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ONE-MAN FORMALDEHYDE

SYNTHESIS SYSTEM

FINAL REPORT

By

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SUMMARY

As a continuation of the Formaldehyde Synthesis Study program, a full-scale formaldehyde synthesis system was designed for a nominal one-man capacity of 200 gm CH_2O/day. The system was fabricated and experimentally tested, and from the data observed a preliminary design for a ten-man system was prepared.

In normal operation carbon dioxide, oxygen, and hydrogen gases were fed to the one-man system, using a sodium tetraborate reaction bed, with nitric oxide gas as the catalyst, and formaldehyde and water were generated. These products were removed by adsorption on a bed of silica gel granules. With recycling, all of the carbon dioxide was converted to formaldehyde. The system operated automatically and continuously during short duration runs, and in a manner compatible with zero gravity operation.

INTRODUCTION

The chemical synthesis of carbohydrates from metabolic wastes is considered a promising method for generating a portion of man's normal food requirements for space missions of long duration. Specifically, the production of sugars and glycerol, from metabolic CO_2 combined with H_2 and O_2 generated by water electrolysis, offers a physico-chemical synthesis technique which has the potential to operate successfully within the constraints of spacecraft ecologies.

This investigation has been concerned with the continued study of the production of formaldehyde from CO_2, H_2 and O_2, as an intermediate in the synthesis of carbohydrates. A working model of a one-man synthesis system has been designed on the basis of data developed in prior investigations of laboratory and breadboard system models. The one-man system was subsequently fabricated and experimentally tested, and the design of a ten-man system was prepared on the basis of observed test data.

Program Objectives

The objectives of the investigation of the one-man formaldehyde synthesis system were:

1. To develop the design for a full-scale operational formaldehyde synthesis system, having a nominal capacity of 200 gm CH_2O/day.
2. To fabricate an automatic operational system based on the developed design, compatible with the zero-gravity constraints of the spacecraft environment.

3. To test proper component and overall system performance, and to develop operating data.
4. To prepare the preliminary design of an automatic multi-man system from observed test data.

Approach

In the initial phase of the program a series of preliminary tests were conducted to provide data on a) catalyst gas control and supply, b) effective separation of product formaldehyde from the synthesis system in a manner feasible for zero-gravity operation, and c) automatic control of the synthesis system.

Nitric oxide removal from the recycle gas entering the methane synthesis reactor was investigated. If NO is allowed to reach the methanator, it reacts with hydrogen and becomes converted into undesirable NH_3 gas. Thus, successful nitric oxide adsorption on Molecular Sieves, Type 13X, allowed its use as the catalyst in the one-man system.

Silica gel beds were tested for adsorption of both formaldehyde and water from the recycled product gas stream. Successful adsorption and regeneration by heating provided the required means for continuous product removal, compatible with zero-gravity operation.

The composition of the gas streams entering the main formaldehyde synthesis reactor and the auxiliary methane synthesis reactor are complex, and must be within specific ranges for proper system performance. Automatic control of these compositions by feed gas flow regulation and product removal programming were comprehensively tested on the breadboard system and satisfactory techniques were developed.

After the preliminary tests were completed the detailed design of the one-man system was prepared. A primary component in the system was the formaldehyde synthesis recycle gas heat-exchanger; its design was based on the heat-exchanger in the prior breadboard system. The remaining major components were also predicated primarily on components in the breadboard system. Specific materials of construction, such as Inconel 600, were required to withstand the reaction temperatures in the presence of recycle gases.

The automatic controls for the system were designed to allow completely un-manned operation after start-up. Specific gas sensors and temperature monitors adequately controlled the entire system in totally automatic operation.

Tests were conducted on the one-man system to show basic performance and capacity, to verify controlled operation, to demonstrate zero-gravity feasibility, and to provide data for the multi-man design. An automatically controlled production rate equivalent to one-man capacity was measured, but internal heat transfer efficiencies were less than expected. Upon completion of tests the design for a ten-man system was prepared on the basis of observed data.

PRELIMINARY TESTS

A series of preliminary tests of various parts of the formaldehyde synthesis system were conducted to show operational characteristics and feasibility for sustained operation. These tests were concerned with a) catalyst gas control and supply, b) effective separation of product formaldehyde and water, and c) automatic system control.

Catalyst Gas Control and Supply

The catalyst gases found suitable for the formaldehyde generation reaction in prior phases of testing were nitric oxide and ozone. Nitric oxide was the more effective catalyst, and in contrast to ozone, was not destroyed in the formaldehyde reaction. The NO concentration remains constant in the closed main recycle loop and any replacement required would be due only to leakage. However, in the auxiliary recycle loop where carbon dioxide is reduced to methane, NO reacts with H_2 and is reduced to NH_3 regardless of the methanation catalyst used. Not only is the NO catalyst continuously removed from the system, but undesirable by-product NH_3 is also introduced into the recycle system.

Previous attempts to remove NO before it entered the methanator were only partially successful. Although $NaClO_3$ on activated alumina was found to remove NO completely, regeneration to release NO was impossible. Thus, the adsorbed NO was permanently lost and has to be replaced.

The purpose of continued investigation was to find a solid NO adsorbent which would be regenerable and able to release NO in a controlled, gradual manner, thus maintaining the proper catalyst concentration in the recycle system, and continuously reusing the catalyst gas.

Solid adsorbents which were thought to be capable of removing NO by physical adsorption were selected and subjected to screening tests. Gas mixtures approximating the composition of the recycle gas stream and containing about 2000 ppm of NO were passed through a 40 cc bed of each adsorbent maintained at room temperature (24°-27°C), while the concentration of NO in the intake and in the exhaust were monitored. The results of this screening are summarized in Table 1 indicating that type Molecular Sieves 13X warranted further investigation.

TABLE 1

ADSORPTION OF NO_x ON SOLID ADSORBENTS

Adsorbent.	Results
Activated Alumina	Up to 63% of NO removed
Silica Gel	Usually about 30%, sometimes up to 60% of NO removed
Molecular Sieves, 3A	No removal of NO
Molecular Sieves, 4A	Erratic. Up to 90% of NO removed for a short time.
Molecular Sieves, 13X	97-99.5% of NO removed.

A series of tests were performed to identify the parameters and to determine the optimum conditions for removal of NO from the gas stream by Molecular Sieves 13X. Preliminary tests indicated that the level of NO removal was the same regardless whether 1/16" or 1/8" diameter pellets were used; to minimize the pressure drop, only 1/8" diameter pellets were used in further testing.

At a given temperature, the adsorption of various components from a multicomponent gas stream depends on their relative adsorptivities and partial pressures. In a typical recycle gas containing 5-10% O_2, 30% CH_4, and 60-65% CO_2, nitric oxide at 0.2% is only a minor constituent and its adsorption will be strongly influenced by the adsorptivities of the major components, in this instance, carbon dioxide. For instance, a Molecular Sieve 13X bed exposed to a gas stream of the above composition, immediately becomes saturated with CO_2 adsorbing up to approximately 15 % by weight. Consequently, all the tests were performed with gas mixtures having a nominal composition of a typical recycle gas as given above.

Testing indicated that the adsorption of NO on Molecular Sieves 13X requires the presence of oxygen in the gas stream, indicating that NO has to be converted into NO_2 which is the probable species adsorbed. The influence of oxygen on the adsorption of NO is illustrated by tests shown in Table 2. These tests indicate that NO adsorption does not occur in the absence of oxygen. Conditions favoring the attainment of equilibrium for the conversion of NO into NO_2, such as high O_2 concentration, low temperature, and long contact time, would improve the removal of NO from the gas stream.

The dependency of the NO adsorption on gas flow rate is shown in Table 3. At low gas flows, changes in the flow rate show little effect on NO removal; however, when the superficial gas velocity approaches 2 cm/sec or higher, there is a marked increase in the NO passing through the bed unadsorbed.

The adsorption of NO on Molecular Sieves 13X depends on the geometry of the adsorbing bed and a minimum bed length is required to obtain satisfactory removal of NO. Table 4 lists adsorption data for four different beds operating

TABLE 2

INFLUENCE OF O_2 ON THE REMOVAL OF NO BY MOLECULAR SIEVES 13X

Conditions

Adsorbent Bed:	40 cc, 120 mm long, 22 mm dia., 1/8" pellets, 24°-27°C
Gas Composition:	CH_4 27-29.5% O_2 as indicated NO as indicated, nominal 2000 ppm CO_2 remainder
Gas Flow Rate:	200 cc/min, superficial velocity 0.88 cc/sec

O_2 Concentration, %	NO Concentration, ppm		Remarks
	Input	Product	
0	2040	2040	
0.2	2400	2400	
5.3	2280	50	
9.7	1865	40	
14.7	1640	0	
15.0	1810	10	

TABLE 3

DEPENDENCY OF NO_x ADSORPTION ON MOLECULAR SIEVES 13X ON GAS FLOW VELOCITY

Conditions

Adsorbent Bed: 40 cc, 120 mm long, 22 mm dia., 1/8" pellets, 24°-27°C

Gas Nominal Composition:		
	CH_4	30%
	O_2	as indicated
	NO_x	2000
	CO_2	balance

Gas Flow, cc/min	Superficial Velocity, cm/sec	O_2 Conc., %	NO, ppm	
			Intake	Product
100	0.44	4.9	2200	30
100	0.44	10.6	1650	0
200	0.88	6.0	1920	10
200	0.88	9.5	2040	20
428	1.88	5.3	1920	140
456	2.00	9.3	1800	60
630	2.76	4.9	1800	390
666	2.92	10.2	1450	100

with gas of the same composition. When NO is adsorbed the saturated portion of the bed becomes yellow; thus, the advancing of the saturated portion toward the effluent end of the bed can be followed visually. The distance of the saturated zone from the effluent end at the time of breakthrough was measured and is indicated in Table 4 as length of the mass transfer zone. With bed No. 1, breakthrough occurred within less than an hour indicating that the mass transfer zone was longer than the bed. Because of lower superficial gas velocity, the mass transfer zone of Bed No. 4 was shorter than the others. An approximate length of the mass transfer zone at various velocities can be obtained by plotting data obtained as shown in Figure 1, which indicates minimum length of the bed required for the removal of NO from the gas stream as a function of the superficial gas velocity.

The breakthrough capacity of a Molecular Sieves 13X bed for NO removal depends on its length beyond the mass transfer zone, i.e., the saturated portion of the bed. Data obtained with three beds indicate that the saturated portion of a fresh 13X Molecular Sieve bed is able to adsorb at least 51.4 cc of NO per cc of its volume or 0.1 gram of NO per gram of sieves before the breakthrough occurs.

Desorption experiments were tailored to determine the conditions necessary for a controlled, gradual release of NO from Molecular Sieves 13X beds previously saturated to breakthrough. Gas mixtures of typical recycle gas composition but containing no NO were passed through a saturated bed at a rate of 200 cc/min in a direction reverse to that used for adsorption and the concentration of NO in the effluent determined periodically. Initial tests indicated that when the desorption is attempted isothermally, very large amounts

TABLE 4

INFLUENCE OF BED GEOMETRY ON THE ADSORPTION OF NO ON MOLECULAR SIEVES 13X

Conditions

Beds: 1/8" pellets, 24°-27°C

Gas Nominal Composition:		
	CH_4	30%
	O_2	5%
	CO_2	65%
	NO	2000 ppm

Gas Flow: 200 cc/min

Mol. Sieves 13X Bed				Superficial Gas Velocity, cm/sec	NO, ppm			Hrs. to Break-through	Length of MTZ, cm
No.	Vol., cc	Dia., cm	Length, cm		Intake	Product Avg.	Product Range		
1	30	2.2	9	.88	1720-2040	65	30-70	0	
2	40	2.2	12	.88	2120-2700	40	20-80	11	10.8
3	100	2.2	30	.88	1800-2670	2	0-10	165	10.0
4	100	4.2	7.5	.25	2040-2670	13	0-20	96	5.0

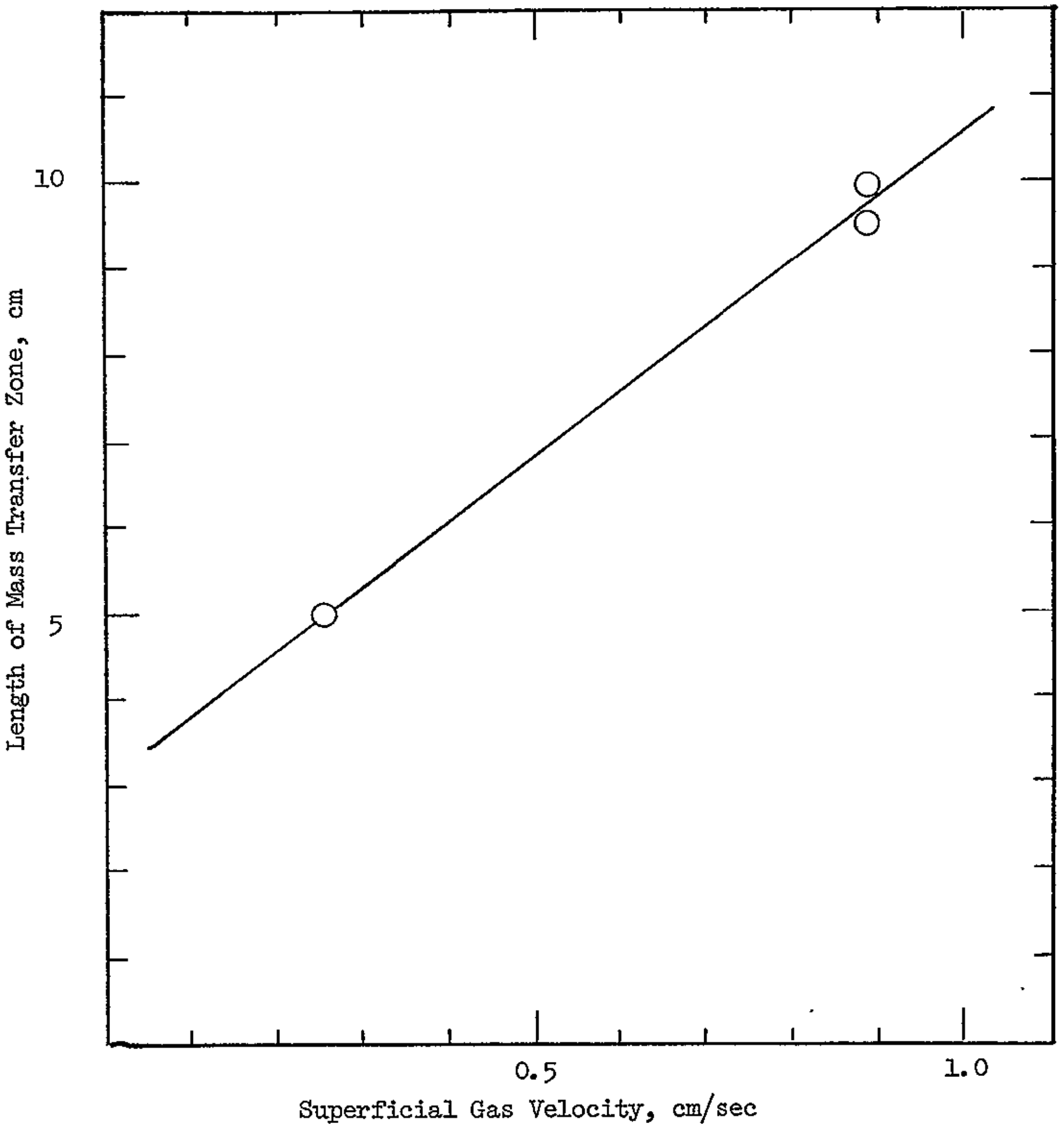


Figure 1. DEPENDENCE OF THE LENGTH OF MASS TRANSFER ZONE ON SUPERFICIAL GAS VELOCITY FOR NO ADSORPTION ON MOLECULAR SIEVES 13X

of NO are desorbed during the first few minutes and then the desorption curve decays very rapidly. On the other hand, the concentration of NO in the desorbing gas can be maintained at a desired level by continuously increasing the bed temperature in a programmed manner.

The adsorption-desorption experiments showed that Molecular Sieves 13X could be used to maintain the catalyst gas concentration in the main recycle system without appreciable losses or need for make-up additions of fresh NO. However, the amount of NO removed from the stream entering the methanator is only 7.5 g/day for the one-man system, or about 6 lbs/year. A bed containing 600 grams of molecular sieves would suffice for 5 days of operation before reactivation by desorption is required. The desorption process involves heating to about 200°C and discharge to overbaord vacuum for 2-4 hours. The conclusion of testing was that regeneration of NO is not as efficient as merely carrying stored NO (or NO_2) as expendables. Thus, approximately 10 pounds of expendables would supply all of the catalyst gas needed for one year of operating with no power requirement or complex system components.

Separation of Product Formaldehyde and Water

Testing in prior phases had shown silica gel capable of separating product formaldehyde and water from the main recycling gas stream by selective adsorption. General quantitative data on bed capacity were developed but not to an extent sufficient for design of a larger separator.

To develop additional design data, the simultaneous adsorption of formaldehyde and water on silica gel was further investigated in this phase by operating the original breadboard formaldehyde system under actual synthesis conditions. A tube containing 100 cc of granular silica gel backed by four vapor traps immersed in a dry-ice-acetone bath was located in the main recycle system at the outlet of the formaldehyde reactor. Any CH_2O and H_2O passing through the adsorption column was collected in the vapor traps. The efficiency of the adsorption column was designated as the percent of total produced CH_2O retained on the column. Silica gel has a greater affinity for water than for formaldehyde, and the water adsorbed from the gas stream gradually displaces formaldehyde. For this reason, the overall breakthrough capacity of an adsorption column was determined by the appearance of CH_2O in traps contacting the gas exiting the adsorption column.

The breakthrough capacity of the silica gel adsorption bed depends on the gas composition, adsorption temperature, linear gas velocity, and bed length. Since the composition of the recycle gas remains essentially constant, adsorption characteristics obtained during actual formaldehyde synthesis depend only on other variables. Although the adsorption of CH_2O improves with lowering of temperature, successful recovery from the recycle gas can be made only within a relatively narrow temperature range. When the product gas is cooled to approximately 25°C, paraformaldehyde begins to condense before reaching the adsorption bed. On the other hand, formaldehyde desorption begins at 50-55°C. Normally, the heat of adsorption raises the temperature of the adsorption zone by approximately 10-15°C. Therefore, for satisfactory removal of CH_2O, the temperature of the recycle gas entering the adsorption bed must be between 25°C and 40°C. During the adsorption experiments, the temperature of the gas entering the silica gel bed generally ranged between 28°C and 37°C. No CH_2O adsorption trends due to temperature were observed in this range.

The influence of bed geometry on the removal of CH_2O was investigated with three beds of different diameters but containing the same amount of granular silica gel. Experimental results, summarized in Table 5 , indicate that the degree of CH_2O removal depends both on the superficial velocity of the gas and on the adsorption bed length. Decreasing superficial velocity increased the percent of CH_2O removal; however, when the length of the bed becomes short, as illustrated with bed 3, the CH_2O removal drops significantly even with low superficial velocities. In this case, the geometry of bed 2 allows an acceptable degree of CH_2O removal without excessive pressure drop experienced with a longer bed.

The dependency of CH_2O removed by granular silica gel on the adsorption time is shown in Figure 2. If 95% removal is assumed as the lowest acceptable limit, then a 100 cc bed is capable of removing formaldehyde from the recycle gas passing through the adsorption bed at a rate of 5 liters/min for 3 hours, i.e., recovering CH_2O from a total of 900 liters of recycle gas.

Attempts were made to increase the breakthrough capacity of the granular silica gel bed by precondensing the CH_2O as solid paraformaldehyde on solid surfaces at room temperature. The vapor pressure of paraformaldehyde was higher or about equal to that of CH_2O in the recycle gas and very little condensation occurred.

The use of a charcoal bed before the silica gel was also investigated. Although the degree of CH_2O removal was increased, it was due apparently only to an increase in the total adsorption bed volume. A special form of silica gel, Mobil Sorbeads, was investigated; however, under the same conditions as for granular silica gel, only 62-75% removal of formaldehyde

TABLE 5. INFLUENCE OF BED GEOMETRY ON THE REMOVAL OF CH_2O

Bed bulk volume	100 cc
Space velocity	3000 $hr.^{-1}$
Gas flow	5000 cc/min
Adsorption time	3 hrs

	Silica Gel Bed		
	1	2	3
Bed diameter, cm	2.2	2.5	3.1
Bed length, cm	26.4	20.4	14.0
Superficial gas velocity, cm/min	1320	1040	702
Number of tests	3	6	2
CH_2O adsorption, % of total	92.5	95.0	89.7

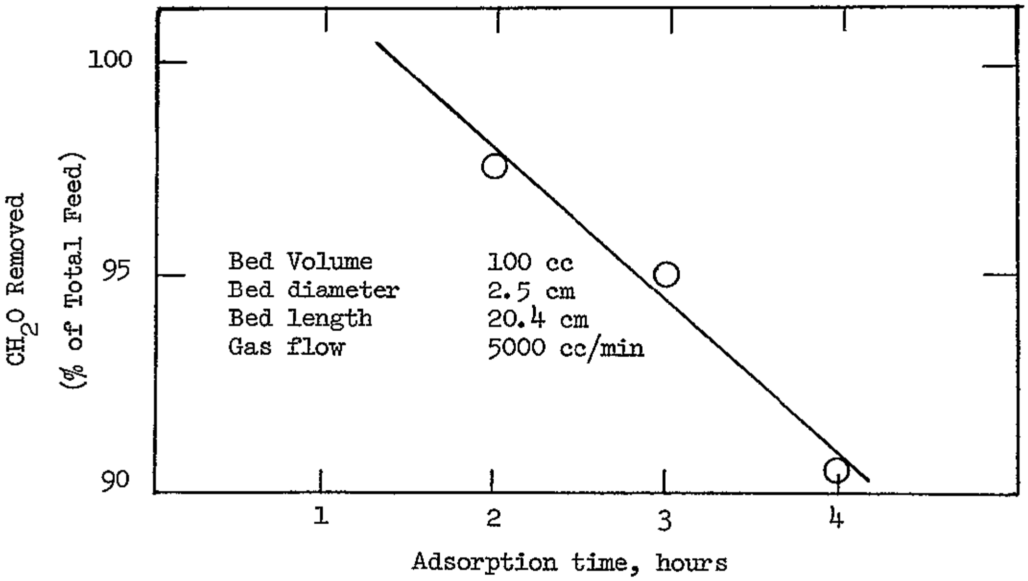


Figure 2. DEPENDENCY OF CH_2O REMOVAL ON THE ADSORPTION TIME

was achieved.

Granular silica gel adsorption beds saturated with CH_2O and H_2O can be regenerated by slowly heating up to 175°-200°C while passing a stream of dry gas through the bed, preferably in the opposite direction to adsorption flow. Desorption of CH_2O begins at approximately 50°-55°C; however, only after reaching 175-200°C is essentially complete removal of CH_2O and H_2O from the bed achieved. After cooling to room temperature, the regenerated silica gel bed is again suitable for further adsorption of CH_2O and H_2O.

Repeated adsorption and desorption of a granular silica bed did not indicate any deterioration or diminishing of adsorption capacity. All tests indicated that granular silica gel would operate satisfactorily to separate both products, formaldehyde and water, from the recycling gas stream, by using a multiple bed configuration with continuous recycling.

Automatic System Operation

A series of performance tests were conducted on the breadboard system to develop start-up and operating procedures for automatic system control during continuous formaldehyde synthesis.

All experiments were performed with a main recycle gas flow of 5000 cc/min, an oxidation reactor temperature of 675°C, and a methanator reactor temperature of 315°C. A Molecular Sieve 13X bed was used to adsorb NO from the gas stream entering the methanator; and, consequently, NO was present only in the main recycle loop. Manual controls were employed during start-up; however, a procedure for entirely automatic regulation of the flow of feed gases was developed and used during actual runs.

System operation was initiated by purging and filling the entire system with CO_2 while operating the recycle pump; concurrently, the temperature of the formaldehyde reactor was raised to about 620°C and the temperature of the methanator to 315°C. Hydrogen flow through the methanator was started and maintained at about 100-150 cc/min until the methane concentration within the whole system reached 40-45%.

Initial addition of H_2 caused an increase in the internal pressure of the system proportional to the rate of H_2 flow. This problem was alleviated by employing a ballast chamber having a volume equal to approximately 10% of the volume of the entire system. Gas flow to the methanator is diverted initially through the H_2 chamber, introducing H_2 into the system without any increase in pressure. Later, only H_2 is permitted to flow through this container so that it is refilled with H_2, ready for the next start-up.

When the CH_4 concentration reached 40-45%, O_2 and NO were introduced into the system by diverting a portion of the recycle gas stream through a gas chamber containing enough O_2 and NO to give the desired concentrations in the recycle system. The automatically controlled feed lines of CO_2, H_2, and O_2 were then opened, and the reaction started by raising the temperature of the oxidation reactor to 675°C.

This manual start-up procedure was found to be satisfactory; it allowed the operator to raise the concentrations of O_2, CH_4, and NO to desired levels before each run without increasing the internal pressure to levels which would require venting. In this manner the integrity of the closed system was maintained both during start-up and actual sustained operation.

During the entire run, the feeds of CO_2, H_2, and O_2 were regulated automatically. The production and subsequent removal of CH_2O and H_2O from the gas phase causes a decrease in system pressure which actuates a diaphragm flow regulator controlling the CO_2 feed to the system. Feed of H_2 is based on the CH_4 concentration in the recycle gas to the formaldehyde reactor. Since there is an excess of CO_2 in the system at all times, the formation of CH_4 and its concentration are regulated by controlling the flow of H_2 to the methanator. The concentration of CH_4 in the recycle system is monitored continuously by a LIRA non-dispersive infrared analyzer (Mine Safety Appliance Co.); the output from the analyzer was used to activate a solenoid valve controlling the H_2 input flow. A Beckman polarographic oxygen analyzer monitored the oxygen concentration in the recycle gas entering the formaldehyde reactor, and actuated the solenoid valve controlling O_2 input flow.

The concentrations of O_2 and CH_4 in the recycle gas were checked periodically by anron-line gas chromatograph. Generally, the concentrations of both O_2 and CH_4 were maintained within acceptable fluctuation ranges, approximately ±5% for CH_4 and ±2% for O_2, throughout experiments of 180 min. duration. Operations in this manner showed the feasibility of automatic sustained formaldehyde synthesis.

DESIGN OF ONE-MAN SYSTEM

The design of the one-man formaldehyde synthesis system was based on data developed during operation of the breadboard prototype system, on results of preliminary tests of system components described in the previous section, and on theoretical and scale-up calculations for mass-transfer, heat-transfer, and pressure-drop.

Design Objectives

The primary design objectives were:

a) Operation with continuous synthesis of formaldehyde.

b) Separation of product formaldehyde and water on continuous or semi-continuous basis compatible with zero-gravity operation.

c) Automatic operation of system with un-manned controls.

d) Operation of system with no external heating of reactors after start-up.

e) Convenient arrangement of system components for ready accessibility for servicing or replacement.

System Components

Continuous synthesis of formaldehyde required that both the formaldehyde and the methane reactors, the product separator, and the recycle blower be designed with high reliability and a minimum of moving mechanical components.

The major system components and primary controls are listed as follows.:

a) Formaldehyde synthesising catalytic reactor and counter-flow heat-exchanger.

b) Methane synthesising catalytic reactor and counter-flow heat-exchanger.

c) Cycling separators for removal of formaldehyde and water products.

d) A centrifugal blower for circulation of all gas streams.

e) Nitric oxide adsorber bed.

f) O_2, CO_2 and H_2 feed gas controls.

g) System instrumentation.

The conceptual schematic design for the formaldehyde synthesis system is shown in Figure 3 Gas flow rates and temperature levels are indicated at various points in the system. A gas blower circulates the recycle gas at a flow rate of 50 liters/min at ambient temperature, and at essentially ambient pressure. Pressure drop in the system at this flow rate would approximate 2" to 3" H_2O. Methane and oxygen in the recycle stream pass into the main reactor and combine to form formaldehyde and water as the primary products, and carbon dioxide as a by-product.

Additional feed CO_2 and by-product CO_2 are converted to CH_4 in the methane synthesis reactor. To accomplish this, a portion of the recycle gas, approximately 2 liters/min, is diverted from the main recycle stream and mixed with feed H_2. This mixture is then preheated in a counter-flow heat exchanger to 260°C; it then enters the methanator where CO_2 reacts with H_2 to produce CH_4 and H_2O. The temperature of the methanator is maintained at 320°C by passing a sufficient amount of air through a cooling-jacket around the reactor shell. The exit hot air stream at 200-250°C can be utilized if

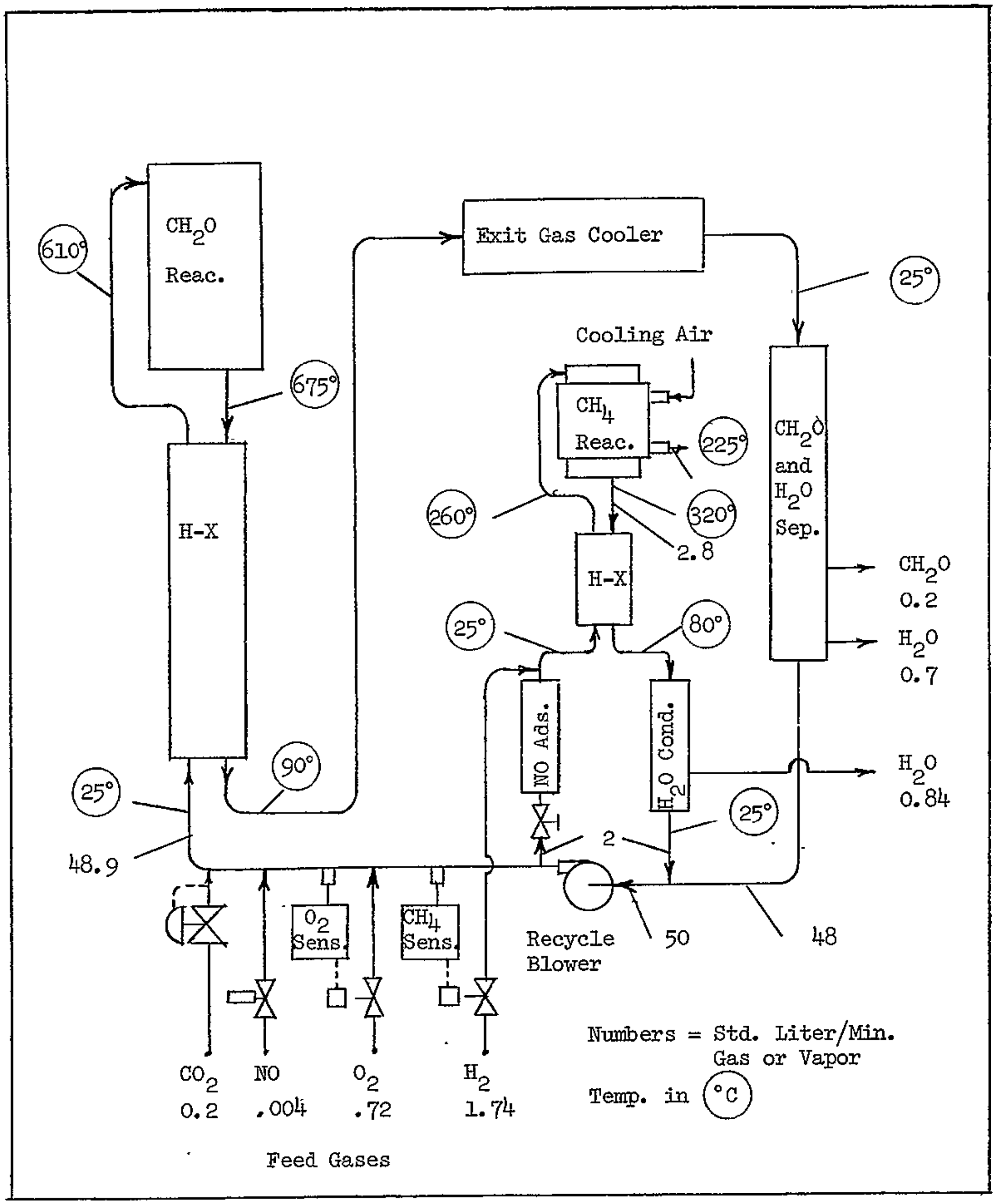


Figure 3. ONE-MAN FORMALDEHYDE SYNTHESIS SYSTEM SCHEMATIC

needed to supplement electrical heating during desorption of the beds used to remove CH_2O and H_2O products from the system. The methanated product exits the reactor and is cooled in the counter-flow heat-exchanger. After approximately 95% of its water content is removed in an air cooled condenser, it is returned to the main recycle stream.

Feed O_2, CO_2, and make-up NO are added to the recycle gas stream. The stream then enters the main counter-flow heat exchanger, becomes preheated, and passes into the main formaldehyde reactor at a temperature of 610°C. The formaldehyde synthesis reaction then occurs, with a temperature increase to 675°C. The recycle stream containing product CH_2O and H_2O leaves the reactor, passes through the counter-flow heat exchanger, and exits at approximately 90°C.

The recycle stream must be cooled to approximately 25°C for satisfactory separation of CH_2O and H_2O. The amount of heat removed at this point is rejected to the surroundings, or to an external cooling loop.

As noted previously, separation of product CH_2O and H_2O from the recycle gas stream is achieved by simultaneous adsorption on a silica gel column. Since the adsorbate is retained on the column, it is compatible with zero gravity conditions and is readily available for further use by thermal desorption. The desorbed product consists of CH_2O and H_2O in approximately 1:2 ratio by weight. Uninterrupted operation necessitates the use of at least two, and possibly three, adsorption columns. While one column is used for the removal of CH_2O and H_2O from the process gas stream, the other is regenerated by heating to approximately 200°C; and the third is cooled back to ambient temperature. The third bed may be eliminated by using larger beds and combining the heating-cooling functions into one operation. The cycling time of the columns is dependent mainly on the time required for desorption and cooling; this time also dictates the size of the columns required for the complete removal of CH_2O and H_2O. Since H_2O is adsorbed preferrentially, the breakthrough capacity is determined by the appearance of CH_2O in the exit gas. However, because the product gas composition is essentially constant, automatic cycling on a time basis instead of on the basis of gas composition is simpler and more reliable.

Since the removal of CH_2O and H_2O from gas stream can be effected only at approximately ambient temperatures, the entire gas stream in the recycle system must be first cooled from the reaction temperature to ambient temperature. The stream must then be reheated again to 610°C for the reaction to proceed. Both the formaldehyde and the methane synthesis reactions are exothermic, and for the one-man system, produce approximately 3880 cal/min. Formaldehyde synthesis produces 2640 cal/min which is sufficient to raise the total recycle gas stream temperature by 100-130°C, and to maintain the reactor at temperature once the required 610°C level is reached. Methane synthesis produces 1240 cal/min, which is more heat than is needed for maintaining the reactor at the desired temperature of 320°C. Excess heat must be removed.

Overall system heat losses are due to loss of sensible heat in the gases leaving the heat exchangers, and to loss through the reactor walls and insulation. The estimated losses through the insulation will be approximately 2000 cal/min, while the sensible heat loss will range from 1300 to 1600 cal/min, depending on the efficiencies of the heat exchangers and the temperatures of the exiting gas streams. By using a suitable physical arrangement of the components, efficient heat recuperators, and efficient insulation, the system has the capability of operating without outside heating of the reactors or recycle gas, after both reactions have been initiated.

To attain a high degree of heat conservation, the formaldehyde reactor with its heat exchanger and the methane reactor with both internal and external heat exchangers should be assembled in one insulation module. This entire module will be designed to provide minimum heat loss but with accessibility to all components. Small cartridge heaters both in the main and in the methanation reactors are utilized for preheating during start-up, and make-up heating, if required, during normal operation. All other components, namely, the CH_2O and H_2O separator, NO adsorber, flow control valves, regulators, recycle blower and piping will be situated outside of the insulation reactor module. The power required for recycling the gas, desorption of CH_2O and H_2O, and instrumentation will be supplied externally.

Formaldehyde Reactor and Heat-Exchanger Design

The primary objective of the design of the formaldehyde reactor and heat-exchanger sub-system was to configure these components to meet the following performance criteria:

1. To maximize production of formaldehyde and minimize production of carbon oxides in the system.
2. To preheat incoming recycle gas from ambient to the 610°C level required at the reactor inlet.

3. To cool recycle gas leaving the reactor at 675°C down to approximately 90°C to allow subsequent minimal further cooling to 25°C for removal of product formaldehyde and water.
4. To minimize pressure drop across the reactor and heat exchanger, attempting to keep total Δ p below 2" H_2O.
5. To minimze total heat loss through insulation and in the exiting gas stream, attempting to keep this total below the 515 BTU/hr. released by the exothermic reaction within the reactor, thus allowing operation with no external heat input, after start-up is achieved.

Formaldehyde Reactor. - The formaldehyde reactor configuration was based on the configuration of the breadboard model. The breadboard reactor zone was a 1" diam x 5" high cylinder filled with reaction promoting material. The one-man reactor was scaled up to a 3" diam x 5-1/2" high reaction zone, to give approximately ten times the capacity of the breadboard reactor, since the one-man recycle flow rate was to be ten times the rate in the breadboard system. Three 100-watt heating rods were located in a 2-inch zone above the reaction zone for start-up.

Construction Materials. -- Examination of the breadboard model which was constructed from stainless steel, Type 321, indicated considerable corrosion, particularly at the hottest portion of the heat exchanger. Nickel base alloys such as Inconel and Hastelloy, which are more resistant to oxidation at the reaction temperature than stainless steels, were considered as alternates. Because of poor workability and unavailability in desired forms, Hastelloy metals were eliminated.

Tests conducted with a formaldehyde reactor lined with Inconel 600 sheet, indicated that the presence of Inconel 600 lining did not impair the production of formaldehyde. The lining itself was slightly tarnished but showed no scale formation and had only negligible weight gain indicating little or no reactivity with the recycle gases. Inconel 600, therefore, was found suitable for the construction of both the formaldehyde reactor and the heat exchanger.

Another lining material which also showed little corrosion in tests at actual operating conditions, and which did not impair the production of CH_2O, was Alonized stainless steel. An Alonized stainless is one into which aluminum has been diffused by heat-treatment to form a 0.010-0.015" thick outer layer of stainless-aluminum alloy which is resistant to oxidative corrosion at elevated temperatures. This material was also considered suitable for construction, but only for the formaldehyde reactor.

A reactor was fabricated from Alonized stainless steel, and a shell for the heat-exchanger from Inconel 600. During construction, pinhole leaks were discovered at several points along the weld seam between the alonized stainless steel reactor and the Inconel 600 heat exchanger shell. All attemps to seal the leaks both by welding and by high temperature brazing were unsuccessful, apparently because of the composition of the alonized alloy. As noted above, the alloy is highly corrosion resistant due to the protective surface metal oxide formed on heating. The surface coating appeared to interfere intermittently with welding, and to prevent completely any attempts at high temperature brazing, since the brazing flux could not remove the oxide to provide a fresh metal surface for bonding.

When all attempts at sealing leaks were unsuccessful, the alonized reactor was removed from the heat-exchanger, and an Inconel 600 reactor was fabricated instead.

Heat-Exchanger Design. - The one-man heat exchanger design was based on the operation of the breadboard system. The amount of heat transferred across the heat exchanger in the breadboard system was calculated from the gas flow rate and gas stream temperature changes as follows:

$Q = W C_p \Delta T$

W = 5 liters/min = 6 gm/min (approx. 0.1 man capacity)

C_p = 0.35 cal/gm°C, the nominal heat capacity at 300°C for a 54% CO_2, 30% CH_4, 6% O_2, 5% H_2 and 5% CO, recycle gas mixture.

ΔT = 600° - 25° = 575°C, inlet gas side or,

675° - 80° = $\underline{595°C}$, outlet gas side;

585°C Average

$Q = 6\,(.35)\,(585) = 1200$ cal/min = 280 BTU/hr.

The breadboard system heat-transfer surface area for 19 tubes, 9 inches long, and 1/8 inches in diameter, was 0.47 ft^2, and for an average temperature difference of 65°C (149°F) the overall heat transfer coefficient was:

$$U = Q/A\Delta T = (280 \text{ BTU/hr})/(0.47 \text{ ft}^2)\,(149°\text{F})$$

$$= 4 \text{ BTU/hr °F ft}^2$$

This is equivalent to a gas-film coefficient of 8 BTU/hr°F ft^2 since the coefficients on both heat-exchange surfaces are essentially equal.

Assuming the same heat-transfer coefficients and operating temperatures would apply for the one man system, a total surface area of 4.7 ft^2 would be required, if similar parameters, primarily the Reynolds and Prandtl number, are maintained. In a direct 10:1 scale-up, a heat-exchanger containing 190 tubes 9 inches long, and, 1/8" in diameter would provide analogous heat transfer. However, to provide a margin of safety and to minimize pressure drop, 240 tubes, 13 inches long 1/8" in diameter, were specified to give approximately 9 ft^2 of heat-transfer surface for the nominal one-man heat-exchanger in a tube and shell configuration. Since all flows are in the laminar region the effect on heat-transfer coefficients of the resulting 25% change in the Reynold's number is negligible.

The tubes were spaced to provide a hydraulic radius for the shell side equivalent to that of the tube side of the exchanger so that heat-transfer coefficients and pressure drop parameters would be the same on both sides. Upon examining the anticipated total system heat losses and volume of insulation needed to keep these losses below the 515 BTU/hr rate of generation in the reactor, an alternate configuration for the heat-exchanger was considered. In this alternate, the straight shell and tube configuration would be changed to a shell and tube arrangement wrapped spirally around the outside of the main reactor body. This arrangement is shown in Figure 4.

The number of tubes in the spiral heat exchanger was cut in half to 120 but the length was increased to 26 inches, thus giving the same heat transfer surface area. The tubes were arranged in three layers of 40 each, giving a rectangular heat exchanger cross-section approximately 7 inches high x 5/8 inch thick.

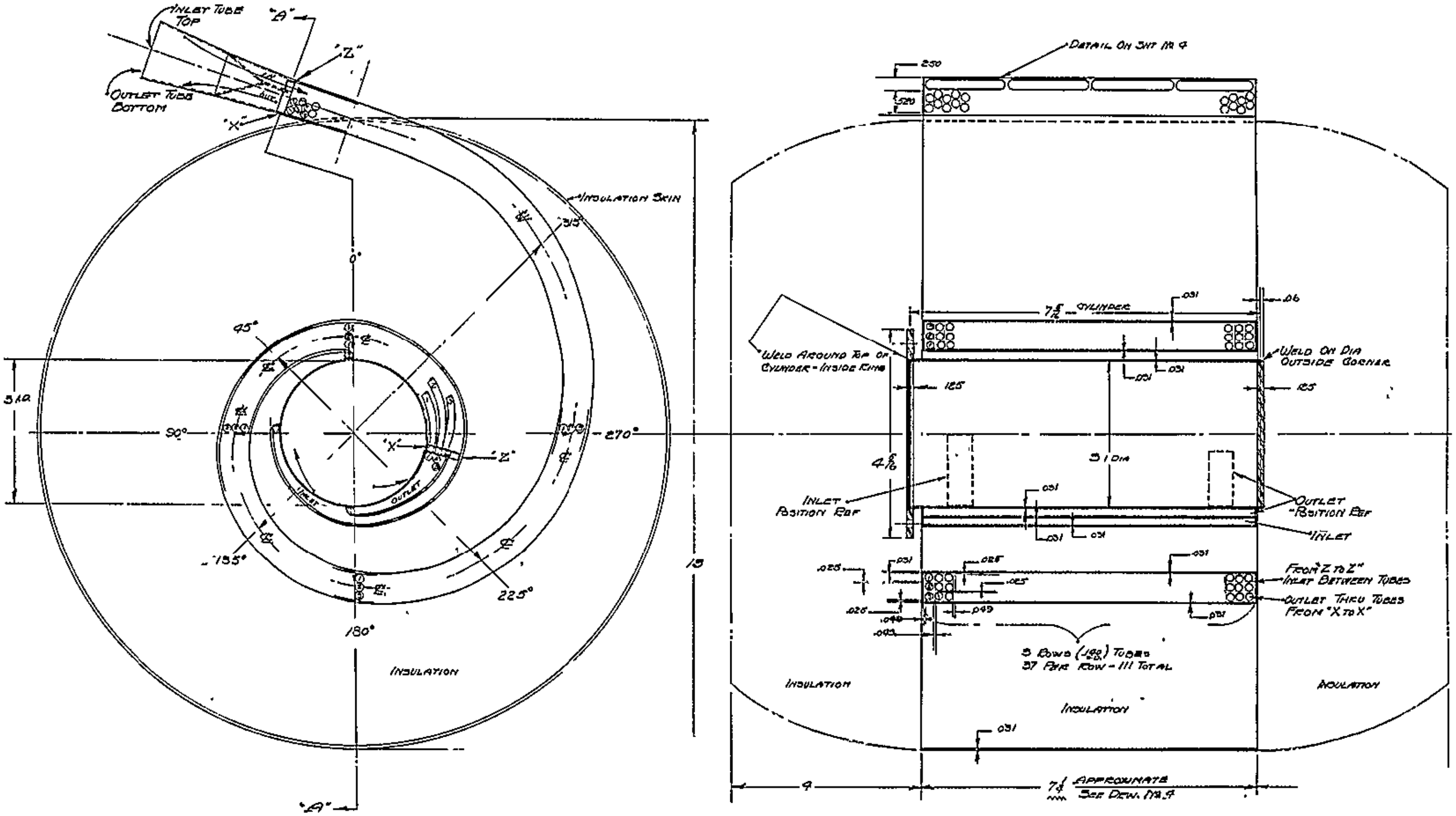


Figure 4. FORMALDEHYDE REACTOR WITH SPIRAL HEAT-EXCHANGER

Calculations for the insulation thickness around the 3-inch diameter x 7-inch high formaldehyde reactor shell at 675°C showed that at least a 5-inch thick layer was required to keep losses at a reasonable level. If the straight tube and shell heat-exchanger were used it too would require this thickness of insulation, at least at the high temperature end. The resulting cylindrical volume of the insulated reactor and heat-exchanger was 13" in diameter and 26" high.

In an attempt to minimize this volume the alternate spiral heat exchanger configuration was considered, since it could be wrapped around the reactor and, theoretically, located within the reactor insulation at a position where the average surface temperature of the heat-exchanger coincided with the insulation temperature. The heat-exchanger would thus operate essentially adiabatically in an environment continually maintained at the same temperature as the heat exchanger surface.

The insulation material chosen for use around the reactor and heat-exchanger was Min-K, type 1301 and for the bottom and top ends was Thermo-Flex Type RF. The properties of these materials are listed in Table 6.

TABLE 6. PROPERTIES OF JOHNS-MANVILLE THERMAL INSULATION MATERIALS

Material	Useful to °F	Form	Density lbs/cu. ft.	Therm. Conductivity BTU/hr. Ft^2 (°F/in.)
MIN-K, Type 1301	2000	Molded block	16	0.24
Thermo-Flex RF 600	2000	Fiber felt	6	.47-.62

Fabrication of the spiral configuration was not completed due to difficulties involved in attaching the heat-exchanger to the reactor in a manner which would allow access to seams and joints for leak-repair. Complex and costly weldments or castings would have been required for this purpose, and assembly and delivery time were not compatible with the program scope.

Consequently, the basic design of the straight tube and shell heat-exchanger configuration was used instead of the spiral configuration. To minimize overall system height the reactor and heat-exchanger were positioned side by side rather than end to end. The resulting required insulation volume for the subsystem is 18" wide, 14" deep and 22" high, instead of 14" in diameter and 32" high.

The arrangement of the formaldehyde reactor with a straight shell and tube heat exchanger is shown schematically in Fig. 5. and a photograph of the assembled unit is shown in Fig 6. Both the formaldehyde reactor and the heat exchanger were constructed from Inconel 600 as individual units to be assembled into a single subsystem. The reactor is 7-15/16" high, 3" in diameter, and has a 0.031" thick wall fitted with inlet and outlet ducts. The reaction zone is 5" high. The blind flange sealing the top of the reactor contains three 100 watt cartridge heaters for preheating the intake gas during startup. The shell and tube heat exchanger located next to the reactor is 15" high and 3-1/8" in diameter, with a 0.018" thick wall. It contains 241 tubes; each tube is 13" long, with a 0.14" outside diameter and a 0.010" wall. Thermocouple wells are provided to measure temperatures at the inlet, middle, and outlet of the reactor, and both gas streams at the high-temperature end of the heat-exchanger.

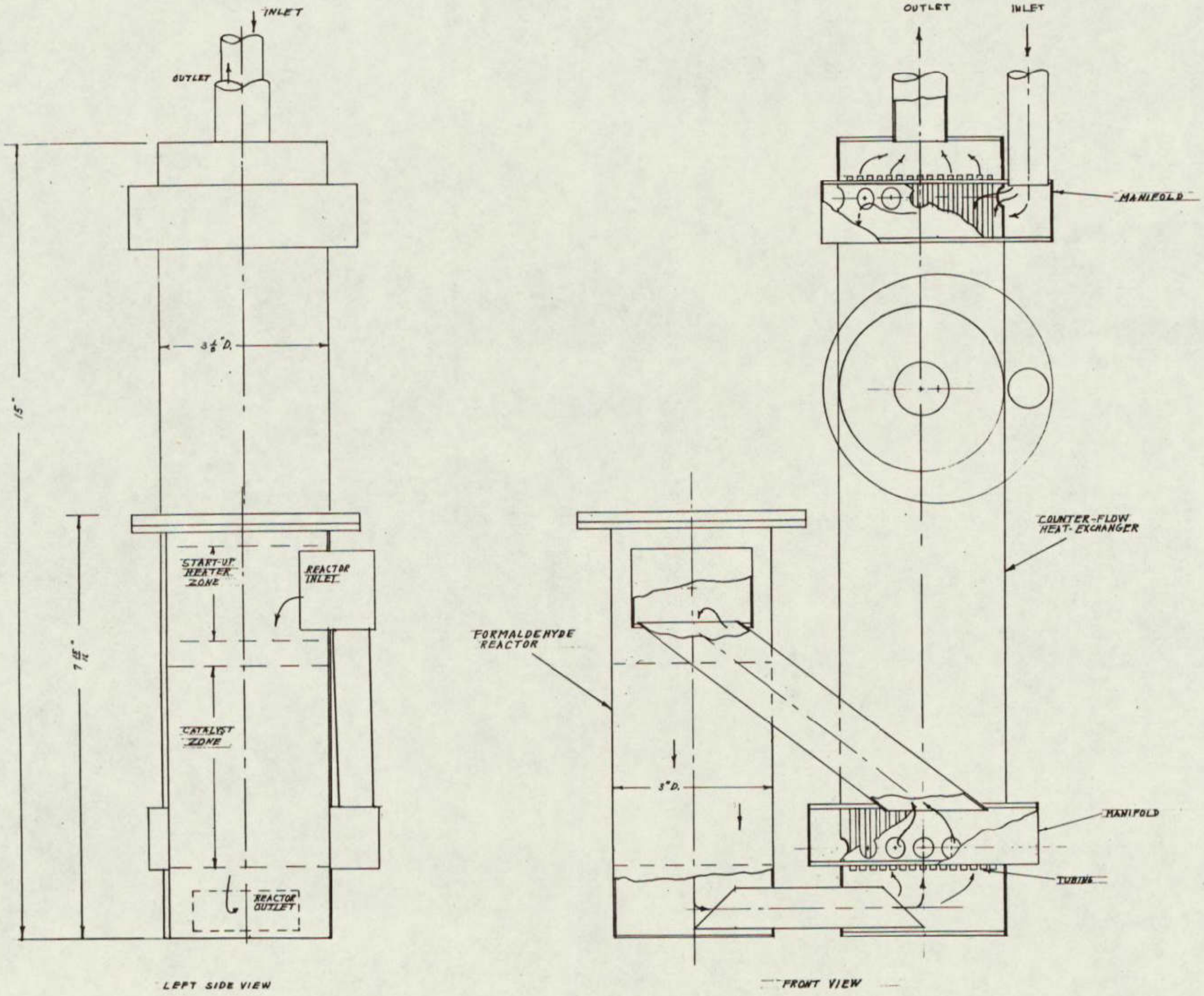


Figure 5. FORMALDEHYDE REACTOR AND STRAIGHT HEAT-EXCHANGER

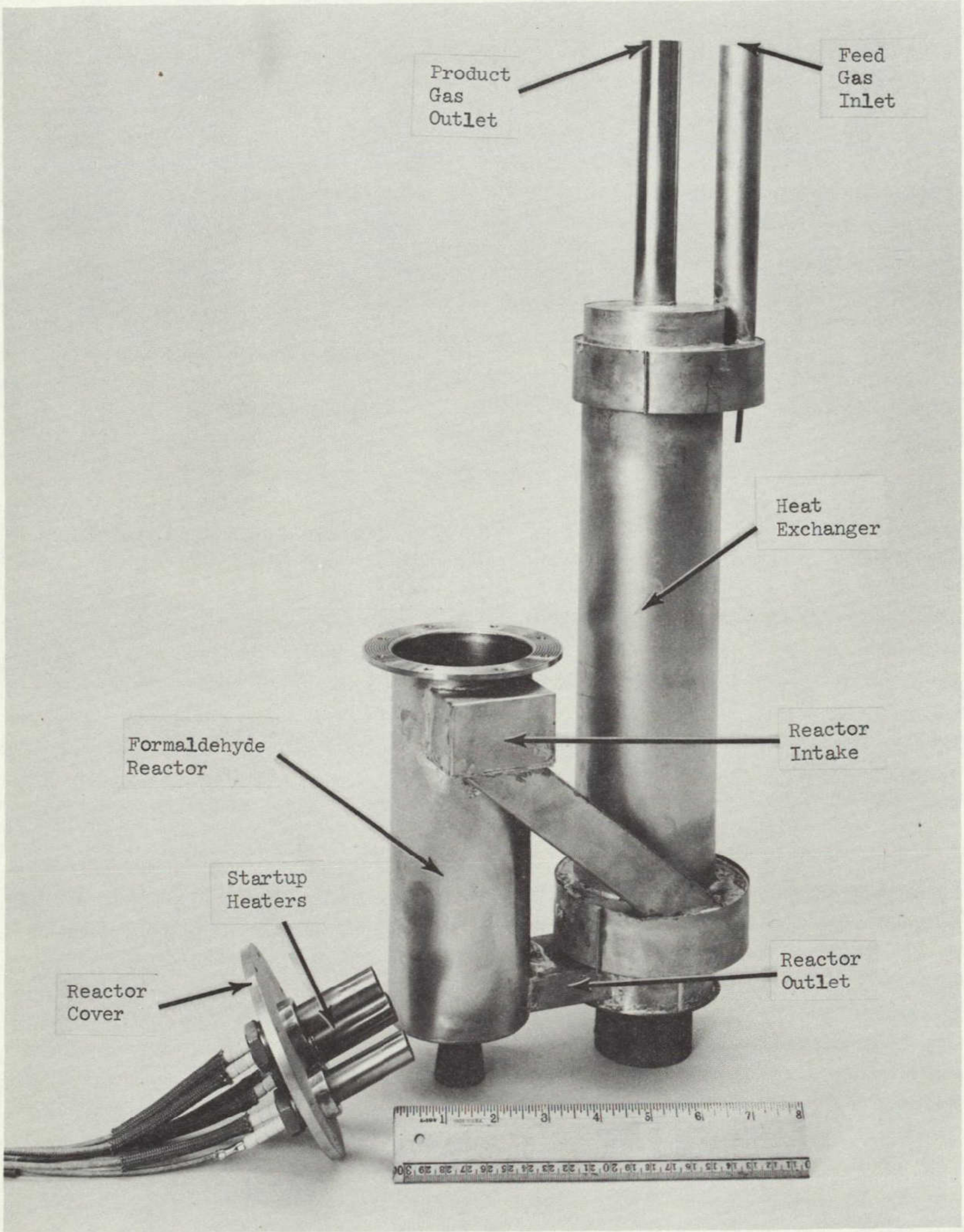


Figure 6. FORMALDEHYDE REACTOR HEAT-EXCHANGER

As noted before, the sub-system is insulated with MIN-K Type 1301 insulation around the reactor and hot end of the heat exchanger, and with Thermo-Flex RF insulation around the colder portions of the heat exchanger and ends of the sub-system.

The anticipated pressure drop across both sides of the straight heat-exchanger at a flow of 50 liters/min, and at operating temperatures, will be approximately 0.5" H_2O. The anticipated heat losses from the complete system will be due to a) insulation losses, b) loss by conduction along the length of the heat exchanger, and c) sensible losses in the exit gas stream. These losses were estimated at 150, 190, and 180 BTU/hr respectively, for a total of 520 BTU/hr. which is the approximate rate of heat generation in the reactor. On this basis, operation with no thermal input would be feasible.

Methane Reactor and Heat-Exchanger Design

The primary function of the methane reactor is to convert feed CO_2 and by-product CO_2 (from the formaldehyde reaction) to CH_4. The CH_4 is then returned to the formaldehyde reactor for conversion by oxidation to product formaldehyde. CO_2 is reduced by H_2 in the reactor to form CH_4 and H_2O. The reaction occurs at 320°C with over 99% conversion in a single pass; it is highly exothermic releasing 290 BTU/hr during normal operation of the one-man system.

The methane reactor and heat-exchanger subsystem was designed to meet the following performance objectives:

1. To produce approximately 215 gm/day of CH_4 from CO_2 and H_2 for use as feed to the main formaldehyde synthesis reactor.
2. To preheat incoming feed gas from 25°C to the 320°C level needed to initiate the CH_4 synthesis reaction.
3. To cool exiting product gas from the final reaction temperature level of 320°C to 115°C for subsequent cooling to 25°C to condense by-product water.
4. To provide for continuous cooling of the reactor to maintain the 320°C exit gas temperature level required for complete single-pass reaction.
5. To provide for transfer of the heat removed from the reactor to a separately located formaldehyde adsorption bed being heated during regeneration.

Methane Reactor. - The methane reactor configuration was based on that of the breadboard model. The breadboard reaction zone was a 3/4" diam. x 5" high cylinder filled with 1/8" cylindrical pellets of catalyst, namely, nickel oxide coated on alumina, a standard Sabatier reaction catalyst. Again the one-man reactor was a ten-fold scale-up to give approximately ten times the capacity of the breadboard methane reactor.

The exit temperature of the breadboard reactor was maintained at 320°C by direct loss through the insulation to the surroundings; no other external cooling was necessary. This mode of cooling was feasible since the reactor was only 3/4" in diameter, but was not feasible for the one-man reactor.

To achieve rapid and consistent cooling in the one-man reactor, the catalyst zone was fitted with a 5" high aluminum core containing 19 cylindrical holes 9/16" in diameter for the 1/8" catalyst pellets. The core fitted snugly within the 3-1/4" diameter stainless reactor. A cooling - jacket was located around the reaction zone, for circulation of cooling air. In this configuration the reactor would operate essentially under isothermal conditions, and excess heat from the reaction would be transferred rapidly to the reactor shell walls, and into the cooling gas passing through the jacket.

Feed Heat Exchanger. - The incoming gas stream must be heated to approximately 260°C. to sustain the reaction between CO_2 and H_2. A counter-flow shell-and-tube heat-exchanger was used for this purpose, with feed gas entering at 20°C and leaving at 260°C; exiting reaction product gas at 320°C exchanged with the feed gas, leaving the tube side of the exchanger at approximately 80°C.

The shell-and-tube heat-exchanger consists of 19 tubes, 7-1/4" long by 1/8" diameter and 0.006" wall, in a 3/4" diameter by .018" thick shell. In start-up the incoming feed gas stream is heated by a 250-watt cartridge heater located in the tubing connecting the heat-exchanger feed outlet to the reactor inlet.

A schematic of the methane synthesis reactor along with the counter-flow heat-exchanger, the start-up heater and ducting, and the reactor cooling jacket is shown in Figure 7. A photograph of the unassembled fabricated unit is shown in Figure 8.

Construction Materials. - The entire reactor assembly, other than the reactor core, was constructed from stainless steel. The reactor core was fabricated from aluminum. The sub-system assembly was integrated with the main formaldehyde reactor and heat-exchanger sub-system into a single insulation envelope to minimize overall system weight and size. The assembly was covered with a three-inch thick layer of Thermo-Flex RF insulation.

Formaldehyde Separator Design

The removal of formaldehyde and water from the recycle gas stream could be achieved by two different methods; adsorption by a silica gel bed, or condensation on cool surfaces. Both methods were investigated and found capable of removing CH_2O and H_2O from the recycle gas stream. With both methods, two or more cycling separators are required; while one separator is used to remove CH_2O and H_2O, the others are being regenerated.

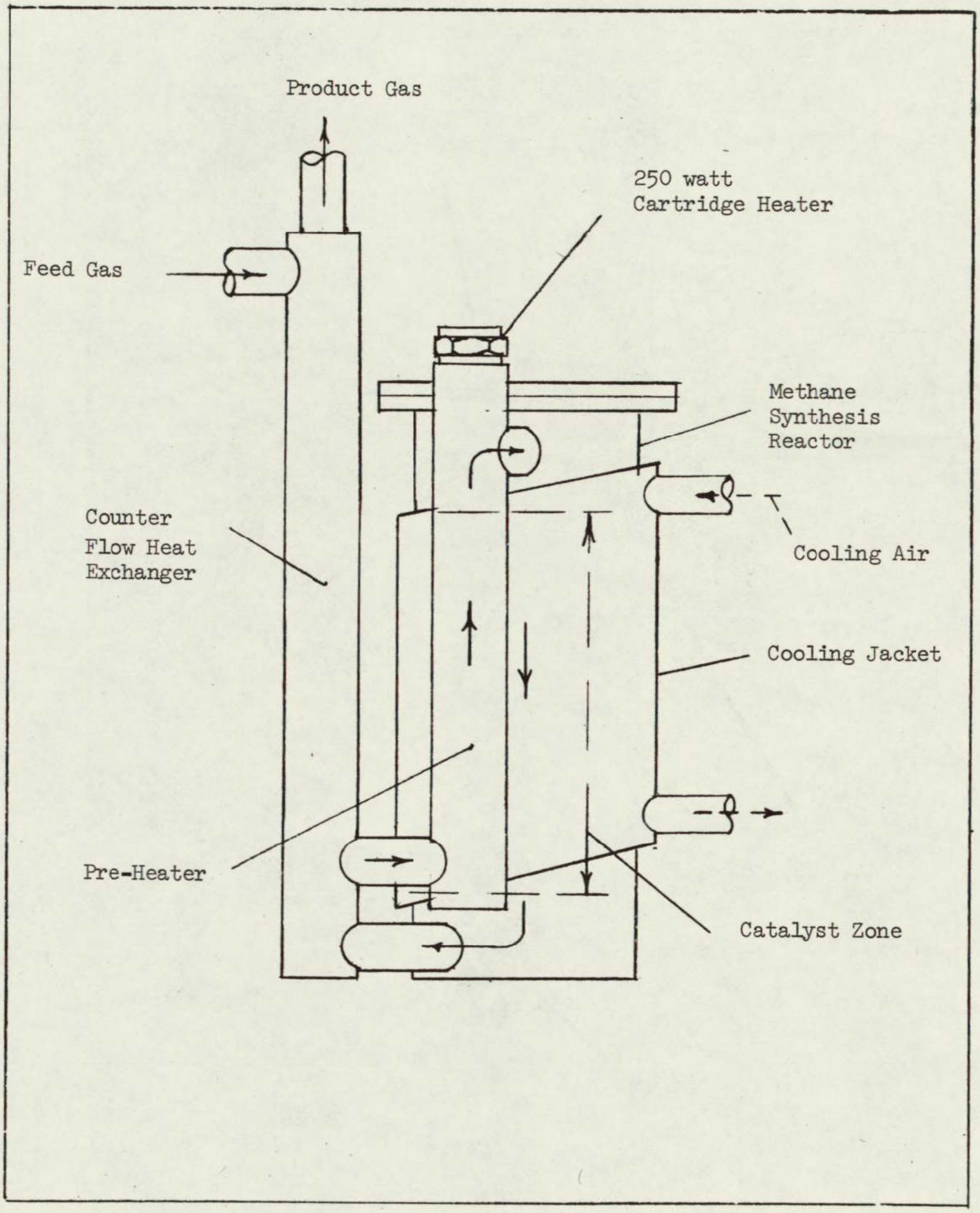


Figure 7. METHANE SYNTHESIS SYSTEM SCHEMATIC

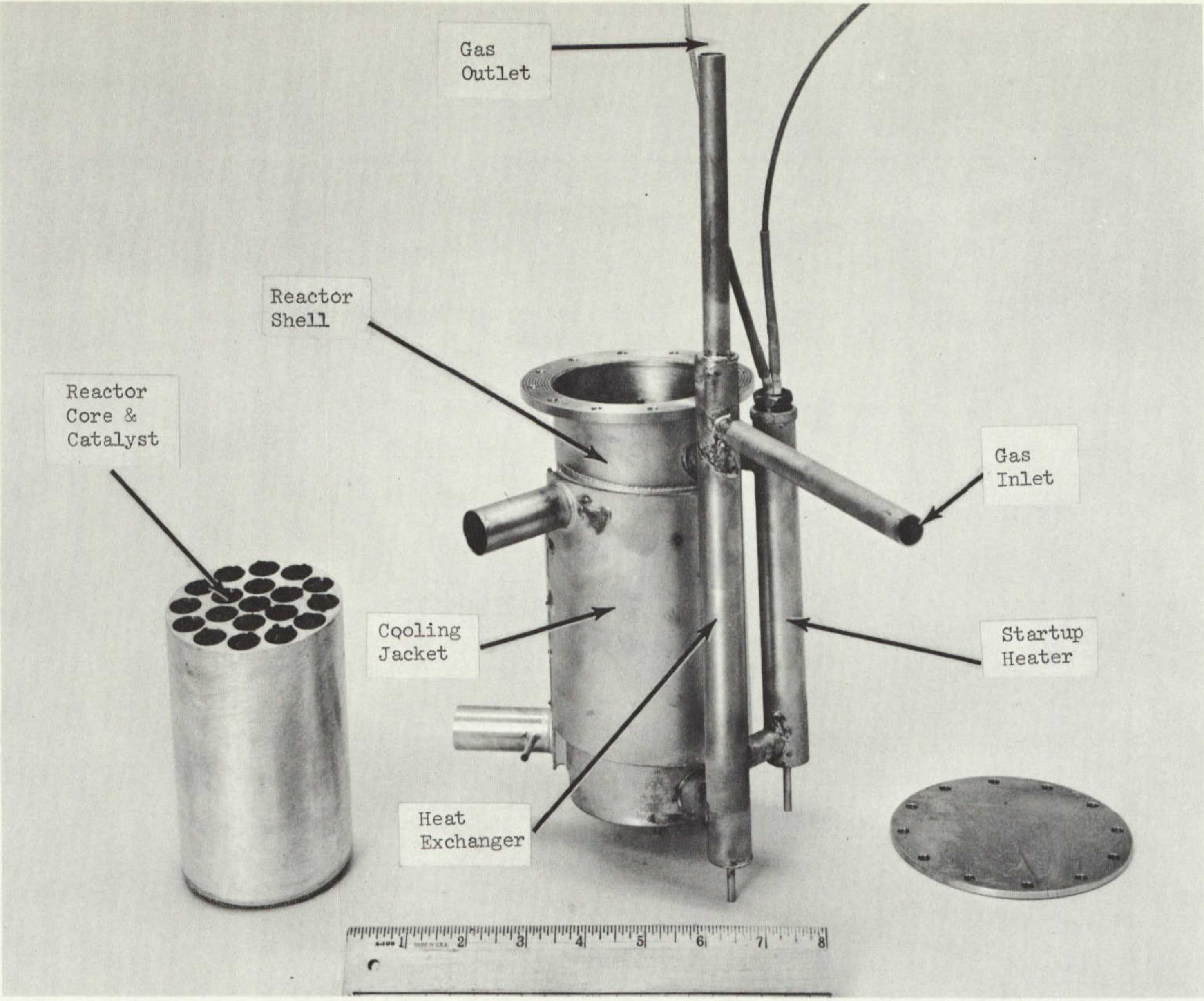


Figure 8. METHANE SYNTHESIS SYSTEM ASSEMBLY

The dimensions of a silica gel adsorption bed depend on the pressure drop which can be tolerated by the system and the length of the adsorption - regeneration cycle which is practically possible. For example, in a nominal one-man formaldehyde system, two beds 8" long by 3-1/2" diameter each containing 800 g granular silica gel and cycling every 90 min. would be required. Effective adsorption of CH_2O and H_2O is achieved at temperatures slightly above ambient with essentially 100% removal of both products. Complete regeneration requires heating up to 200°C, which would in turn require an input of at least 150·BTU/hr just to heat the silica gel bed in the 90 min. cycle time. However, adsorption on silica gel involves only solids and gases and, therefore, is very satisfactory for zero gravity conditions.

An an alternate; satisfactory removal of CH_2O and H_2O from the recycle gas stream can be obtained by direct condensation on cool surfaces. The completeness of CH_2O removal depends on the temperature and on the surface area. Condensers cooled to 1° - 2°C were found to remove approximately 95% of the CH_2O present in the recycle system. A portion of the CH_2O condenses on the cool walls in the form of solid paraformaldehyde; the remainder condenses with water forming a formaldehyde solution. Cooling below 0°C removes both CH_2O and H_2O in a solid form.

Removal of solid paraformaldehyde from the condenser is achieved by circulating water heated to approximately 90°C through the condenser. This temperature level could be achieved by utilizing the hot exit gas from the methanator cooling jacket. A condenser with a surface area of approximately 360 sq. inches would be required to remove the CH_2O and H_2O; however, the internal product collection volume may be made sufficiently large to require only infrequent cycling for regeneration.

The advantages and disadvantages of both these methods are compared in Table 7. Primarily because of zero-gravity operational complications, the silica gel bed was chosen over direct condensation.

TABLE 7. COMPARISON OF ADSORPTION AND CONDENSATION METHODS FOR CH_2O AND H_2O SEPARATION

Method	Advantages	Disadvantages
Adsorption on Silica gel	1. Operation is satisfactory for zero gravity conditions 2. Beds remove 100% of CH_2O	1. Energy is required for regeneration at 200°C level 2. Cycle is short
Condensation on cooled surfaces	1. Energy is required for regeneration at 90°C 2. Unit is capable of removing at least 95% of CH_2O 3. Cycle is long 4. Pressure drop is low	1. Zero gravity operation would be complicated 2. Solid paraformaldehyde separates from liquid solution

<u>Separator Configuration.</u> --The separator design employing two silica gel beds was utilized for actual operation. Each bed was sized to be large enough for one-hour of adsorption, and for heat-up and cool down to accomplish desorption-regeneration within the same cycle time. The beds were 8 inches high 3 inches in diameter filled with approximately 600 gm of 4-8 mesh silica gel granules. Pressure drop across one bed at 50 liters/min flow approximated 0.5" H_2O.

Each bed was heated with a 400-watt electrical heater wrapped around the entire cylindrical bed. The beds were not insulated.

Cycling Controls. - The inlet to each bed was fitted with a solenoid valve; direction of flow to either bed was effected by energizing the respective solenoid. An electric timer could thus switch flow from one-bed to the other on a cyclical basis. The pressure drop across the open solenoid valve at 50 liters/min approximated 0.5" H_2O.

In normal operation recycle gas flowed through one bed until it became saturated; the time interval is based upon an increase in bed temperature, at the outlet end, to 50°C, signifying the arrival of the adsorption temperature front. The cycle timer then de-energizes the inlet solenoid on the adsorbing bed, and energizes the inlet solenoid on the other bed.

The inlet end of each bed is fitted with a small exhaust line leading to another smaller solenoid valve. The exhaust solenoid opens on beginning of desorption-regeneration, and some of the CH_2O free recycle gas leaving the opposite adsorbing bed back-flushes through the desorbing bed and exits via the exhaust solenoid. Both exhaust solenoids and heaters cycle in proper coordination with the inlet solenoid valves, thus functioning to provide automatic adsorption-desorption on a continuous basis.

The exhaust line from the beds delivers the CH_2O-H_2O product in a highly concentrated form (carried by a low-flow stream of recycle gas) for subsequent further use as required. The carrier recycle gas may be returned ultimately to the main recycling system. A schematic drawing of the separator sub-system is shown in Figure 9.

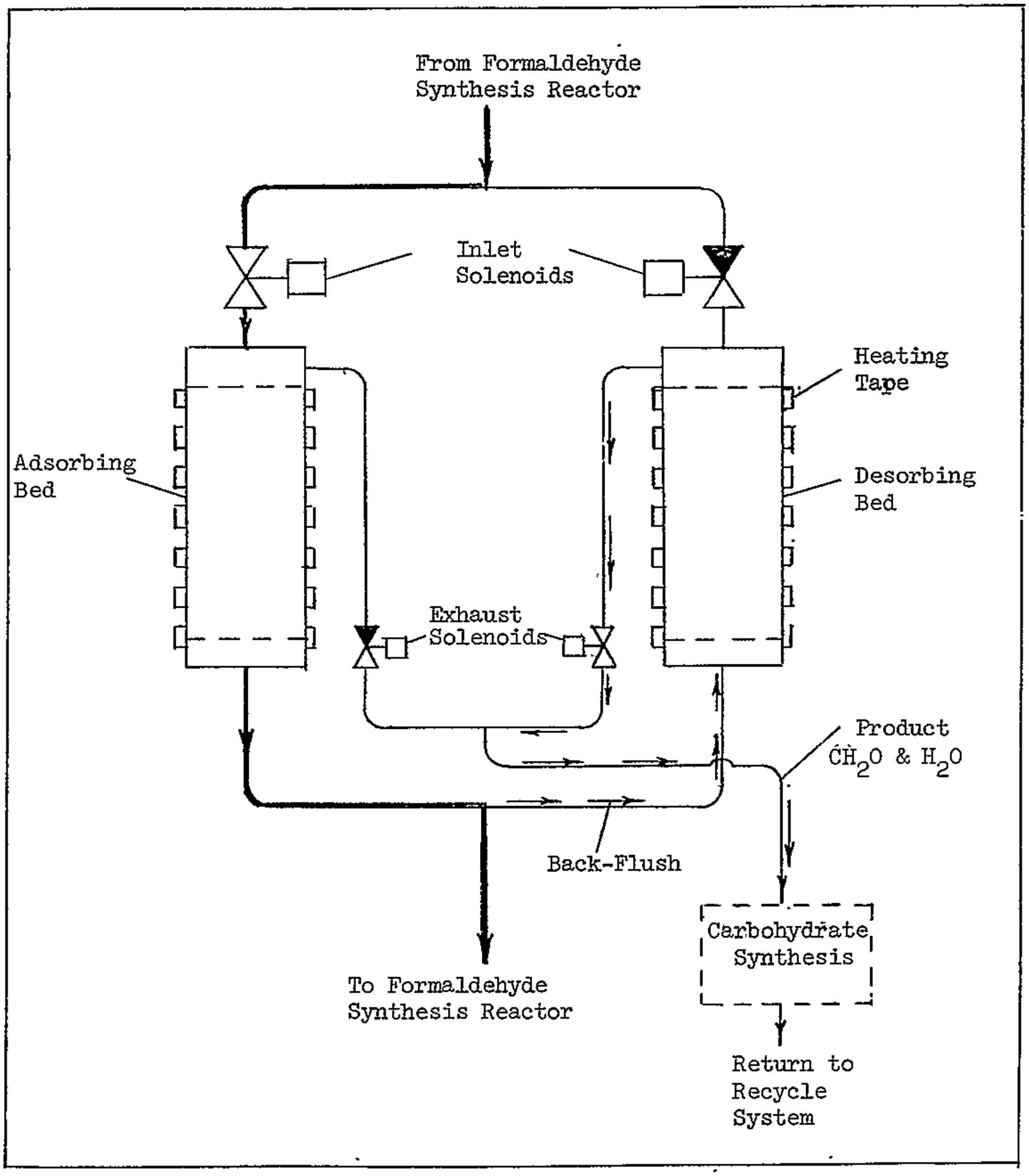


Figure 9. CH_2O - H_2O SEPARATOR SCHEMATIC

Recycle gas is designated for back-flush of the system because it is conveniently suited and available for this use. However, by including several additional valves, back-flushing could be accomplished with any of the system feed gases, namely O_2, CO_2 or H_2.

In this mode of operation an additional line would be added to the bottom of each bed for introduction of flush gas. Solenoid valves would then be added to the outlet line from each bed so that the bed could be totally isolated from the system. Similarily, smaller solenoid valves would also be added to the inlet flushing lines. In operation, back-flush gas would be added for a short time to purge recycle-gas from the bed prior to commencement of heating. Purged recycle gas and back-flush gas would return to the system loop. After purging and start-up of heating, the flush-gas would divert to the formaldehyde usage or processing unit; flush-gas would then either be vented or returned as feed to the recycle system.

EXPERIMENTAL TESTS AND DATA ANALYSIS

System Configuration

The major components of the one-man formaldehyde synthesis system were assembled in the configuration shown in Figure 10. The formaldehyde reactor and heat-exchanger and the methane reactor and heat-exchanger were housed completely within the insulation envelope. All other components, connecting ducting, and metering indicators were located outside and attached to the support structure of the envelope. The upper right quarter of insulation surrounding the methane reactor sub-assembly is removable in sections to provide access to both the methane and formaldehyde reactors and start-up heaters.

The direction of flow as indicated is for normal operation. In the formaldehyde separator the #1 bed is adsorbing. The inlet valve to the #2 bed is closed, and the bed is undergoing desorption, with back-flush gas exiting through the #2 flush valve. In a total food synthesis system the CH_2O and H_2O condensers shown would be replaced by the synthesis subsystem which uses CH_2O as a feed to generate carbohydrates.

A positive displacement meter was used to monitor recycle flow, but would be replaced by a differential pressure gauge for flow indication in the final system. With the exception of the condensers, the system, as shown, is suitable for zero-gravity operation.

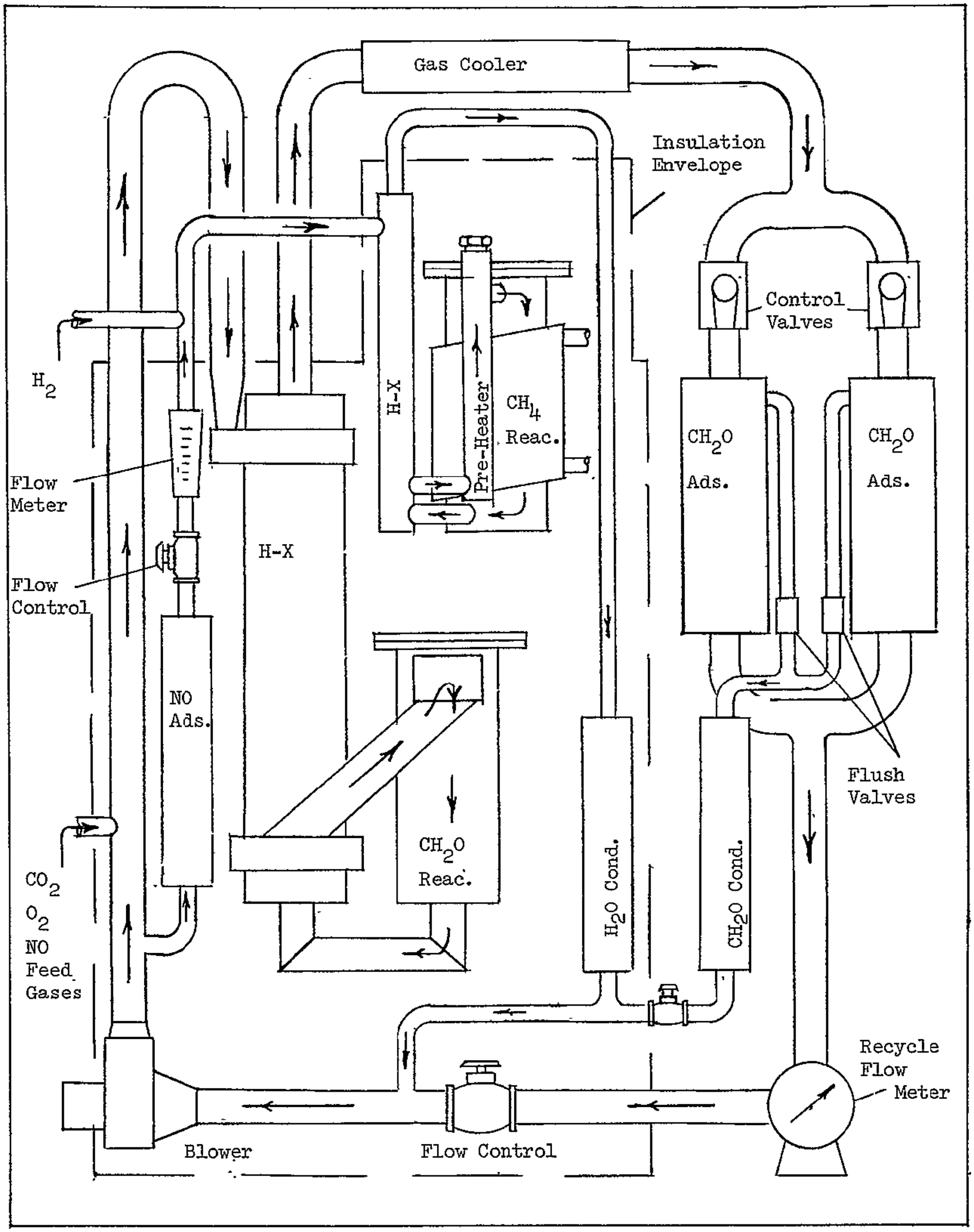


Figure 10. ONE-MAN FORMALDEHYDE SYSTEM OVERALL CONFIGURATION

Monitoring Equipment

Gas Sensors and Analysis. - The following instruments were used to monitor the recycle gas composition and to actuate solenoid valves regulating the input of feed gases.

a) LIRA infrared analyzer, model 300, Mine Safety Appliance Co. capable of monitoring CH_4 in concentrations 0-100%.

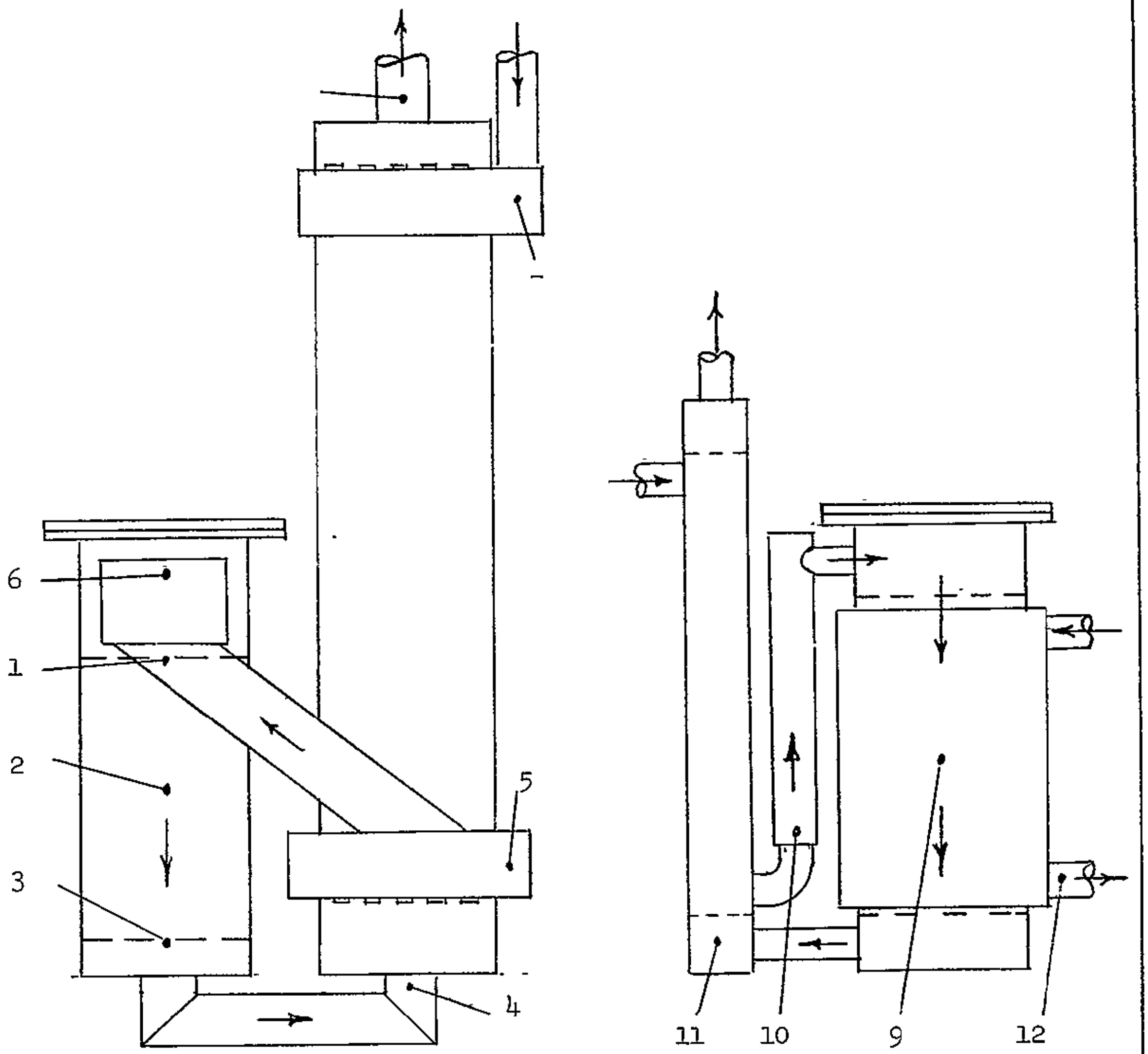
b) Beckman polarographic oxygen analyzer, using a 0-25% O_2 concentration range.

c) Gardsman (West Instrument Corp.) "on-off" controllers, which were activated by the outputs of LIRA and Beckman analyzers, actuated solenoid valves regulating the input of H_2 and O_2, respectively.

d) Bastian Blessing pressure sensitive gas regulator, sensitive to ± 1" H_2O pressure changes for direct control of CO_2 feed.

e) The performance of these sensors was checked periodically by analyzing gas samples by an in-line gas chromatograph, Aerograph Model A-90-P using a 6 ft. silica gel column maintained at 75°C, using helium as the carrier gas.

Temperature Sensors and Control. - Temperatures of various strategic locations within the system were measured by Chromel-Alumel thermocouples and recorded continuosly by a Daystrom-Weston, 12 point recorder. The locations of thermocouples are show schematically in Figure 11 . Thermocouple #2 was connected to a Gardsman stepless controller (West Instrument Corp.) and thermocouple #9 to a Gardsman proportionating controller, and were used to control the formaldehyde reactor and the methanator temperatures, respectively, both during preheating and during the actual testing.



Formaldehyde Reactor-Heat Exchanger

1	Reactor Bed In
2	Temperature Control
3	Reactor Bed Out
4	Product In (hot)
5	Feed Out (hot)
6	To Preheater
7	Feed In (cold)
8	Product Out (cold)

Methanator

9	Temperature Control
10	Feed Preheated
11	Product to Ht. Exch.
12	Cooling Gas Out

Figure 11. LOCATION OF THERMOCOUPLES

Flow Indicators. - The total recycle flow was measured by a Sprague displacement gas meter, Type 175 and the recycle flow through the methanator by a "Gilmont" ball flowmeter with a 0-12 l/min range. All other flows were indicated by "Gilmont" ball flowmeters of the following capacities:

O_2 flow,	0-2000 cc/min
H_2 flow,	0-2000 cc/min
CO_2 flow,	0-2000 cc/min
NO flow,	0-80 cc/min
Methanator cooling,	0-25 l/min
Silica Gel desorbing,	0-2000 cc/min

System Testing

Startup Procedures. - The system was prepared for testing by recycling gas through the entire system while it was being purged with CO_2; concurrently, both the formaldehyde and the methanation reactors were being preheated. To avoid overheating of the preheater elements, recycle gas flow through the formaldehyde reactor was maintained at about 20-25 l/min and through the methanator at about 10 l/min. With the formaldehyde reactor preheaters fully energized (115 V) i.e. delivering 300 watts, the top of the reaction bed became preheated to the required startup temperature of 600°C in about 3.5 - 4 hours. The methanator preheater, with voltage set at 50 V for delivering the 55 Watts required, preheated the methanation catalyst bed to a startup temperature of 260°C in approximately 1.5 hours. When the temperature of the methanator reached 260°C, the recycle flow through it was reduced to 2 l/min. and H_2 flow started at a rate of approximately 400 cc/min. The methanation starts immediately and the temperature of the methanator increases, eliminating further need for preheating. At this H_2 flow rate, the desired methane concentration of at least 30% in the system is reached in about 40 minutes. The H_2 flowrate is kept relatively low during the startup methanation because faster flow results in an excessive increase of the internal pressure.

When the top of the formaldehyde reactor bed reached 600°C, nitric oxide was admitted into the system at a rate of 30 cc/min for one minute, which provided enough NO to give a 0.2% concentration in the recycle gas. Since NO is continuously lost by being adsorbed on Molecular Sieves 13X bed in the methanation loop regardless whether the CH_4 oxidation has started or not, the NO concentration is maintained by adjusting its flow to 4 cc/min immediately after the initial addition. Then the flow of O_2 was started at a rate of about 300 cc/min. until its concentration reached about 6%. Normally, such addition of O_2 would raise the internal pressure of the system by about 24" H_2O; however, if the top of the reaction bed is preheated sufficiently, some reaction takes place immediately on adding oxygen and removes CH_4, minimizing the increase in internal pressure. The initiation of the CH_4 oxidation reaction is manifested by a slow drop in the CH_4 concentration, a sudden increase in the reaction bed temperature, and more significantly, a continuous drop of internal pressure. These manifestations indicate that the reaction is proceeding and a test has begun.

Test Procedures. - During the entire run, the feeds of CO_2, H_2 and O_2 were regulated automatically using the monitoring and control equipment described in the previous section. At the beginning of a run, feed gas valves of each controller were adjusted to provide cycling between suitable minimum and maximum flow rates for satisfactory automatic control of the recycle gas composition under all conditions, i.e. ranging from practically no reaction through an intermediate to a fast reaction rate. Thus, the minimum flows for O_2 and H_2 were adjusted just to offset their reaction in the methanator, with no reaction in the formaldehyde reactor; their maximum flows were high enough for the highest CH_4 oxidation rate expected from preliminary testing. Feed of CO_2 was adjusted to range from 0 to about 1000 cc/min and was self adjusting between these values according to the need for maintaining a constant pressure. The flow rate of NO was maintained constant during the entire run. Once the flow rates of feed gases were set properly, the desired gas concentrations were maintained throughout the entire test automatically by the monitoring equipment.

The temperatures of both formaldehyde and methanation reactors were controlled automatically using control thermocouples situated in the center of each bed. The formaldehyde reactor required electrical heating during these runs; however, the methanator had to be cooled to maintain the proper bed temperature at 260°C.

The duration of each test was determined by the time required to saturate one silica gel adsorption bed. The adsorption of CH_2O and H_2O raises the temperature of the silica gel bed at the adsorption zone from ambient to 50°-55°C, depending on water concentration in the gas. This adsorption zone moves down the silica gel bed, creating a moving hot front which reaches the exit end of the adsorption bed when it becomes saturated. Thus, when the temperature at the exit end of adsorption bed reached 50°-55°C, one run was terminated and another started by simply switching the product gas flow through another adsorption bed.

Regeneration of Adsorption Beds. - The regeneration of a saturated silica gel bed was started immediately after the completion of a run. A small stream, usually 150-200 cc/min, of the recycle gas leaving the adsorbing bed is diverted to backflush the saturated bed while it is heated up to 200-210°C by an external heater. This backflushing gas stream carries the desorbed vapor into an air-cooled condenser backed by three ice-water cooled condensers, where water vapor and formaldehyde condense as a solution. The backflush gas, with essentially all the formaldehyde removed from it, exits the condensers and returns to the main recycle gas stream.

Heat-up of the bed to 200°C to begin desorption usually takes from about 50 to 80 min, depending on the power input to the electric heating tape. Power was set to maintain the outer shell temperature at 225°C in all tests. Before being reused the desorbed bed must be cooled to approximately ambient temperature. If only the desorption flow of 150-200 cc/min is used, the cooling requires several hours; however, when approximately 1/2 of the recycle gas is diverted through the desorbed bed, it reaches ambient temperature in about 75 min; the total stream of recycle gas cools the bed to ambient in about 25-30 min. The minimum regeneration time for the silica gel bed.achieved during testing was about 80-90 minutes.

Test Results. - Test results and experimental conditions are summarized in Table 8. The system was operated at a total recycle flow velocity of 31.1 - 36.7 l/min with 28-34 l/min being recycled through the formaldehyde reactor and 2-3 l/min through the methanator. The recycle gas composition

TABLE 8. - TEST RESULTS - ONE-MAN FORMALDEHYDE SYNTHESIS SYSTEM

Test No.	Total Recycle Flow, l/min	Test Length, min	Formaldehyde Production					Formaldehyde Reactor Conditions												
			Soln. Vol., cc	CH_2O wt.%	CH_2O Wt g	CH_2O Rate, g/hr	Recycle Flow, l/min	Recycle Gas Comp. Range, %						Bed Temperature, °C			Heat Exchanger Temp., °C			
								NO	O_2	N_2	CH_4	H_2	CO_2[a]	To Preheater	In	Out	Feed In	Feed Out	Prod. In	Prod. Out
1	32.5	150	55	4.7	2.6	1.0	28.5	0.1	6.0-6.5	6.8-9.0	26.0-26.6		57-61	470-610	610-690	540-660	43-49	390-550	520-660	190-215
2	32.5	30	62	3.1	1.9	3.9	30.5	0.1	6.0	9.5	26.6		56	610-630	680-690	660-680	49-60	550-590	660-680	215-240
3	32.5	90	49	8.8	8.0	5.3	29.5	0.1	5.2-7.8	9.0-11.5	24.5-29.6		51-61	470-550	600-650	530-610	38-43	380-480	500-540	180-205
4	32.5	90	58	5.2	4.7	3.1	29.5	0.1	5.5-6.2	12.2-14.4	23.3-26.5		53-59	550-610	640-660	600-640	43-49	480-530	540-590	205-215
5	32.5	60	41	5.8	2.4	2.4	30.0	0.1	3.6-5.8	3.8-5.8	27.8-30.2		59-65	510-570	620-660	550-600	43	400-470	530-590	180-200
6	32.5	30	36	4.4	1.6	3.2	30.0	0.2	5.8	5.8	27.8		60	560-570	650-660	600-620	43	470-480	590-600	205-210
7	31.1	60	30	7.5	2.2	2.2	29.1	0.29	5.4-5.8	7.4-9.0	26.6-30.0	1	54-60	490-530	600-630	530-570	38-43	390-430	510-560	175-190
8	31.1	60	28	11.5	3.2	3.2	29.1	0.28	5.4	9.2-10.2	28.4	1	55-56	520-530	620-630	570-580	43	430-450	560-570	195
9	32.5	60	16	11.5	1.7	1.7	30.5	0.3	5.4-7.3	6.0-6.4	27.8-28.4		58-61	490-530	610-640	540-590	43	390-430	520-580	140-160
10	36.7	30	30	5.9	1.8	3.6	34.7	0.3	5.4	8.0	27.2		59	530-550	640-650	590-600	43	430-450	580-590	155-165
11	31.0	20	25	6.7	1.7	5.1	29.0	0.31	5.6	17.0	30.3		47	510-570	630-670	550-620	43	420-460	540-600	140-145
12	36.7	20	21	4.6	1.0	3.0	34.7	0.31	5.5	16.0	29.0	2	47	570-620	670-700	610-640	43	460-500	600-640	145-160

[a] CO_2 values calculated by difference.

TABLE 8. - TEST RESULTS - ONE-MAN FORMALDEHYDE SYNTHESIS SYSTEM - Continued

Test	Methane Reactor Conditions							Feed Gas Flow Ranges[e],			
No.	Recycle	Reactor Temperatures,			Cooling Gas		Product				
	Flow,	In	Center[b]	Out	Flow,	Temp.,[c]	H_2O,[d]	O_2	NO	CO_2	H_2
	l/min	°C	°C	°C	l/min	°C	cc	cc/min	cc/min	cc/min	cc/min
1	4	260-315	290	325-390	20	230-325			2	0 to 400	
2	2	300-315	290	375-380	20	310-315	92		2	"	
3	3	240-265	290	310-345	20	210-270			2	"	
4	3	230-265	290	310-315	20	210-215	98		2	"	
5	2.5	230-250	290	280-310	20	165-195		200-500	3	"	120-800
6	2.5	250-255	290	310-315	20	205	17	200-700	3-6	"	120-800
7	2	250-260	290	310-330	20	205-245		200-500	4	"	120-800
8	2	260	290	310	20	205-210	57	200-500	4	"	120-800
9	2	260-280	290	325-350	18	220-245		200-500	4	"	120-800
10	2	255-265	290	330-340	18	225-245	45	200-500	4	"	120-800
11	2	255-265	290	325-350	18	210-225		420-750	4	0 to 1000	120-800
12	2	265-290	290	350-370	18	225-245	7	420-750	4	"	120-800

b. Center temp. is setting of the thermocouple used for controlling heaters; no heating was needed during runs and the temperature remained at or above the control setting.

c. Gas temp. leaving cooling jacket; inlet temp. was constant at 80°F (ambient).

d. Measurements were made every second test, therefore each value represents product H_2O of two tests and includes H_2O produced during startup methanation.

e. Feed gas flow ranges indicate the minimum and the maximum flow settings of control valves.

was maintained at 5.5 - 6% O_2, 26-30% CH_4, 4-17% N_2 47-60% CO_2, and 0.1-0.3% NO. The temperatures of the formaldehyde reactor ranged from 600°C to 700°C; however, they were usually in the 600°-650°C range. Because the time required for CH_2O and H_2O desorption from the silica gel separator bed was much longer than the adsorption to saturation, truly continuous operation could not be achieved; instead, tests were obtained in pairs, and test duration was the total time available for adsorption of product by the two silica gel beds.

The formaldehyde production rates observed range up to 5.3 g/hr, i.e. equivalent up to 127 grams per day. The lower than anticipated formaldehyde production is attributable mainly to low recycle gas flow rates which reached only about 62% of the originally planned 50 l/min. Since the formaldehyde production rate is directly proportional to the recycle gas flow rate, raising the recycle gas flow to the required 50 l/min rate would allow operation at the anticipated goal of 200 g/day of formaldehyde.

Although the recycle gas composition was controlled automatically, periodic checks of composition were made by an in-line gas chromatograph. To indicate the range of recycle gas composition, the lowest and the highest values for each gas during each run obtained by gas chromatographic analysis are given in Table 8.

Temperature ranges observed during each run in the formaldehyde reactor, heat exchanger, and methanator are included in the Table, indicating the lowest and the highest values observed during each test.

The feed gas flow ranges indicate the highest and the lowest flows used for each gas. Automatic flow controllers, operating on an "on-off" principle, determined the length of time each gas was supplied at the lowest and at the highest flow rates to maintain the required concentration.

Data Analysis

Formaldehyde Production. - The formaldehyde production rates obtained with this system range up to 5.3 g/hr. or 127 grams per day. This observed formaldehyde production rate was obtained with a recycle gas flow of approximately 30 l/min., i.e. only about 60% of the planned flow rate of 50 l/min. Since the formaldehyde production is essentially directly proportional to the volume of gas flowing through the reactor, raising the flow rate to 50 l/min. would boost the formaldehyde production rate up to 200 g/day even if the same degree of overoxidation remains prevalent. It can be expected that the shortening of reaction gas residence time in the high temperature zone would cause an additional increase in the formaldehyde yield.

The total amount of water produced was approximately two to four times higher than could be expected from the amount of formaldehyde separated from the recycle gas by the adsorption beds. This imbalance in the production of CH_2O and H_2O indicates an unexpectedly high degree of overoxidation of the CH_2O formed. From the data available, it is impossible to determine with certainty the specific cause of this excessive overoxidation; however, several possible causes, listed in probable order of importance are:

1. Too long a residence time for the reacting gas mixture within the hot zone, causing decomposition and further oxidation of the CH_2O formed,

2. Incomplete CH_2O removal by the adsorbing bed, and subsequent return of some CH_2O to the hot reaction zone, where it becomes oxidized to CO_2 and H_2O,
3. Catalytic effects of the metallic walls, which are partially covered with an oxide film, in the reactor, outlet duct, and hot end of the heat exchanger, causing direct oxidation of CH_4 to CO_2 and H_2O.

Item 2, the return of unadsorbed CH_2O to the hot zone, should contribute little to the overoxidation. Results with runs in which the CH_2O adsorption beds were saturated to a point where H_2O was condensing for a considerable length of time in the gas lines downstream of adsorbers did not differ appreciably from those where the run was terminated immediately upon start of CH_2O condensation. Since the temperature of the adsorption bed indicates the degree of total saturation and also determines the amount of CH_2O which can be adsorbed, it appeared that the point at which significant amounts of unadsorbed CH_2O escaped back into the recycle system was not reached in any of the runs.

Catalytic effects of the hot walls on the direct oxidation of CH_4 to CO_2 and H_2O also can be considered minimal. When a typical recycle gas containing about 30% CH_4, 6% O_2, and 64% CO_2, but no nitric oxide catalyst gas was recycled with all system components at typical reaction temperatures, (formaldehyde reactor at approximately 650°C), the rate of H_2O production observed was insignificant at only 0.8 g/hr., compared to a minimum of 18 gm/hr under synthesis condition.

The formaldehyde reactor preheater, and outlet duct all remained at or near the reaction temperature, constituting an extended length hot zone. It is estimated that, with the recycle gas flows used in these tests, the residence time of the reacting gas in the hot zone is from 2.0 to 2.2 sec., compared with the residence times of 0.5-0.7 sec. in preliminary investigations with the laboratory and breadboard reactors. Since the residence time in this reactor was 3-4 times longer than in the other reactors where good formaldehyde yields were obtained, it is possible that too long a residence time is the primary cause of formaldehyde decomposition and overoxidation to CO_2 and H_2O.

Data Correlation. - From the data available, no correlation was apparent relating the primary operating conditions of flow rate, temperature, and catalyst concentration, with the CH_2O production. Recycle gas flow rates and composition were held essentially constant during all the runs. Temperature varied from 600° to 700°C at the intake end and 530° - 680°C at the outlet end of the reaction bed; however, no clear trends in CH_2O production appeared related to these temperature variations. The same was true with the NO concentration which varied from 0.1% to 0.3% in different runs. It is possible that any trends because of changes in temperature or NO concentration were masked by the very high degree of overoxidation experienced.

The CH_4 oxidation rates experienced in these tests, approximated from the water produced, are 2-4 times higher than those observed during prior experiments with small reactors. Since essentially all the CH_4 underwent the usual gas phase oxidation route involving $CH_4 \longrightarrow CH_2O \longrightarrow CO \longrightarrow CO_2$, (heterogeneous catalytic oxidation was shown to be minimal) the amount of

CH_2O produced momentarily was actually considerably higher than in prior tests. Thus by, shortening residence time or by fast cooling of the product gases it may be possible to raise the formaldehyde production rate well above the target value of 200 g/day.

Heat Exchanger Performance. - Although the design of the formaldehyde reactor heat-exchanger was based on a direct scale-up of data obtained from the heat-exchanger used in the breadboard model, the one-man heat-exchanger did not perform with as high an efficiency as expected. Performance of the one-man heat exchanger compared with that used in the breadboard unit is shown in Table 9. The calculated efficiency of the one-man unit is only 57%,

TABLE 9. COMPARISON OF HEAT-EXCHANGER PERFORMANCE OF BREADBOARD MODEL AND ONE-MAN SYSTEM.

	Feed, °C			Product, °C			Calculated Efficiency, %
	In	Out	ΔT	In	Out	ΔT	
Breadboard	25	600	575	675	80	595	80
One-Man System	43	450-500	Avge: 470	550-600	150-200	Avge: 400	54

compared with 80% observed in the breadboard model. On re-examination of original experimental data of the breadboard model, it was discovered that there might have been an error in the temperature measurement of the product outlet; however, if there was an error, it could have raised the product outlet temperature by 50°C at the most. Even the assumption of such an error is insufficient to explain the disparity between the performances of the heat exchangers, both designed using the same assumptions.

Because of poor performance of the heat-exchanger, feed gas entering the preheater section of the formaldehyde reactor was at a lower temperature than anticipated. The result of this was that the recycle gas could not be preheated sufficiently during startup if a recycle flow of 50 l/min. was used. Sufficient preheating could be achieved only with recycle gas flow rates of up to 30-32 l/min. Even with this recycle gas flowrate, during the actual tests, the feed gas was not preheated by the heat exchanger to the desired kindling temperature of 620°C, but only to 500°C before entering the formaldehyde reactor.

Because total flow was below the design value the heat of reaction was insufficient by itself to maintain the system at the proper temperature. Therefore, continuous heating of the reactor by means of the startup heaters was needed during all the tests. It was estimated that 188 watts were required to raise the recycle gas temperature from 450°-500°C measured at the feed exit from the heat-exchanger to 600-650°C observed at the top of the reaction bed. Experimentally, the measured power required to maintain the temperature ranged from 193 to 300 watts.

Since product was not cooled sufficiently before leaving the heat exchanger, it had to be cooled additionally before entering the formaldehyde separators; otherwise, adsorption of formaldehyde would not occur.

The available data fails to indicate an apparent reason or explanation for the lower than anticipated efficiency of the heat-exchanger. Since the formaldehyde reactor and the heat-exchanger were situated side-by-side, only about 1-1/2" apart, it can be assumed that there was some heat transfer from the hot reactor to the shell of the heat-exchanger. This would help to explain the fact that the observed Δ T of the feed was lower than Δ T of product, and that the product was exiting at a temperature higher than expected. However, such additional heat transfer to the shell side should also tend to preheat the feed gas to temperatures higher than anticipated, but in actuality the opposite was observed.

Methane Reactor Performance - The entire methane synthesis subsystem performed essentially as anticipated in the design, and produced enough methane to maintain a constant level in the recycle gas. Outside heating was required only to preheat the catalyst bed to its kindling temperature; once the methanation reaction had started, excess heat was released. This not only eliminated the need for outside heating but, as anticipated, required cooling to prevent overheating of the catalyst bed.

Although the controller for the reaction heater was set for a bed-center temperature of 290°C, methane reaction always started at about 260°C and quickly increased the catalyst bed temperature above the control point so that heater was never used during the runs. To prevent over-heating of the catalyst bed, the temperature of the gas leaving the methane reactor was generally maintained in the 310 - 350°C range by adjusting the external cooling air flow. The aluminum reactor core acted as an efficient heat transfer medium preventing local over-heating, as evidenced by smooth temperature curves regardless of the H_2 flow cycling or adjustments in flow of the cooling air.

The counter-flow gas heat exchanger operated properly, cooling the product gas from 310 - 350°C to an outlet temperature of 80° - 100°C, and preheating the feed gas (recycle plus hydrogen) from ambient to approximately 260°C. Thus, the feed gas entering the catalyst bed was at the required kindling temperature.

The water produced in the methanator was condensed in condensers, cooled by ambient air, having an approximately 730 cm^2 cooling surface. Normally, the collected water is clear, odorless, and has a pH of 6-7. However, the combined product of runs # 9 and 10 had a pH of 8 and a faint ammonia odor, indicating that the NO adsorber had approached the breakthrough point. The combined product of runs # 11 and 12 had a sharp NH_3 odor and a pH of 9, clearly indicating that the NO adsorber was saturated, and admitting NO to the methanator.

NO Control. - The loss of NO catalyst gas from the recycle gas stream is constant and is only due to its removal from that part of the recycle stream going to the methanator; therefore, a constant flow of NO feed was sufficient to control its concentration. The Molecular Sieves 13X bed removed essentially all the NO from the recycle gas entering the methanator and performed as expected from preliminary experiments. From the volume and the geometry of the adsorption bed, it was estimated that it should remove NO for approximately 7-10 hrs. As anticipated, breakthrough of NO was observed after 11 hours, as indicated by the presence of NH_3 in the product of methanation during runs # 11 and 12.

Automatic Control Performance. - The automatic controllers regulated the flow of feed gases satisfactorily and maintained the recycle gas composition within acceptable limits. Taking into account all the tests the average fluctuations in the concentrations were ± 1.4% for O_2, ± 2.5% for CH_4, and

± 5% for CO_2; however, a couple of widely fluctuating runs increased the average range while a majority of the individual tests showed much smaller variations.

The output of oxygen and methane sensors located at the feed gas inlet into the heat exchanger actuated "on-off" type controllers for O_2 and H_2. flows, respectively. Therefore, the flows of O_2 and H_2 were not steady but fluctuating between the "high" and the "low" flow and only the length of time at each flow was varied to maintain the required concentration. Although the flow of O_2 varied between the "low" of 200 cc/min and the "high" of 500-700 cc/min. and that of H_2 between 120 and 800 cc/min, there was sufficient mixing; no sudden fluctuations in any gas concentration were observed.

The feed of CO_2 was controlled directly by a pressure sensitive regulator which was self-adjusting and maintained the CO_2 flow within the range of 0-1000 cc/min according to need. Since CO_2 is removed from the system only after it becomes converted into CH_2O, the adsorption of formaldehyde causes a total system pressure drop which is reflected in the pressure sensitive regulator, ultimately causing the flow of feed CO_2.

Blower Performance. - A Globe Industries, Inc. minature A.C. Centrifugal blower, type C-19A-535, size 2, operating at 400 cps frequency and 115 volts, with a 0.08 mfd 1000 WVDC capacitor, was used in all the tests. This blower is designed to deliver an even, non-pulsating flow of gas and draws only 27-30 watts of power; it is able to deliver up to approximately 60 l/min. against a back pressure of 4" H_2O.

The blower worked well, developing a ΔP of ~ 5.5" H_2O across its pressure and suction ends while mounted in the system. No deterioration of performance was observed after cumulative total of about 80-100 hours of operation. This type blower appears to be well suited for use in scale-up to a multi-man system.

Formaldehyde Separator Performances. The formaldehyde separation subsystem was designed for continuous operation using a 2 hr adsorption-desorption cycle. In actual tests, continuous operation, could not be achieved for two reasons. First, the rates of H_2O production in these tests were several times higher than in normal operation. Although the total capacity of the adsorbing bed was found to be essentially as anticipated, it became saturated in less than 2 hours, sometimes even in 20 minutes. Second, the desorption of a saturated bed took longer than 2 hours. Since the heat transfer within the silica gel bed was poor, with heating accomplished by tapes wound around the adsorption bed shell, it took more than 1 hour to reach the final desorption temperature of 200°C, and even longer to cool back to the near ambient temperature needed for the next adsorption cycle.

The separation of both formaldehyde and water was achieved by passing the entire product gas stream precooled to about 25-28°C through a silica gel adsorption bed initially at ambient temperature. Adsorption of water raises the temperature in the adsorption zone to 40° - 45°C. As a portion of the adsorption bed becomes saturated, the adsorption zone moves downstream. Thus, the saturation can be followed by observing the movement of the hot zone through the adsorption bed; when the hot zone reaches the exit end, the adsorbing bed is completely saturated. Usually, a run was terminated when the temperature near the exit end of the adsorption bed reached approximately 45°C. Some runs were continued beyond this point; in these cases, the temperature of the adsorption bed exit increased further and when it reached about 60°C, condensation of H_2O was observed downstream of the adsorbing bed indicating that no water at all was being removed. The movement of the hot zone through the adsorbing bed could be utilized for automatic cycling by switching to a fresh bed when the temperature near the exit reaches a preset limit.

Desorption was facilitated by backflushing the desorbing bed, which was being heated up to 200°C with a small stream (150-200 cc/min) of the recycle gas leaving the adsorbing bed. This stream of gas picked up the desorbed formaldehyde and water vapors and carried them to a series of condensers where CH_2O and water were condensed to a solution. The flushing gas, relieved of CH_2O and H_2O, was returned to the recycle gas stream. The first condenser, having a surface area of about 400 cm^2, was cooled by ambient air, followed by three condensers, having surface areas of about 240 cm^2 each, cooled by an ice-water bath. Over 90% of the CH_2O and H_2O condensed as a solution in the air cooled condenser, some condensation occurred in the first two and practically none in the third of the ice-water-cooled condensers. The efficiency of the CH_2O and H_2O condensation was checked by locating a dry-ice-acetone cooled trap after the last of the ice-water cooled condensers; however, only insignificant condensation was observed in this trap indicating effective removal of CH_2O and H_2O in the condensers.

When the desorbing bed reached 200°C, it was kept at this temperature for 10-15 min. and then cooled back to ambient temperature, in preparation for the next adsorption cycle. When cooling was accelerated by increasing the backflushing gas stream flow rate, up to about 15 liters/min, the required time was still in excess of 1 hour.

The observed performance indicated that the size of the adsorption bed should have been sufficient for 2 hours of normal operation. However, to reduce the time of desorption to less than 2 hours, changes improving the heat transfer through the bed, such as internal fins and internal heating lines should be made. A formaldehyde separator of this size should then be sufficient for a continuous, cycling operation, provided the problem of overoxidation is resolved and the rates of H_2O formation return to normally expected levels.

PRELIMINARY DESIGN OF A
MULTI-MAN FORMALDEHYDE SYNTHESIS SYSTEM

The preliminary design of a multi-man formaldehyde synthesis system considers the design aspects of a) synthesis reaction parameters, b) heat-transfer conditions, c) power, weight, and volume requirements, and c) system operation and configuration. The design is based nominally on a ten-man system for convenience but can be scaled up approximately proportionately to twenty or thirty-man capacity without significant error.

Synthesis Reaction Parameters

In the multi-man system the primary formaldehyde synthesis reaction parameters that determine maximum synthesis rates are a) total recycle flow rate, b) reactor inlet gas stream composition and catalyst concentration, c) reactor temperature, and d) CH_2O removal efficiency.

For a ten-man system synthesizing 2000 gm/day of formaldehyde, the total recycle flow rate should be approximate 500 liters/min ($\sim$ 18 cfm). The average nominal feed rates for CO_2, O_2, H_2, and NO would be 2.0, 7.5, 19.0 and 0.05, liters/min, respectively. In a system of this size flow controllers would be required which provide a modulated on-off control for each feed gas. Proportional controllers do not appear essential to sustained operation. An infra-red sensor for CH_4, and an ion-migration sensor for O_2 would control H_2 and O_2 feeds respectively, while a total pressure sensor would control the CO_2 feed. The same sensors thus monitor and control system feed gas composition along with controlling feed gas flow.

Since the concentration and feed rate of NO are very low, the feed of nitric oxide can be closely controlled at a specific level by fixed orifice and will not require a continuous NO sensor. Daily routine would require verification of the proper NO concentration with an expendable sniffer-type sensor at specific points: a) outlet from the NO adsorbing bed in the methane synthesis loop, below 10 ppm required; b) recycle gas inlet feed to the formaldehyde synthesis loop, 2000 ppm required; Manual corrections would be made as required.

Total recycle flow rate would be sensed by pressure difference across the system; this differential would be used to control flow by means of a motor-driven valve. Total flow failure would shut-off power and thus all feed gas flow to the system, requiring a manual reset operation as part of start-up.

Temperatures of the formaldehyde and methane reactors would be controlled manually during start-up. When reaction temperature and nominal production rates were reached external heating would stop. In the event of over temperature in either reaction the total system power would shut off. The reaction temperature limit in the formaldehyde reaction is 700° C and in the methane reactor, 340° C.

The formaldehyde adsorption bed temperature should approximate 25°C for adequate adsorption. Consequently, the silica gel bed, after desorption by heating to 200°C and flushing, must have approximately 25% of the length of the bed pre-cooled at the inlet end to 25°C, or lower, before adsorption commences. Flushing gas flow should be sufficient to displace the total desorption bed gas once every two minutes.

Heat Exchanger Design Conditions

Efficient operation of the formaldehyde synthesis system entails proper performance of five separate heat-transfer functions. These five are:

1. Formaldehyde reactor inlet-outlet gas heat-exchange.
2. Methane reactor inlet-outlet gas heat-exchange.
3. Methane reaction heat-dissipation to a cooling gas.
4. Exiting recycle-gas heat-dissipation to cooling gas or liquid.
5. a) Formaldehyde separator heat-up during desorption.
   b) Formaldehyde separator heat-dissipation during cool-down prior to adsorption.

In addition, the reactors and separators require adequate minimal weight and volume insulation indicating a possible need for a vacuum-jacket type insulation system for the higher-temperature components.

The nominal operating design conditions for the respective heat-exchangers are as follows:

1. Formaldehyde Heat Exchanger; Counter Flow, Gas-to-Gas

   Feed Gas Δ T: 25°C to 600°C
   Product Gas ΔT: 765°C to 100°C
   Heat Transfer Rate: 30,000 BTU/hr.
   Mass Flow Rate: 600 gm/min ($\sim$18 scfm)
   Allowable Total Pressure Drop: 1.0" H_2O

2. Methane Heat-Exchanger: Counter Flow, Gas-to-Gas

Feed gas ΔT: 25°C to 265°C

Product gas ΔT : 320°C to 80°C

Heat Transfer Rate: 1,000 BTU/hr.

Mass Flow Rate: 25 gm/min. ($\sim$.75 scfm)

Allowable Total Pressure Drop: 1.0" H_2O

3. Methane Reactor Cooling: Forced Convection, Gas-to-Solid

Gas ΔT: 25°C to 225°C

Heat Transfer Rate: 3,000 BTU/hr. (Cooling)

Mass Flow Rate: 200 gm/min ($\sim$6 scfm)

Allowable Total Pressure Drop: 0.5" H_2O

4. Exit Recycle-Gas Cooling: Natural Convection, Gas-to-Air, or Forced Convection, Gas-to-Water

Gas ΔT: 100 C to 25°C

Air ΔT: 20°C to 25°C, or

Liquid ΔT: 5°C to 80°C

Heat Transfer Rate: 3200 BTU/hr.

Gas Flow Rate: 600 gm/min ($\sim$18 scfm)

Air Flow Rate: 10,000 gm/min, or

Water Flow Rate: 140 gm/min

5. a. Formaldehyde Separator Heat-Up: Forced Convection, Solid-to-Gas,

Solid ΔT: 25°C to 200°C.

Gas ΔT: 225°C to range of 25° to 200°C
(non-steady state)

Heat Transfer Rate: 2000 to 100 BTU/hr.

(non-steady state)

Gas Flow Rate: 200 gm/min (~6 scfm)

(from methane-reactor cooling)

Allowable Pressure Drop: 0.5" H_2O

b. Formaldehyde Separator Cool-down: Forced Convection, Solid-to-Air

Solid ΔT: 200 C to 25°C

Gas ΔT: 25°C to range of 200°C to 25°C

(non-steady state)

Heat Transfer Rate: 2000 to 100 BTU/hr.

(non-steady state)

Air Flow Rate: 200 gm/min (~ 6 scfm)

Allowable Pressure Drop: 0.5" H_2O

The nominal design characteristics of insulation for the reactors and separators depend on selection of conventional or vacuum-type insulation. The feasibility of using vacuum-type insulation is dependent on the envelope design. Larger volumes of the reactors and separators indicate considerable weight and volume savings for the vacuum-type insulation as indicated in Table 10.

TABLE 10. INSULATION CHARACTERISTICS

	k, BTU/hr °F Ft.	Density, lb/ft^3
Johns Manville Thermo-Flex RF 600	.47-.62	6
Johns Manville Min-K 1300	.24	16
Linde "Super Insulation" at 10 micron vacuum,	.0005	17

Initial desing of the insulation envelope will be based on the use of "super insulation" materials.

System Configuration and Operation

The overall configuration and operation of the multi-man system is based on the one-man system. The major components in the system would be as follows:

1. Formaldehyde synthesis reactor and heat-exchanger, with vacuum-insulation envelope.
2. Methane synthesis reactor and feed gas heat-exchanger, with external cooling jacket, and vacuum insulation envelope.
3. Formaldehyde product separator with internal heat-exchangers, and vacuum insulation envelope.
4. Exit recycle gas stream cooler.
5. Main recycle gas stream blower.
6. Cooling air stream blower.
7. CO_2, O_2, and CH_4 sensors and controllers, integrated with the CO_2, O_2 and H_2 feed systems, respectively.
8. Recycle gas flow-sensor and flow-control valve.
9. Temperature, flow, and heater-cycling indicators, and overall system instrumentation.

These system components would be assembled in a configuration similar to that of the one-man system, with the exception that the formaldehyde and methane reactors would be insulated as separate units rather than in the same insulation envelope, to more conveniently utilize vacuum-type insulation.

The formaldehyde reactor and heat-exchanger should be located end-to-end as with the breadboard system, rather than side-by-side as with the one-man system. This arrangement entails a larger dimension for the sub-system, but provides for better heat conservation and shorter high temperature contact time for exiting product gases.

Centrifugal blowers should be used to circulate the recycle gas and cooling air streams. Total recycle system pressure drop should be approximately 3" H_2O. Accordingly, the recycle gas ducting should be 2" - 3" in diameter, and all heat-exchangers designed to operate under laminar flow conditions.

The multi-man system would require manual start-up similar to that for the one-man system, and would then continue in normal operation in the automatic mode. Off-normal operation of blowers, heaters, feed gas sub-systems, or over-temperature of the reactors or separators would occasion automatic shut-down of the system, and require manual correction and start-up to return to normal operation. A schematic of the multi-man system is shown in Figure 12 .

Estimated System Weight, Volume, and Power

The major components of the system should be fabricated from the same materials used in the one-man system. Inconel 600, or Hastelloy X where feasible, should be used for the formaldehyde reactor and heat-exchanger. All other system components, except the methane reactor core, should be built from 304 or 321 stainless steel; the methane reactor core should be aluminum.

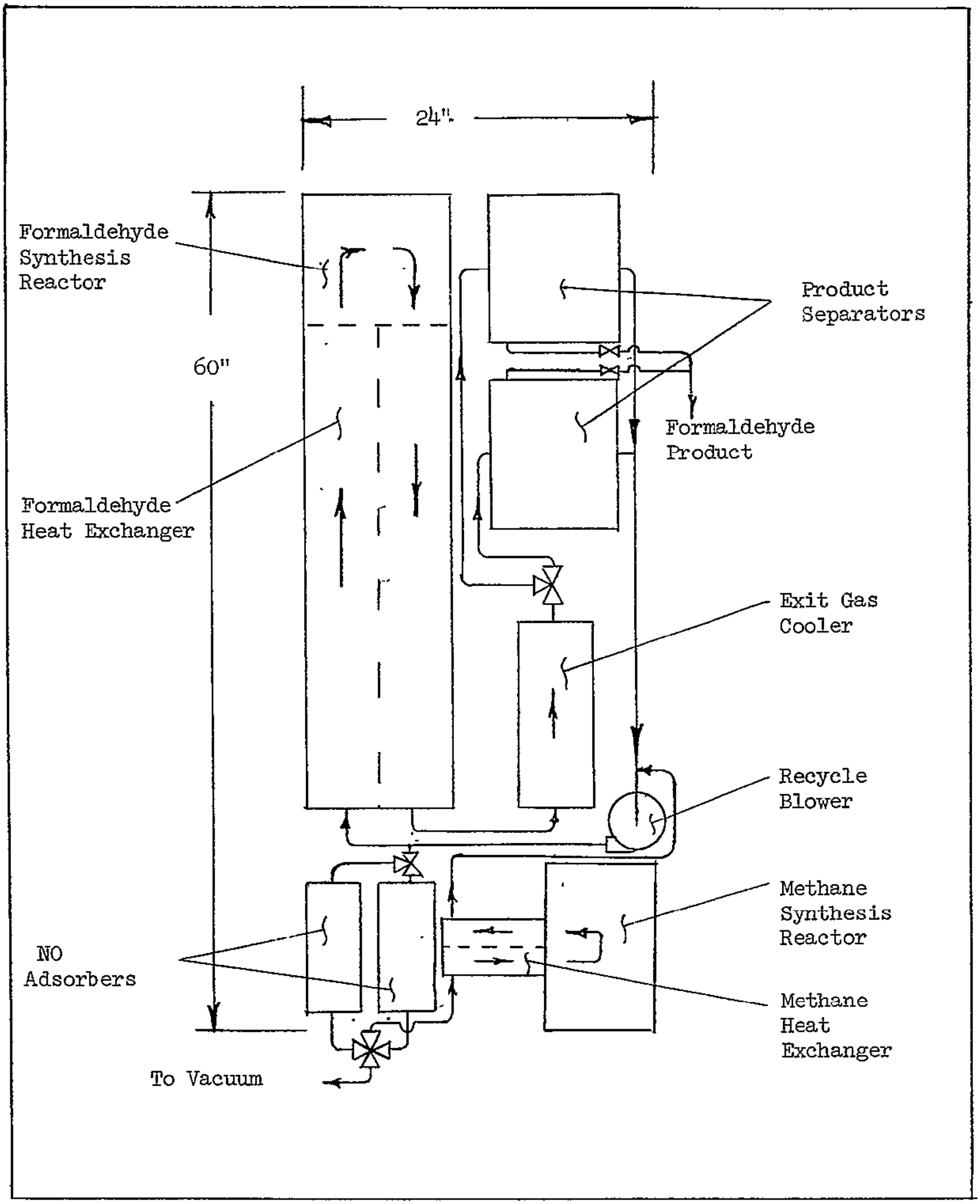


Figure 12. MULTI-MAN SYNTHESIS SYSTEM SCHEMATIC

The estimated dimensions and weight, uninsulated, of the major system components, are as follows, based on a 10-man formaldehyde synthesis capacity of 2000 gm/day:

1. Formaldehyde Reactor:

   Diameter: 9.5 inches

   Overall Height: 7.0 inches

   Reaction Zone: 5.0 inches

   Reactor Volume: 350 in^3

   Bed Material Wt.: 8 lb.

   Reactor Weight: 3 lb.

2. Formaldehyde Heat-Exchanger:

   Diameter: 9.5 inches

   Overall Height: 40 inches

   Weight: 18 lb.

3. Methane Reactor:

   Diameter: 9 inches

   Overall Height: 7.0 inches

   Reaction Zone: 5.0 inches

   Reactor Core: 9" diameter aluminum cylinder, 5" high
   166" square holes, 1/2", on 5/8" center

   Catalyst Volume: 240 in^3

   Catalyst Weight: 6 lb.

   Core Weight: 10 lb.

   Reactor Shell Weight: 6 lb. (Including cooling-jacket)

4. Methane Heat-Exchanger:

Diameter: 3 inches

Height: 12 inches

Weight: 2 lb.

5. Formaldehyde Separators - Two Beds and Internal Heat-Exchangers

Diameter: 10 inches, each

Overall Height: 12 inches

Adsorber Height: 10 inches

Adsorbent Weight: 12 lb., each

Bed Weight: 8 lb., each

6. Exit Recycle Gas Cooler:

Diameter: 10 inches

Length: 22 inches

Weight: 10 lbs.

7. Insulation - Vacuum Type

Theoretical calculations indicate a 1/4" thick layer of insulation at a 10 micron vacuum, will provide adequate insulation for all components needing insulation, assuming satisfactory insulation support and vacuum integrity. The additional weight of a cylindrical 1/4" thick annular insulation envelope for each component is as follows:

a) Formaldehyde Reactor and Heat-Exchanger: 5 lb. and support of 5 lb = 10 lbs

b) Methane Reactor and Heat-Exchanger: 2 lb + 2 lb of support = 4 lbs

c) Formaldehyde Separators: 2 lb + 2 lb of support = 4 lbs

8. Nitric Oxide Catalyst Sub-System

For 1 year of operation 30 lb. of NO are required utilizing a 6 lb.

container. Two adsorbing beds of Molecular Sieves 13X, 2 lb. each, operate on a 5 day regeneration cycle.

9. Blowers, Ducting, and Instrumentation:

The two centrifugal blowers required for the system weigh approximately 2 lb. each. Ten feet of 3" diameter connecting and ducting are needed, weighing approximately 12 lb. Control valves for recycle flow and formaldehyde separator direction weigh approximately 15 lb., when recycle gas is used for back-flushing of the desorbing separator bed. Remaining gas sensors, flow control valves, and temperature indicators weigh approximately 20 lbs., and support framework 10 lb.

System Weight. - The total weight of components listed approximates 180 lbs., as follows:

a.	Formaldehyde Reactor and Heat-Exchanger; Insulated	-	38 lbs
b.	Methane Reactor and Heat-Exchanger, Insulated	-	28
c.	Formaldehyde Separators, Insulated	-	44
d.	Nitric Oxide Catalyst Sub-System	-	40
e.	Exit Gas Cooler	-	10
f.	Blowers, Ducting and Instrumentation	-	60
			220 lbs.

System Volume. - The total envelope to contain all of the listed components is 64" high by 24" wide by 18" deep, for an overall volume of 16 cu. ft.

System Power. - The power required for normal system operation, after start-up is complete, will be essentially that required for operation of the recycle and cooling air blowers, and for system instrumentation.

Total blower power is:

a) Recycle System:	
Two 10 cfm blowers at 3" H_2O,	60 watts
b) Cooling Air	
One 10 cfm blower at 3" H_2O,	30 watts
	90 watts
Instrumentation (Averaged value)	110 watts
	200 watts

In start-up, two 1000 watt heaters are needed for the formaldehyde reactor, and one 500 watt heater for the methane reactor. The length of start-up time will approximate three-hours under normal conditions, based on operation of the one-man system. Thus total start-up power is 2700 watts for three hours.

The weight, volume, and power estimates shown are for a non-optimized working model assembled from commercial off-the-shelf type components.

CONCLUSIONS AND RECOMMENDATIONS

Based on experimental data obtained previously with a small, bench-scale breadboard prototype model, a nominal one-man formaldehyde synthesis system was designed, fabricated, and tested. Based on operation of the one-man system the following conclusions were made:

1. Testing of the full-scale system demonstrated the feasibility of producing formaldehyde at a rate equivalent to 200 g/day.

2. Automatic controls performed as required, and the recycle gas composition was maintained within acceptable variation limits.

3. The methane synthesis subsystem operated as required with no external heating needed after startup; in fact, the subsystem required cooling and thus acted as a convenient heat source for other subsystems.

4. Continuous separation of product formaldehyde and water was shown to be feasible by using two automatically cycling adsorption beds.

5. Molecular Sieves 13X were found suitable for complete, selective adsorption of NO from the recycle gas, but only in the presence of at least 2-3% O_2. The Molecular Sieves 13X bed effectively removed all NO from the recycling gas entering the methane synthesis loop.

6. Nitric oxide is superior to ozone as a gaseous catalyst because ozone is completely destroyed during each pass through the reactor. Replenishing of O_3 would involve high weight and power penalties, while only a small supply

of stored NO and light weight storage and supply equipment are required.

7. The measured efficiency of the formaldehyde recycle gas heat exchanger was less than the design value anticipated from direct scale-up from the breadboard model. Possible reasons for the lower efficiency are: excessive heat loss by conduction along the heat exchanger body, proximity to the high temperature formaldehyde reactor, or channeling on both the shell and tube sides of the heat exchanger.

8. The maximum recycle gas flow rate at which the required reactor inlet temperature could be reached with the reduced heat exchanger efficiency was approximately 60% of the required design value. Correspondingly, the formaldehyde production rate was slightly over 60% of the nominal rate.

9. Although a normal amount of formaldehyde was generated, up to four times the amount of normal water was generated, indicating a high degree of over-oxidation in the formaldehyde synthesis system. The cause of over-oxidation was apparently the lower recycle gas flow rate and the resulting high residence-time for product gas at or above the 600°C level.

10. After starting, the power requirement for supplemental heating of the formaldehyde reactor corresponded to the amount of heat lost due to the inefficient operation of the heat exchanger. No external power was required for the methanation subsystem. Thus, with adequate heat exchanger efficiency the primary power requirement for the total operating system would approximate 30 watts for the blower.

11. The preliminary design of a ten-man system, based on these data, indicates a total volume of 16 cu. ft., a weight of 220 lbs., and a power requirement of 200 watts, using commercially available components.

Recommendations

The results of the tests conducted on the one-man system indicated where modifications or additional tests are required to improve the formaldehyde production rate and the overall heat-transfer efficiency of the integrated system. The following recommendations are suggested to achieve these general objectives:

1. A series of tests should be conducted at varied operating conditions namely recycle gas flow rate, formaldehyde synthesis reactor temperature, feed gas composition, and reactor bed material to determine the effects of these conditions on formaldehyde production and overoxidation in the one-man system.

2. Specific tests should be conducted on the one-man system with the primary objectives of reducing overoxidation of methane to CO_2 and increasing the ratio of formaldehyde product to carbon dioxide by-product.

3. The formaldehyde recycle gas heat-exchanger should be tested to determine the cause of low heat-transfer efficiency. Re-design and modifications should be performed, as required.

4. The formaldehyde reactor and heat-exchanger should be reconnected in an end-to-end configuration to minimize product gas residence-time at elevated temperatures, and to eliminate cross-directed heat transfer from the reactor walls to the heat-exchanger walls.

5. Vacuum-jacket type insulation should be tested for feasibility in the multi-man system.

6. The feasibility of recovery of NO adsorbed on Molecular Sieves should be investigated in anticipation of larger crew sizes and longer duration missions.

NASA - Ames N70-23429

Moffett Field, California
April 3, 1970

Program Code 127-53-15-04-00-21

From Ames
To NASA Representative
Scientific & Technical Information Facility

Subject: Transmittal of Contractor Report: "One-Man Formaldehyde Synthesis System" Final Report by P. Budininkas and G.A. Remus, General American Transportation Corporation, 7449 North Natchez Avenue, Niles, Illinois.

1. The subject report prepared under Contract NAS 2-3889 has been reviewed at Ames and is recommended for release in STAR as CR 73432.

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Enclosure: 1 cy subject report

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