Feasibility of Regeneration of Carbohydrates in a Closed-Circuit Respiratory System

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Several of the steps of a possible carbohydrate regeneration system have been investigated experimentally. Carbon dioxide separated from the cabin atmosphere would be mixed with excess hydrogen and exposed to a glow d.c. discharge in a water-cooled reactor at a pressure below atmospheric. Conversion to carbon monoxide has shown values up to 90% in a single pass. The study of the generation of formaldehyde from mixtures of carbon monoxide and hydrogen in silent discharges showed the yield to increase with flow rate, power input, and magnetic field applied; maximum yield was obtained at unit ratio of the volume concentrations of the reactants. Formaldehyde condenses readily to sugars in slightly alkaline solutions at moderately elevated temperatures. At least 13 different sugars have been identified chromatographically. About 63–64% of one sample appeared to be hexoses; 17% of the same sample was xylose.

Introduction

An integrated ecological system for the support of life in space is by its nature highly complex, and a number of variations would be possible. In the following, we will be concerned only with the feasibility of the regeneration of carbohydrates using water and gases present in the atmosphere of the closed system traveling in space. Table 1 contains a first rough estimate of the power requirements for carbohydrate regeneration under the conditions imposed. An over-all energy utilization of the order of 4% is indicated, but some improvement may be feasible.

The estimates of Table 1 are based on an assumed consumption of 1.52lb hexoses/man-day and give a total power requirement of about 2.8 kw/man-day.

The approach considered is based on the fact that digestion of food yields carbon dioxide, which, after reduction to the monoxide, may be reduced further to formaldehyde. Several catalysts are available that cause the condensation of formaldehyde to various sugars, which, with or without interconversion in the body, should be acceptable as food. A four-step method of synthesis of these sugars is visualized:

1) Isolation of the carbon dioxide from the cabin atmosphere as a pure gas.

2) Conversion of the carbon dioxide to the monoxide. An excess of hydrogen is added to the dioxide, and the mixture is passed through a high-temperature glow discharge. Intermediate pressure (below atmospheric) and a fairly high voltage are needed. (It has been shown that silent discharge at atmospheric pressure would give a low degree of conversion and would, therefore, require a high rate of recycling).

3) Reaction of carbon monoxide with hydrogen to give formaldehyde. The gas mixture formed in the glow discharge is passed directly into a silent discharge to produce formaldehyde. A high-power yield should be attainable, but it is necessary to add water to prevent polymerization. The formation of traces of methyl alcohol and various hydrocarbons may be anticipated.

4) Condensation of the formaldehyde to sugars. As is well known from data in the literature, the condensation of formaldehyde to give "formose" sugar proceeds readily at moderate temperatures in the presence of various alkali and alkaline earth hydroxides and heavy metal salts. At completion of the condensation reaction, the hydroxides would be removed by electrodialysis, the sugar acetals split by hydrolysis, and free formaldehyde removed by inverse osmosis under pressure.

We are not concerned in the present paper with the technique for accomplishing step 1) of the foregoing nor with the design and operation of electrolytic cells for the generation of hydrogen and oxygen. However, it might be noted that the latter cells must be able to rotate to achieve separation of gas and liquid phases at weightlessness. They could consist of parallel thin segments arranged radially and containing alternate positive and negative electrodes separated by conventional-type diaphragms. The gases liberated could be led out through separate manifolds connected with opposite ends of a hollowed-out center shaft.

Reduction of CO_2 to CO

The equilibrium constant K for the reaction between carbon dioxide and hydrogen to give the monoxide and water has been computed for a large temperature range by Kassel.[1] Since its value increases rapidly with the temperature, a high degree of conversion should be attainable in a glow discharge.

The first reactor used had a shell comprised of three concentric Vycor tubes separated by ceramic rings and removable one at a time. The assembly was enclosed in a 3-in. Pyrex pipe provided with metal flanges. The exit electrode was designed for fast quenching of the gas stream, and either a water-cooled, thin-walled copper tube or a solid rod of graphite served as the anode. The electrodes were held in deep packing glands and could be raised or lowered about 10 in. The

Table 1 Power required for carbohydrate regeneration for a crew of five

Process	Quantity, lb/day	Power, kw
Distillation of water	60	0.3
Extraction of carbon dioxide	38	1.2
Production of oxygen	27	2.0
Production of hydrogen	3.4	2.0
Production of carbon monoxide	12	2.0
Production of formaldehyde	13	4.8
Production of sugar (60% yield)	7.8	2.0
Total power requirement (5 men)		14.3

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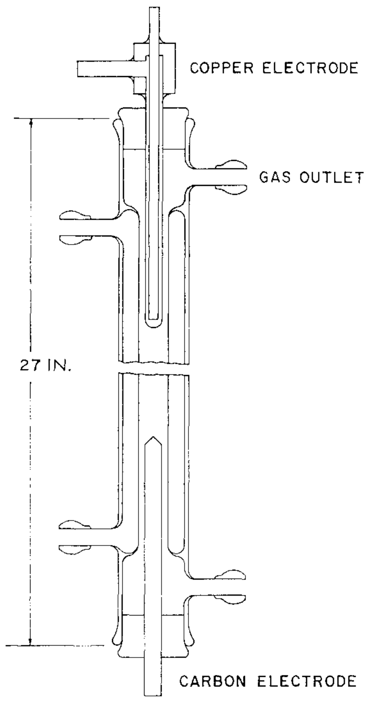


Fig. 1. Glass reactor for conversion of CO_2 to CO.

d.c. power supply (Model F6005-A1R from Precision Measurements, Inc.) was controlled by a series regulator type 889-A power tube for a plate dissipation of 10 kw. The grid bias voltage was controlled with a General Radio type 1205-B adjustable, regulated power supply adapted for the purpose. The output current was measured in milliamps in four different ranges. When this reactor was operated, the center Vycor tube started to emit an intense visual radiation a short time after the discharge had been initiated, but the degree of conversion of the carbon dioxide was low. Removal of the innermost Vycor tube raised the yield of carbon monoxide strongly. Further removal of the next size larger Vycor tube increased the yield even more, and it was decided to change over to the water-cooled all-glass reactor shown in Fig. 1.

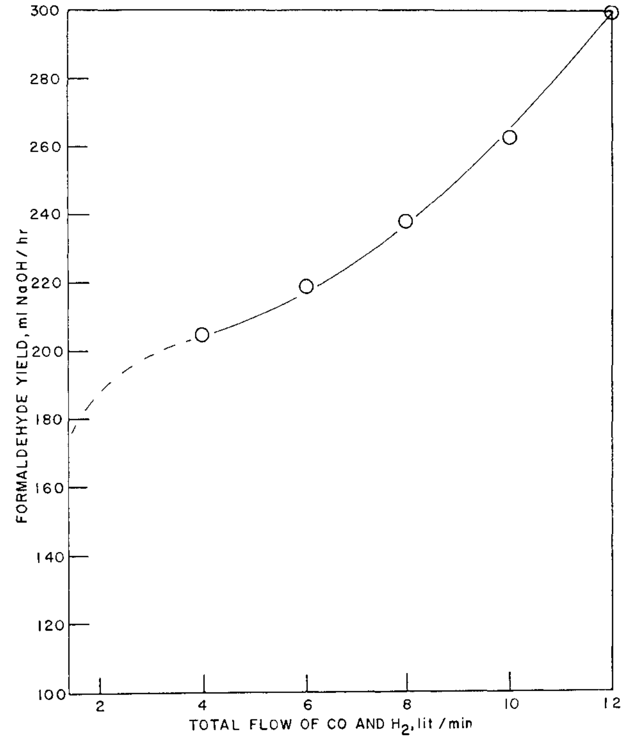


Fig. 2. Yield of CH_2O at various gas flow rates using the all-glass reactor.

Table 2 Conversion of carbon dioxide to the monoxide as a function of the composition of the feed gas

Gas feed ratio, H_2/CO_2	Degree of conversion, $CO/(CO + CO_2)$
1.0	0.534
1.3	0.650
2.0	0.814
3.0	0.893
4.0	0.864
5.0	0.800

The reactor of Fig. 1 has one water-cooled electrode of copper tubing and one graphite electrode. The latter seemed to be inert to the discharge and suffered a negligible loss of weight after use over a considerable length of time. The inner diameter of the reactor tube proper was 0.785 in. The shell was made of Pyrex pipe, and it should be able to withstand severe vibration or mechanical shock. The weight of the reactor with electrodes was 1344 g. The data obtained seemed to indicate that the degree of conversion varied linearly with the pressure within the range employed.

The effect of variations in the volume ratio of hydrogen to carbon dioxide in the feed gas on the degree of conversion is indicated by the data in Table 2. The degree of conversion appears to go through a maximum of 90% at a hydrogen/carbon dioxide ratio of about 3:1. A higher degree of conversion should be attainable by increasing the distance between the electrodes, but the power yield would be lowered. An increase in operating pressure would decrease the size and weight of the vacuum pump employed.

The "power yield" at maximum conversion was about 38 g of CO/kw-hr consumed in the discharge. At conversions of only 80%, yields per kw/hr several times higher are readily attainable by using higher flow rates. An appreciable fraction of the energy dissipated in the discharge would be recoverable as heat.

Generation of Formaldehyde

The thermal stability of formaldehyde is low, and it decomposes quantitatively at higher temperatures. Since a silent discharge occurs over a short distance but a broad area, the temperature of the neutral gas remains near that of the surroundings. By various means this may be regulated over a wide range, making it feasible to generate formaldehyde continuously at ordinary temperatures, provided that its tendency to polymerize on the walls enclosing the discharge is prevented. By steady absorption of the formaldehyde as it is produced in saturated water vapor or in a flowing aqueous phase, this may be accomplished. The partial vapor pressure of formaldehyde over its aqueous solutions is small at low concentrations, as shown in Table 3; hence the amount of formaldehyde decomposed in the gas phase of a silent discharge would be small. Even if the rate of decomposition on the discharge is considerably larger than its rate of formation, it should still be possible to obtain good power yield, so long as its concentration in the gas phase is maintained at as low a level as possible by adequate cooling.

Most of the measurements were carried out using a reactor of conventional design but mounted inside a long solenoid

Table 3 Partial vapor pressure of formaldehyde above its aqueous solutions

	Temperature in °C				
Formaldehyde weight, %	15	30	45	60	75
	Vapor pressure in mm Hg				
1.0	0.02	0.08	0.26	0.84	2.78
2.0	0.04	0.16	0.51	1.65	5.46
3.0	0.07	0.24	0.74	2.40	7.94
4.0	0.09	0.30	0.96	3.10	10.2
5.0	0.11	0.37	1.20	3.89	12.9

wound on a 6.3-cm-i.d. thin-walled micarta tube having a length of 95 cm. The reactor's center tube was 5 cm. o.d. and 4.6 cm i.d., 80 cm long (active surface), and the mantel tube was 6 cm o.d. and 5.52 cm i.d. To provide some degree of cooling for the solenoid, it was centered on a micarta ring carried by six thin spokes held in a flange mounted on top of a 6-in. Pyrex pipe cross and then enclosed in a 36-in. long, 6-in. i.d. Pyrex pipe. A blower was placed on one of the inlets to the cross to prevent the solenoid from overheating when used at 15 A over an appreciable length of time. Water vapor was added to the gas stream by bubbling it through a water column maintained at constant temperature.

Some data obtained at approximately constant current and voltage are summarized in Sec. A of Table 4 and illustrated graphically in Fig. 2. Without any apparent increase in the power consumption, the yield of formaldehyde increases rapidly with the flow rate. The effect of current (at varying voltage) with constant CO and H_2 flows is shown by Sec. B of Table 4 and in Fig. 3. The amount of formaldehyde present was determined by adding a measured amount of 0.1333 N NaOH and a few cubic centimeters of hydrogen peroxide, warming the solution to about 60°C on a water bath and then back titrating to neutral with 0.1 N HCl. A series of titrations using samples with known formaldehyde content showed the method to be capable of high accuracy. Because of the limitation imposed by the range of the flowmeters employed, no measurements could be obtained at flow rates above a total of 12 liters/min, but extrapolation to a recycle ratio of 6 would seem to indicate the possibility of relative yields corresponding to 1200–1500 cc NaOH titer solution/hr.

It would seem probable that, with a given reactor, circuit constants, and current frequency, only minor changes of the power factor would occur over a wide current range. The large increase in yield with increasing flow rate and power input should enable us to get much higher yields than any measured at levels presently beyond our reach.

Table 4 Yields of formaldehyde in an all-glass reactor

I, ma	P, kw	Flow, liters/min CO	H_2	Yield, CH_2O[a]	Water, T, °C
A. Constant power and constant CO/H_2 flow ratio					
145	2.11	2	2	204	78
143	2.07	3	3	219	76
140	2.07	4	4	238	76
140	2.09	5	5	262	76
138	2.07	6	6	300	80
B. Varying power with fixed CO and H_2 flows					
17	0.13	6	6	105	66
31	0.27	6	6	122	69
45	0.43	6	6	138	61
71	0.77	6	6	179	65
89	1.04	6	6	201	69
120	1.63	6	6	249	77
145	2.19	6	6	299	66
163	2.59	6	6	320	70
C. Constant power and total flow, varying CO/H_2					
130	1.86	1.5	10.5	172	63
128	1.81	2	10	179	60
139	2.02	3	9	240	66
133	2.01	4	8	292	62
138	2.07	6	6	300	80
150	2.28[b]	8	4	305[b]	65
170	2.65[b]	9	3	324[b]	68
D. Varying power, constant flows, with magnetic field					
40	0.33	6	6	104	63
44	0.37	6	6	123	62
61	0.63	6	6	167	73
81	0.99	6	6	222	61
109	1.58	6	6	323	65
131	2.08	6	6	339	63

[a] Yield given as cc 0.1333 N NaOH/hr.

[b] Correcting these two values to the average power for the five preceding ones, we obtained yields of 287 and 244, respectively, as plotted in Fig. 4.

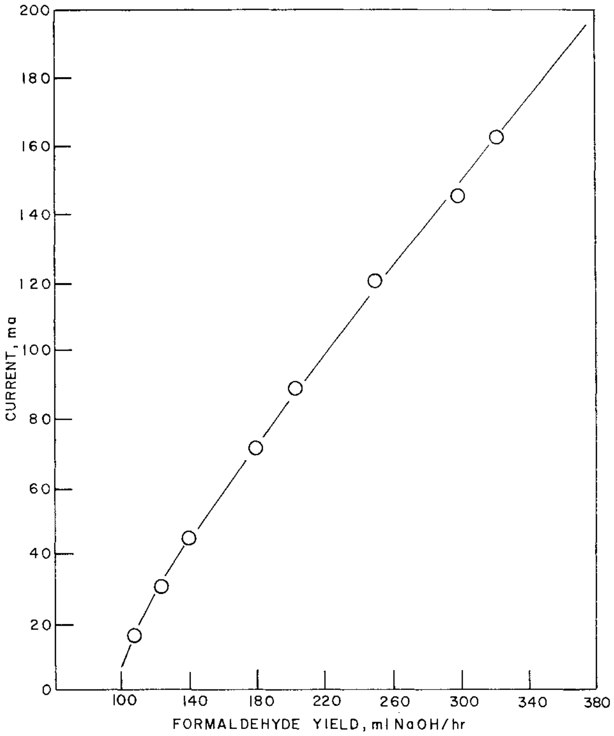


Fig. 3. Yield of formaldehyde at varying current, constant flow, and gas composition.

It was shown previously that, when mixtures of hydrogen and carbon dioxide are exposed to a glow discharge under certain conditions, maximum conversion to carbon monoxide and water was obtained when the feed ratio of the reacting gases was close to 3. The law of mass action is generally inapplicable to reactions in glow discharges, and it is doubtful that a thermodynamic equilibrium dependent on temperature is set up in any type of reaction taking place under similar circumstances. The generation of formaldehyde will be carried out using the gas mixture leaving the glow discharge reactor, and it is important to know the concentration ratio of carbon monoxide to hydrogen at which maximum yield is attained. Section C of Table 4 summarizes some yield measurements carried out at a series of different ratios for the CO and H_2 concentrations at a constant total flow of 12 liters/min, while the power input was maintained approximately constant. In Fig. 4 the yield data have been plotted against the H_2/CO ratio to the left and the CO/H_2 ratio to the right of center.

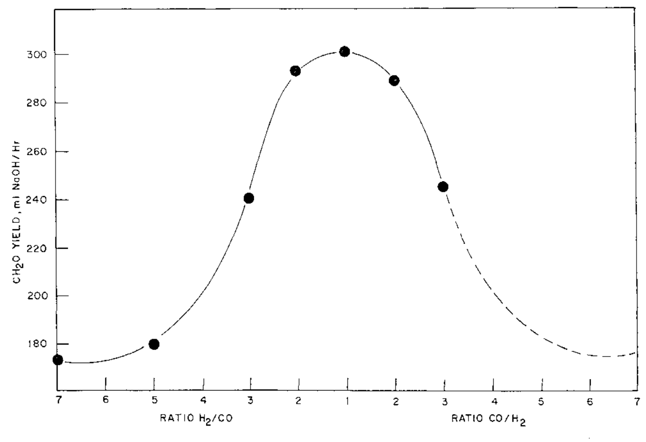


Fig. 4. Yield of formaldehyde at various CO/H_2 ratios, constant power input, and total gas flow.

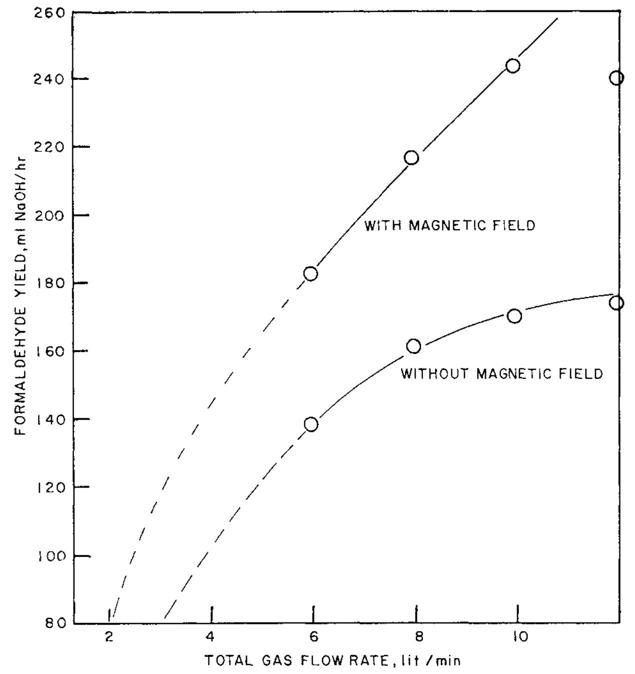


Fig. 5. Yield of CH_2O at various flow rates, with and without magnetic field using metal center electrode.

As a general rule the rate of any homogeneous chemical reaction taking place in an electric discharge is high, with a half-life of the order of fractions of a millisecond. This is probably also true in the case of the generation of formaldehyde. In the case of the data given in Table 4, the residence time of the gas mixture at a total flow of 12 liters/min, would be about 6 sec. Since virtually complete equilibrium would be attained in a few milliseconds, large increases in flow rate would give steadily increasing yields of formaldehyde per unit of time. The problem might shift over from that of generation to that of collecting formaldehyde without appreciable losses at high recycle ratios.

Charge carriers moving in a steady magnetic field tend to assume a circular motion, and in combination with their linear velocity they will follow a helical path. At high angular velocities of a charge carrier, the number of kinetically successful collisions may be enhanced, or, in other words, the yield of a given reaction would increase. However, part of the apparent magnetic effect may be caused by changes of the power factor of the discharge current. Section D of Table 4 summarizes some yield measurements with varying power input, constant gas flow, and using d.c. to generate the magnetic field. Comparison of these data with those in Sec. B shows that the yield of formaldehyde is greatly increased by the presence of a magnetic field. This is shown even more strongly by the data given in Table 5 and represented graphically in Fig. 5. To obtain these data, the center tube of the all-glass reactor was replaced by a water-cooled brass tube having nearly the same outer diameter. The power factor of the discharge turned out to be very small, as shown by the unusually low currents and voltages in the primary coil of the variable transformer, although substantial values for both were recorded for the discharge. The current through the discharge was difficult to control and easily exceeded 300 ma when the discharge became activated. However, despite the unexpectedly low power factor, substantial yields were obtained.

Table 5 Yields of formaldehyde, with and without magnetic field, in glass reactor with metal center electrode

I, ma	P kw	Flow, liters/min CO	H_2	Yield, CH_2O^a	Water, T, °C
A. Without magnetic field					
232	2.25	3	3	138	80
237	2.44	4	4	161	74
>300	>3.12	4	4	243	68
257	2.57	5	5	168	68
>300	>3.12	5	5	255	69
278	2.72	6	6	172	62
>300	>3.12	7	7	269	60
B. With magnetic field					
208	2.10	3	3	182	84
205	2.07	4	4	216	72
220	2.24	5	5	243	77
215	2.17	6	6	240	70

[a] Given as cc 0.1333 N NaOH/hr.

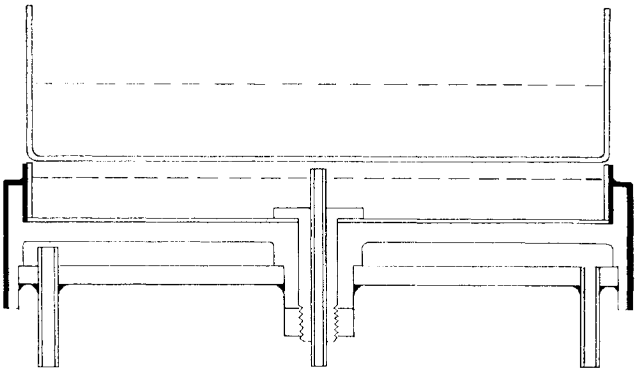


Fig. 6. Diagram of the reactor for study of the formation of CH_2O in the presence of a liquid phase.

A diagram of a small reactor operating with a static liquid phase and using the bottom of a crystallizing dish to spread the discharge over the surface of the water is shown in Fig. 6.

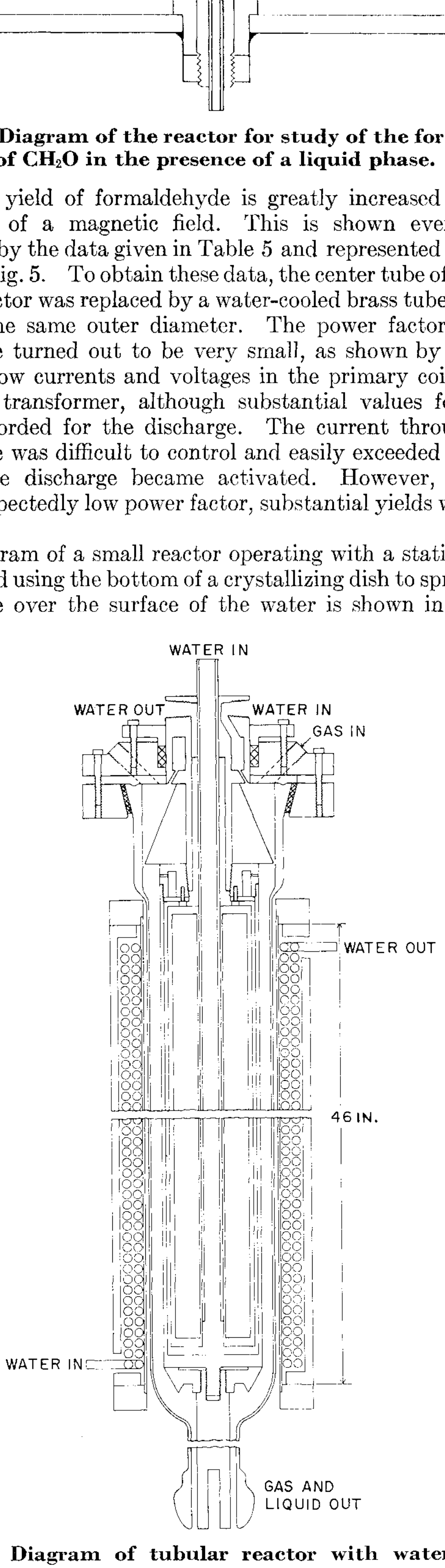


Fig. 7. Diagram of tubular reactor with water-cooled solenoid.

The data obtained with this reactor were somewhat erratic, but a number of them showed unexpectedly high power yields. Therefore, a larger reactor of the same type was built in such a way that the water was made to flow uniformly over the edge of a 16-in. micarta ring, and a trough with a glass bottom was suspended over the water surface using gage blocks to adjust the distance between them.

A few measurements of the yield of formaldehyde in a silent discharge in the latter reactor have been summarized in Table 6. The distance between the top edge for the water retaining ring and the underside of the etched plate glass disk was adjusted to 0.313 in. (The actual distance between the plate and the water surface was somewhat smaller, but it could not be measured easily. Test runs with a slightly shorter distance caused wetting of the glass disk, and most of the current passed directly through the liquid.) Yields are of the same order of magnitude as the highest values obtained with the all-glass tubular reactor, but they were obtained with a discharge area of only 1100 cm^2 as compared to 1450 cm^2 for the tubular reactor, a difference of about 24%. At weightlessness in outer space it is necessary to employ a spinning reactor generating a coherent, flowing aqueous phase. The flat-plate reactor simulates to a considerable extent the behavior of such a space reactor.

Production of Formaldehyde in an End-Closed System

An integrated laboratory unit was built for continuous production of formaldehyde from CO_2 and H_2, using a high recycle rate of the gas stream from the silent discharge and diverting part of this gas to the glow discharge in order to prevent buildup of CO_2 content because of the steady removal of CO and H_2 as formaldehyde dissolved in water. A new tubular reactor (Figs. 7 and 8) and also a new flat-plate reactor (Fig. 9) were built for this unit. Both were designed to come within a factor of 2 or 3 of the size required to give an adequate amount of carbohydrates for a crew of five, assuming that 50% of the sugar may be nondigestible.

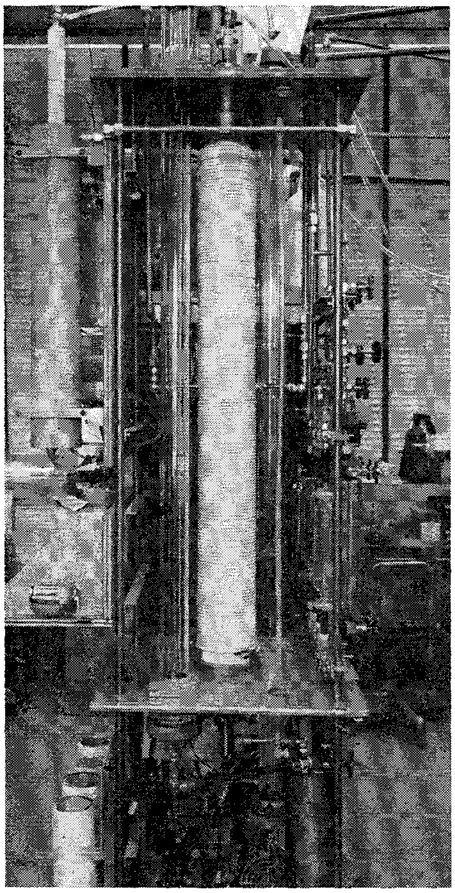


Fig. 8. Photograph of tubular reactor with solenoid.

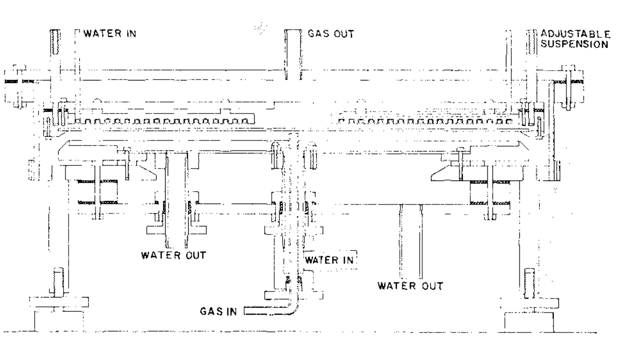


Fig. 9. Diagram of 24-in. flat-plate reactor.

Carbon dioxide in the atmosphere, assumed to be removed at the same rate it is liberated, would be fed into the processing system as a practically pure gas. This requires that the first step of the process be adjusted to the rate of formation of formaldehyde in the second step. The amount of formaldehyde generated per pass of the gas mixture coming from the glow discharge depends on the dimensions of the reactor, its current, voltage and power factor, and on the flow rate, composition, temperature, and pressure of the gas. In general, since the rate of formation of formaldehyde is very much smaller than that of CO, the gas mixture passing through the silent discharge must be recycled several times. At constant power input, the yield of formaldehyde increases proportionately with the flow rate and is roughly proportional to the power consumed. Adjustment of the two reactions should not on this account offer any particular difficulties. However, because of the necessity of recycling, another factor must be considered. To obtain maximum degree of conversion of CO_2 it is essential that the H_2/CO_2 ratio in the feed gas is close to 3. However, the generation of formaldehyde requires an H_2/CO volume ratio of unity to attain maximum yield. Hence, a compromise must be made between the reactant ratios of the two reactions, and a further adjustment must be made with regard to the amount of power dissipated in each reaction. At a degree of conversion of carbon dioxide of 80%, the amount of power consumed is less than one-third of the amount dissipated to attain a conversion of 90%. Operating the glow discharge to give a lower degree of conversion will require that the formaldehyde be generated at a correspondingly higher power input, using a reactor with large active surface area and as low a recycle rate as possible. The CO_2 present in the recycle gas is converted to some extent to CO in the silent discharge, but its total concentration will increase steadily. Therefore, part of the recycle gas must be returned to the glow discharge to keep its CO_2 concentration of carbon dioxide at a sufficiently low level to prevent appreciable interference with the generation of formaldehyde. The increase in the amount of power dissipated in the glow discharge on this account should be small. To decrease losses of formaldehyde due to decomposition in the silent discharge, it is essential that ample amounts of water are recycled for its absorption and that the temperature of the exit gas is lowered before it re-enters the reactor.

To allow greater versatility in handling operating conditions at high gas recycle ratios, the new tubular reactor was

Table 6 Yields of formaldehyde using reactor with flat glass plate

I, ma	P, kw	Flow, liters/min CO	H_2	Yield, CH_2O[a]	Water, T, °C
124	1.72	2	2	240	28
122	1.61	4	4	290	28
138	1.85	6	6	320	28
136	1.79	8	8	360	28

[a] Given as cc 0.1333 N NaOH/hr.

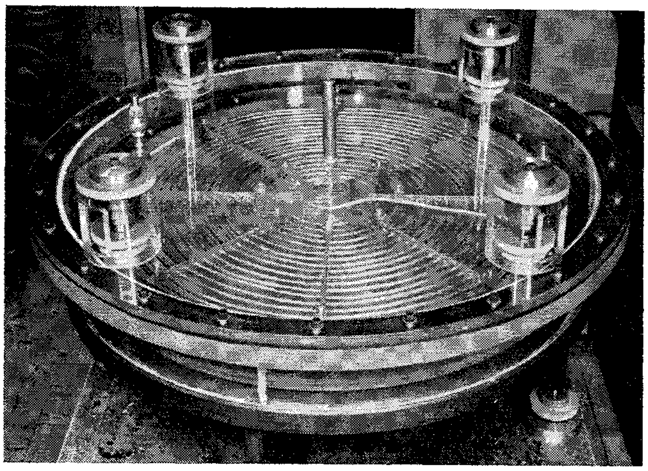


Fig. 10. Photograph of flat-plate reactor.

built with an inner diameter twice as large as that of the ones employed previously, and its length was increased by about 12 in. Figure 7 shows a schematic diagram, and Fig. 8 is a photograph of the reactor enclosed in its solenoid. The top section was designed to allow flow of water either along the inside wall of the glass mantel tube or the surface of the center electrode made of thin-walled brass tubing. (As a third alternative, the gas stream could be moistened by bubbling it through a 20 in.-deep column of water maintained at constant temperature.) To get water to flow over the surface of the center electrode, its top closing disk was threaded to screw into the brass tube and a shallow groove was cut into its periphery. Along the center of this groove were drilled a number of small holes to connect with an inner deep groove, which could be covered with a brass plate to stop water from flowing out. Since the inner volume of the center electrode is relatively large, a closed, centered insert was provided to decrease the amount of liquid required for operation of the system. The liquid flowing out of the reactor is drained into a small tank from which it is recirculated using an insulated pump. The stream is divided between two flow meters, and the temperature of each stream is controlled by a glass heat exchanger provided with a linear coil containing 45 ft of tubing.

The new flat-plate reactor (Fig. 9) has an active surface area about 2.5 times larger than that of the first one of this type built, and it was improved considerably with respect to various details. The method of suspending the glass plate was unchanged, but the cooling coil above it was lifted up from the surface of the glass to get a more uniform discharge and to avoid accidental impacts or stresses that might cause it to break. The coil was mounted by soldering it to eight radial supports slotted at $\frac{1}{2}$-in. intervals to the same depth and width as the diameter of the tubing employed. The water inlets and outlets for the cooling coil and the four height-adjustment rods for the plate-glass assembly were all provided with packing glands (not shown) to avoid gas leakage. The circular wall enclosing the top section of the reactor was made of a double sheet of annealed Plexiglas premolded to its outer diameter. The bottom part of the Plexiglas wall was held in place tightly by a double ring of $\frac{1}{8}$-in. cold-rolled steel and sealed both inside and outside to the supporting micarta disk with an epoxy resin. The top outer micarta ring also was sealed to the Plexiglas in a similar manner. The adjustment of the distance between the underside of the glass plate and the surface of the liquid flowing out below was accomplished using the small turrets designed for the purpose and shown on the top of the reactor in Fig. 10. The supporting screws could be adjusted with a precision close to 0.001 in. by using gage blocks. Retightening of the packing glands could be made without disturbing either the height or the tilt of the glass plate.

The Condensation of Formaldehyde to Formose Sugar

This process has been studied extensively in recent years. Kusin[2,3] and Langenbeck[4] showed that primary formation of a series of oxy-oxo compounds like dioxyacetone, glycol aldehyde, and glyceraldehyde probably represents early rate determining steps of the condensation process. Pfeil and Schroth[5] found that the rate of reaction is a function of the nature of the cation of the alkali hydroxide employed and that it increases strongly with increasing dilution of the formaldehyde solution—a most unusual behavior. They also studied the effect of various alcohols, ethylene glycol, glycerol, glucose, dioxane, etc., and were able to show that, with respect to the formaldehyde present, the reaction is monomolecular. They suggest as initiating mechanism that a complex compound is formed between the metal hydroxide and an oxy-oxo compound generated by the formaldehyde. The complex compound is assumed to react with free formaldehyde to form various new species among which have been found a whole series of sugars. Pfeil and Ruckert[6] have identified chromatographically the following sugars in the final reaction product: glucose, mannose, fructose, arabinose, ribose, galactose, sorbose, rhamnose, xylose, lyxose, and others. An indication of the presence of a heptose in very minute quantities was also found. No evidence was obtained for a reversal of the formation of hexoses. On the contrary, these sugars seemed to accelerate the condensation of the formaldehyde. To quote from their paper:

> Only when all formaldehyde present has been used up, is the degradation of the ketopentoses and tetroses initiated. Isomerizations and epimerizations of the sugars continue in such a manner that the finished syrup contains predominantly pentoses and hexoses. The appearance of a yellow coloring coincides with an accelerated formation of hexoses, which represents the last phase of the main reaction.

P. W. Mitchell of the FMC Corporation has made a further study of the foregoing process and devised a simple apparatus to carry out the condensation reaction on a continuous basis. The alkaline formaldehyde solution was pumped through a coil immersed in a constant-temperature water bath. After leaving the coil, the solution was first cooled, then deionized using a column of mixed-bed ion exchange resins. The effluent, which had a very low conductivity, was then concentrated in a flash evaporator at 50°C and a pressure of about 15 mm Hg. When calcium hydroxide was used as a catalyst, a large share of the amount present was removed as carbonate in an intermediate step. The final product was a slightly yellow, highly viscous syrup with a sweet taste. The yield of material on an anhydrous basis from one batch was 77%. The placement of the spots on a paper chromatogram of the

Table 7 Approximate composition of the sugar from formaldehyde; study by P. W. Mitchell

Component, number	Weight, %	Possible identity	Osazone melt. p., °C	Osazone, type
1	0.4	glycollic aldehyde	...	...
2	1.1	glyceraldehyde	...	...
3	1.8	dihydroxyacetone	126–129	triose
4	3.2	erythrose, threose, erythrulose	147–149	tetrose
5	2.5	xylulose	183–187	pentose
6	6.5	ribose, dendroketose	159–176	pentose
7	17.2	xylose	186–188	pentose
8	16.5	fructose, mannose	173–177	hexose
9	17.5	sorbose, arabinose	147–149	hexose
10	16.8	glucose	183–185	hexose
11	8.5	galactose	142–144	hexose
12	4.4	...	167–179	hexose
13	<2	heptulose	...	...

synthetic sugar mixture, together with those produced by authentic sugars, is shown in Fig. 11. The approximateco mposition of the synthetic sugar mixture in terms of 13 different components found to be present is given in Table 7. The large percentage of xylose is of particular interest.

Biological Testing of Formose Sugar

This testing was carried out under the direction of T. J. Russell of Bio Dynamics, Inc., Edison, New Jersey. One group of ten weanling albino rats was given a balanced synthetic diet containing formose sugar, a second group was given a diet wherein the formose sugar was replaced with cellulose flour having zero nutrition value, and a third group with normal diet was used as control. Growth data for each group are shown plotted in Figure 12, where the top curve represents data for the control and the bottom one data for the test diet.

Moderate to severe diarrhea was common to all animals in the group fed formose sugar, but this symptom was absent in the other two groups. Postmortem examination of the animals in the first group revealed marked distension of the stomach by undigested food, suggesting the possibility that formose sugar inactivates the gastric enzymes responsible for partial digestion preceding passage of food into the intestines. In addition, the presence of undigested food in the beginning of the intestines suggests that intestinal enzymes were affected as well.

Attempts by Mitchell to separate formose sugar in a number of fractions and to test them individually for toxicity seemed to indicate that they all showed about the same degree of toxicity. However, all species present in formose sugar have a high degree of solubility in water, and the degree of separation attained with the method employed may easily have been insufficient to lower the concentration of the toxic components in any one of the fractions to such an extent that their biological effects were suppressed. A somewhat simpler explanation of the toxic effects based on well-known chemical behavior of the species present would seem to be more plausible.

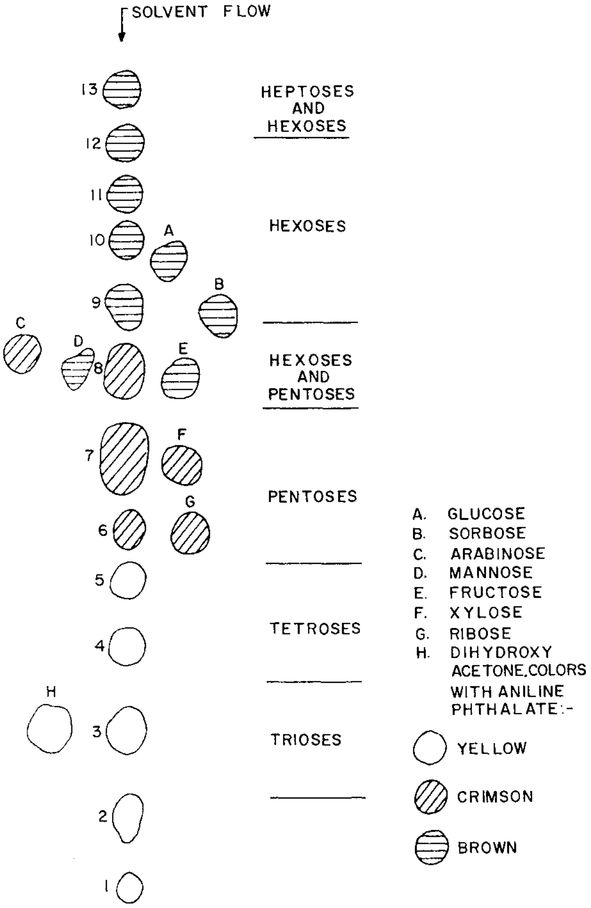


Fig. 11. Chromatogram of synthetic sugar mixture and some authentic sugars.

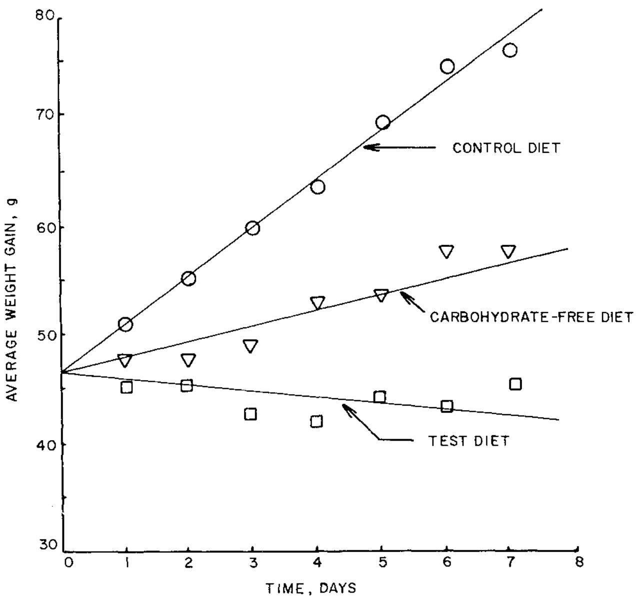
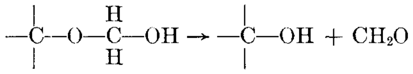


Fig. 12. Curves for growth rates of weanling rats fed various diets.

Aldehydes and alcohols generally react exothermally under formation of semiacetals. Any semiacetals formed by carbohydrates with formaldehyde would thus appear to be quite stable giving a high degree of probability to the assumption that formose sugar contains considerable quantities of this type of substances. When they are broken down by the acidic gastric juices, relatively large amounts of formaldehyde would be released, causing strong toxic effects. This conclusion is strongly supported by the fact that all weanling rats fed on a diet containing formose sugar, casein, and agar solution had stomachs and intestines grossly swollen with what appeared to be undigested food. As is well known, agar solutions coagulate and casein hardens rapidly in the presence of formaldehyde.

The formation and decomposition of carbohydrate semiacetals is likely to be a kinetically intricate problem to solve. In general, semiacetals seem to form in basic and decompose in acidic solutions. Removal of the catalyst producing the formose sugar by electrodialysis followed by acidifying the solutions obtained would set the stage for their breakdown to carbohydrates and free formaldehyde according to the general reaction



$$-\overset{|}{\underset{|}{C}}-O-\overset{H}{\underset{H}{C}}-OH \rightarrow -\overset{|}{\underset{|}{C}}-OH + CH_2O$$

The rate of reaction is most likely to increase with the temperature and probably with decreasing pH of the solution. To avoid the use of acids that subsequently would be difficult to remove if necessary, the possibility of splitting the semiacetals by saturating the neutral formose solution with carbon dioxide under moderate pressure and raising the temperature should be considered. There are only a few older data available on the hydrolysis of alkyl acetals, but recently Wolford made some measurements of the rate of hydrolysis of $CH_3 \cdot CH(OC_2H_5)_2$ in water-acetone solutions and found it to be extremely sensitive to the concentration of hydrogen ions present.

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Radiation Shielding Considerations in Manned Spacecraft Design

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A procedural analysis that minimizes the space radiation hazard is described for all engineering phases up to hardware design and illustrated by reference to its application in recent studies. Radiation dosages are shown to differ significantly among different spacecraft configurations for the same mission. Estimated radiation dosage levels also vary significantly, depending on the degree of detail to which the spacecraft and body models have been designed. In view of the important mission-configuration-dosage relationships that have been found and the detailed body-radiation tolerances now specified, an efficient treatment of the radiation hazards to manned spaceflight must begin during preliminary design. Detailed inputs must come from system design groups early enough to allow the radiation analysis results to be used in the final determinations of external configuration, materials, and inboard profile.

Introduction

SPACE radiations have received considerable attention during recent years—and have been cited, at various times, as a factor limiting or prohibiting manned space flight, or as being completely insignificant. Depending on the attendant conditions, any of these observations may have been correct.

For a narrower definition of the hazard, we must analyze the characteristics of the mission and the spacecraft in some detail. Such an analysis requires 1) a model of the ambient radiation environment (see the Appendix), 2) a model of the spacecraft or body which interacts with the environment, and 3) the physical relationships that describe the interactions.

Some model environment and spacecraft data will be discussed, not because the data are new but rather to indicate the analytical procedures necessary to the proper consideration of radiations in spacecraft design. At the same time, it is demonstrated that the analysis should begin during the feasibility studies and may well be continued, with expanding detail, in an iterative manner through all of the engineering phases. The analysis requires considerable input data from other technical areas and in turn provides inputs to those areas. It is extremely important that these "feedback" loops be established early.

In this paper, the analytical procedure is discussed for four phases: feasibility studies, preliminary design studies, preliminary design, and design.

Feasibility Studies

The radiation hazard to materials and components is expressed in terms of the incident flux; for man it is usually expressed as dosage absorbed. It is therefore useful to convert the environment from a distribution of particle fluxes to radiation dosage as a function of a standard absorber (a crude representation of the spacecraft). This has been done using several computer programs,[1, 2] which calculate the interactions of the input environment data with the input interacting body data (in this case, hollow spheres of aluminum).

Plots of dose vs aluminum absorber obtained from these programs are shown in Fig. 1 for different constituents of the radiation environment. The effect of orbital parameters on radiation dosages in the Van Allen belts is shown in Fig. 2. The effect of the geomagnetic field in screening out solar flare particles for the May 10, 1959 solar flare is shown in Fig. 3. The proton energy cutoffs used in the preparation of these data were obtained from the solar plasma model of Obayashi and Hakura as given in Ref. 3.

We can now make a first evaluation of the radiation hazard, using as an example a two-week equatorial earth orbit at 600-naut-mile altitude. Table 1 shows a radiation dosage

Table 1 Preliminary estimate of radiation for two-week equatorial orbit at 600 naut miles

Source	Dosage, REM, for aluminum shield thickness, g/cm² 2	6	10
Van Allen belt protons	223	120	85
Secondary neutrons	2	3	4
Van Allen belt electrons	0	0	0
Secondary X-rays	13	9	8
Artificial belt electrons	31,230	0	0
Secondary X-rays	185	159	154
Cosmic rays	~1	~1	~1
Solar flare protons	0	0	0
Total dosage	31,654	292	252

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