CHEMICAL FOOD SYNTHESIS SYSTEMS FOR SPACECRAFT

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Abstract

The life support system requirements for long duration manned space missions have been examined. Hybrid systems that use both biological and chemical processes for food synthesis from metabolic wastes may be feasible and competitive with systems that use stored food. This paper describes a typical, conceptual, configuration of a closed life support system. Specific processes for the synthesis of formaldehyde, glycerol, carbohydrates, and ethanol are discussed. Work currently under way to develop technology suitable for synthesis of such materials is briefly described.

Introduction

Initial efforts (1,2) to develop regenerative life support systems for use in long duration manned space missions began in the 1950's. These studies were directed toward the development of biological systems which would provide oxygen and potable water from metabolic waste products. While the emphasis in this early work was directed toward the use of photosynthetic gas exchangers (reclamation of oxygen from carbon dioxide), attention was also given to the utilization of the by-product biomass as a protein food source, and it was shown that man can tolerate up to 20 percent of his diet as a biomass comprised of algae. More recently, work was begun on the chemical synthesis of foods for manned spacecraft.

Based on work of the late nineteenth century, Akerlof and Mitchell (3) studied the synthesis of simple carbohydrates from materials that could be obtained from human metabolic waste products in a spacecraft. They synthesized formaldehyde from carbon monoxide and hydrogen in a silent electric discharge reactor and condensed it in the presence of calcium hydroxide to form a complex mixture of carbohydrates called formose sugar. They fed the mixture to rats and found it to be toxic.

In conjunction with other programs related to the development of life support systems for long duration space missions, NASA sponsored studies to define feasible methods for regenerating foods from metabolic wastes. This paper summarizes the conclusions of these studies and discusses work currently under way to synthesize foods chemically.

Closed Life Support System

In Table 1, typical metabolic input-output relationships for man are listed. As mission durations increase and crew sizes become larger, it will be advantageous to reclaim more and more of the metabolic wastes. A recent study (4) demonstrated the necessity of reclaiming oxygen and water in one-year, four-man-crew missions with expendables replenished every 90 days. Even with this degree of reclamation, some 14-15 percent of the wastes lost must be offset by means of stored food.

Manned Mars encounter missions would probably require approximately 500 days and a 10-man crew. With the present technology for reclaiming water and oxygen, nearly 3,200 kg of food would be needed. Our closed life support system studies were directed toward determining the configuration and the engineering feasibility of a regenerative life support system with a total weight requirement significantly less than that for a system which used stored food.

The assumptions made to guide our studies are listed in Table 2. They are somewhat restrictive and not necessarily representative of what might be imposed in an actual long duration space mission. For example, the power penalty of 50 kg/kW is only an estimate of what might be available by 1980. The studies' conclusions are presented in reference 5. The following briefly summarizes the results of these studies.

As a basis for comparison, a representative physicochemical system with stored food was defined that would be suitable for long duration missions. As the basic system, it provides the processes necessary for temperature and humidity control, waste treatment, CO_2 collection, concentration and reduction, water reclamation and purification, water electrolysis for oxygen production, and other provisions for personal hygiene and sanitation. A block diagram of the basic system is shown in Figure 1. Generally, a completely regenerative system would utilize all the techniques of the basic system and, in addition, would require the food synthesis system.

Because the technology for the basic system was more developed, primary attention in the study was given to the analysis of concepts for waste processing, chemical food synthesis, and biological food synthesis. Candidate systems considered were based on such concepts as photosynthetic systems including algae, duckweed, plants, etc.; microbiological systems including hydrogen and methane fixing bacteria, fungi, and yeasts; and chemical systems including carbohydrate, fat, protein and alcohol synthesis processes. From these, essentially two classes of completely regenerative systems evolved; in the first, all the food is synthesized biologically; and in the second a hybrid process of both biological and chemical processes is used.

From the viewpoint of weight and power, the biological system is preferred over the hybrid. However, the use of the biological system is based on the assumption that man can tolerate a high level of protein in his diet. There are indications that a high protein diet consumed over a long period imposes physiological stresses, such as increased water turnover. Since the hybrid system can produce a diet with components in more conventional proportion, it is considered to be a preferable approach.

The caloric requirement and the desirable composition of the diet are relatively well established (6). There is some variation, however, in recommended allowances and actual consumption. For example, a minimal protein requirement of 35 g per day for a 70 kg man is considered adequate. The adult American, however, prefers considerably more and his average diet provides around 100 g. The 35 g diet supplies approximately 7-8 percent of the total daily caloric requirement, while the 100 g diet supplies 18-20 percent. The remainder of the caloric needs is met through essentially equal quantities of fat and carbohydrate. Fat provides 9 calories per g, compared to 4.5 for protein and carbohydrate. From weight and volume considerations, it would be advantageous to construct a diet with a high fat content. An upper dietary limit of 50-percent fat has been suggested (7) since more may prove to be physiologically detrimental.

Our predisposition then has been to prefer a closed system that would furnish a normal calorically constituted diet. A simplified schematic diagram of such a system is shown in Figure 2. Its principal features are a urine processing system, a solid and fecal waste processing system, a bacterial (Hydrogenomonas eutropa) protein synthesis system, and chemical reactors for carbohydrate synthesis. A specific fat synthesis process is not shown. For this scheme, the assumption was made that the required fats would be provided from stored supplies. A later section of the paper discusses a fat synthesis concept currently being investigated.

Since the intent of this paper is to examine chemical synthesis, the waste processing and bacterial systems are only briefly discussed. The function of the waste processor is to treat and condition raw urine and fecal material into a form acceptable as the nutrient medium for the bacterial system. The bacterial system includes the necessary culture apparatus, pumps, and controls to recombine the waste nitrogen, sulfur, carbon, hydrogen, and oxygen into protein. A system is also shown for processing the protein-rich bacteria into an acceptable food. As yet, the requirements for this are undefined.

The Hydrogenomonas system does not require light for growth as do the algal photosynthetic systems. It obtains its energy for growth from the recombination of hydrogen and oxygen. A photosynthetic system is hampered by many inefficient steps. The conversion of electrical energy to light is about 20 percent efficient, and the utilization of light by the active photosynthetic cell is about 20 percent. A net efficiency results which is something less than 4 percent. The Hydrogenomonas process power requirement is largely a function of that necessary to electrolyze water to provide hydrogen and oxygen. Current electrolysis systems for spacecraft are approximately 50-60 percent efficient. Assuming other process inefficiencies and losses, the bacterial system should be some five or six times more efficient than a photosynthetic system under the conditions of the assumptions stated earlier.

The remaining sections of the paper present an account of our activities in chemical food synthesis.

Formaldehyde Synthesis

As noted in Figure 2, a process for the synthesis of formaldehyde is needed because formaldehyde is an intermediate material for the synthesis of carbohydrates. Our studies showed that formaldehyde was also an intermediate in some processes for fat synthesis. Since many of the unit operation problems associated with the synthesis of formaldehyde were common to other processes, it was considered appropriate first to attempt a solution here rather than choose specific fat or carbohydrate synthesis processes. If successful, the technology developed could be directly applicable to other concepts.

Formaldehyde is produced extensively and economically by two significantly different approaches. Usually, carbon monoxide and hydrogen form methanol and methanol is oxidized to form formaldehyde.

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$CH_3OH + \frac{1}{2} O_2 \longrightarrow HCHO + H_2O$$

In the other method, mixtures of hydrocarbons, including methane, are oxidized to form formaldehyde.

$$(C_nC_{2n+2}) + nO_2 \longrightarrow nHCHO + nH_2O$$

The product also contains many other organic compounds and the yield of formaldehyde is considerably less than that of the methanol process. In Germany formaldehyde is produced commercially from methane alone. The technique is evidently influenced by economical factors related to the availability of reactants.

The spacecraft technique is also influenced by various factors. Economics is one, but simplicity of operation is more important. Figure 3 shows the processes which would be involved if the methanol system were adopted. Most noticeable are the high temperature and/or pressure reactors for producing carbon monoxide and synthesizing methanol. Also shown is a separator for removing unreacted gases after methanol is converted to formaldehyde. The advantages of this technique are that reaction conditions are well known and yields are high. Disadvantages are the high pressures and temperatures required and the gas-liquid phase separation problems.

The methane technique is shown in Figure 4. There are relatively high temperature reactors, but the reactions are all carried out at ambient pressure. Yields are less than with the other process and the need for gas-liquid separation still exists. Typical catalysts, such as ozone or nitrous oxide, may be difficult to produce or control in a spacecraft. The major disadvantage of this approach, however, is that complete oxidation of methane to carbon dioxide and water is much more favored thermodynamically.

Other processes for producing formaldehyde were also considered. The complexities of the necessary processes and uncertainties of various steps in the processes caused their rejection for further serious consideration as candidate methods. Formaldehyde synthesis by both the methane and methanol route is currently being investigated in the laboratory. To date, attempts to synthesize formaldehyde via the methane route have been discouraging. It is too early to comment on progress via the methanol route.

Glycerol Synthesis

Normal fat, protein, and carbohydrate which make up our diets are generally composed of long chain complex molecules. To simplify the synthesis process, an effort was made to identify simpler molecules which would satisfy nutritional requirements. Glycerol is such a material. Feeding studies (8) have been conducted with rats to determine tolerable levels of glycerol in the diet. This work suggests that glycerol can provide up to 40 percent of the caloric requirement with no ill effects.

In a study (9) primarily directed toward an analysis of the synthesis of fats, techniques for the synthesis of glycerol were also investigated. In passing, it should be noted that a process which involved the synthesis of ethylene from carbon monoxide, polymerization to α-olefines via the Ziegler growth reaction, conversion to fatty acids by oxidative ozonolysis, and combination with glycerol to form edible glycerides was defined as the most feasible technique for lipid synthesis. However, the process is considered to be too complex for spacecraft use, and it is probable that work to pursue synthesis for such use will not be undertaken.

Four methods (10) of glycerol synthesis were examined: (a) direct hydrogenation of carbon monoxide, (b) synthesis from acetylene and formaldehyde, (c) trimerization of formaldehyde, and (d) hydrogenolysis of carbohydrate. The examination of these techniques was quite extensive and only the conclusions of the investigation will be discussed. The first method

$$3CO + 3H_2 \longrightarrow \begin{array}{ccc} CH_2 & CH & CH_2 \\ | & | & | \\ OH & OH & OH \end{array}$$

is conceptually simplest. However, the reaction favors the formation of ethylene glycol and requires pressures in excess of 1,000 atmospheres.

The second, synthesis from formaldehyde and acetylene, follows the reaction sequence:

$$HC \equiv CH + HCHO \xrightarrow{Cu(C{\equiv}CH)_2} HC \equiv CCH_2OH$$

$$HC \equiv CCH_2OH \xrightarrow{H_2} H_2C = CHCH_2OH$$

$$H_2C = CHCH_2OH \xrightarrow{H_2O_2} \begin{array}{ccc} CH_2 & CH & CH_2 \\ | & | & | \\ OH & OH & OH \end{array}$$

All steps in this method are well known, are considered fairly reliable, and give high yields; but the method is undesirable because it is complex and involves handling hazardous material.

The last two processes are considered to offer more promise. In trimerization of formaldehyde, three carbon sugars and hydroxy ketones are formed by the condensation of formaldehyde. They are then hydrogenated to glycerol.

$$HCHO \xrightarrow{Base} \begin{array}{c} HOCH_2CHCHO \\ \quad\quad | \\ \quad\quad OH \end{array} + \begin{array}{ccc} CH_2 & CO & CH_2 \\ | & & | \\ OH & & OH \end{array}$$

$$\begin{array}{c} HOCH_2CHCHO \\ \quad\quad | \\ \quad\quad OH \end{array} + \begin{array}{ccc} CH_2 & CO & CH_2 \\ | & & | \\ OH & & OH \end{array} \xrightarrow{H_2} 2\begin{array}{ccc} CH_2 & CH & CH_2 \\ | & | & | \\ OH & OH & OH \end{array}$$

Generally, the problems associated with this concept are related to stopping the first reaction at the three-carbon stage. The formation of pentoses and higher sugars proceeds readily under favorable conditions. The second reaction proceeds above 100 atmospheres. The usual problems of product separation and high pressure and temperature reactors contribute to the overall complexity of this process for spacecraft use.

The final process for glycerol synthesis, hydrogenolysis of carbohydrates, is similar to trimerization of formaldehyde process. Formaldehyde is allowed to condense to higher sugars. They are reduced to polyhydric alcohols, and the alcohols are further hydrogenated to form glycerol.

$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{H_2} \begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

$$\begin{array}{l} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{H_2} \begin{array}{l} 2CH_2CHCH_2 \\ \;\;|\quad\;|\quad\;| \\ OH\;OH\;OH \end{array}$$

The second reaction occurs more readily at 100 to 200 atmospheres pressure. However, ethylene glycol and propylene glycol are also formed, and the process is complicated by the usual separation problems.

<u>Carbohydrate Synthesis</u>

The main technique for synthesis of carbohydrate has been introduced in the discussion of glycerol synthesis, that is, condensation of formaldehyde. The first observation of the formation of sugars was reported in 1861 (11). Intervening work is summarized by Shapira (5, p. 175). The major disadvantage of this method is that it is nonspecific; that is, three-, four-, five-, and six-carbon sugars may be formed. Furthermore, optically active isomers of the sugars form. Naturally occurring sugars are composed of the D isomers. However, during synthesis, equal quantities of L isomers form. Little is known of their caloric value or of their possible toxicity. While the toxicity of the L form is not known, studies (3,8) in which the synthetic mixture was fed have been relatively unsuccessful. Presently, it is not known whether the mixture itself is toxic or if formaldehyde may still be in the product. Efforts are currently under way to purify the mixture further in order to resolve the question. Studies were recently initiated to study carbohydrate synthesis by passing formaldehyde through a catalyst matrix with optically active sites. It is hoped that this work will lead to synthesis of a sugar mixture of the D isomer optical form.

An alternative approach to carbohydrate synthesis via the formaldehyde route is to stop the condensation at an intermediate stage (as was necessary with glycerol synthesis). The products are reacted in the presence of a base to form fructose and sorbose.

$$\text{Formaldehyde} \xrightarrow{\text{Base}} \text{DL-glyceraldehyde} + \text{dihydroxyacetone}$$

$$\begin{array}{l}\text{DL-glyceraldehyde} \\ + \text{ dihydroxyacetone}\end{array} \xrightarrow{\text{Base}} \text{DL-fructose} + \text{DL-sorbose}$$

Sorbose is poorly tolerated in the diet and an additional process for its removal would have to be introduced. Since this approach required the development of essentially the same techniques as does the process previously described, there was no particular advantage foreseen in pursuing it at the present.

Ethanol Synthesis

One other process is worthy of consideration for a spacecraft chemical food synthesis system. Studies of the nutritive and toxicological properties of ethanol indicate it has a high caloric value, and with suitable supplement of protein and carbohydrate, and a controlled rate of consumption, it might provide a substantial part of man's caloric requirement.

Ethanol production could result from the following reaction (12):

$$3CO + 3H_2 \longrightarrow C_2H_5OH + CO_2$$

The conditions for this reaction are 150°-200° C and 10-20 atmospheres pressure. Under these conditions, a product is formed which is 4 to 8 percent ethanol. The processes required for an ethanol plant are shown schematically in Figure 5. Ethanol synthesis requires considerable recycling of by-products which discourages laboratory studies of the process.

Unit Operations

The ability to synthesize foods, chemically, in a spacecraft will depend in large part on the solution to unit operations problems. Figure 5 is typical of synthesis processes; there are requirements for high pressure, high temperature reactors, gas-liquid and liquid-liquid separation, heat exchangers, and process controllers, pumps, etc. The problem is further compounded by the constraints of power, weight, volume, and zero gravity. Also, consideration must be given to the necessity for long term reliable performance, for the crew may not be able to operate and maintain a complex chemical plant.

Generally, our approach has been to investigate processes that are not used conventionally. Our selections have been based on the consideration of possible, and preferred, mechanical simplicity. In investigating these processes considerable effort is required to prove or disprove work previously reported in the literature, for example, the work related to synthesizing formaldehyde by methane oxidation. Further, new technology or processes must be generated. The probability of synthesizing suitable carbohydrates would be greatly increased if a simple process for the resolution of racemic mixtures were developed.

Solutions to these problems are not yet in hand. Space missions which are postulated for the next two decades consider durations of such magnitude that regenerative systems to some degree may be essential. In addition to the requirements of future space missions, the technology developed may be applicable to more immediate problems of the world's food supply.

Literature Cited

1. Robinette, Joan, ed., "Biologistics for Space Systems Symposium," AMRL TDR-62-116, Wright Patterson AFB (1962).
2. Miller, R. L., and C. H. Ward, "Algal Bioregenerative Systems," SAM TR-66-11, Brooks AFB (1966).
3. Akerlof, G. C., and P. W. Mitchell, J. Spacecraft, 1, 303 (1964).
4. Armstrong, R. C., "Life Support Systems for Space Flights of Extended Time Periods," NASA CR-614, Washington, D.C. (1966).
5. Conference on the Closed Life Support Systems, NASA SP-134 (1967).
6. Recommended Dietary Allowances, National Academy of Sciences, National Research Council, Publication 1146 (1964).
7. Calloway, D. H., Presentation at 46th Annual Meeting of the American Dietetic Society, Philadelphia (1963).
8. Shapira, Jacob, Presentation at 52nd Annual Meeting, American Association of Cereal Chemists, Los Angeles (1967).
9. Frankenfeld, J. W., "Study of Methods for Synthesis of Fatty Acids and Lipids from Metabolic Wastes Aboard a Spacecraft," Final Technical Report, Contract No. NAS2-3708 (1967).
10. Ibid., 94.
11. von Butlerow, A. M., Ann., 120, 295 (1861).
12. Emmett, Paul H., ed., "Catalysts," vol. 4, p. 113, 217, Reinhold (1960).

TABLE 1

Man's Metabolic Requirements

Input, g/day		Output, g/day	
Water	2,900	Water	3,080
Oxygen	825	Carbon dioxide	1,010
Food	635	Solid wastes	270

TABLE 2

Closed Life Support System Study Constraints

Mission duration	1 to 3 years
Crew size	10 to 100 men
Gravity	Zero or reduced
Spacecraft orientation	Random
Power penalty	50 kg/kW
Atmosphere	Standard
Processes	Chemical and/or biological

BASIC LIFE SUPPORT SYSTEM WITH STORED FOOD

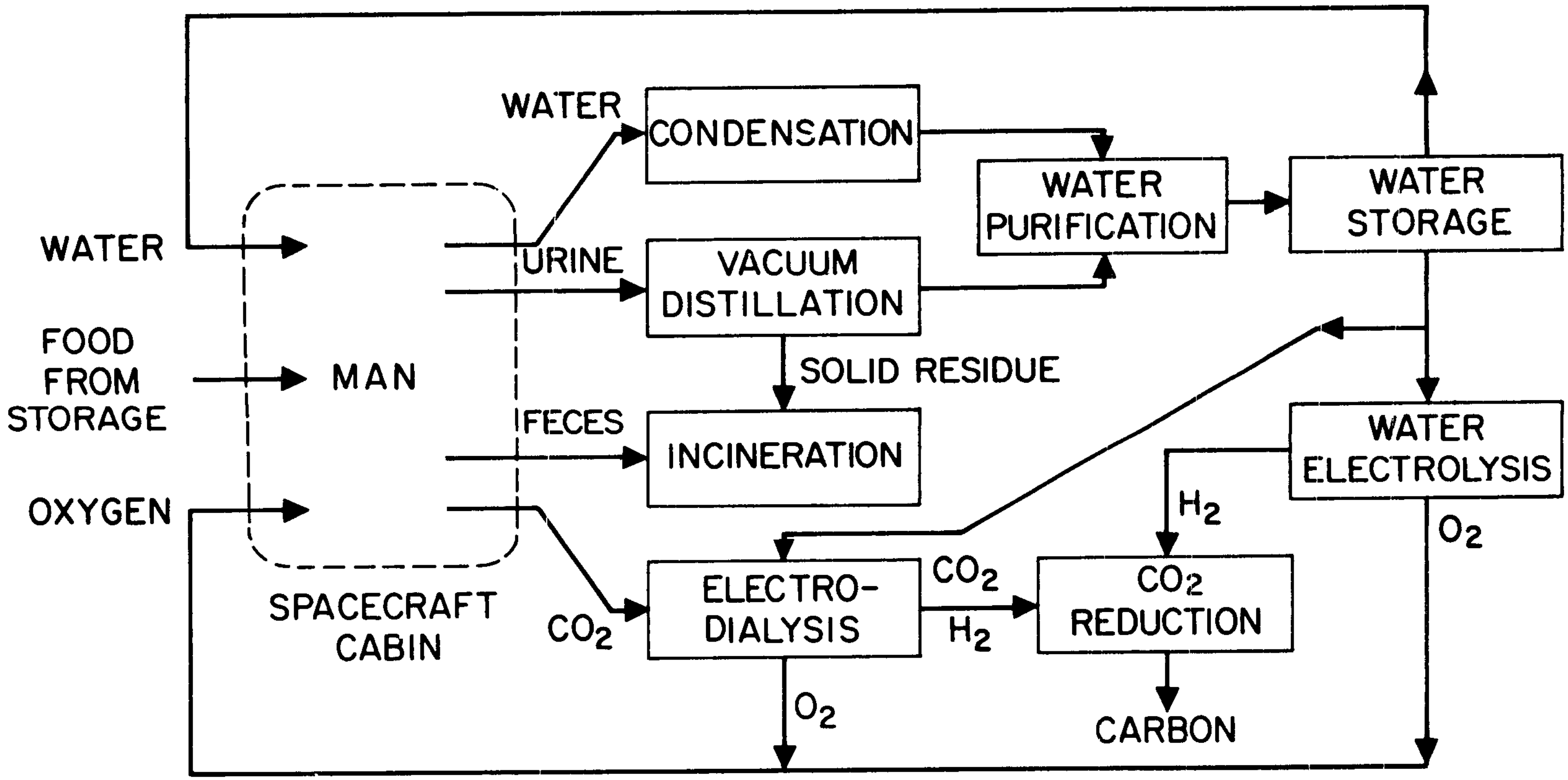

Figure 1.

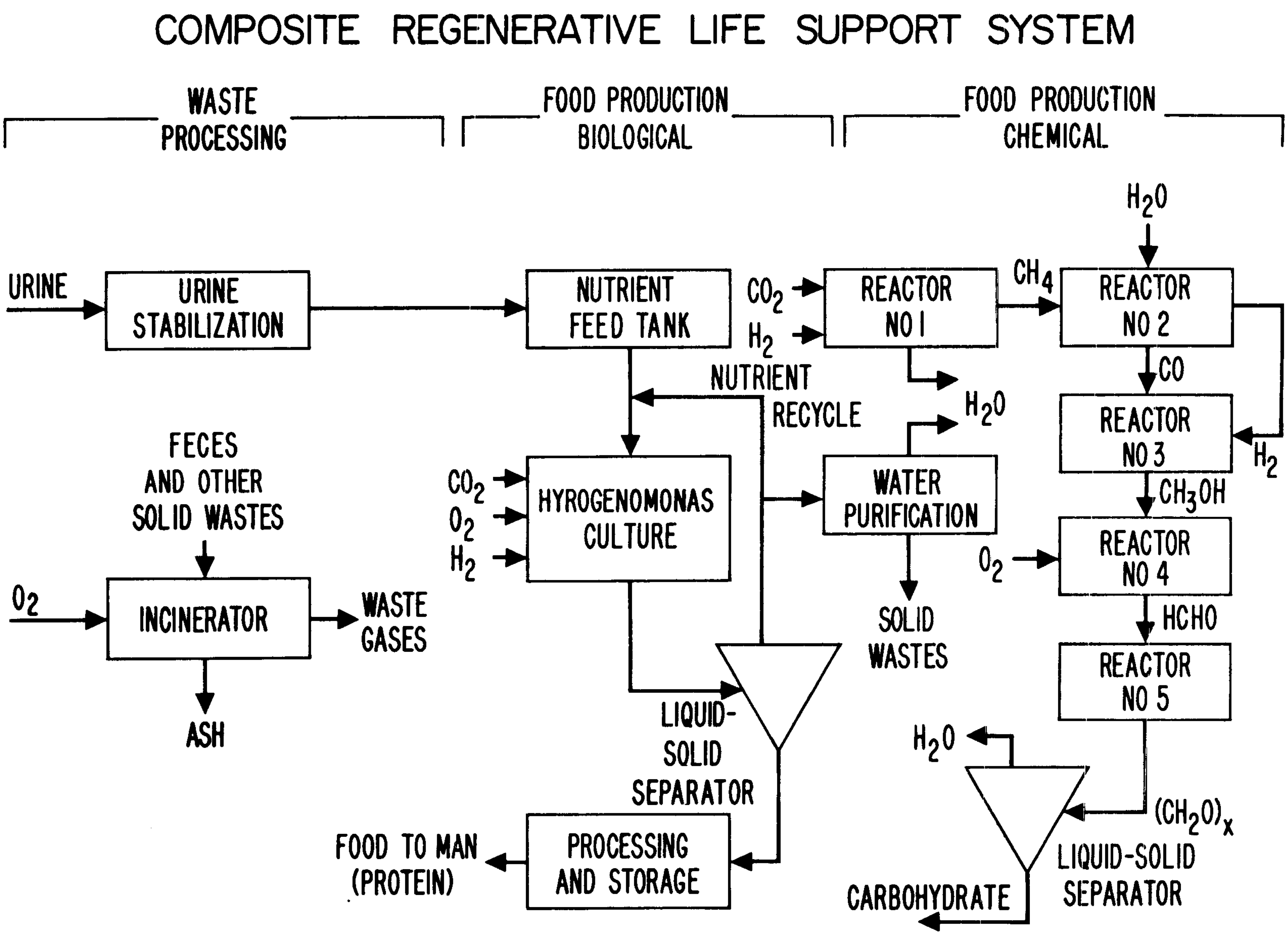
COMPOSITE REGENERATIVE LIFE SUPPORT SYSTEM
WASTE PROCESSING
FOOD PRODUCTION BIOLOGICAL
FOOD PRODUCTION CHEMICAL
URINE
URINE STABILIZATION
NUTRIENT FEED TANK
CO_2
H_2
REACTOR NO 1
CH_4
H_2O
REACTOR NO 2
CO
REACTOR NO 3
H_2
CH_3OH
REACTOR NO 4
O_2
HCHO
REACTOR NO 5
$(CH_2O)_x$
LIQUID-SOLID SEPARATOR
H_2O
CARBOHYDRATE
NUTRIENT RECYCLE
H_2O
WATER PURIFICATION
SOLID WASTES
CO_2
O_2
H_2
HYROGENOMONAS CULTURE
LIQUID-SOLID SEPARATOR
PROCESSING AND STORAGE
FOOD TO MAN (PROTEIN)
FECES AND OTHER SOLID WASTES
O_2
INCINERATOR
WASTE GASES
ASH

Figure 2.

FORMALDEHYDE SYNTHESIS WITH METHANOL INTERMEDIATE

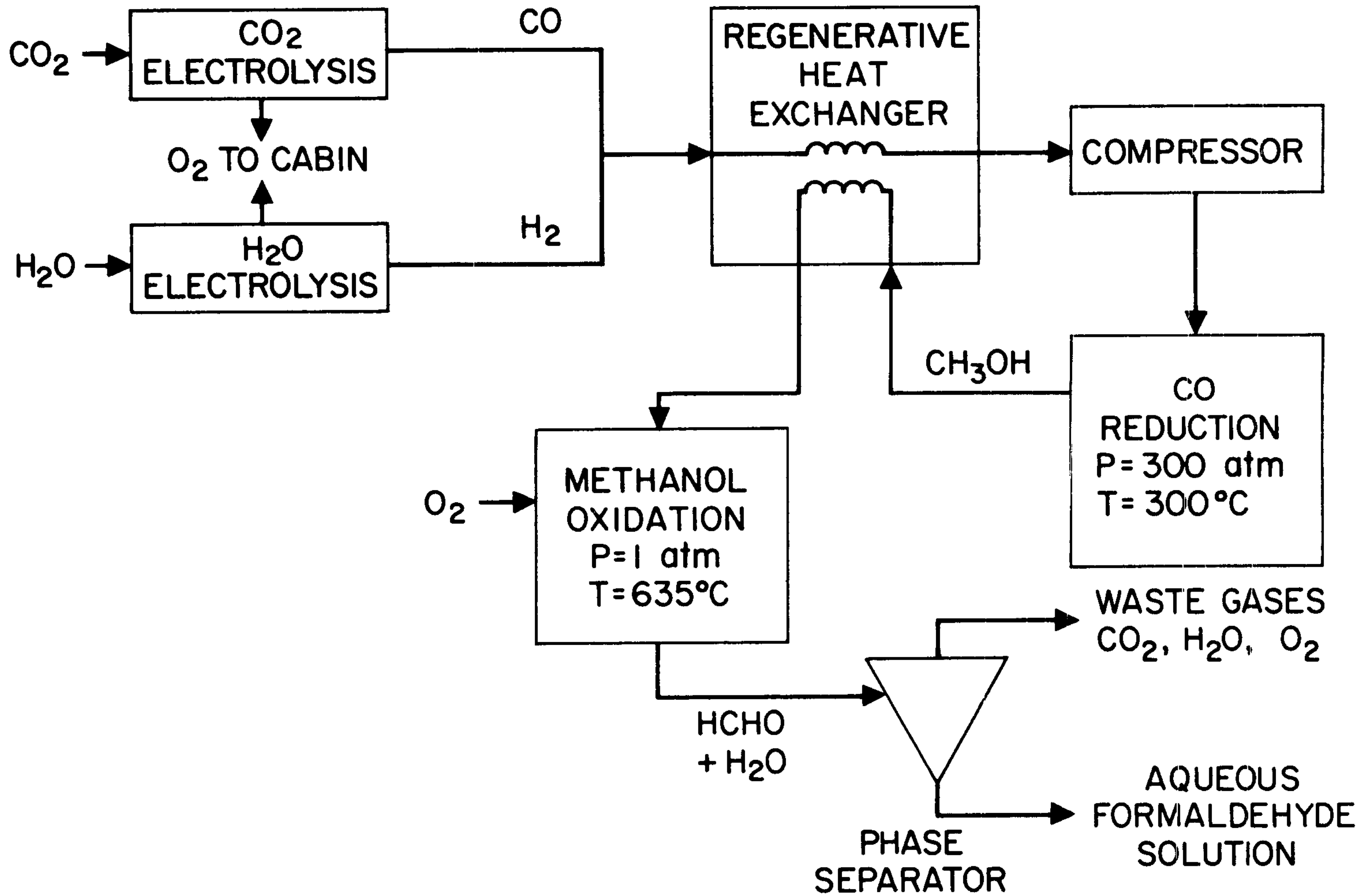

Figure 3.

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FORMALDEHYDE SYNTHESIS WITH METHANE INTERMEDIATE

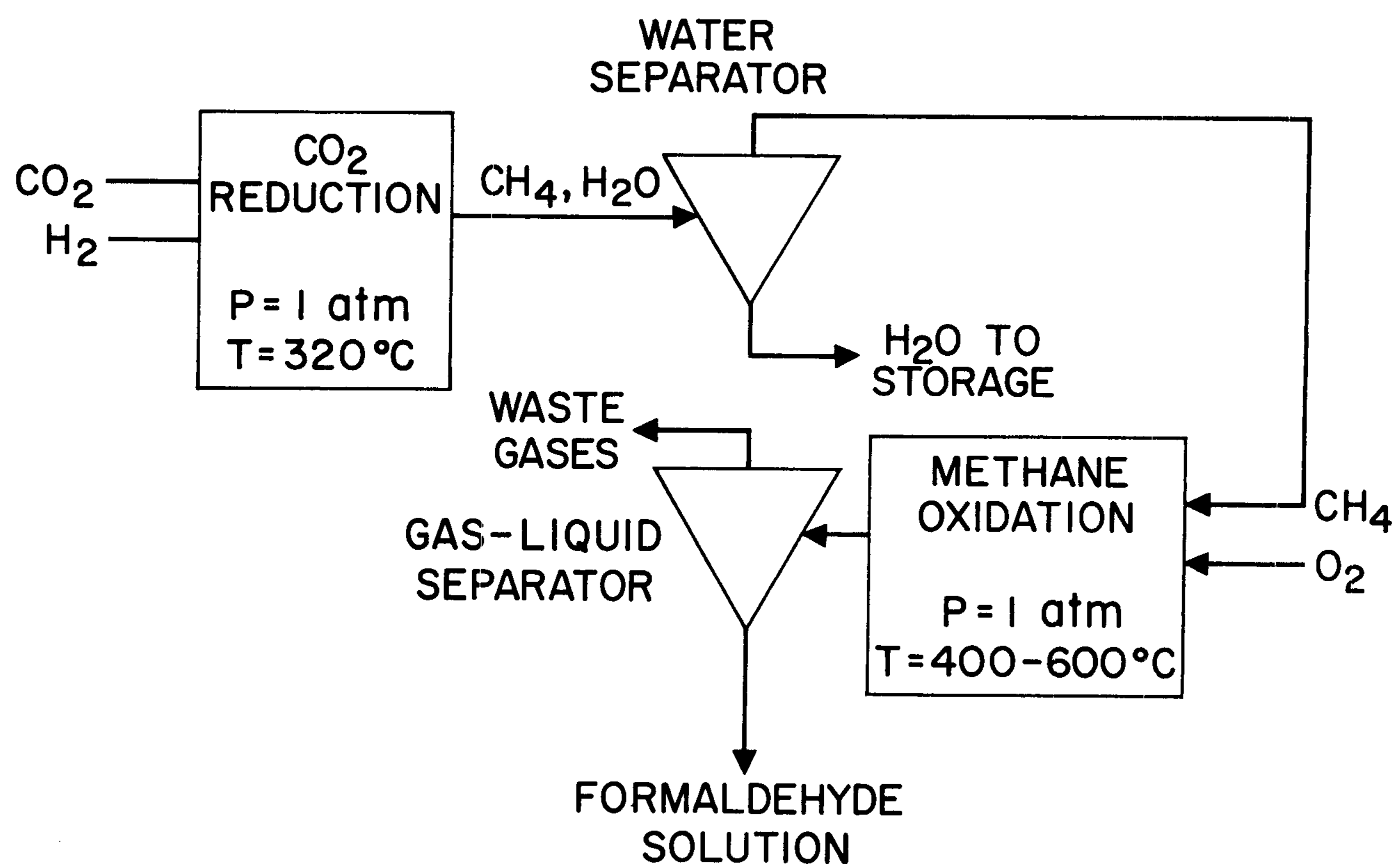

Figure 4.

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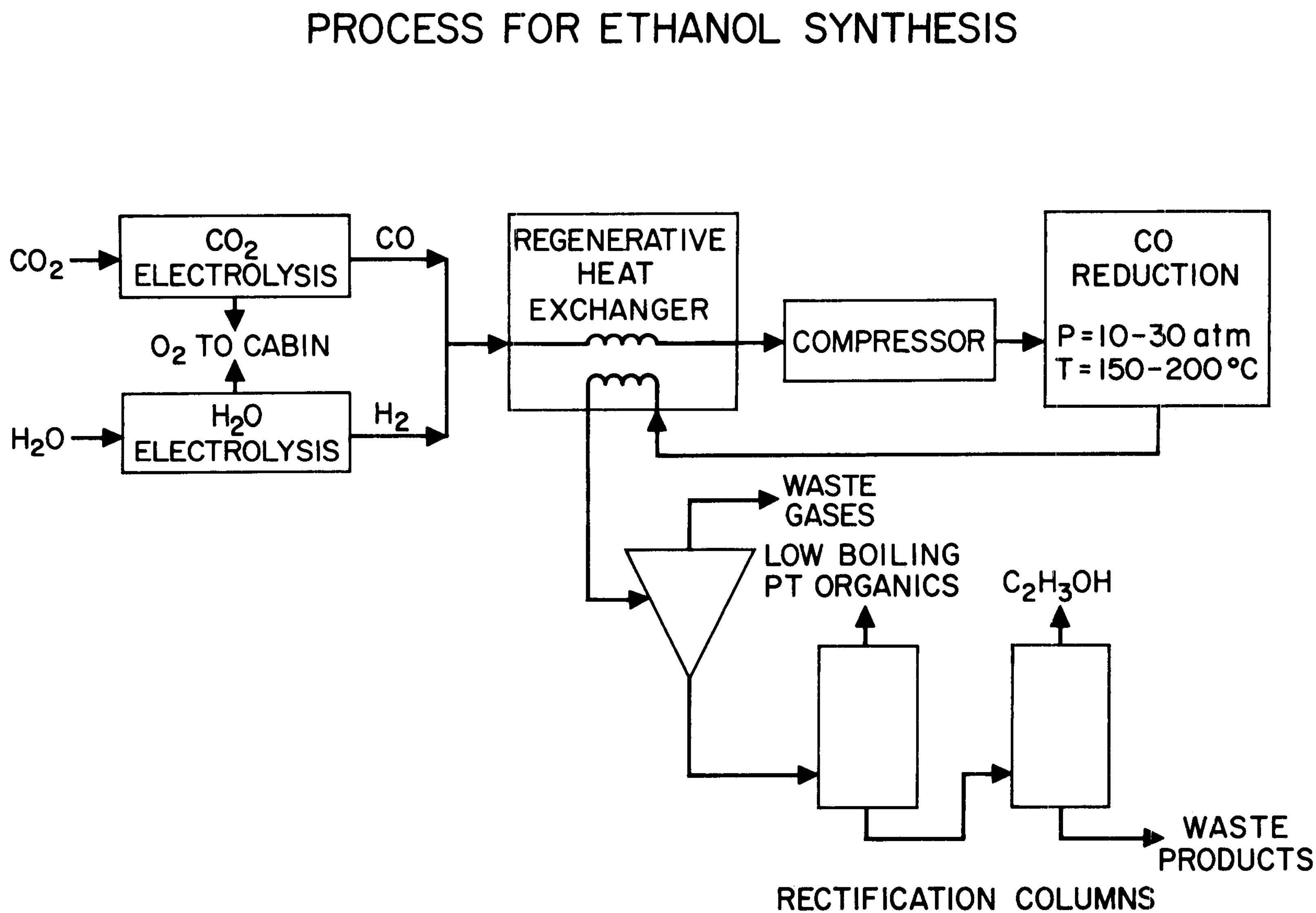

Figure 5.

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