18.9	0.20	0.0	78.6	2.25

TABLE 3. REACTANT GAS CARBON DIOXIDE CONTENT VS. CATALYST BED DEPTH

Run No.	Space velocity, $hr.^{-1}$	H_2/CO mole ratio	CO_2 analysis, vol.%		
			Top third	Mid third	Outlet
45	500	4.0	0.4	0.0	0.00
46	750	4.0	1.6	0.0	0.00
47	1000	4.1	2.7	0.3	0.00
48	1481	4.0	4.6	0.8	0.05
51	2010	4.1	3.8	0.2	0.00
55	1000	3.0	4.9	1.0	0.35
57	1500	3.0	6.1	3.6	2.25

Heat dissipation is one of the major problems associated with the reaction as it is highly exothermic. This problem was minimized by making the reaction chamber small in diameter (0.527 in. ID) in relation to its length (38.5 in.). This design provided a large surface area for cooling and a minimum distance for the reacting gases to travel from the center of the chamber to the cooling surface. Fins were provided on the outside of the tube to furnish additional cooling surface. For convenience, air was used as the cooling fluid. In a lunar installation, a fluid such as Dowtherm or a molten salt, would be recirculated through an exchanger or radiator to dissipate the heat of reaction.

REDUCTION OF CARBON MONOXIDE WITH HYDROGEN

The reaction of carbon monoxide with hydrogen to form methane and water was studied using a nickel-on-kieselguhr catalyst. The data for these runs are presented in Tables 1 to 5, and Figures 4 to 6. The various parameters which were studied are detailed in the following paragraphs.

Temperature

Some catalyst activity was noted as low as 200 C; the catalyst was found to be very active at 250 C, so that very excellent conversions were obtained. Therefore, all the runs were made at a nominal catalyst bed temperature of 250 C, except Run 57 which was made at 350 C. An attempt was made during Run 57 to increase the conversion by increasing the temperature at a 3:1 hydrogen-carbon monoxide mole ratio and a 1,500-hr-1 space velocity; the conversion of carbon dioxide to methane and water decreased as the temperature was increased.

Pressure

The first nine runs were made at atmospheric pressure. The conversions were nearly complete at a 4:1 mole ratio even with space velocities of 1,000 hr-1. It was only at lower hydrogen-carbon monoxide mole ratios that the conversions decreased sufficiently to require raising the catalyst bed pressure. The last three runs were made at 6.1 atm to approach complete conversion at a 3:1 ratio. In comparing Runs 54 and 55 (see Table 1), it can be seen that increasing the pressure from 1 to 6 atm decreased the carbon dioxide yield from 0.8 to 0.4% and correspondingly increased the yield of water and methane.

Hydrogen-Carbon Monoxide Mole Ratio

The effect of hydrogen-carbon monoxide mole ratio on conversion and yields can be seen in *Figure 4*. At a space velocity of 1,000 hr-1, at 250 C and 1.0 atm, the catalyst gave complete conversion of carbon monoxide and carbon dioxide until the hydrogen-carbon monoxide mole ratio was decreased to less than 3.5:1. The carbon monoxide conversion remained complete but the carbon dioxide yield increased; at a 3:1 ratio, the carbon dioxide yield was approximately 2%.

TABLE 4. REDUCTION OF CARBON MONOXIDE WITH HYDROGEN (CARBON MONOXIDE CONVERSION AND PRODUCT YIELD)

Run No.	Impurity mole % in H_2 stream	H_2/CO mole ratio	Space velocity, $hr.^{-1}$	Catalyst bed pressure, atm.	Catalyst bed temp., °C.	Material balance, %	CO conversion, mole %	Normalized product yield, mole %		
								H_2O	CH_4	CO_2
63b	None	3.00	1000	6.1	254	99.5	100.0	97.6	99.0	0.95
64c	0.1 COS	3.00	1000	6.1	254	97.1	100.0	96.4	98.2	1.65
66b	1.0 NO	2.98	1005	6.1	255	98.8	100.0	98.6	97.2	1.87
66c	1.0 NO	3.44	1120	6.1	252	100.8	100.0	100.0	100.0	0.00
67b	0.5 PH_3	3.09	1024	6.1	249	100.6	100.0	97.2	98.2	1.52

TABLE 5. REDUCTION OF CARBON MONOXIDE WITH HYDROGEN (PRODUCT GAS ANALYSIS)

Run No.	Composition of Product Gas, vol. %						
	H_2	H_2O	CO	CH_4	CO_2	NH_3	N_2
63b	6.0	0.20	0.0	92.9	0.9	—	—
64c	5.0	0.20	0.0	93.2	1.6	—	—
66b	4.0	0.20	0.0	93.3	1.8	0.2	0.5
66c	21.8	0.20	0.0	77.2	0.0	0.3	0.5
67b	10.0	0.20	0.0	88.4	1.4	—	—

The effect of hydrogen-carbon monoxide mole ratio on the product gas composition can be seen in *Figure 5*. No carbon monoxide could be detected in the outlet gas for any of these runs. Within this range, the carbon dioxide content of the gas increased logarithmically as the hydrogen-carbon monoxide mole ratio was decreased below 3.5:1 (to about 1.5% at 3:1). The theoretical product yield at a 3:1 ratio is 100% methane, 0% hydrogen. The catalyst gave 86% methane, 13% hydrogen at the 3:1 ratio.

Space Velocity

At a 4:1 mole ratio, no carbon dioxide was formed at space velocities up to 2,000 hr-1. At a 3:1 ratio, the carbon dioxide yield increased rapidly as the space velocity was increased above 1,000 hr-1.

Material Balance

With the exception of two runs, all overall material balances for the runs (see Table 1) were under 100%. Most of the low material balances can be attributed to low water recoveries. Because the catalyst is known to be a good absorbant for water, it has been hypothesized that
some of the water is slowly adsorbed on the catalyst. In order to prove that this was the case, a long duration run (Run 49) was made (see *Figure 6*). The water production, which fluctuated about %0.5 g/hr, gradually increased throughout the run (dotted line). After 30 hr, the liquid water production rate was 19.2 g/hr (about 96% of theoretical). At the rate of increase of water production (0.01 g/hr), it would have taken about 100 hr before the actual water production rate equalled the theoretical production rate. For long runs, the water balance should be no problem and it is hypothesized that the small amount of water adsorbed on the catalyst may help to prevent carbon formation.

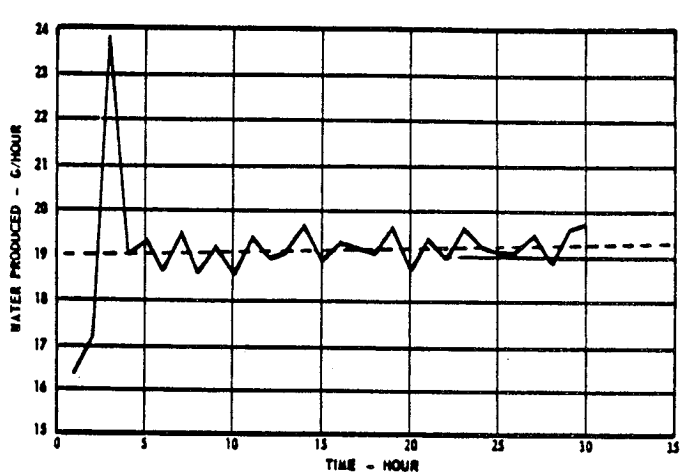

Fig. 6. Water production rate vs. time for Run 49 (1,000 hr.$^{-1}$ space velocity; 250° C.; 1 atm.; 4 : 1 mole ratio).

Sulfur

Almost any form of sulfur in the reactant gases will be converted to nickel sulfides and thereby poison the catalyst and reduce its activity. Carbonyl sulfide (COS) was selected for evaluation for convenience and its stability in steel gas cylinders. A high concentration of sulfur in the hydrogen reactant gas (0.1 vol% COS or fifty-nine grains of sulfur per 100 std cu ft) was used in these tests. This concentration is approximately 1,000 times the normal allowable limit of sulfur in the feed gas to Fischer-Tropsch units and permitted the extent of sulfur poisoning of the catalyst to be determined in a relatively short time (22 hr).

Run 63b (see Tables 4 and 5) was made with freshly reduced catalyst to provide a basis for comparison at a fairly high space velocity and a low hydrogen-carbon monoxide mole ratio. Run 64 was made with 0.1 vol% COS in the hydrogen stream. The data for Run 64c (see Table 4) were taken after 22 hr of operation with 0.1 vol% carbonyl sulfide in the hydrogen stream. In this length of time, 3.08 g of sulfur, equivalent to 3.9 wt% of the nickel in the catalyst, was charged to the catalyst bed, and the product gas composition had changed only slightly (CH_4 yield dropped from 98.9 to 98.2%, H_2O yield dropped from 97.5 to 96.4%), and CO_2 yield increased from 0.95 to 96.4%). During the progress of the run, the activity in the top 6 in. of the catalyst bed was observed to gradually decrease. This was evident by the downward movement on the catalyst column of the major temperature peak. Analysis of the catalyst after the run showed that almost all the sulfur was removed in the first 6 in. of the bed, leaving the balance of the 32 in. for near-normal conversion.

Oxides of Nitrogen

A newly reduced batch of catalyst was used for Run 66 (see Tables 4 and 5) in which 1 vol% nitrogen oxide (NO) was added to the hydrogen stream. The data for Run 66b were taken after approximately 7 hr of operation; at a 2.98:1 hydrogen-carbon monoxide mole ratio, good conversion was obtained (for this low ratio). The data for Run 66c were taken after about 10 hr of operation; at a 3.44:1 mole ratio, conversions were 100% to methane and water, showing that the catalyst was not damaged. The temperature peak did not progress down the column during the run. It was, therefore, concluded that this nitrogen oxide would not injure the catalyst. The nitrogen oxide was reduced under the conditions of the reaction. About 2 wt% ammonia was found in the water condensed out from these runs. Additional nitrogen and ammonia were also found in the vapor phase. The nitrogen material balances showed that about 75 wt% of the nitrogen oxide was converted to ammonia, the balance being converted to nitrogen.

Phosphorus

In Run 67 (see Tables 4 and 5), 0.5 vol% phosphine (PH_3) was added to the hydrogen stream. This run was stopped after less than 3 hr of operation, at which time the catalyst activity was falling and the pressure drop across the reactor was increasing rapidly (0 to 30 in. vP in 30 min). In Run 76b, in which the data were taken after about 2 hr of operation, the conversion was still good but it was starting to drop off rapidly. Inspection of the catalyst from the run showed that the majority of the phosphorus was deposited on the first third of the bed; the second third of the bed contained some phosphorus, and the bottom almost none. The data show that phosphorus is a most active catalyst poison and it will have to be removed from the reactants prior to contact with the nickel catalyst.

Other Impurities

Time did not permit the study of other possible poisons. High concentrations of water in the reactants are known to affect adversely column equilibrium if not actually to poison the catalyst. Carbon dioxide is not a poison; it is normally present to some extent in the product gases. Nitrogen gas and ammonia have also been present in low concentrations without damage to the catalyst.

Heat Balance

In all runs, the majority of the heat was released in the top third of the bed; however, in several runs at high space velocity (1,500 or 2,000 hr-1) and/or low hydrogen-carbon monoxide mole ratios (3:1), enough heat release took place in the second third of the catalyst bed to require some cooling. At the highest space velocities, temperature control was very difficult, due to the large amount of cooling air required (up to 100 std cu ft/hr) to maintain the nominal catalyst bed temperature. In future designs, this problem will be solved either by providing multiple carbon monoxide entry points or by providing multiple cooling fluid entrances.

PRESSURE DROP

The pressure drop across the catalyst bed with the catalyst was excellent. It did not go up with time even at hydrogen-carbon monoxide mole ratios as low as 3:1. Run No. 49 was continued for 31 hours without shutdown; the pressure drop did not increase a measurable amount during this prolonged period. The absence of a pressure buildup indicated no carbon deposition and a long, useful catalyst life.

Catalyst Life

The catalyst was still active when it was removed after fourteen runs (110 hr). As can be seen from the tabulation below, analyses on the catalyst before and after use showed no carbon deposition.

Time, hr	Carbon content of catalyst C-0765-1001-1, wt%
0	5.08
110, Top one-third	5.02
110, Mid one third	5.11

As stated previously, there was no pressure buildup during the run, so this would not be a limiting factor on the life of the catalyst. However, impurities in the feed (discussed later) may prove to be the limiting factor in the life of this catalyst. Temperature control is also very vital because carbon is definitely deposited on the catalyst at higher temperatures (400 C and up). Catalyst life would probably be extended if the catalyst bed operating temperatures were started low when the catalyst is new and active and then gradually raised as the catalyst activity declines.

Catalyst Bed Depth

At low space velocities, only the top inch or two of the catalyst bed was involved in the major portion of the reaction. As the space velocity was increased, more and more of the bed was involved until, at very high space velocities and low hydrogen-carbon monoxide mole ratios (Runs 55 and 57), the full length of the catalyst bed was not able to achieve complete conversion of carbon dioxide into methane and water. This is best shown by carbon dioxide gradients in the reactor taken for the various runs as reported in Table 3. Two additional advantages of a deep catalyst bed are: it allows for a margin of safety as the catalyst ages and becomes less active; and it allows the top of the bed to act as a guard chamber to remove various catalyst poisons.

Impurities in the Feed Gas

Most catalysts are subject to poisoning by various impurities. Nickel is known to be poisoned by sulfur and phosphorus. Therefore, it was necessary to determine the extent that these and other poisons can be tolerated in the reactant gases.