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RESEARCH AND DEVELOPMENT STUDY RELATED TO THE SYNTHESIS OF FORMALDEHYDE FROM CO_2 AND H_2

FINAL REPORT

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SUMMARY

Formaldehyde is an intermediate in the synthesis of edible carbohydrates from CO_2, O_2 and H_2 derived from crew member metabolic wastes on spacecraft missions. Methods of accomplishing the synthesis of formaldehyde from CO_2 were studied, and the $CO_2 \longrightarrow CH_4 \longrightarrow CH_2O$ route was selected as the most suitable for spacecraft conditions.

The partial oxidation of methane by oxygen was investigated using both solid and gaseous catalysts. The highest formaldehyde yield was achieved with gaseous nitric oxide catalyst; the yield was 2.5% of the methane admitted to a single pass reactor.

The feasibility of converting CO_2 into formaldehyde was demonstrated with a recycle system entailing two reactors. A methanation reactor converted feed and by-product CO_2 into CH_4; the CH_4 in turn was oxidized to formaldehyde in an oxidation reactor. With recycling, essentially 100% conversion of CO_2 to formaldehyde was achieved at ambient pressures. The product formaldehyde and water were separated and removed either as solid paraformaldehyde and ice or adsorbed on solid adsorbents. The system is compatible with zero gravity operation.

INTRODUCTION

For space missions of long duration, the major weight contribution to life support is stored food. The weight of food necessary to support a multiman crew on a space flight suggests that the major portion should be supplied by regenerative methods, utilizing man's metabolic wastes (ref. 1). To supply the solid portion of man's normal food requirements, a separate method will be needed for the synthesis of each of the three primary food categories, carbohydrates, proteins, and fats.

In the present state-of-the-art, physicochemical synthesis of foodstuffs may have some advantages over biological systems. A chemical process is more reliable and controllable, and seems to have lower weight and power penalties. The chemical synthesis of carbohydrates from metabolic wastes is considered more promising than the synthesis of proteins and fats (ref. 39).

This investigation has been concerned with one aspect of carbohydrate synthesis: the production of formaldehyde (CH_2O), which is an intermediate in the synthesis of sugars and glycerol, from metabolic CO_2 combined with H_2 and O_2 generated from waste water electrolysis.

Program Objectives

The objectives of the research and development program for synthesis of formaldehyde from carbon dioxide and hydrogen were:

1. To conduct a literature survey and to investigate theoretical considerations, and from these to determine the most appropriate methods, chemical reactions, and catalysts for accomplishing the synthesis of formaldehyde from carbon dioxide and hydrogen, compatible with space-

craft usage.

2. To perform laboratory tests of the selected methods and to introduce modifications of the processes and catalysts leading to improved formaldehyde yields and minimum by-product formation.
3. To select the most promising method, and to develop and operate a laboratory reactor demonstrating the feasibility of formaldehyde synthesis.
4. To investigate the separation and purification of formaldehyde product, preferably in solid form.
5. To assemble a breadboard system and obtain operating data and to prepare the preliminary design of a prototype model.

Approach

An extensive survey of literature was carried out to identify the possible methods of CH_2O synthesis from CO_2 and H_2 and to determine their applicability to spacecraft conditions. The following routes of CH_2O synthesis were considered:

1. Direct Reduction

   (a) $CO_2 + 2H_2 \longrightarrow CH_2O + H_2O$

   or

   (b) $CO + H_2 \longrightarrow CH_2O$

2. Methanol Intermediate:

   (a) $CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$

   (b) $2CH_3OH + O_2 \longrightarrow 2CH_2O + 2H_2O$

3. Formic Acid Intermediate:

   (a) $CO_2 + H_2 \longrightarrow CHOOH$

   (b) $2CHOOH \longrightarrow CH_2O + CO_2 + H_2O$

4. Methane Intermediate:

(a) $CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$

(b) $CH_4 + O_2 \longrightarrow CH_2O + H_2O$

The oxidation of methanol to formaldehyde (reaction 2b) is very well known (ref. 3) and over 90% of commercially synthesized formaldehyde is produced by this technique. The methanation of carbon dioxide (reaction 4a) also was adequately investigated earlier (ref. 2) and a catalyst developed which produces over 99% conversion in a single pass at temperatures of about 200°C. Therefore, these two reactions were not investigated during this program.

The literature survey and thermodynamic calculations indicated that high pressure reaction systems would be necessary to overcome unfavorable thermodynamics at atmospheric pressure for the direct reduction, the methanol intermediate, and the formic acid intermediate methods. In contrast, the favorable thermodynamics for the formation of CH_2O at atmospheric pressure via the methane route indicate that this can be accomplished entirely at ambient pressures and in the gas phase. Consequently, the methane route was considered more suitable for spacecraft application than the other three routes, and was investigated in detail.

The first step of the CH_2O formation, the methanation of CO_2, can be easily accomplished (ref. 2); the major problem, therefore, was one of finding a suitable method for partial oxidation of CH_4 to CH_2O in acceptable yields. To accomplish this, a comprehensive literature search was carried out, various claims for conversion of CH_4 to CH_2O were catalogued, and each one was critically evaluated. Also, theoretical considerations predicting the CH_2O yields and conditions for their improvement were surveyed. Then various solid and gaseous catalysts were screened in laboratory systems using single pass flow reactors. The most promising of all the catalysts were gaseous O_3 and NO which provided 1.0-2.5% CH_2O yields. These were further tested in recycle systems, and yields of up to 25-30% were achieved.

Finally, an integrated recycle system was developed for converting CO_2 and H_2 into CH_2O. In this system a Sabatier reactor converted CO_2 and H_2 to CH_4; the CH_4 was then partially oxidized to CH_2O in a second catalytic reactor. Under proper recycle conditions, and at entirely ambient pressures, essentially 100% of the CO_2 fed into the system was converted to CH_2O which was either condensed to solid paraformaldehyde or adsorbed directly on adsorbents for separation and recovery.

A breadboard prototype model was fabricated and tested to measure power requirements and obtain operating data. From these data the preliminary design of a flight prototype model was prepared.

SELECTION OF EXPERIMENTAL APPROACH

A literature survey revealed three feasible routes for the synthesis of formaldehyde from CO_2 and H_2: 1) direct reaction to CH_2O, 2) formation of CH_3OH with subsequent conversion to CH_2O, and 3) production of CH_4 followed by oxidation to CH_2O. A fourth possibility, the formation of formic acid with subsequent reduction to CH_2O, existed but its feasibility was low. Commercially, most of the CH_2O is produced by catalytic oxidation of CH_3OH; some CH_2O, particularly in European countries, is obtained from the partial oxidation of CH_4. However, successful commercial methods did not appear to lend themselves to spacecraft applications.

The problem of selecting the most suitable route for providing acceptable yields of CH_2O under space conditions was approached by first making an extensive literature search and reviewing all reported reactions, conditions, CH_2O yields, and catalysts used. The advantages and disadvantages of each method under spacecraft restraints were considered and used to select the specific route of CH_2O synthesis for a detailed experimental investigation.

Direct Reduction of Carbon Oxides to Formaldehyde

Because of its potential simplicity, the formation of CH_2O in a direct, one step gas phase reduction of CO_2 or CO by H_2 appeared readily adaptable to spacecraft usage. However, the formation of CH_2O from carbon oxides and H_2 is thermodynamically unfavorable. The free energies for these reactions, ΔF_r, are positive and become more positive with an increase in temperature, as indicated in Table 1. From thermodynamic data, Fischer (ref. 4) calculated the CH_2O yields from CO and H_2 obtainable at various temperatures and pressures as shown in Table 2. The equilibrium for a direct reduction of CO_2 by H_2 to CH_2O is still more unfavorable.

It has been proposed (ref. 5) that CH_2O is an intermediate in the formation of CH_3OH from CO_2 and H_2 under high pressures. Therefore, in the presence of H_2, CH_2O would become converted to CH_3OH. To avoid this, an extremely selective catalyst having high activity for CH_2O formation at low temperatures is required. Although solid catalysts such as Mn, Sn, Sb, Ni, Fe, Co, Cu, Pd, and Pt have been proposed in the literature and in patents, Neuman and Biljcevic (ref. 6) reinvestigating these claims could not find any of practical value.

The formation of CH_2O from CO and H_2 under silent electric discharge has been investigated previously (ref.7,8). It is known that electric discharges may enhance the reaction rates and, thus, bring the reactions to equilibrium, even at low temperatures. The reported yields of CH_2O are of the order of 0.3% based on the CO passed through the reactor (ref. 8); however, this value seems to be too high from the thermodynamic standpoint. An earlier investigation (ref. 7) indicated that besides CH_2O, some CO_2, saturated hydrocarbons, and unsaturated hydrocarbons are formed during the reaction of CO and H_2 under a silent electrical discharge condition.

The review of literature and thermodynamic considerations indicate that only negligible yields of CH_2O can be expected from a direct reduction of CO_2 (or CO) by H_2 under atmospheric pressure. Even if suitable catalysts could be found, the very high pressures needed to achieve practical CH_2O yields would make this reaction difficult to implement under spacecraft conditions.

TABLE 1

FREE ENERGIES OF CH_2O FORMATION FROM CO_2 AND CO

Reaction	ΔF_r, kcal/mole	
	298°K	1000°K
$CO_2 (g) + 4H_2 (g) \longrightarrow CH_2O (g) + H_2O (g)$	+13.4	+27.6
$CO (g) + H_2 (g) \longrightarrow CH_2O (g)$	+ 6.5	+26.9

TABLE 2

YIELDS OF FORMALDEHYDE FROM A DIRECT CO AND H_2 REACTION

[From ref. 4]

Temp., °K	Mol % CH_2O in Product		
	1 atm	100 atm	1000 atm
300	0.002	0.16	1.6
400	0.001	0.06	0.6
500	0.0005	0.01	0.3

Formaldehyde Synthesis with Methanol as an Intermediate

The CH_3OH route of CH_2O production is a two step operation where carbon oxides are first converted to CH_3OH and then CH_3OH is oxidized to CH_2O. The conversion of CH_3OH to CH_2O is a successful process and is being used extensively for commercial production of CH_2O (ref. 3). It involves passing CH_3OH vapor and air mixture over solid catalysts at essentially atmospheric pressure and absorbing the CH_2O formed in water scrubbers. The usual catalysts are silver, copper, or iron-molybdenum oxides. The reaction proceeds at 450°-600°C with yields of formaldehyde ranging from 83 to 92% of the CH_3OH reacted. The process, if run under suitable conditions, produces practically no side reactions, the only products being CH_2O, H_2O, and unreacted CH_3OH.

The investigation of the CH_3OH route was centered mainly on the second step, i.e. the formation of CH_3OH from CO_2 and H_2. The reaction of CO with H_2 has been studied extensively; however, literature on the reaction of CO_2 and H_2 to form CH_3OH is relatively scarce (ref. 9, 10, 11). The free energy of reaction of CH_3OH formation from carbon oxides is influenced both by temperature and pressure; high conversions to CH_3OH can be obtained at elevated pressures. For instance, a ZnO catalyst containing 0.25% Fe_2O_3 produces CH_3OH at 300-500°C and 200-210 atm; a Cu-Al_2O_3 catalyst gives best results at 285-400 atm pressures. Recently, a low pressure methanol process utilizing a copper-base catalyst and operating at about 50 atm and temperatures of 200-300°C was announced (ref. 12).

Both theoretical considerations and experimental evidence available in the literature indicated that the formation of CH_3OH directly from CO_2 or CO is impractical under atmospheric pressure at temperatures associated with presently used catalysts. Thermodynamic equilbrium calculations give a maximum conversion to CH_3OH of only 0.7% at 225°C considered to be the lowest practical operating temperature. The production of CH_3OH from CO_2 at atmospheric pressure would become thermodynamically possible only at temperatures below 100°C; however, the reaction velocities are too low at this temperature with presently available catalysts.

Formaldehyde Synthesis with Formic Acid as an Intermediate

In the production of CH_2O by the CHOOH route CO and H_2 are first converted to CHOOH which is then reduced to CH_2O. The thermodynamics for the reaction $CO_2 \text{ (g)} + H_2 \text{ (g)} \longrightarrow \text{CHOOH (g, or l)}$ are not well known; however, the free energy of reaction at 298°K is estimated to be $\Delta F_{298} = +11$ kcal and can be expected to become more positive with an increase in temperature (ref. 13). Several methods for the production of CHOOH from CO_2 and H_2 have been claimed: a) electrolytic reduction using a halogen acid electrolyte (ref.14), b) reduction of CO_2 by lithium borohydride in ether solution (ref. 15), c) reduction of CO_2 using a Raney nickel catalyst in liquid solution (ref. 16). Formic acid may be converted to CH_2O using a tin oxychloride catalyst (ref. 17). In view of the thermodynamics the overall process does not appear to offer a high potential yield. Also, the complexity and liquid-gas phase process conditions of the above mentioned claims do not provide the basic simplicity of system design and operation desired for spacecraft conditions.

Formaldehyde Synthesis with Methane as an Intermediate

The route of CH_2O production with CH_4 as an intermediate consists of two steps: the first step, the methanation of CO_2, is well known (ref. 2) and requires no further investigation. Using a ruthenium catalyst, up to 99% conversion of CO_2 to CH_4 can be obtained at moderate temperatures (190-200°C) and at atmospheric pressure. The problem, then, was one of finding suitable methods for the second step, the partial oxidation of CH_4 to CH_2O in acceptable yields.

The partial oxidation of CH_4 to CH_2O has been the subject of numerous investigations (ref. 3, 18, 19) using solid catalysts, gaseous catalysts, and various non-catalytic devices. The free energy of the reaction of methane oxidation to formaldehyde has a large negative value (ΔF_r = approx. -70kcal in the 25°C to 800°C temperature range) at atmospheric pressure. Therefore, thermodynamically, the reaction should proceed essentially to completion at all convenient temperatures; however, it has been shown (ref. 20) that the rate of CH_4 oxidation becomes appreciable only at temperatures above 600°C. At these temperatures, two problems arise and complicate the process of CH_2O production. One is that CH_2O becomes unstable and tends to decompose above 400°C; the other is that further oxidation of CH_2O to CO_2 takes place. A large part of the literature deals not so much with attempts to increase the rate of CH_2O production but with methods for preventing decomposition and further oxidation of the CH_2O formed. Because of these tendencies the reported CH_2O yields are relatively low, ranging from 2 to 4% of the CH_4 feed per pass, but these yields can be improved considerably by reusing the unreacted CH_4 and O_2 in a recycle system. In fact, a process has been described for CH_2O production, involving partial oxidation of CH_4, and reportedly is being used in the U.S.S.R. to produce 3000 tons/year of formaldehyde (ref. 21).

The $CO_2 \longrightarrow CH_4 \longrightarrow CH_2O$ system was selected for experimental laboratory investigation as the most suitable for spacecraft conditions and constraints. While CH_2O yields from CH_4 oxidation are not as high as those obtainable from oxidation of CH_3OH, the CH_4 route has the following advantages:

a) The entire process proceeds at atmospheric pressure in the gas phase using either solid or gaseous catalysts.

b) Since it operates at atmospheric pressure, the process requires no high pressure equipment entailing high power and weight.

c) The by-products are CO_2, CO, H_2O, and possibly H_2, which can be separated and reused.

d) Satisfactory over-all yields of CH_2O can be obtained with a recycle system.

METHANE OXIDATION

A comprehensive literature search was carried out and copies of articles and publications pertaining to the oxidation of CH_4 to CH_2O were obtained for detailed study and review. Efforts were made to secure as complete a collection as possible of publications on the subject. Over 90% of all U.S. and foreign articles and patents, mostly in their original languages, were obtained and evaluated. The remainder consisted of either obscure publications generally not available in the U.S., articles which seemed to have little pertinence, or repeat patents issued in various countries but covering the same subject. It is interesting that most of the articles on the oxidation of CH_4 to CH_2O have been published outside of the U.S., the early ones being mostly British or German, with the Russian publications accounting for more than one half of the published material after World War II.

Various processes utilize gaseous catalysts, alone or in conjunction with solid catalysts. The gaseous catalysts claimed include O_3, NO_2, NO, HNO_3, Cl_2, HCl, SO_2, and others; of these the most promising appeared to be ozone and nitric oxide. While single pass operation results in low CH_2O generation, recycling increases the overall CH_2O yield considerably. The Gutehoffnungshütte process, utilizing a gaseous NO catalyst, was reported in operation on a pilot plant scale in Rumania (ref. 22), with yields of about 9.7%. A similar process is being used in the U.S.S.R. producing 3000 tons/year of formaldehyde (ref. 21).

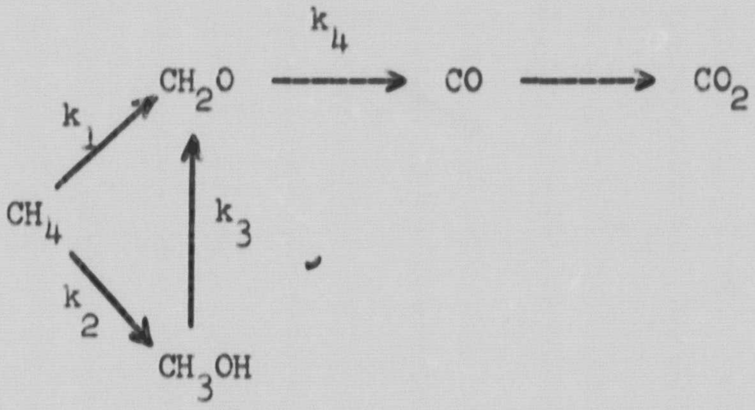
The most promising system appeared to be the so-called Hibernia process (refs. 22, 23) which utilizes a solid catalyst and ozonized oxygen or air. It was claimed that the process can convert up to 40% of the methane into formaldehyde. The claimed advantages of the process are high conversion to formaldehyde, low operating temperature (106°C), ease of removal of the unreacted ozone, if any, from the product, and the absence of by-products. However, there are reports (refs. 24, 25) indicating that the Hibernia process either does not work as claimed or cannot be repeated without additional information.

Most of the miscellaneous methods described for the production of formaldehyde have never achieved any significant success. Claims of formaldehyde production in the presence of an electric discharge may actually be due to catalytic action of nitrogen oxides or ozone formed in the gas mixture.

Gas Phase Oxidation

The partial oxidation of CH_4 to CH_2O has been studied by numerous investigators (refs. 3, 18, 19). The problem of gas-phase methane oxidation has been reviewed in detail and a reaction mechanism postulated by Semenov (refs. 26, 27) which establishes the overall process for going from CH_4 through oxygenated intermediates to the final oxidation product carbon dioxide. According to this mechanism, the oxidation of CH_4 is a degenerate, branched chain reaction where $OH\cdot$ and $HO_2\cdot$ are considered to be the chain carrying radicals; CH_2O and traces of methanol are the oxygenated intermediates. The $OH\cdot$ radical is believed to be the active radical (ref. 28). The $HO_2\cdot$ radical is converted, particularly on acidic surfaces, to H_2O_2 which changes to $OH\cdot$. Thus, it appears that conditions favoring the formation of $OH\cdot$ radical may provide the optimum CH_2O concentrations.

In a gas mixture containing CH_4 and O_2, chain carrying radicals can be produced by heating; however, their production is enhanced by the use of initiators such as an NO molecule. The steady state relationship during the oxidation of CH_4 may be represented by :



where $k_1 = 9k_2$, $k_2 = k_3$; and $k_4 = k_1 + k_3$ (ref. 29). A dynamic equilibrium is achieved where, as is typical for an intermediate, the concentration of CH_2O reaches a certain maximum level, depending on reaction conditions, after which further CH_2O formation serves only to increase overall oxidation to carbon oxides. Figure 1 is a qualitative representation of this behavior under varying conditions of temperature, initiator (NO) concentration, and residence time.

The best efficiency is achieved by operating at conditions which just approach the maximum CH_2O formation but do not go beyond it. There is indication (ref. 28) that at this point the ratio of CH_4 going to CH_2O to that oxidized further to carbon oxides is of the order of 40:60; various literature sources indicate that under these conditions the maximum yields of CH_2O reach 2-4% of CH_4 in the gas.

Although the general features of the mechanism for the oxidation of CH_4 are established, various problem areas remain unresolved. The theoretically calculated maximum rate of reaction depends on the second power of the CH_4 and on the first power of O_2 concentrations (ref. 27),

$$w_{max} = k\left[CH_4\right]^2\left[O_2\right]$$

However, the experimentally observed powers range from 0.4 to 2.3 for CH_4 and from 0.5 to 2.7 for O_2. Apparently this change of kinetic dependence on con-

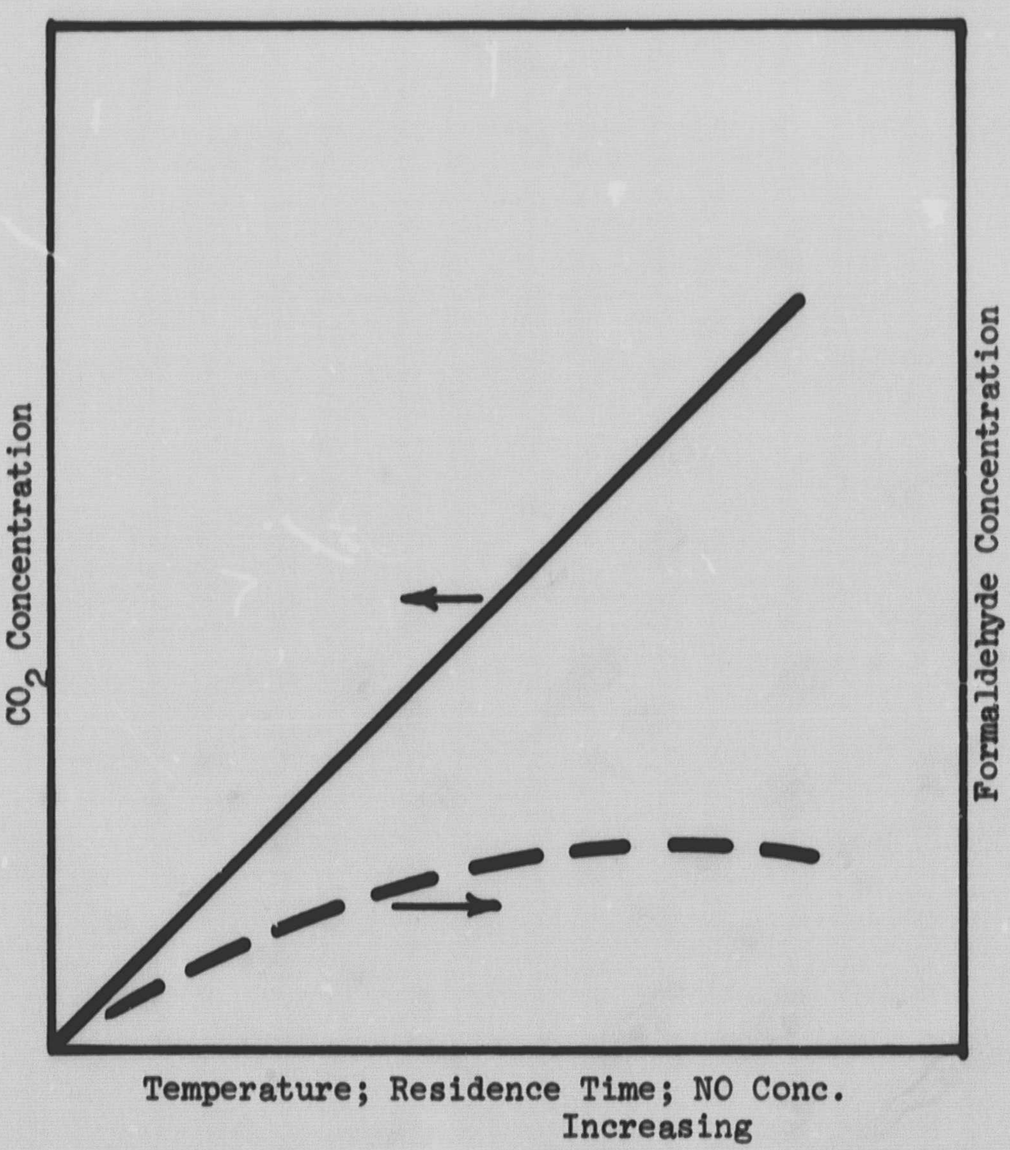


Figure 1. DEPENDENCY OF PRODUCT CH_2O-CO_2 RATIO ON CONDITIONS OF CH_4 OXIDATION

centrations is peculiar to degenerate, branched chain reactions and changes with the reaction temperature. Another problem affecting CH_2O yields is the chain lengeh, which is an indication of the probability of formaldehyde formation. Semenov (ref. 26) considers a chain length of 100, while the work of McConkey and Wilkinson (ref. 28) indicates a chain length for oxidation to CH_2O of approximately 10 and for complete oxidation between 15 and 30. Some results reported in German patent literature would indicate a chain length of several hundred; however, this is considered unlikely because of the simultaneous increase of the rate of attack on CH_2O by the radicals. The third problem is the degree of influence of CO on the course of reaction, since this may become significant in recycle systems where the CO concentration is expected to increase to high values. Apparently, the effect of CO depends on the CH_4 concentration (refs. 27, 28). In systems having low CH_4 concentration, the $OH\cdot$ and $HO_2\cdot$ radicals attack the CO molecule, oxidizing it to CO_2. However, at high CH_4 concentrations the probability of a collision between the radical and a CO molecule is minimized because the concentration of radicals is being reduced by an increased number of collisions with CH_4 which result in increased production of CH_2O.

Heterogeneous Catalytic Oxidation

In heterogeneous catalytic reactions, generally, old bonds are broken and new ones formed only by species chemisorbed on the catalyst surface. During the reaction there is competition among reactants, intermediates, and final products, for the active sites on the surface of a catalyst.

In heterogeneous catalytic oxidations of hydrocarbons such as CH_4, one of the difficulties encountered is the occurrence of unwanted consecutive reactions such as $CH_4 \longrightarrow CH_2O \longrightarrow CO_2$. A probable reason for this lies in the nature of CH_4 and of the desired end product, CH_2O. In hydrocarbon oxidation, products which can be obtained in high yields are those which possess a chemical stability comparable with that of the parent compound. The stability of CH_2O is very much lower than that of CH_4; CH_2O is unstable and decomposes thermally at 400°C which is where oxidation of CH_4 just begins to be appreciable. Another significant factor lies in the ease of chemisorption of CH_2O; it is chemisorbed more readily and with greater affinity than CH_4 on the usual oxidation catalysts. Based on these reasons, it has been anticipated that CH_2O formed during partial oxidation of CH_4 will be oxidized to carbon oxides more easily than the parent CH_4, and that a method for selectively arresting oxidation is required.

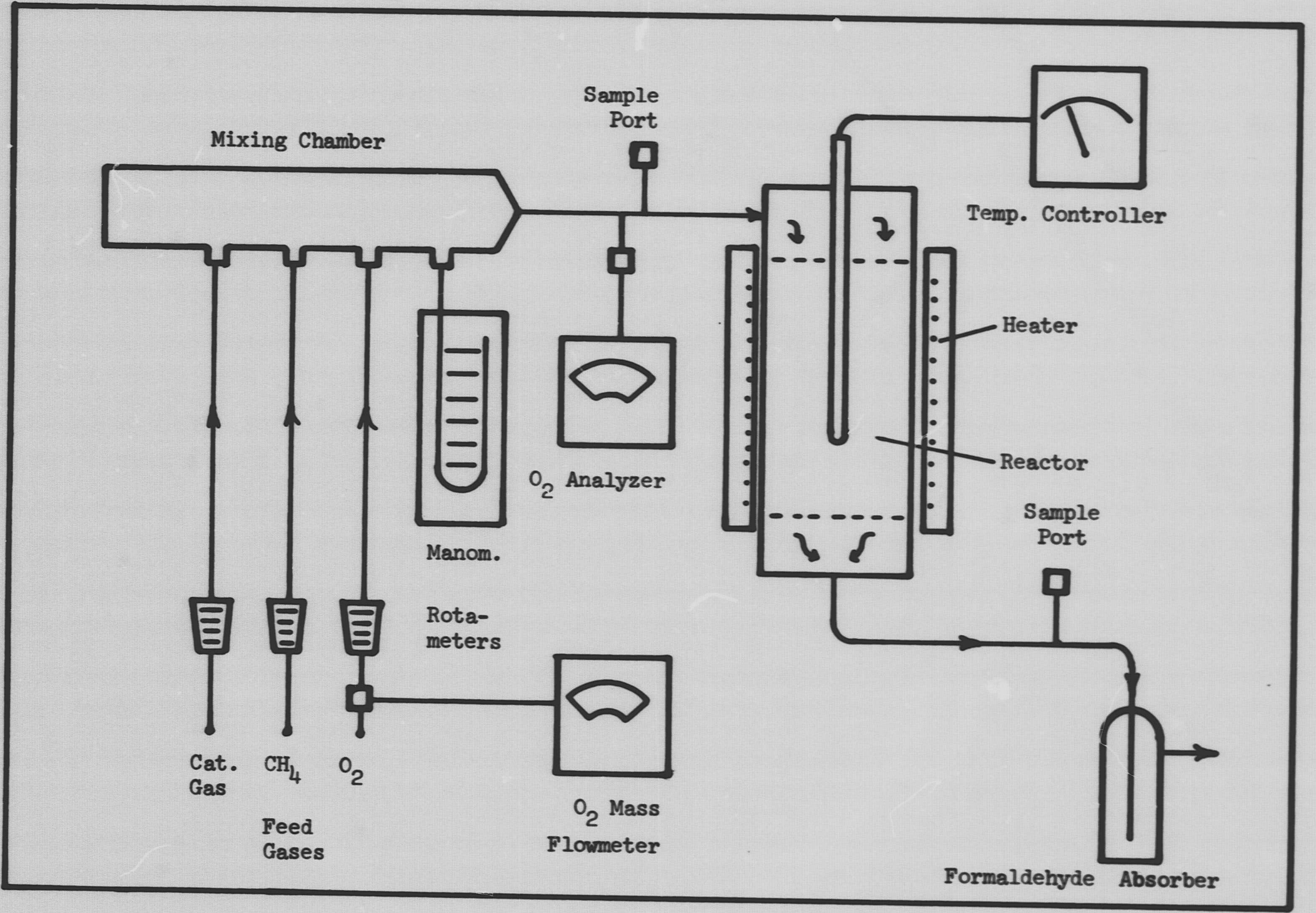
Attempts have been made by many investigators to obtain satisfactory yields of CH_2O by partial oxidation of CH_4 using various solid catalysts. Generally, results were poor, and whenever any success was reported, it seemed to depend not so much on a selection of a catalyst as on attendant experimental conditions, such as high space velocities, rapid cooling of the product, or catalyst configuration which apparently helped to prevent further oxidation of CH_2O formed.

SINGLE PASS REACTORS

All single pass experiments with both solid and gaseous catalysts were performed in a single-pass, flow type system shown schematically in Figure 2. Usually, the reactor consisted of a Vycor glass tube, approximately 18" long, with a one-inch inside diameter; although several experiments were performed using somewhat smaller or larger diameter tubes. A four-inch long reaction zone was heated to the desired temperature by an electric heater surrounding the Vycor tube. A movable thermocouple inserted into a well at the longitudinal center of the reaction tube permitted temperature measurement at various levels of the reaction zone. Since there were temperature gradients toward both ends of the reactor, the reaction temperature was measured at the hottest spot, which was approximately the center of the bed. When testing solid catalysts, a bed of known volume, usually 40 cc, was located at the center of the heated reaction zone.

Metered streams of CH_4 and either O_2 or air were premixed and fed into the reaction zone. The flow rates of each gas were measured with flowmeters which were periodically calibrated with absolute wet-test meters. Methane used was C.P. grade, while O_2 and air were high-purity grades.

Certain CH_4-O_2 and CH_4-air mixtures are explosive under the experimental conditions of this investigation. The reported flammability limits for CH_4-O_2 are 5.4% to 59% CH_4 and for CH_4-air mixtures 5.4% to 14% CH_4 (ref. 30). Therefore, all experiments were performed with gas mixtures containing CH_4 outside of these flammability limits. To avoid formation of gas mixtures which may become explosive, the O_2 concentration was monitored continuously by a Beckman polarographic oxygen analyzer.



. Figure 2. SINGLE PASS REACTOR SCHEMATIC

The reaction product was passed through a gas washing bottle containing a known amount of water where condensables such as CH_2O, CH_3OH, and H_2O vapor were absorbed. The amount of CH_2O formed was determined from analysis of the resulting solution. The results were expressed in percent yield of CH_2O, which was calculated as the number of moles of CH_2O formed divided by the number of moles of CH_4 fed into the system.

A complete analysis of the gas and of the condensables was conveniently achieved by gas chromatographic techniques using a thermal conductivity detector. Two parallel columns, both kept at 121°C, allowed a complete analysis. Separation of H_2, O_2, N_2, CH_4, and CO was obtained with a 5A Molecular Sieve column. A Porapak N column was used for separating CH_2O, H_2O, CH_3OH, and CHOOH collected in a water solution; the Porapak N also separated CO_2 from the other permanent gases.

All single pass tests were of either one or two hour duration. To facilitate the screening of solid catalysts, the concentration of formaldehyde collected in the gas wash bottle was determined by a colorimetric method using either a Nessler's or a modified Schiff reagent (ref. 3). Only runs producing CH_2O yields of approximately 0.1% or more were further considered and a complete analysis of the gas then performed.

Solid Catalysts

A listing of solid catalysts mentioned in the literature as being suitable for the partial oxidation of CH_4 to CH_2O was prepared. These catalysts were tested to determine their capacity for CH_2O formation, under essentially identical conditions. It was hoped that comparison of various materials would provide sufficient information to develop a form of classification indicating those catalyst properties which increase CH_2O production. All the solid catalysts tested gave low (under 0.1%) CH_2O yields, except etched SiO_3 (0.78%) and WO_3 (0.32%); this led to the conclusion that satisfactory yields of CH_2O cannot be expected from solid catalysts, and that no substantial behavior classification could be established.

A summary of the experimental results obtained with solid catalysts tested is given in Table 3; only the best result achieved with each catalyst is listed. The activity of each catalyst was tested at 425, 536, and 650°C using space velocities of 450 hr^{-1}, 900 hr^{-1}, and 1,200 hr^{-1}. Initially, the feed gas composition was varied from 95% O_2 and 5% CH_4 to 10% O_2 and 90% CH_4; however, most of the experiments were performed using a feed consisting of 47.50% O_2 and 52.5% CH_4. The most effective catalyst was found to be the etched walls of a Vycor glass tube, producing up to a 0.78% yield of CH_2O. Tungsten oxide was second giving up to 0.32% yields, while all other solid catalysts produced only very small yields of CH_2O. With the exception of silica, all other catalysts initiate complete oxidation of CH_4 at 536°C.

Ozonized Oxygen

Partial oxidation of CH_4 to CH_2O with ozonized O_2 by the so-called Hibernia process using activated barium peroxide in the reaction beds at 100-300°C was reported as producing up to 40% yields with coke oven gas, and up to 9.7% yields with pure CH_4 (refs. 22, 23). The catalyst bed consists of BaO_2 powder activated either by addition of 0.5% Ag_2O alone or with 1% Na_2O_2 deposited on unglazed procelain chips so that the resultant mass contains about 10% BaO_2 by weight.

TABLE 3

SUMMARY OF CH_2O PRODUCTION FROM CH_4 USING SOLID CATALYSTS

Active Ingredient	Catalyst Description[(a)]	Highest Yield[(b)] %	Remarks
Etched SiO_2	Etched wall of the Vycor reaction tube, 23 mm I.D., 4" long	.78	
Etched SiO_2	Same as #1; tube filled with 6 mm etched Vycor tubes	<.002	
Etched SiO_2	Same as #1; reaction zone filled with etched silica boiling chips	<.002	
Al	Al fluoride; H-Al-1101 T 1/4	Trace	
Ag	4% Ag on alumina; H-Ag-0101 E 1/8	Trace	
Ba	Ba fluoride; H-Ba-0201 T 1/8	0.05	
Cu	CuO; H-Cu-0307 T 1/8	.12	
Co	39% Co on kieselguhr; Co-0108 T 1/8	<.002	Stable temp. impossible.
Cr	Cr oxide ($Cr^{(vi-iv}$) on activated alumina; CERLOX catalyst	<.02	Stable temperature cannot be maintained
Cr	Chrome Alumina, 33% Cr_2O_3; H-Cr-0304 T 1/8	0	Stable temperature impossible above 425°C.
Fe	20% Fe_2O_3 on alumina; H-Fe-0301 T 1/8	0	Stable temp. difficult to maintain above 370°C.
MnO_2	19% MnO_2 on activated alumina; H-Mn-0201 T 1/8	<.002	
Mo	10% MoO_3 on high activity alumina; G-Mo-1201 T 1/8	<.02	
Ni	15% Ni in oxide form on activated alumina; H-Ni-0302 T 1/8	<.002	Flashing. Temp. control impossible.

TABLE 3. - Continued

SUMMARY OF CH_2O PRODUCTION FROM CH_4 USING SOLID CATALYSTS

Active Ingredient	Catalyst Description (a)	Highest Yield (b) %	Remarks
Pt	Platinum oxide on alumina, 0.1% Pt; G-T-309	<.004	Temp. runaway above 316°C
Ti	86% TiO_2 with alumina; H-Ti-0102 T 1/8	<.04	Temp. control difficult above 425°C
V	10% V_2O_3 on inert alumina; H-V-0501 S 1/4	<.03	
V	10% V_2O_3 on high activity alumina; H-V-0601 T 1/8	<.02	
V	10% V_2O_3 on silica-alumina; H-V-0701 T 1/8	0	Temp. control difficult above 316°C
W	10% Wo_3 on activated alumina; H-W-0101 T 1/8	.32	Flashing when 587°C is reached
W	95% WO_3; H-W-0602 T 1/8	.1	Temperature control problems
Zn	24% Zn oxide on activated alumina; H-Zn-0701 T 1/8	<.002	Temperature control very difficult
$Na_2B_4O_7$	Sod. tetraborate on porcelain	Trace	
BaO_2	10% BaO_2, 1% Na_2O_2, 0.5% Ag_2O on porcelain	0	
Co-Cu	5% of Co+5% Cu as oxides on alumina; H-Co-0901 T 1/8	<.004	Local overheatings

TABLE 3. - Concluded

SUMMARY OF CH_2O PRODUCTION FROM CH_4 USING SOLID CATALYSTS

Active Ingrdient	Catalyst Description [(a)]	Highest Yield [(b)]	Remarks
Cr oxide	Cr^{vi-iv} oxides, Ba oxide, Ba chromates on activated alumina; CERLOX 8615 catalyst	<.02	Stable temp. cannot be maintained
Ni-W	6% Ni, 19% W sulfided on alumina; H-Ni-4303 E 1/12	<.02	

(a) Prefixes H and G indicate Harshaw and Girdler catalysts, respectively, followed by catalog number. All others, catalysts prepared in this laboratory.

(b) Yield = Moles of CH_2O formed/moles of CH_4 in feed.

A series of experiments was performed to ascertain the workability of the Hibernia process and investigate other possible catalysts using ozonized O_2. The ozone (O_3) was generated by Type O3Cl ozonator manufactured by the Ozone Research and Equipment Corp., Phoenix, Arizona. This ozonator employs a high voltage silent discharge and is capable of converting up to 4-5 volume % of the O_2 to O_3. The concentrations of O_3 in gas were determined by standard iodometric titrations.

BaO_2 Catalyst. - The BaO_2 catalyst was prepared following the Hibernia process description by mixing dry powder materials to give a mixture containing 98.5% BaO_2, 1% Na_2O_2, and 0.5% Ag_2O by weight. This material was tested in the following configurations:

1. Catalyst powder was mixed intimately with a fine porcelain powder in a 1:10 weight ratio and pressed into 1/4" tablets.
2. Porcelain chips were slightly moistened and sprayed with a light coating of the catalyst powder, providing a minimal thickness of catalyst.
3. Moistened porcelain chips were mixed with the catalyst powder so that the final product consisted of porcelain chips coated with a thick coating of the catalyst powder.
4. Pure catalyst powder was supported in a fused silica boat.

Since extensive investigation using BaO_2 made in the U.S.A. gave meager CH_2O yields, a BaO_2 sample was obtained from Remy and Company, Hamburg, Germany. Two catalysts were prepared from this German made BaO_2 and tested: a) finely ground BaO_2 powder was deposited on moistened porcelain Berl saddles, b) a blend consisting of 98.5 wt. % BaO_2, 1 wt % Na_2O_2, and 0.5 wt % of Ag_2O was deposited on silica wool.

A large number of tests were performed with the BaO_2 catalyst using feed mixtures containing 53% CH_4 and 47% ozonized O_2. The temperature of these tests ranged from 95°C to 535°C and the flow rates of the feed gas mixture were varied from space velocities of 9 hr^{-1} to space velocities of 3600 hr^{-1}. The ozone concentrations ranged from o.05% to 1.4% by volume of the feed.

In spite of numerous attempts and variations in the experimental conditions, and in the preparation of the reactor bed material, high CH_2O yields claimed by German patents could not be repeated. In most of the experiments only traces of CH_2O were produced; the best yields obtained were meager, reaching only up to 0.3% of the CH_4 input. Other investigators (refs. 24, 25) who tried to verify the Hibernia process also failed to obtain any significant amounts of CH_2O.

Other catalysts. - Direct oxidation of CH_4 with O_3 does not produce CH_2O (ref. 31); therefore, any promoting effect exercised by O_3 is either in the activation of a solid catalyst or in initiation of radicals for possible chain reaction of the CH_4 oxidation. The Hibernia process, although impossible to verify, seems to be based on the activation of BaO_2 catalyst by O_3. Two other reaction beds, porcelain pellets coated with alkali borates and boron nitride chips, which gave fairly good results with other chain initiators (such as NO described in the next section) have been tried and gave results which were considerably better than those obtained with BaO_2 beds.

Partial oxidation of CH_4 to CH_2O in the presence of porcelain Berl saddles coated with alkali borates was investigated in the temperature range of 315°C-705°C, with air-CH_4 mixtures containing from 17% to 40% CH_4, and at space velocities ranging up to 7500 hr^{-1}. Maximum CH_2O production was obtained at temperatures of 650-705°C. At these temperatures, the yields of CH_2O depend on the ozone concentration in the feed gas; for instance, with 30% methane and 0.1% O_3 in feed, the observed yields are approximately 0.4%; with 0.3% O_3, yields increase to 0.8%; and with 0.6% O_3 yields reach 1.1% of the CH_4 feed.

Under given conditions, the highest CH_2O yields were observed at low CH_4 concentrations in the feed gas. Figure 3 shows CH_2O yields obtained at a reaction temperature of 705°C, a space velocity of 7500 hr^{-1}, and a 0.4 % O_3 concentration in the feed gas. When ozonized O_2-CH_4 feed is used instead of ozonized air-CH_4, the CH_2O yields obtained are somewhat lower. For instance, at up to 705°C and 1% O_3, the yield of CH_2O is only 0.5%. Because of the need to operate outside of the explosive range, the O_2-CH_4 feed must contain at least 53-60% CH_4. Thus, the lowering of CH_2O yield can be attributed to a high CH_4 concentration.

A bed of boron nitride chips was tested at 698°C and space velocities ranging from 8000 hr^{-1} to 10,000 hr^{-1} using a mixture of CH_4, O_2, and air as a feed. The feed gas consisted of 20-30% CH_4 and 15-30% O_2, with the remainder being N_2; the ozone concentration was 0.28-0.35%. The observed CH_2O yields ranged from 0.76 to 0.90% of the input CH_4.

When air is passed through the ozonator, some nitrogen oxides are formed. Analysis of these nitrogen oxides is difficult because O_3 interferes with the analytical methods. Nevertheless, it was established that the concentrations of NO formed in the ozonator are in the neighborhood of 100 ppm, but that they have no significant effect on the CH_2O yields.

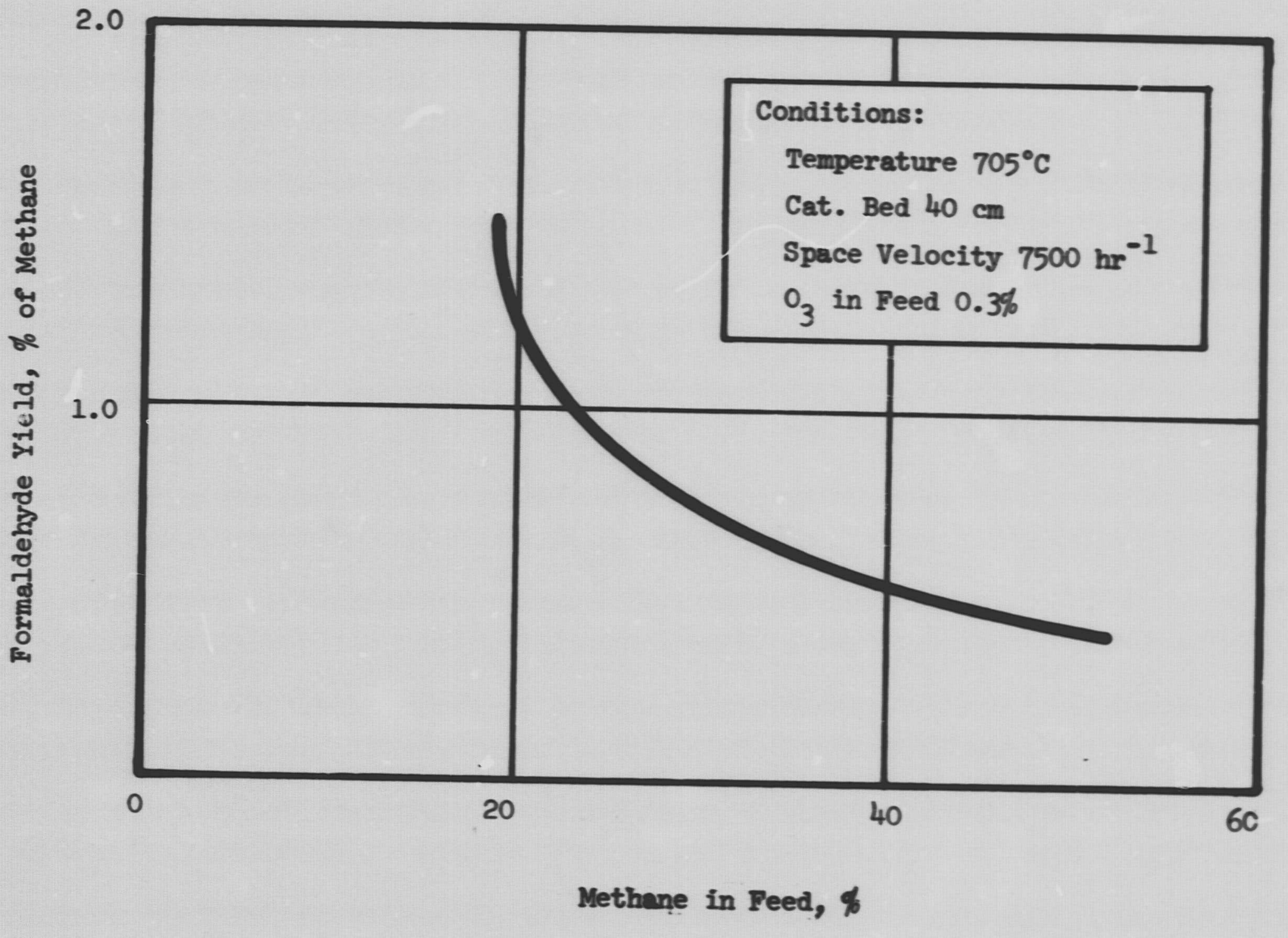


Figure 3. SINGLE PASS YIELDS OF CH_2O WITH O_3 AND ALKALI TETRABORATE BED

Nitric Oxide Gaseous Catalyst

The use of nitrogen oxides as homogeneous gas phase catalysts for the partial oxidation of CH_4 to CH_2O has been reported by several investigators, primarily Germans and Russians (refs. 3, 18, 19, 26, 27). Generally, the reported yields of CH_2O based on CH_4 in the feed gas are low and range from about 1% to 2.8% in single pass reactors. The total yield can be increased by employing either several reactors connected in series or a recirculating system. Enikolopyan et al (ref. 32) have obtained yields of CH_2O reaching 7.4% of CH_4 in the feed using three consecutive reactors and up to 18.5% in a recirculating system, with an 8-fold recycling of the gases. A German patent issued to Gutehoffnugshütte (ref. 33) claims a 65% yield of CH_2O using a 28 fold recirculation of the gas mixture.

There is no universal agreement on the best feed gas composition or the reaction temperature. The reported feed gas compositions range from CH_4-air ratios of 3.7:1 to 1:3 and CH_4-oxygen ratios of 3:1 to 1:1. The best reaction temperatures reported in the literature range from 380°C to about 650°C. Most of the reports, however, agree that nitric oxide concentrations of 0.08-0.25% are sufficient to produce good yields of CH_2O. Although some processes use empty heated reaction vessels, there seems to be sufficient indication that when the reaction zone is packed with supports coated with alkali tetraborates, the reaction becomes more reproducible and results in higher CH_2O yields.

The use of NO as a homogeneous gas phase catalyst for the partial oxidation of CH_4 to CH_2O was investigated using single pass reactors having reaction zones packed with 6 mm porcelain Berl saddles coated with potassium or sodium tetraborate. Activated alumina, silica gel, high surface silica boiling chips, and Tamer tabs boiling stones were tested as support materials for the alkali tetraborate but were found to give lower results than porcelain Berl saddles. Both O_2-CH_4 and air-CH_4 feed mixtures were investigated to find the optimum experimental conditions giving not only the maximum CH_2O yields based on CH_4 in feed, but also the highest mass production of CH_2O.

Oxygen-CH_4 feeds. - The dependence of CH_2O yields on the feed gas composition has been investigated by using feed gases containing 5%, 53%, 66%, 80%, and 90% CH_4, the remainder being O_2. Since O_2-CH_4 mixtures containing 5%-35% CH_4 are explosive, this composition range was not investigated. Runs were obtained at a temperature range of 540°C-620°C and space velocities ranging from 2200 hr^{-1} to 3750 hr^{-1}. Under these conditions, the highest CH_2O yields were obtained at 620°C, and this was the highest temperature at which the reaction zone could be safely maintained. A further increase in the reaction temperature caused a sudden increase in the formation of CO and CO_2 to concentrations reaching 50% of the product, with accompanying release of heat and runaway temperatures. In general, the reproducibility of results, was poor with O_2-CH_4 mixtures; however, the averages of several runs clearly indicate the trends of product composition.

Average values of CH_2O yields obtained at the best temperature (620°C) and space velocity (3750 hr^{-1}) are depicted in Figure 4 which illustrates the dependency of CH_2O yields on CH_4 concentration.

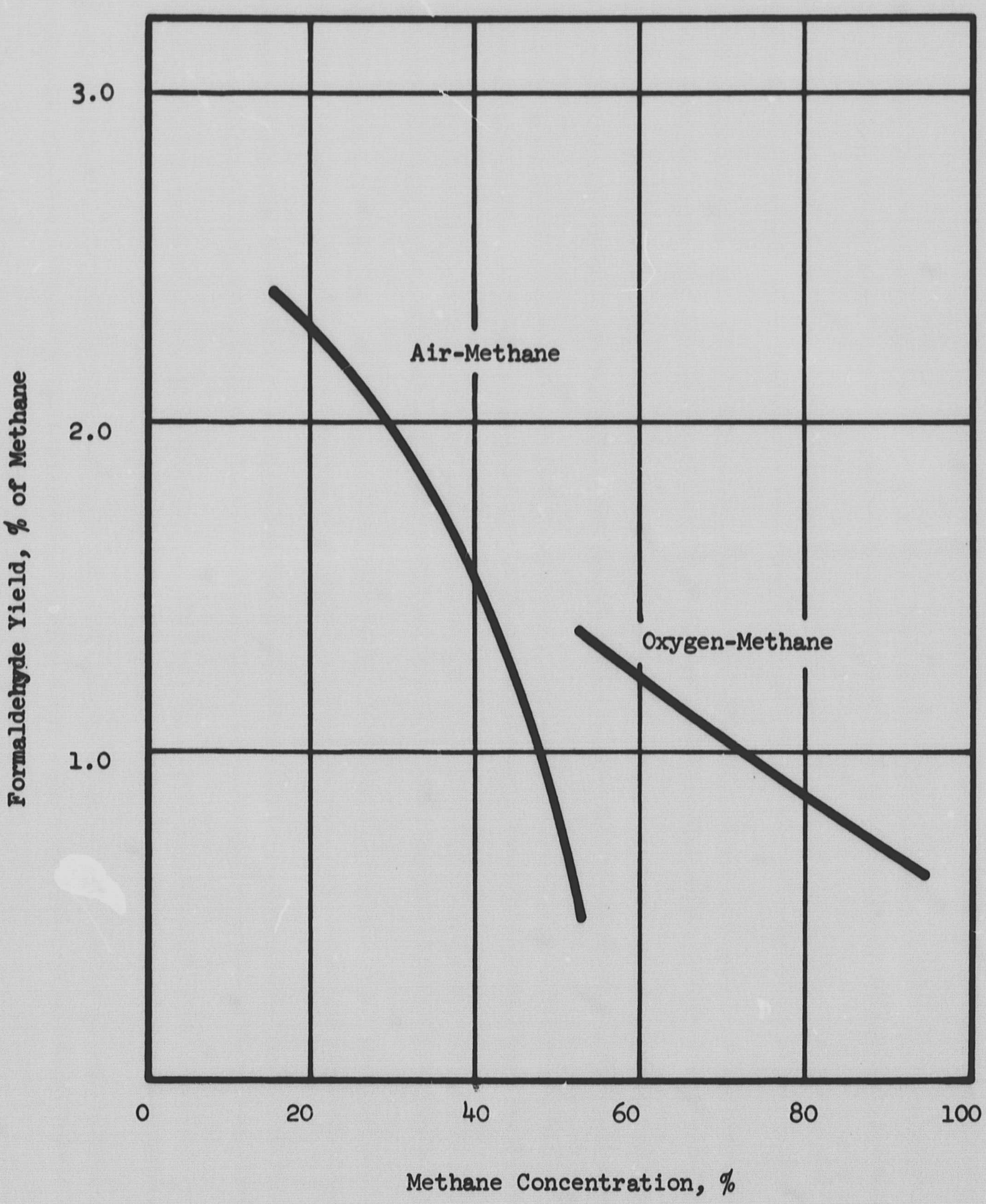


Figure 4. DEPENDENCY OF CH_2O YIELDS ON CH_4 CONCENTRATION WITH NO CATALYST

Air-CH_4 feeds. - The dependence of CH_2O yields on feed gas composition, reaction temperature, and space velocity was investigated with air-CH_4 mixtures. The NO concentration was 0.2% by volume in all the experiments. Data were obtained using feed gas containing 20%, 30%, 40%, and 50% CH_4 in the temperature range of 594°C-705°C, and space velocities ranging from 2250 up to 7500 hr^{-1}. The explosive range of air-mehtane mixtures lies between 5% and 14% CH_4; therefore, compositions below 20% CH_4 were not investigated.

The average CH_2O yields obtained at various temperatures, space velocities and CH_4 concentrations are summarized in Figure 5. The CH_2O yield depends on the space velocities at temperatures 594°C and 621°C; however, at 650°C and higher temperatures, the CH_2O yield appears to be independent of space velocities in the range investigated. These results indicate that the yield of formaldehyde does not increase when temperatures higher than 678°C are used. The yield of CH_2O decreases with an increase in CH_4 concentration in the feed gas, as illustrated in Figure 4.

Numerous experiments indicated that a more controlled operation was achieved with air-CH_4 than with O_2-CH_4 feed, i.e. with an inert diluent in the reaction gas. Better temperature control, lower conversion to carbon oxides, and much less chance of ignition or explosion have been experienced with air-CH_4 mixtures as compared with O_2-CH_4 mixtures. Since operation of a recycling system was expected to cause a build-up of carbon oxides in the recirculating gas, tests were made to determine to what extent the yield of CH_2O would be influenced if N_2 were replaced by CO_2. Single pass experiments were performed using a feed gas consisting of a mixture containing 30% CH_4, 14.7% O_2, 55.3% CO_2, and 0.2% NO. This mixture has the same concentrations of O_2 and CH_4 as that of 30% CH_4 in air, except the N_2 is replaced by CO_2. It was found that

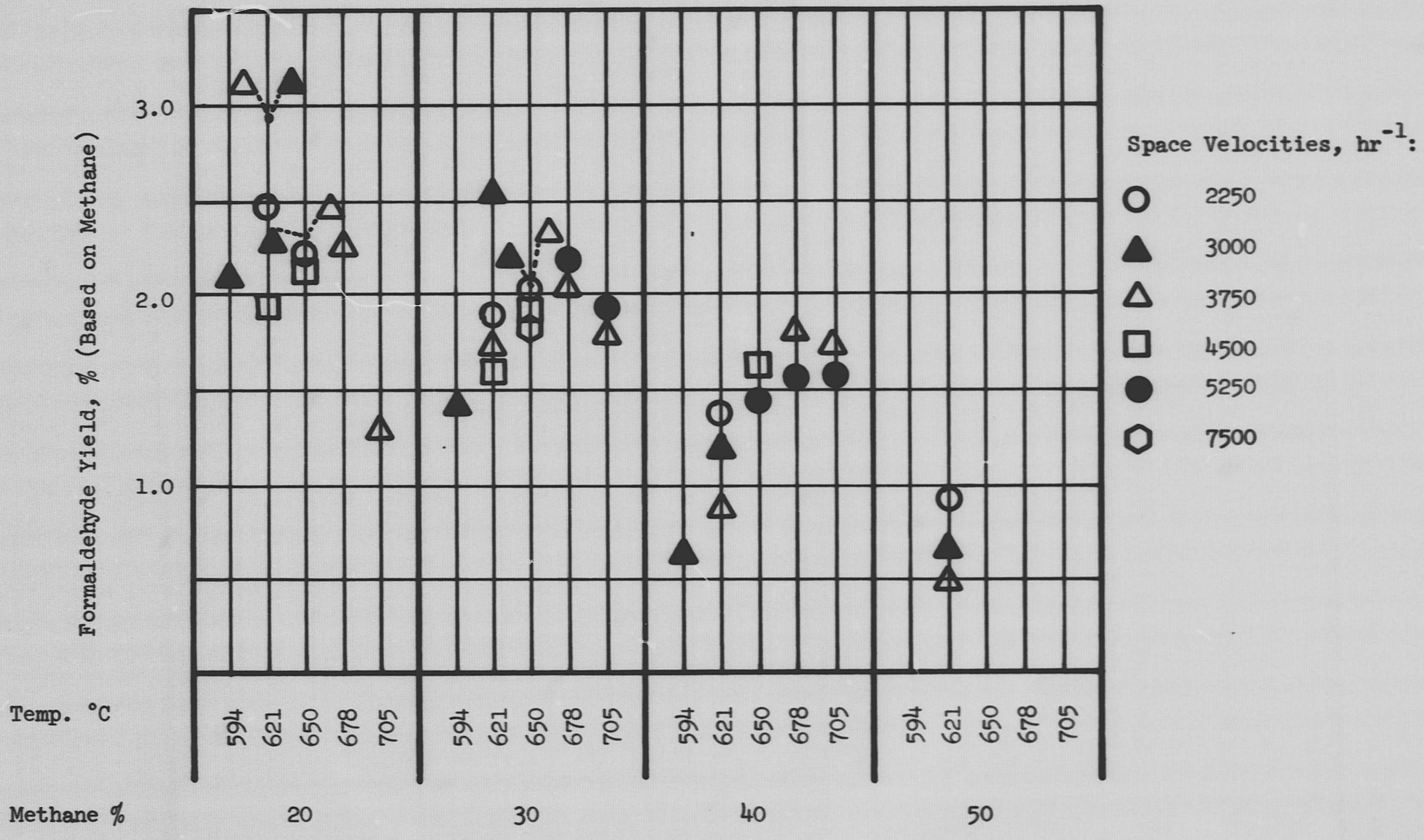


Figure 5. SUMMARY OF CH_2O YIELDS WITH NO CATALYST AND AIR-CH_4 FEEDS

CO_2 does not inhibit the formation of CH_2O and the replacement of diluent N_2 by CO_2 did not change CH_2O yields. For example, a run conducted with a CH_4-O_2-CO_2 mixture at 610°C and space velocity of 5250 hr^{-1} produced a 2.2% yield of CH_2O, while an air-30% CH_4 feed under the same conditions gave a 2.1% yield.

Analysis of total nitrogen oxides ($NO + NO_2$) in the feed gas and in the product gas indicated that there was no measurable loss of NO_x during the CH_4 oxidation in a single pass reactor.

Reaction beds other than alkali tetraborate. - Besides alkali tetraborates, several other reaction beds were tested in conjunction with NO gaseous catalysts. These beds were selected because of their reported beneficial effects in chain reactions associated mainly with minimizing over-oxidation to carbon oxides. Sodium silicate was reported effective in producing high CH_2O yields, ranging from 1.3 to 4.3% of CH_4 per pass in a recycle system (ref. 34); however, these claims appear to be refuted on theoretical grounds (ref. 28).

Experimental results with several reaction beds tested are summarized in Table 4; the results show that none of these approached or surpassed the yields of CH_2O obtainable with alkali tetraborate beds, with the exception of boron nitride which gave excessive CO.

TABLE 4

YIELDS OF FORMALDEHYDE OBTAINED WITH VARIOUS REACTION BEDS AND NO CATALYST

Reaction Bed	Temp. Range, °C	Yield of CH_2O, %	Remarks
$AlPO_4$ pellets	540	0.22	Product contains 0.2% CO_2 and 0.8% CO.
KNO_3 on silica-alumina	650	0.67	Product contains 0.9% CO_2 and 1.6% CO.
KNO_3 on porcelain Berl saddles	650-705	1.3-1.5	Product contains no CO_2 and 0.1-0.3 CO.
Na_3SiO_3 on porcelain	400-705	up to 0.7	Product contains up to 0.2% CO_2, 0.2% CO
BN pellets	650	2.2	Product contains 0.2% CO and 4.4% CO_2.

RECYCLE SYSTEMS

Single pass experiments demonstrated that significant yields of CH_2O can be obtained only with O_3 and NO initiators used in conjunction with solid beds. The CH_2O yields amounted to only 1.0-2.5% of the CH_4 feed; this was too low for a practical CH_2O production system. Only a small portion of the reactants is used up per pass; consequently, the total yield could be increased by recycling the unreacted gas mixture.

Recycle experiments were performed with the same reactor configuration used in single pass tests. However, after removing product CH_2O and H_2O, the remaining gases were continuously returned by a pump to the intake of the reactor. Make-up feed gases were added to the recycle system in proportions required to maintain the composition desired for feed to the reactor. A portion of the recycle gas was vented downstream of the CH_2O separator to maintain constant system pressure. Normally, the recycle system was operated at temperatures, catalyst gas concentrations, and reactor inlet gas compositions giving the maximum CH_2O production. The recycle gas flow was maintained at 5000 cc/min, equivalent to a space velocity of 7500 hr^{-1}; the recycle ratio, defined as the volumetric ratio of recycle gas flow to feed gas flow, was varied by changing the feed gas flow.

Recycle System Using Ozone

In these experiments, O_2-CH_4, air-CH_4, and O_2-CH_4-diluent (N_2 or CO_2) mixtures were investigated. Oxygen or air were passed through an ozonator and then mixed with the other feed gases prior to entering the reactor. Since O_3 is completely decomposed in the reaction zone, the entire amount of O_3 required to maintain its concentration must be supplied with the feed. It was found that a 0.05%-0.06% concentration of O_3 in the recycle gas is required to obtain significant CH_2O yields. The capacity of the ozonator imposed a limit on the recycle ratio and CH_2O yield obtainable with the system. A feed gas mixture of 40% O_2-60% CH_4 was required to maintain gas entering the reactor at the proper composition of 30% O_2, 60% CH_4, and 10% carbon oxides. With air-CH_4, or O_2-CH_4-CO_2 mixtures, the feed gas mixture contained 31% CH_4 and 14% O_2 which was sufficient to maintain the gas entering the reactor at the proper composition of 12% O_2 and 28% CH_4.

The results of recycle experiments conducted at 705°C with a reaction bed of porcelain Berl saddles coated with sodium borate are summarized in Table 5. CH_2O yield was low with both O_2-CH_4 and air-CH_4 mixtures.

Recycle experiments with a boron nitride reaction bed at 705°C are summarized in Table 6. The CH_2O yield increased with the recycle ratio and reached up to 15.2% at a recycle ratio of 20, with an average yield of 0.62% per pass. The capacity of the ozonator to produce only 4% O_3 in O_2 imposed an upper limit of 20 on the recycle ratios; an ozonator able to produce higher amounts of O_3 in oxygen would allow higher recycle ratios and corresponding higher CH_2O yields.

To determine the feasibility of producing ozone directly in CH_4-O_2 mixtures, gas streams of various composition were passed through a small, air-cooled ozonator; the percent of O_3 produced was determined by iodometric titration. Gases were passed through the ozonator at an average temperature of 0°C with the primary input kept at 90 volts resulting in 12,000 volt potential across the ozonator. The amounts of O_3 produced under various flow conditions

TABLE 5

YIELDS OF FORMALDEHYDE OBTAINED WITH SODIUM BORATE BED AND O_3 IN A RECYCLE SYSTEM

Feed Mixture	Recycle Flow, cc/min	Recycle Ratio	O_3 In System, %	CH_2O Yield, %	
				Total	Per Pass
Oxygen-Methane	5000	5	.31	2.1	.42
" "	5000	5	.21	1.6	.30
" "	5000	5	.29	1.3	.26
" "	5000	10	.15	1.7	.17
" "	5000	20	.08	3.0	.15
Air-Methane	5000	5	.17	2.5	.45
" "	5000	12	.14	2.8	.23
" "	5000	20	.09	4.5	.22

TABLE 6

YIELDS OF FORMALDEHYDE OBTAINED WITH BORON NITRIDE BED AND O_3 IN A RECYCLE SYSTEM

Feed Mixture	Recycle Flow, cc/min	Recycle Ratio	O_3 in System, %	CH_2O Yield, %	
				Total	Per Pass
Oxygen-Methane	5000	10	.16	7.6	.76
" "	5000	20	.06	10.0	.50
" "	5000	20	.06	12.4	.62
" "	5000	20	.08	11.9	.60
" "	5000	20	.09	9.9	.50
" "	5000	20	.09	8.8	.44
" "	5000	20	.09	11.9	.60
Oxygen-Methane-Nitrogen	5000	20	.08	13.5	.68
Oxygen-Methane-CO_2	5000	20	.07	15.2	.76
" " "	5000	20	.06	14.1	.71
" " "	5000	20	.06	12.8	.64

and with different gas mixtures are given in Table 7. These results indicate that the presence of large fractions of CH_4 decreased the ozone production sharply; however, mixtures containing up to 4% CH_4 produced sufficient amounts of ozone for use in the recycle system.

Small amounts of CH_2O, equivalent to yields of 0.04-0.08%, were produced directly in the ozonator with a 40% O_2-60% CH_4 mixture. In one test the product was analyzed for carbon oxides. There were no detectable amounts of CO_2, but the CO concentration was approximately 0.2% of the product gas. The high ratio of CO to CH_2O precluded further investigation of CH_2O generation in this manner.

A mixture of 95% O_2-5% CH_4 was passed through the ozonator at a rate of 500cc/min. The product gas was then passed directly through a reactor containing 40 cc of porcelain Berl saddles coated with potassium tetraborate maintained at 650°C; the CH_2O yield obtained was 0.8%. Therefore, it appeared possible that O_2-CH_4 mixtures containing a low percent of CH_4 could be recycled directly through an ozonator and catalytic reactor; however, the absolute amount of CH_2O formed would be small.

Recycle System Using Nitric Oxide

Experiments were conducted normally at 678°C and at a recycle gas velocity of 5000 cc/min using reaction beds made of porcelain Berl saddles coated with sodium borate. The recycle ratio (recycle gas rate/feed rate) was varied by changing the feed rate. The NO concentration in the recycle gas was maintained at approximately 0.2%. The concentration of CH_4 in the recycle gas varied from 15 to 30%; however, in most of the tests it was in the 20-25% range. The CH_2O yields obtained in the recycle tests are summarized in Table 8. This table shows that the total CH_2O yield increased with increasing recycle

TABLE 7

O_3 FORMATION IN THE PRESENCE OF CH_4

Gas Mixture	Flow, cc/min	O_3, %
O_2	500	1.2
O_2	1000	0.6-0.7
Air	500	0.75
Air	1000	0.33
98% O_2, 2% CH_4	500	1.14
96% O_2, 4% CH_4	500	1.16
40% O_2, 60% CH_4	500	0.01-0.06
80% Air, 20% CH_4	500	0.10

TABLE 8

PRODUCTION OF CH_2O IN A RECYCLE SYSTEM USING NO CATALYST(a)

Recycle Ratio	No. of Tests	CH_2O Yield	
		Total, %	Per Pass, %
4	10	5.75	1.44
5.5	3	7.32	1.33
8.0	3	9.38	1.17
10	12	10.9	1.09
16	1	12.8	0.8
17	13	15.0	0.88
19	15	20.3	1.07
20	8	15.2	0.76
21	3	21.5	1.02
25	53	23.3	.93
25	7	26.9	1.07
30	1	28.9	1.96

a. All tests at 678°C; recycling gas flow 5000 cc/min.

ratio, while the yield per pass decreased reaching an assymptotic limit of approximately 0.9-1.0% per pass. Because the CO concentration in the recycle gas increased with recycle ratio, it seemed that the CH_2O yield per pass had a direct, nearly linear relationship to the CO concentration. However, in tests where CO was removed from the system no increase in CH_2O yield occurred.

A series of tests was performed, all at a recycle ratio of 25, where the concentrations of CH_4 and O_2 were varied to determine the composition of the recycle gas which would result in the highest total CH_2O yield, and which would give the lowest $CO + CO_2$ concentrations. Oxygen concentrations in the range of 5-15% seemed to have no influence on the yield of CH_2O, while an increase in CH_4 concentration showed a small effect, with best overall yields occurring at approximately 30% CH_4 in the recycle gas. This agreed with observations in single pass experiments where the highest production of CH_2O was obtained with gases containing 30-35% CH_4. Both CH_4 and O_2 concentrations influenced the formation of carbon oxides, $CO + CO_2$. Low concentrations of CH_4 and high concentrations of O_2 increased the formation of carbon oxides. It was found experimentally that when the concentration of oxygen in the gas increased to above 9%, the formation of carbon oxides, particularly CO_2, also increased significantly.

The best utilization of reactants in these series was obtained with a recycle gas containing 29% CH_4, and 7% O_2 by volume. At a recycle ratio of 25, the average CH_2O yield was 26.9%; an additional 17.0% CH_4 was converted to CO and 6.5% to CO_2. The ratio of CH_2O to carbon oxides was about 27:23. A ratio of 40:60 has been reported in the literature (ref. 28). It appears that while the total CH_2O yield can be increased by an increase in the recycle ratio and the utilization of CH_4 and O_2 improved by adjusting their concentrations, only up to 50% of the CH_4 feed can be converted to CH_2O, with the remaining amount going to carbon oxides.

SYNTHESIS OF CH_2O FROM CO_2 AND H_2

The recycle system utilizing NO gaseous catalyst converted 25-30% of the CH_4 feed into CH_2O, but also converted another 25% to carbon oxides. The gases vented from the recycle system after CH_2O and H_2O separation consisted mainly of unreacted CH_4, O_2, and carbon oxides. These gases were returned to the feed line entering a Sabatier reactor, in which additional feed CO_2 and the by-product carbon oxides were reduced by H_2 back to CH_4. In this manner, a completely closed, integrated system was achieved which operated to convert feed CO_2, H_2 and O_2 into only CH_2O and H_2O. A schematic of the integrated system is shown in Figure 6.

Partial oxidation of CH_4 was achieved in the main recycle system, in a reactor filled with 40 cc of porcelain particles coated with alkali borates and maintained at 675°C. The reaction products leaving the reactor were cooled and passed through a separator where CH_2O and H_2O were removed. The gas mixture, freed from CH_2O and H_2O, was recycled at a rate of 5000 cc/min at essentially atmospheric pressure. A portion of the recycle gas was vented and passed through the Sabatier methanator where CO_2 and CO were reduced to CH_4 for return to the main recycle loop. The recycle ratio was maintained at 25 by holding the combined flow rate of the feed O_2 and the gas mixture leaving the methanator at 1/25 of the recycle flow.

The methanation reactor consisted of a 40cc bed of nickel on kieselguhr catalyst pellets maintained at 250-320°C. At the low space velocity of approximately 500 hr^{-1}, it was capable of over 99% conversion of carbon oxides to CH_4.

The gas composition in the main recycle loop was maintained at approximately 30% CH_4, 7% O_2, 0.2% NO, the remainder being mostly CO_2 with some CO and small concentrations of N_2 and H_2. To maintain the desired concentrations with-

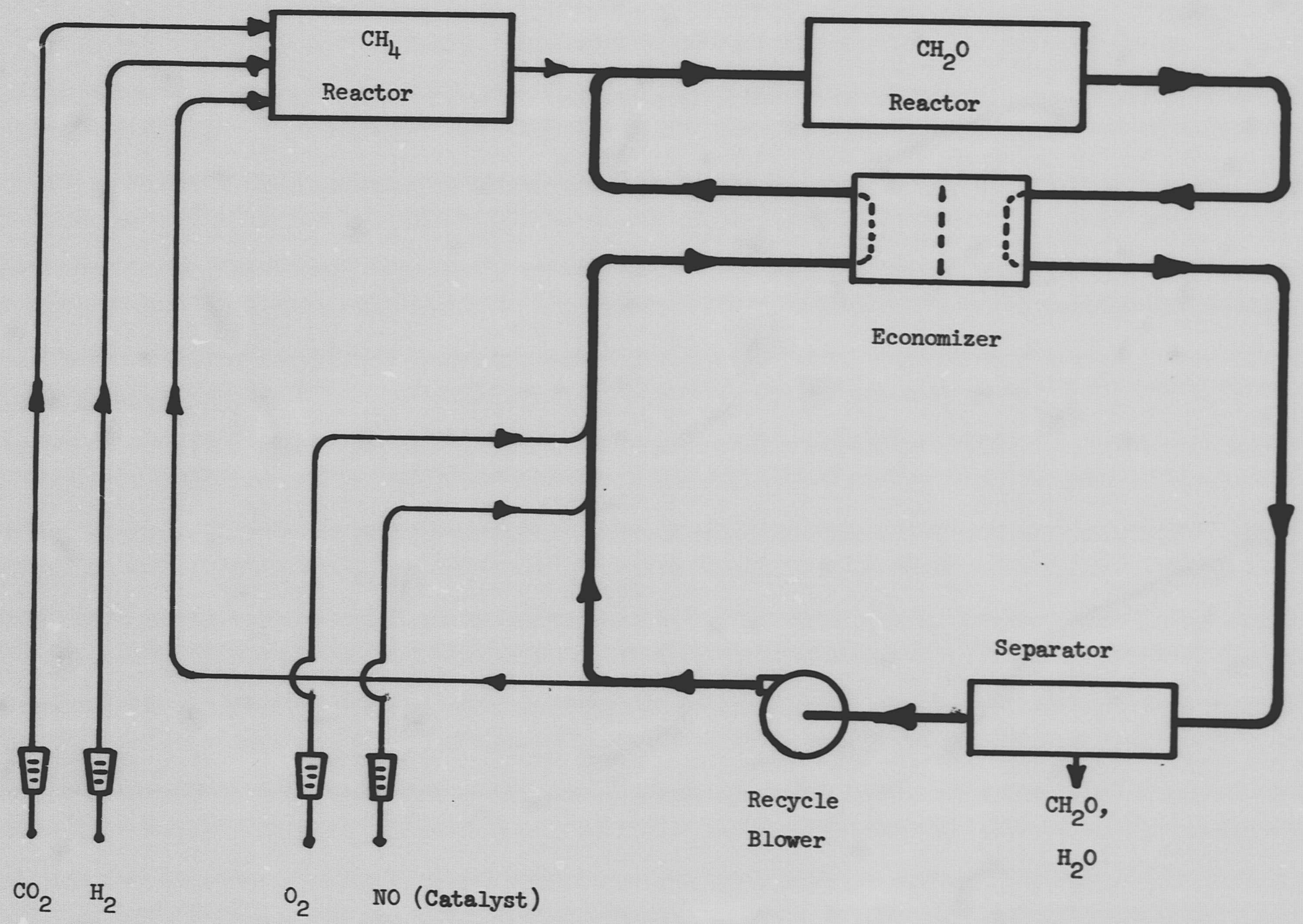


Figure 6. RECYCLE SYSTEM PRODUCING CH_2O FROM CO_2 AND H_2

out changing the internal pressure of the system, the inputs of O_2, H_2, and NO were controlled manually, and the input of CO_2 automatically.

Changes in the O_2 flow were made in accordance with readings of O_2 concentration measured continuously at the formaldehyde reactor outlet by a Beckman polarographic oxygen analyzer. Periodic analyses for CH_4 by a gas chromatograph were used to adjust the flow of H_2. Since there was always an excess of CO_2 in the system, CH_4 formation was regulated by the H_2 input. When the O_2 and CH_4 concentrations were maintained within the desired limits, the CO_2 input could be regulated by a diaphragm valve sensitive to 1" H_2O pressure changes in the system. The removal of CH_2O and H_2O from the gas stream resulted in a pressure drop proportional to the amount of CO_2 used up which actuated the pressure sensitive valve admitting more CO_2 into the system.

The integrated system, operating at a recycle ratio of 25 in a completely closed-loop fashion, i.e. where CO_2, H_2, O_2 and catalyst NO were fed into the system and only CH_2O and H_2O were removed as products, was capable of producing up to 1.5 g/hr (0.05 moles/hr) of CH_2O and converting essentially 100% of the CO_2 feed into CH_2O. Table 9 indicates typical experimentally used feed values and compares them with stoichiometric amounts of feed needed.

Although ultimately all the CO_2 fed into the system becomes converted into CH_2O, the comparison of the experimentally used O_2 and H_2 values with the stoichiometric requirements indicates the overall efficiency of the system. The excess requirements of O_2 and H_2 are due to two factors: (1) over-oxidation of CH_4 to CO_2 with subsequent necessity of reconversion to CH_4, and (2) reaction of O_2 with H_2 in the methanator. The O_2 and H_2 requirements indicate that the ratio of CH_2O to CO_2 formed per pass is 46 to 54, i.e. 46% of the reacted CH_4 goes directly to CH_2O and the other 54% is over-oxidized to

CO_2 which has to be reconverted back to CH_4 for further reaction in the recycle system. Since essentially all of the O_2 in the vented gas stream reacts with H_2 in the methanator, this constitutes another requirement for O_2 and H_2 in excess of the stoichiometric amount.

Separation of CH_2O and H_2O from Product

The removal of CH_2O and H_2O from the reaction product in a manner compatible with zero-gravity conditions was accomplished either by freezing out in cold traps or by adsorption on regenerable solid adsorbers. Neither technique removed any reaction gases from the recycle system.

Gaseous CH_2O, in the presence of water vapor, undergoes a spontaneous and reversible polymerization to solid paraformaldehyde at ambient temperatures. When cold traps are used, most of the CH_2O becomes deposited on the walls as paraformaldehyde which is only slightly soluble in cold water; nevertheless, some CH_2O is frozen out with water. The vapor pressure of paraformaldehyde is such (ref. 3) that a temperature below 0°C, preferably between -10°C and -50°C, is required to obtain essentially complete removal of CH_2O from the gas.

Solid adsorbents which were investigated are listed in Table 10; they removed the CH_2O partially as solid paraformaldehyde, but mostly as adsorbed gas. Silica gel was found to be the most suitable adsorbent for the simultaneous removal of CH_2O and H_2O. Up to 15 wt. % of CH_2O was adsorbed on a silica gel column with 95% efficiency. The silica gel column was repeatedly regenerated with air at 150-250°C to remove all adsorbed CH_2O and H_2O; regeneration by vacuum at room temperature was unsuccessful.

The paraformaldehyde which was adsorbed on the solid adsorbent depolymerizes on heating to gaseous CH_2O; this gas, along with desorbed H_2O vapor was thus

TABLE 9

PRODUCTION OF CH_2O FROM CO_2 AND H_2

	moles/hr			
	CH_2O	CO_2	O_2	H_2
Produced in reactions	0.050			
Stoichiometric requirement for CH_2O production		0.050	0.050	0.200
Overoxidation and reconversion back to CH_4			0.119	0.239
O_2 reacting with H_2 in methanator			0.017	0.034
Total Consumption		0.050	0.186	0.473

TABLE 10

CH_2O ADSORBTION ON VARIOUS ADSORBENTS

Adsorbent	Results
Silica Gel	Adsorbed CH_2O and H_2O. Regeneration temperatures 150-230°C.
Molecular Sieves	Adsorbed CH_2O and H_2O but regeneration temperature was high, about 350°C.
Activated Alumina	Decomposes CH_2O on regeneration by heat.
Anhydrous Calcium Sulfate	Removes all of H_2O but only 40-50% of CH_2O from gas.
Anhydrous Magnesium Perchlorate	Adsorbs H_2O too strongly forming a paste at the inlet of the adsorbent bed.

transferred out of the system and made available for the subsequent processing steps in carbohydrate synthesis.

Nitric Oxide Adsorption

The gaseous NO catalyst for the partial oxidation of CH_4 is not consumed or destroyed to any significant extent; therefore, its concentration remained constant in the recycle gas stream. However, in the vented gas stream, it reacts with H_2 in the methanator and becomes reduced to NH_3. Thus, not only is the catalyst continuously removed from the system requiring continual make-up, but also undesirable by-product NH_3 is introduced into the recycle system.

To remove NO before it entered the methanator, a number of NO adsorbers were investigated. These adsorbers, listed in Table 11, were considered effective for the removal of NO (ref. 35, 36, 37); however, their adsorption capacity seemed to depend on the degree of NO conversion to NO_2; in addition, excess CO_2 appeared to interfere with NO adsorption. $NaClO_3$ on activated alumina was found to remove NO completely and is easy to handle. $CrO_3 + H_2SO_4$ on glass filter paper, although removing NO, was considered less suitable because it tends to lose its activity after adsorbing significant amounts of H_2O. It was not determined whether these adsorbers can be easily regenerated with return of NO to the recycle system.

TABLE 11

NITRIC OXIDE ADSORBERS

Active

- $NaClO_3$ on activated alumina
- $CrO_3 + H_2SO_4$ on glass filter paper

Insufficiently Active

- Molecular sieves
- Silica gel
- Activated carbon
- Chromate on silica gel
- $Fe_2(SO_4)_3$ on activated alumina
- CuCl on activated alumina
- CrO_3 on activated alumina

BREADBOARD PROTOTYPE SYSTEM

A breadboard prototype system, shown schematically in Figure 7, was assembled and tested to obtain data for the preliminary design of a flight prototype model. The overall objectives of testing were to demonstrate the feasibility of CH_2O synthesis from CO_2, to obtain quantitative operational data for scale-up of the system to a one-man capacity unit, and to measure the nominal power requirements.

The operational parameters of the system are summarized in Table 12. The temperature of the reactor was maintained at 670-680°C and the reaction product leaving the reactor immediately entered a gas-to-gas recuperator where product gas was cooled to approximately 75-80°C and the feed gas, flowing counter current, was preheated to 600°C. The product gas, cooled in the gas-to-gas recuperator, then was passed through a CH_2O-H_2O separator and, freed from CH_2O and H_2O, recycled by a diaphragm pump at a recycle flow of 5000 std.cc/min. A portion of the recycle gas was diverted to a methanator where enough CO_2 was converted to CH_4 to maintain the CH_4 concentration at a desired level. The feed rates were manually controlled at the levels indicated in Table 12. Under these conditions, 1.5 g/hr of CH_2O, corresponding to 0.08 lbs/day, were produced.

The main component of the system is the reactor with a gas-to-gas recuperator connected to its outlet, both manufactured from type 321 stainless steel. A detailed sketch of the reactor indicating the dimensions and temperatures at various points during a sustained operation is shown in Figure 8. To minimize oxidation or corrosion of the reactor, a Mullite liner was installed in such a manner that the reactor bed materials do not come into contact

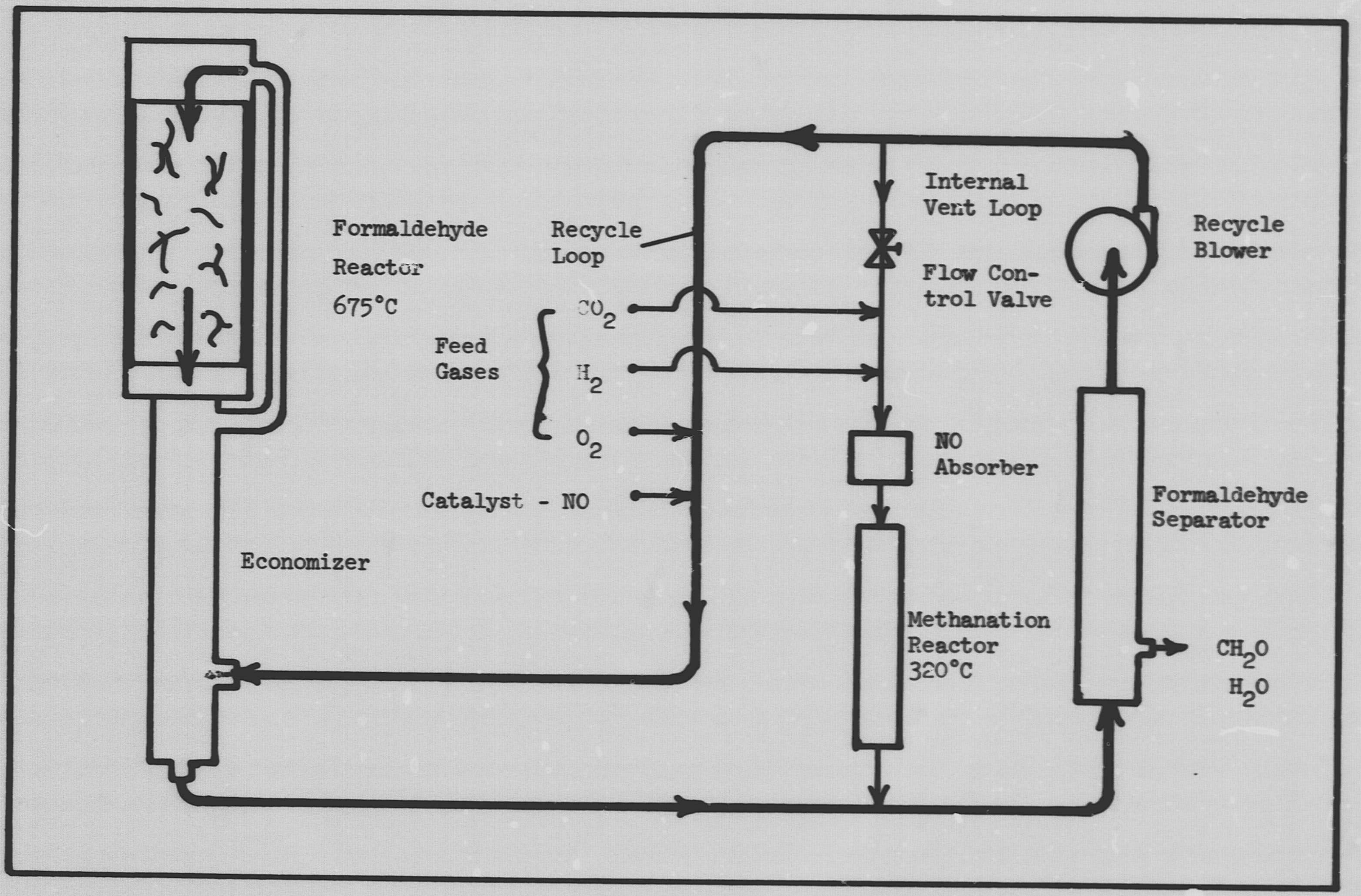


Figure 7. BREADBOARD SYSTEM SCHEMATIC

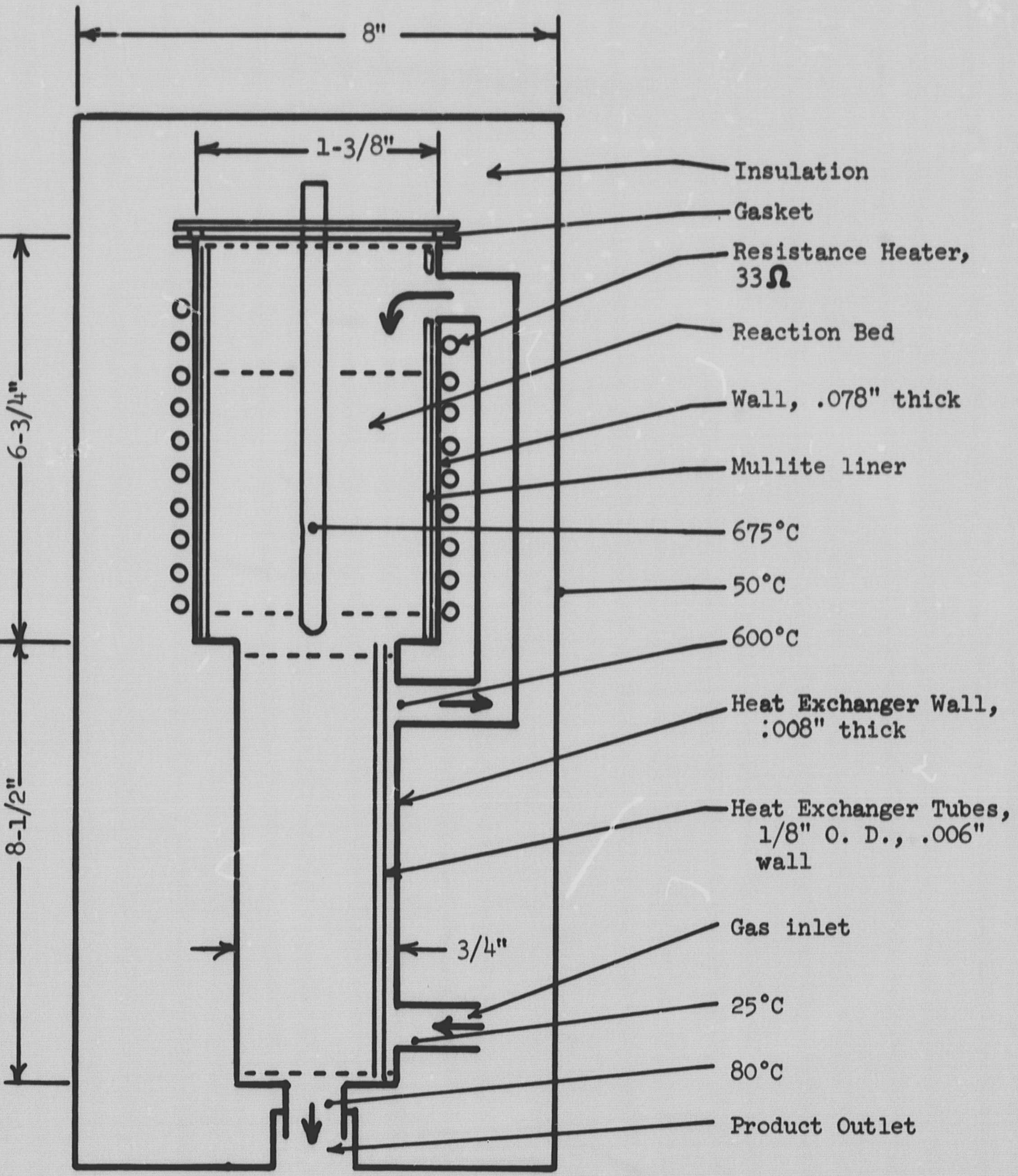


Figure 8. STAINLESS STEEL REACTOR

with the metal walls. A nichrome wire resistance heater wound around the reactor supplied the main heat input. The gas-to-gas recuperator was a tubular heat exchnger containing 19 tubes of 1/8" diameter, having a total surface area of about 60 sq. inches. The entire reactor assembly was insulated with a 3" thick layer of Johns-Manville Thermo-Flex flexible felt insulation.

Both the CH_4 oxidation and the CO_2 methanation are exothermic reactions. However, in this system the extent of reaction is such that only 14.5 watts are released by the oxidation reactions, while theoretically calculated energy required to preheat the reaction gases from ambient to the reaction temperature is 111.4 watts. Experimentally, in prior tests, the heated glass reactor with only superficial insulation and no heat exchanger required approximately 131 watts during normal operation. The nonoptimized, insulated breadboard model required approximately 50 watts to compensate for insulation losses and heat-exchanger inefficiences.

Based on the exothermic energy released by reactions occurring within the CH_4 oxidation reactor, no external heating would be needed after start-up if an 85% effective combined heat-exchanger and insulation system were used. Theoretically, the methanation reactor should generate about 2.5 watts excess heat (ref. 38); experimentally, with the superficially insulated reactor, approximately 19 watts were required to maintain its temperature. The heat input required was again needed to make up for heat lost through the large external surface area of the reactor used for methanation.

Feed gases were obtained from compressed cylinders and the recycle pump was operated well throttled; consequently, no pumping power requirements were measured. The theoretical pumping requirement is 0.15 watts.

TABLE 12

OPERATION OF BREADBOARD PROTOTYPE SYSTEM

CH_2O Production	1.5g/hr
Reaction Beds, Catalyst Volume	
CH_4 Oxidation reactor	40 cc
Methanator	40 cc
Reaction Temperatures	
CH_4 Oxidation reactor	675°C
Methanator	320°C
Feed	
CO_2	20 cc/min
O_2	75 cc/min
H_2	190 cc/min
NO	0.5 cc/min
Feed Flow Control	Manual
Recycle Gas	
Flow	5000 cc/min
Recycle Ratio	25
Composition	
CH_4	20-30%
O_2	6-7%
NO	0.2%
CO_2	remainder
Power Used	
Oxidation reactor	50 watts
Methanator (uninsulated)	Approx. 19 watts
Recycle Blower (theoretical)	0.15 watts
System Operating Pressure	6-10 in. H_2O
ΔP across reaction bed & recuperator at 5000 cc/min	1.5 in. H_2O

PRELIMINARY DESIGN OF PROTOTYPE MODEL

The operation of the breadboard system demonstrated the feasibility of CH_2O synthesis from CO_2, H_2, and O_2 under spacecraft constraints. Based on the experimental data obtained, a preliminary design, shown in Figure 9, was developed for a system able to produce one pound of CH_2O per day. This system would be capable of essentially automatic operation and would supply CH_2O for further use either as solid paraformaldehyde or as the gaseous monomer, CH_2O . The major components of the system are:

1. Formaldehyde synthesizing catalytic reactor and heat-exchanger recuperator assembly with electric heater, thermal insulation, and temperature controls. The reactor is of stainless steel with quartz or porcelain lining, and the heat exchanger, stainless steel.

2. Methanation catalytic reactor with electric heater, thermal insulation and temperature controls. The reactor may be made from light-weight metal such as aluminum.

3. Two CH_2O separators, with switch valves for cycling from adsorption through regeneration. The housing of separators may be made of light-weight metal such as aluminum. Adsorption - desorption cycles every 2 hrs.

4. A nitric oxide adsorber with provisions for cycling and possible regeneration. Housing of the NO adsorber made of aluminum.

5. Constant volume gas circulation blower-pump and flow indicator with controls. Drive motor is to be external to the recycle system.

6. O_2 and CH_4 concentration sensors regulating the supply of O_2 and H_2 feeds and a pneumatic sensor regulating the CO_2 feed.

7. Temperature, flow, and pressure indicators and regulators.

8. Connecting tubing and support framework.

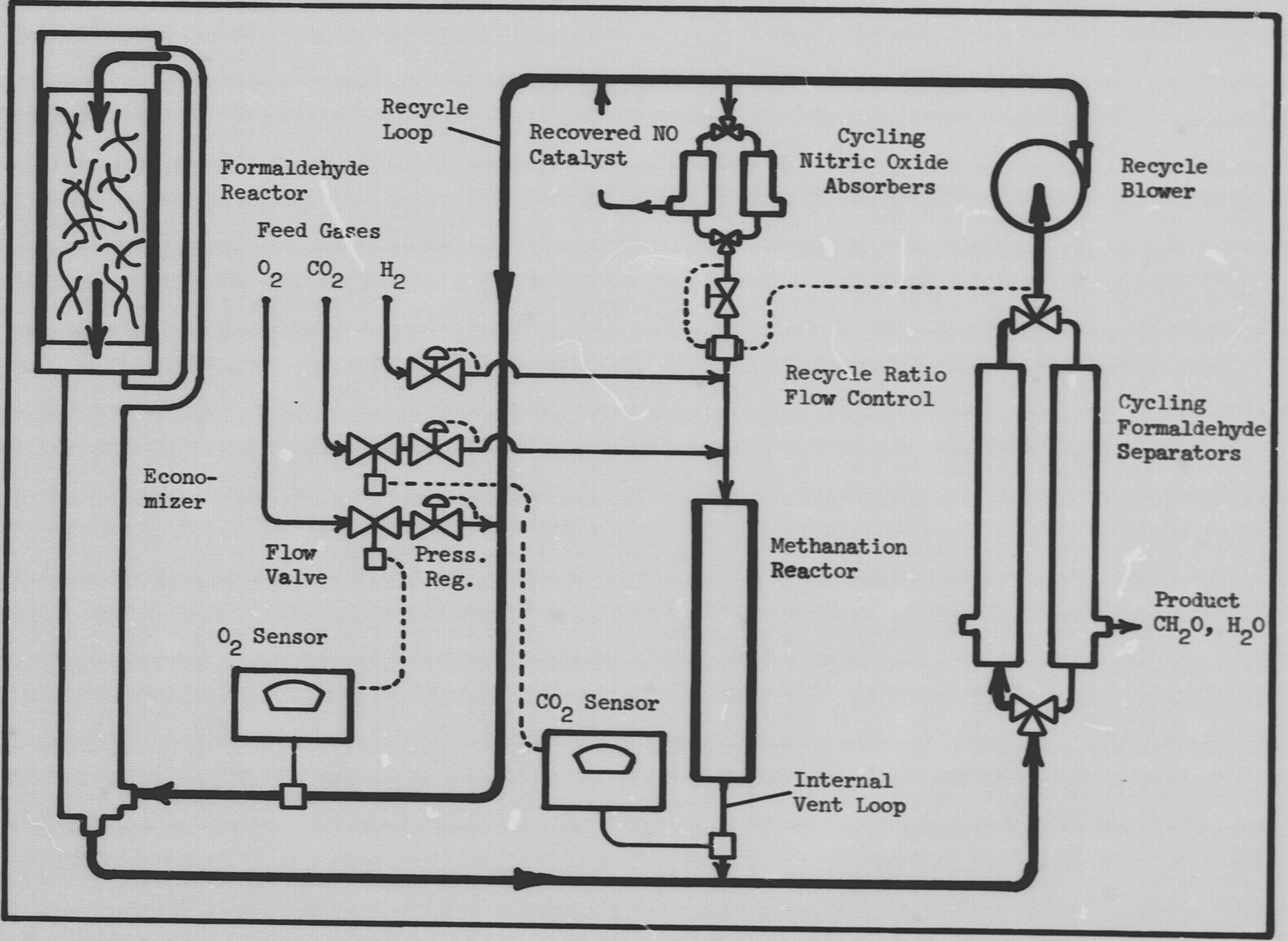


Figure 9. PRELIMINARY DESIGN OF PROTOTYPE

Preliminary estimates of weight and power requirements for a prototype producing 1 lb/day of CH_2O are summarized in Table 13. These values are based on the current observations with the breadboard model and may be somewhat conservative; optimization of the entire system would probably reduce both weight and power requirements.

TABLE 13

PRELIMINARY DESIGN OF PROTOTYPE SYSTEM FOR CH_2O PRODUCTION

Basis: Production of 1 lb CH_2O per day.

A. Weight and Volume

	Beds lbs	Housing		
		lbs	Volume, cu ft	Material
Reactors (insulated)				
CH_4 Oxidation	1.1	1.4	0.330	Stainless steel
Methanation	1.0	0.3	0.083	Aluminum
Gas-to-gas Recuperator (insulated)		2.5	0.405	Stainless steel
Adsorbers				
CH_2O adsorbers (2)	1.4	0.4	0.035	Aluminum
NO adsorber	0.7	0.2	0.017	Aluminum
Controls, connecting tubing, blower, etc.		9.0	0.400	

Total Weight	18 lbs
Total volume of assembled system	1.27 Cu ft

B. Pressure

P of system	6-10 in H_2O
ΔP across oxidation reactor	1.5 in H_2O

C. Power Requirements

Gas recycle pump	1.9 watts
Heating CH_4 oxidation reactor	
70% recovery	355 watts
85% recovery	0
Heating methanator	0

D. Feed Gases:

CO_2	1.47 lbs
O_2	3.95 lbs
H_2	0.63 lbs
NO	0.002 lbs

CONCLUSIONS AND RECOMMENDATIONS

Formaldehyde is an intermediate in the synthesis of edible carbohydrates from CO_2 and H_2O obtained from man's metabolic wastes. An analysis of the various possible methods of formaldehyde production indicated that the carbon dioxide-methane-formaldehyde synthesis system operates under favorable thermodynamic equilbrium at ambient pressure. Therefore, this method was selected for detailed investigation in the laboratory.

Since the process for methanation of carbon dioxide is well known, the investigation centered on the partial oxidation of methane to formaldehyde. Among the various methods tested, the partial oxidation of methane using a gaseous nitric oxide catalyst in conjunction with solid, heated reaction beds gave the most promising results in single pass experiments. The formaldehyde yield ranged between 1.0-2.5%, based on methane input. By recycling the unreacted gas mixture, the effective formaldehyde yield was increased to 25-30%.

An operating laboratory model, incorporating a carbon dioxide methanation reactor and a methane oxidation reactor, was built and tested. Based on operation of the overall system the following conclusions were made:

1. Formaldehyde can be synthesized entirely at atmospheric pressure from CO_2, O_2, and H_2 in a catalytic process with methane as an intermediate.

2. Essentially complete conversion of CO_2 to formaldehyde was accomplished by using an integrated recycle system consisting of a CH_4 oxidation reactor producing CH_2O and a methanation reactor converting CO_2 into CH_4.

3. Product formaldehyde and water can be effectively separated and removed from the system as solids, or adsorbed from the gas phase on

appropriate materials. Formaldehyde condenses as paraformaldehyde, essentially free of by-products. Among the adsorbers tested, silica gel was found to be the most suitable because of both capacity, adsorbing up to 15% of its weight, and ease of desorption.

4. Tests with the operating system demonstrated the zero gravity feasibility of the formaldehyde synthesis process. With 85% effective overall heat-transfer, the high temperature exothermic process requires no additional power for heating.

5. The best catalyst for the oxidation of methane to formaldehyde is nitric oxide; the highest formaldehyde yields were obtained witn NO catalyst and solid beds of alkali tetraborates or boron nitride.

6. Nitric oxide is a feasible catalyst for spacecraft use since it can be generated from waste products such as ammonia or urea. It is unaffected in the methane oxidation reactor but becomes reduced to NH_3 in the methanator. However, the reduction of NO can be avoided by adsorbing it on solid adsorbents before entering the methanator.

7. Ozone produces formaldehyde when used with alkali tetraborate or boron nitride beds; however, it decomposes completely in the reaction zone. Therefore, the entire amount of O_3 must be generated for each pass, limiting the recycle ratio and the ultimate production of formaldehyde to the capacity of the ozonator.

8. Production of O_3 from oxygen is seriously inhibited by the presence of CH_4 in concentrations exceeding 5%.

9. The so-called Hibernia process utilizing O_3 and BaO_2 and claiming

high formaldehyde yields could not be repeated.

10. None of the heterogeneous catalysts investigated produced significant yields of formaldehyde.

11. The best yields of formaldehyde were obtained at 675°C and space velocity of 7500 hr^{-1}, operating with the recycle gas composition at 29% CH_4, 7% O_2, 64% CO_2, and 0.2% NO as the catalyst. These concentrations are not critical and formaldehyde will still be produced, although at lower rates, over a wide range of CH_4 and O_2 concentrations.

12. Gas mixtures containing a diluent, such as N_2 or CO_2, give more reproducible results and are safer to operate with than CH_4 - O_2 mixtures alone.

13. The composition of the reacting gas can be controlled automatically by a system sensing the oxygen and carbon dioxide concentrations, and regulating input carbon dioxide, hydrogen and oxygen feed rates accordingly.

The results of the testing program indicated areas where modifications or additional development appear necessary to improve and increase the efficiency of the synthesis system. Based on these results the following recommendations are made.

1. A larger capacity system, at 1.0 to 2.0 lb CH_2O/day synthesis rate, should be tested in a configuration that minimizes heat loss, and maximizes utilization of the exothermic heat released in the oxidation and methanation reactions. In a larger reactor, surface effects, which increased power requirements and caused excessive over-oxidation of CH_4 in the smaller breadboard model, would be minimized.

2. The overall system should be designed for complete automatic control, requiring minimal attention from crew-members. Specific gas sensors, controllers, and control valves should be utilized to regulate the flow rates of feed gases according to changes in concentrations occurring in the main recycle system. Automatic cycling of the formaldehyde and nitric oxide adsorption beds should be integrated into the control system.

3. Improved utilization of gaseous nitric oxide catalyst is needed. Further investigation should concentrate on searching for a methantion catalyst which does not reduce NO, or on regenerable adsorber capable of releasing NO back into the system. Generation of NO from by-products of spacecraft ecology, such as NH_3 or urea, should also be included in further investigation.

4. The possibility of increasing ozone generating capabilities in pure oxygen and in oxygen-methane-carbon dioxide mixtures should be included in future investigations. Conversion of 10% of the oxygen to O_3 in the gas stream should be the target level of such investigation.

5. The use of vacuum-type insulation, and of a more efficient heat exchanger should be investigated for the purpose of developing a system which could operate with no external heat input after start-up.

6. Both reactor beds should be subjected to duration tests to demonstrate reactor bed life and reliability.

7. Actual power requirement for a 1.0 lb CH_2O/day capacity system should be determined and tests conducted at various synthesis capacities to show a relationship between power and capacity for scale-up to a multi-man system.

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