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DEVELOPMENT
OF A
CARBON FORMATION REACTOR
FOR
CARBON DIOXIDE REDUCTION
BY
GARY NOYES, PhD

FINAL REPORT ON CONTRACT NAS9-16956
BY
HAMILTON STANDARD
DIVISION OF UNITED TECHNOLOGIES CORPORATION
WINDSOR LOCKS, CONNECTICUT
FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LYNDON B. JOHNSON SPACE CENTER
HOUSTON, TEXAS

SEPTEMBER, 1985



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ABSTRACT

Applied research, engineering development, and performance evaluation was conducted on a process for formation of dense carbon by pyrolysis of methane. Experimental research showed that dense (0.7-1.6 g/cc bulk density and 1.6-2.2 g/cc solid density) carbon can be produced by methane pyrolysis in quartz-wool-packed quartz tubes at temperatures of 1100-1300 C. This result supports the condensation theory of pyrolytic carbon formation from gaseous hydrocarbons.

A full-scale Breadboard Carbon Formation Reactor (CFR) was designed, fabricated, and tested at 1100-1200 C with 380-2280 sccm input flows of methane. Single-pass conversion of methane to carbon ranged from 60 to 100 percent, with 89 percent average conversion. The tapered quartz-tube CFR formed 25.7 lb of carbon in the 0.5 cubic foot heated zone of 1.65 lb. of quartz wool packing in 19 days. The product carbon/wool rod was quite hard and rigid and was easily removed from the reactor.

Based on these results, performance was projected for an Advanced Carbon Reactor Subsystem (ACRS) and indicated that the ACRS is a viable option for management of metabolic carbon on long-duration space missions.

FOREWARD

This report was prepared by the Hamilton Standard Division of United Technologies Corporation for the National Aeronautics and Space Administration's Lyndon B. Johnson Space Center in accordance with Contract NAS9-16956, "Development of a Carbon Formation Reactor for Carbon Dioxide Reduction".

Appreciation is expressed to the NASA Technical Monitor, Mr. Robert Cusick of NASA Johnson Space Center, for his guidance and advice.

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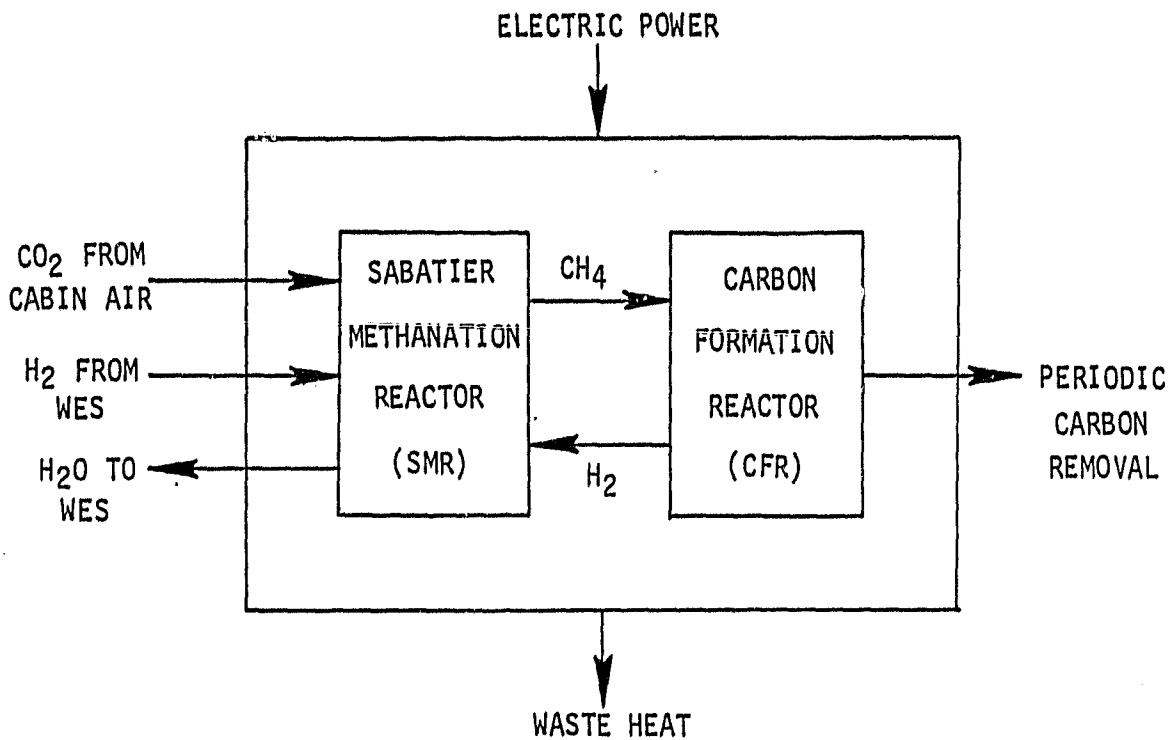
INTRODUCTION

Carbon Dioxide Reduction in Manned Spacecraft

In order to reduce the logistics penalty for air revitalization in manned spacecraft on long duration missions, breathing oxygen must be recovered from metabolic carbon dioxide. After removal from the spacecraft cabin atmosphere by any one of several means, carbon dioxide can be reacted with hydrogen to produce methane and water in a Sabatier Methanation Reactor (SMR) (Ref. 1 and 2). The product water can be condensed and separated from the methane and then electrolyzed into hydrogen and breathing oxygen (Ref. 3 and 4).

In order to reduce the mass of water electrolyzed to the minimum required for breathing oxygen production, hydrogen must be recovered from the SMR product methane to supplement the hydrogen from water electrolysis fed to the SMR. Also, a Space Station probable restriction on venting of carbonaceous gases will preclude venting of methane. To achieve these ends, the methane could be thermally decomposed (pyrolyzed) into hydrogen and solid carbon in a Carbon Formation Reactor (CFR) (Ref. 5).

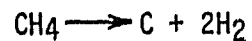
The integration of a CFR and SMR into an Advanced Carbon Reactor Subsystem (ACRS) would perform complete carbon dioxide reduction in a manned spacecraft. As shown in Figure 1, the ACRS would



SMR REACTION



CFR REACTION



OVERALL REACTION

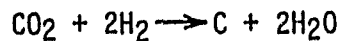


FIGURE 1
 ADVANCED CARBON REACTOR SUBSYSTEM (ACRS)

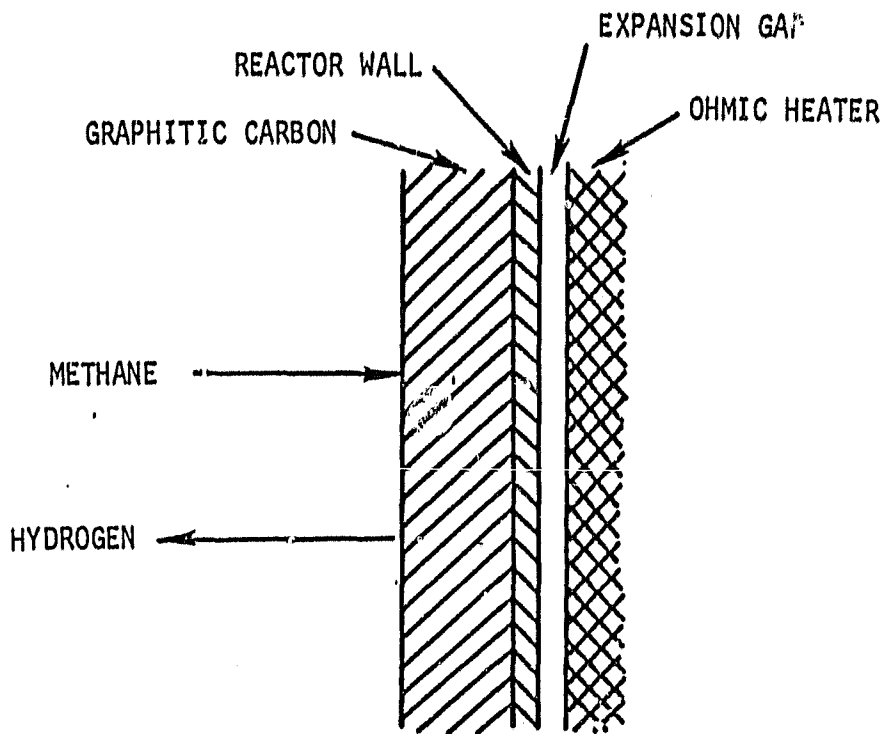
convert carbon dioxide and hydrogen to water and solid carbon. The carbon would be periodically removed from the ACRS and stored on board the spacecraft for final disposal.

To minimize storage volume, the density of the final product carbon must be maximized. In order to eliminate the mass penalty associated with reactor replacement, the CFR must be configured to allow for removal of the formed carbon. Finally, the pyrolysis reaction should exhibit high single-pass conversion of methane to carbon and hydrogen.

The Carbon Formation Process

Methane pyrolysis has been used for many years in the production of carbon black (soot) and synthetic graphite. Recently, researchers at United Technologies Research Center (UTRC) and Hamilton Standard created and patented (Ref. 6 and 7) a technique for formation of high density carbon from methane.

By passing methane through fused quartz tubes heated to elevated temperature, carbon films of varying thickness were formed on the inner wall of the tubes. This process is shown conceptually in Figure 2. As shown in Table 1, the thermodynamics of methane decomposition to carbon dictated temperatures above 1000 C for high equilibrium conversion. Rate data from the UTRC work, as plotted in Figure 3, indicate that temperatures in the range of



REACTION

$\text{CH}_4 + \text{HEAT} \longrightarrow \text{C} + 2\text{H}_2$
 800 W-HR/POUND OF CARBON
 1000-1200 °C TEMPERATURE

CARBON PROPERTIES

CRYSTALLINE GRAPHITE
 DENSE ($\sim 135 \text{ LB/FT}^3$)
 VERY HARD & CONDUCTIVE

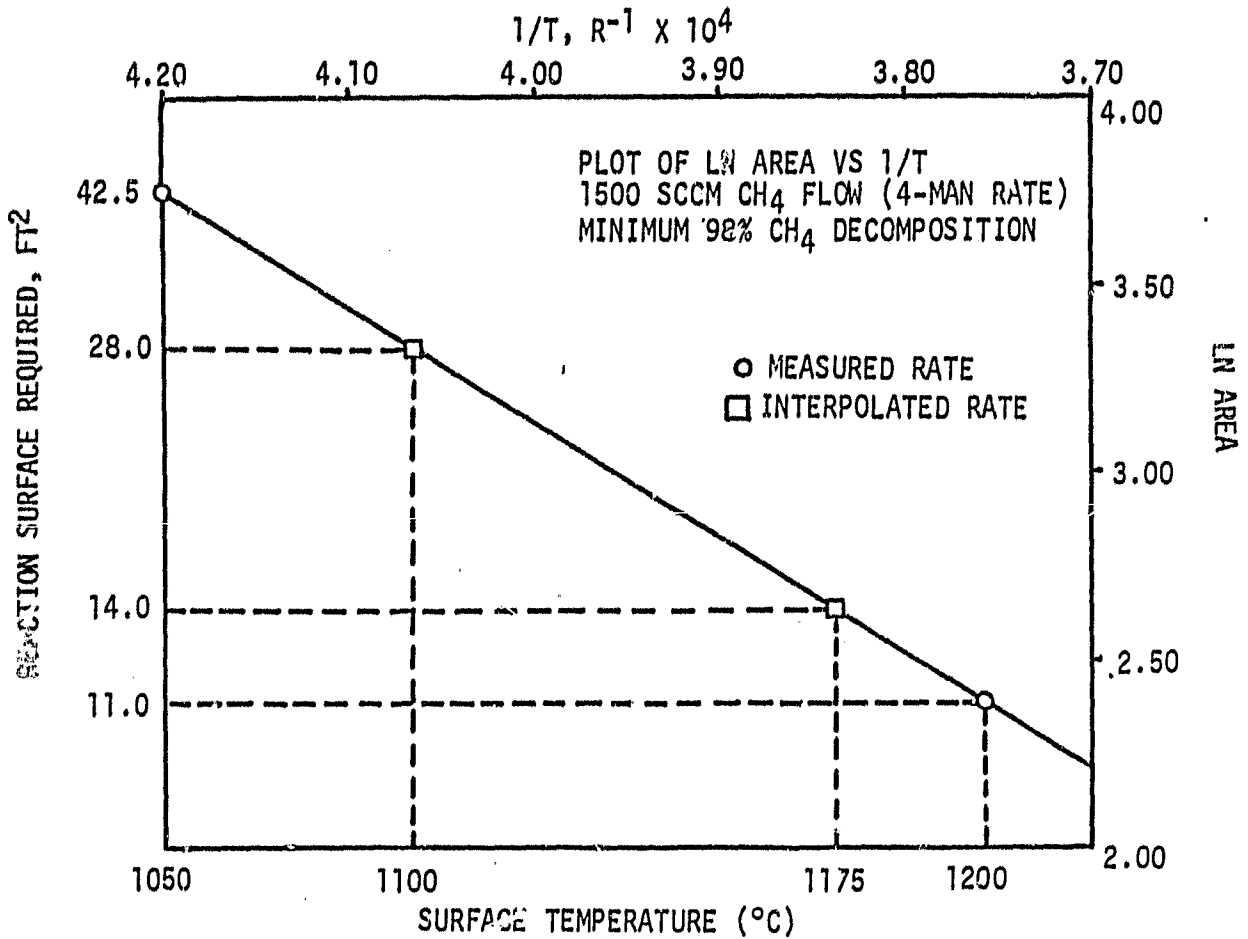
FIGURE 2
 THE IDEALIZED CARBON FORMATION PROCESS

TABLE 1

THERMODYNAMICS OF METHANE CRACKING

TEMPERATURE, C	PERCENT DECOMPOSED
500	31.8
1000	98.2
1150	99.3
1200	99.5
1250	96.6

(DATA FOR GAS-SOLID REACTION FROM JANAF TABLES)



(PRIOR UTRC DATA FOR METHANE DECOMPOSITION ON SILICA GLASS SURFACES)

FIGURE 3
 KINETICS OF METHANE CRACKING

1100-1200 C were required to achieve appreciable carbon formation rate. It was also reported that some undetermined but significant amount of the carbon produced was in the form of light soot.

The hard carbon films, formed on the inner wall of the quartz tubes, separated sporadically from the glass surface upon cooling to ambient temperature. This separation was attributed to the greater shrinkage upon cooling of carbon than of glass. Measured density of the flake carbon was about 2.2 g/cc, the theoretical maximum density of graphite.

Program Objectives and Organization

The above description of the CFR process was the extent of information in-house at Hamilton Standard at the start of the CFR development program. The overall objective of the CFR development program was to expand upon and exploit this base of process understanding to develop a CFR that would (1) minimize volume and mass of consumables required for carbon formation and collection, (2) minimize crew time required for carbon collection and transport, and (3) develop a "white gloves" approach to carbon collection and transport.

The CFR program was organized into the following sequence of tasks: (1) Select CFR concepts for evaluation, (2) Evaluate concepts via laboratory-scale testing, (3) Select a final CFR

concept for development, (4) Design, fabricate, and test a full-scale Breadboard CFR, (5) Perform a conceptual study of SMR/CFR integration, and (6) Recommend further ACRS development activities. The remainder of this report describes the execution and results of these tasks.

REACTOR CONCEPTS STUDY

The purpose of this first phase of the CFR development program was to produce candidate CFR configuration concepts to be experimentally evaluated during the laboratory-scale testing phase of the program.

Requirements Definition and Design Guidelines

The performance requirements for spacecraft application of an ACRS were defined and are presented in Table 2. Compatible performance requirements for the CFR were specified and appear in Table 3. The primary CFR requirement emphasized during this program was minimization of reactor and consumables mass and volume by production of carbon of maximal density.

The ACRS and CFR requirements were then used to develop a set of guidelines to aid in the generation, evaluation, and selection of CFR candidate configuration concepts. These CFR/ACRS design guidelines are presented in Table 4. A functional diagram of the basic ACRS configuration compatible with these guidelines is shown in Figure 4.

TABLE 2
ACRS REQUIREMENTS

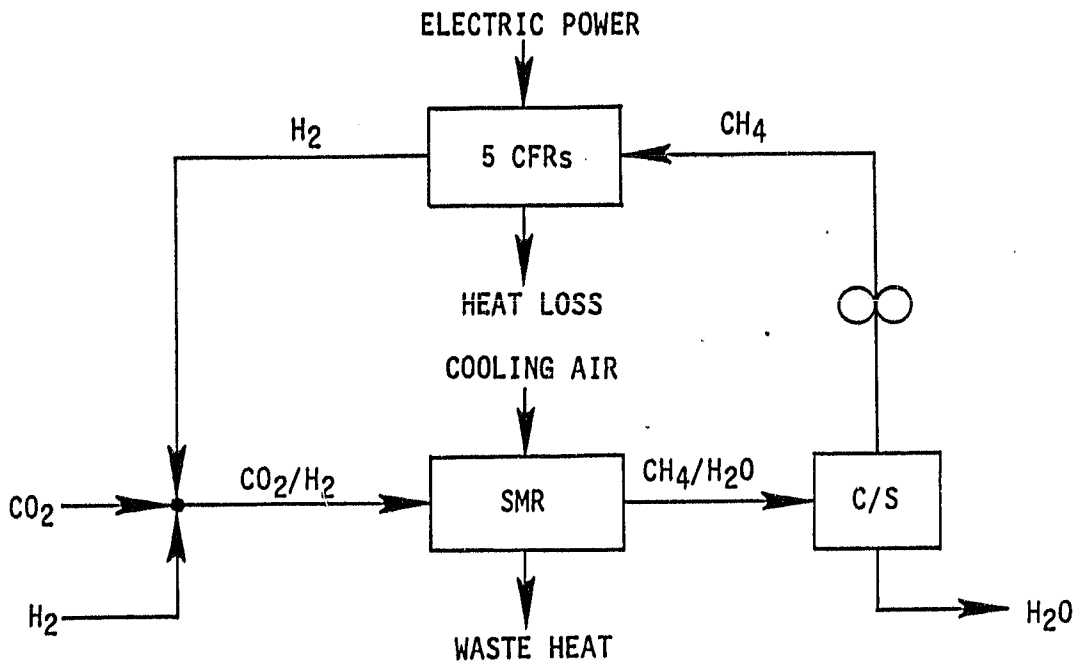
1. As a goal, input CO₂ shall be completely reduced to carbon and water.
2. As a goal, the subsystem shall function properly with input H₂-to-CO₂ molar ratios in the range of 2 to 4.
3. The subsystem shall recover ≥99% of water produced.
4. The subsystem shall provide all required interfaces to the Carbon Formation Reactor.
5. All exposed surfaces shall not exceed a touch temperature of 45 C (113 F).
6. The subsystem shall be designed for minimal weight and power consumption.
7. The subsystem shall be sized at the four-person level, 4.0 kg/day (8.8 lb/day) of CO₂.
8. No CO₂ or CH₄ shall be vented to space during normal subsystem operation.

TABLE 3
CFR REQUIREMENTS

1. As a goal, the reactor shall completely decompose input methane to gaseous hydrogen and solid carbon.
2. As a goal, the form of all carbon produced shall be graphitic: dense, hard and crystalline. If any light carbon soot is produced, it shall be removed completely from the output hydrogen.
3. The reactor shall use a non-expendable catalyst and provide ≥99% separation of carbon from the catalyst; alternatively, the reactor shall use ≥99% of an expendable host with a minimum allowable service interval of 60 man-days (≥90 days as a goal).
4. The reactor shall automatically collect and transfer carbon from the collection vessel to a storage vessel; alternatively, if the collection vessel is the storage vessel, it shall collect carbon for a minimum allowable interval of 60 man-days (≥90 days as a goal).
5. The reactor shall function properly with small amounts of water vapor, dew point ≥25 C (77 F), and varying amounts of hydrogen (as a goal, trace to 2 times the methane flow on a molar basis) in the input gas.
6. All external reactor surfaces shall not exceed a touch temperature of 45 C (113 F).
7. The reactor shall be designed for minimal weight and power consumption. Mass of container for return of carbon to Earth shall be minimized.
8. The reactor shall be sized at the one-person level, 0.36 kg/day (0.8 lb/day) of methane.

TABLE 4
CFR/ACRS DESIGN GUIDELINES

1. The CFR shall form and store carbon at the one-person rate continuously for 90 days. The four-person ACRS shall have five (5) of these reactors, four in operation and one in the carbon transfer sequence.
2. The carbon transfer sequence shall occur four times in 90 days. It shall comprise purging/cooling the carbon-filled reactor, transfer of carbon, and resumption of operation.
3. The CFR shall have a soot filter to insure particulate-free hydrogen output, a regenerative heat exchanger (RHX) to recover heat from the hydrogen outlet, and electrical-resistance heaters to maintain proper reaction temperature.
4. The carbon reactor, soot filter, RHX, and heaters shall be enclosed in a gas-tight enclosure, insulation-filled and pressurized with inert gas so that no pressure differential exists across the reactor wall. All components in this gas-tight enclosure shall be accessible for replacement by removal of insulated cover plate(s).
5. The subsystem shall allow controlled venting to space of process gases. CO₂ or CH₄ shall be vented to space only in the event of SMR or CFR failure.
6. Carbon formation rate shall be controlled by CFR operating temperature. Nominal temperature for a four-person ACRS shall be 1100 C; the maximum temperature (about 1200 C) shall be adjustable sufficient to double the carbon formation rate.



- FOUR MAN ACRS HAS FIVE ONE MAN CFR'S (FOUR ON, ONE OFF LINE)

FIGURE 4
 ACRS FUNCTIONAL DIAGRAM FOR REACTOR CONCEPTS STUDY

CFR Concepts Evaluated

Based on the stated performance requirements and design guidelines, a set of ten CFR configuration concepts were generated and are listed in Table 5 and shown in Figures 5-14. An attempt was made to include all possible CFR geometries and modes of operation. All of the CFR concepts had the potential to meet the stated requirements and guidelines.

The concepts are divided into two basic types by mode of carbon collection and transport. Storage reactor concepts utilize the formation reactor as the collection and transport container; when full of carbon, the storage reactor is replaced. Removal concepts are configured to allow removal of carbon from the reactor formation surfaces; the reactor is a permanent part of the fixed hardware. Carbon removal techniques covered are (1) automatic to storage box or (2) manual to storage bag. Regardless of the manner in which the carbon is collected, crew involvement would always be required to transport the collected carbon from the CFR/ACRS location in the spacecraft to the location for final storage and/or disposal.

The CFR configurations are also differentiated by geometry of carbon formation/collection. Carbon can be formed as cylinders on tube walls, as sheets on planar walls, as coating on fibrous

TABLE 5
CFR CONCEPTS EVALUATED

1. Tube storage reactor, direct heating
2. Tube reactor, manual removal, direct heating
3. Tube reactor, automatic removal, direct heating
4. Carousel tube reactor, automatic removal, direct heating
5. Flat-fin storage reactor, direct heating
6. Flat-plate storage reactor, direct heating
7. Flat-plate reactor, automatic removal, direct heating
8. Wool-in-tube storage reactor, indirect heating with argon
9. Fibers-in-tube storage reactor, indirect heating with hydrogen
10. Entrained-particle storage reactor, indirect heating with hydrogen

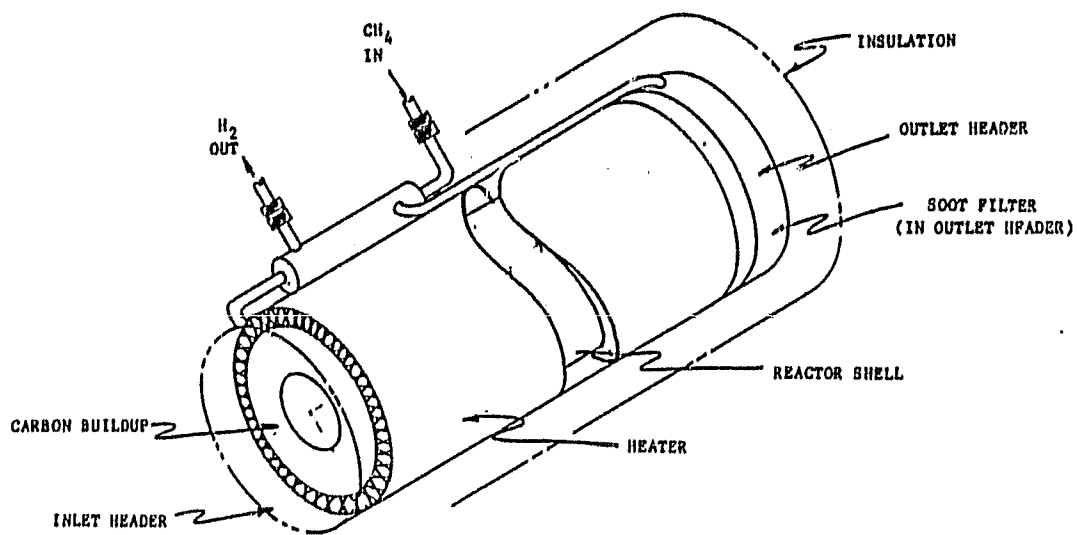


FIGURE 5
TUBE STORAGE REACTOR

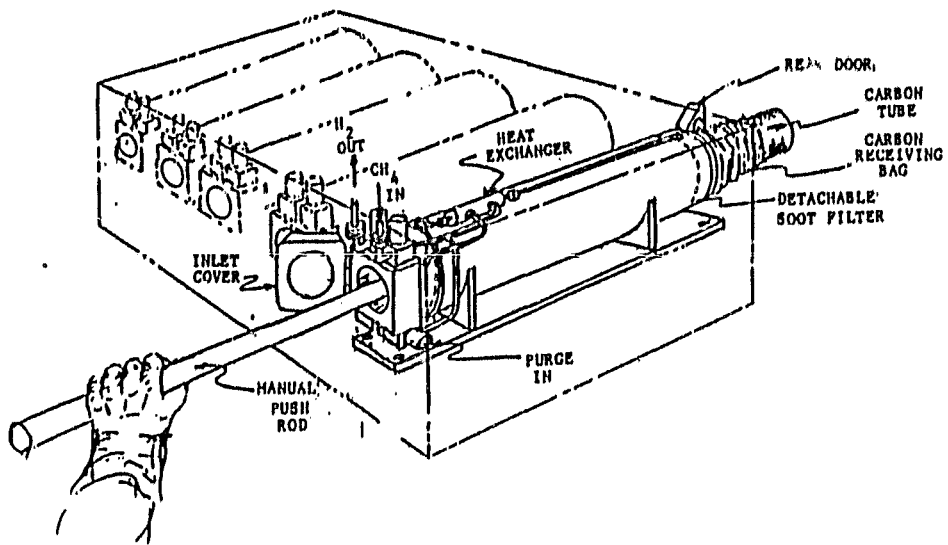


FIGURE 6
TUBE REACTOR, MANUAL REMOVAL

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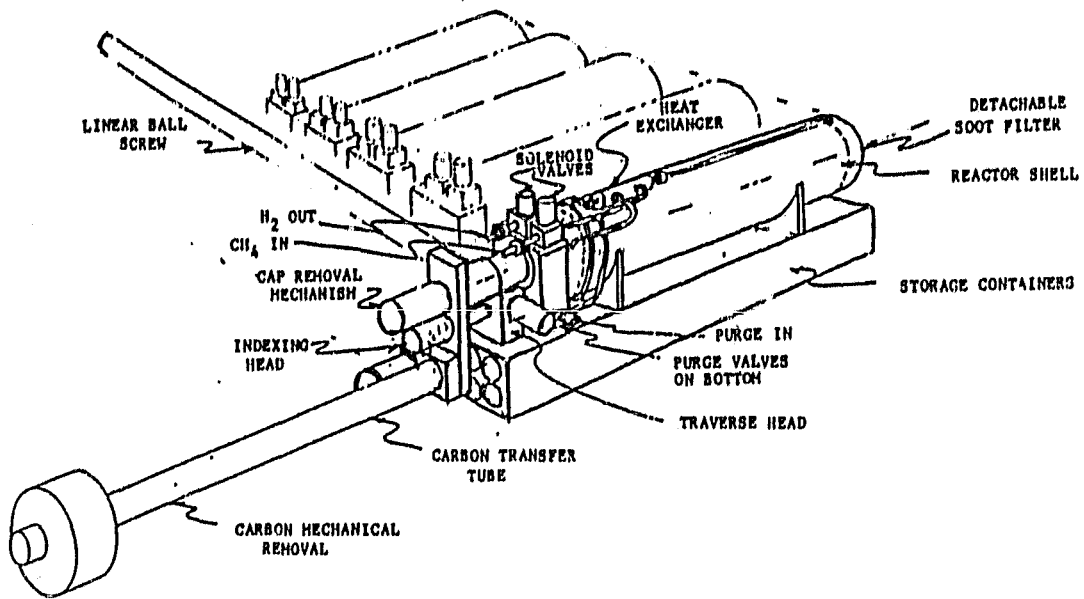


FIGURE 7
TUBE REACTOR, AUTOMATIC REMOVAL

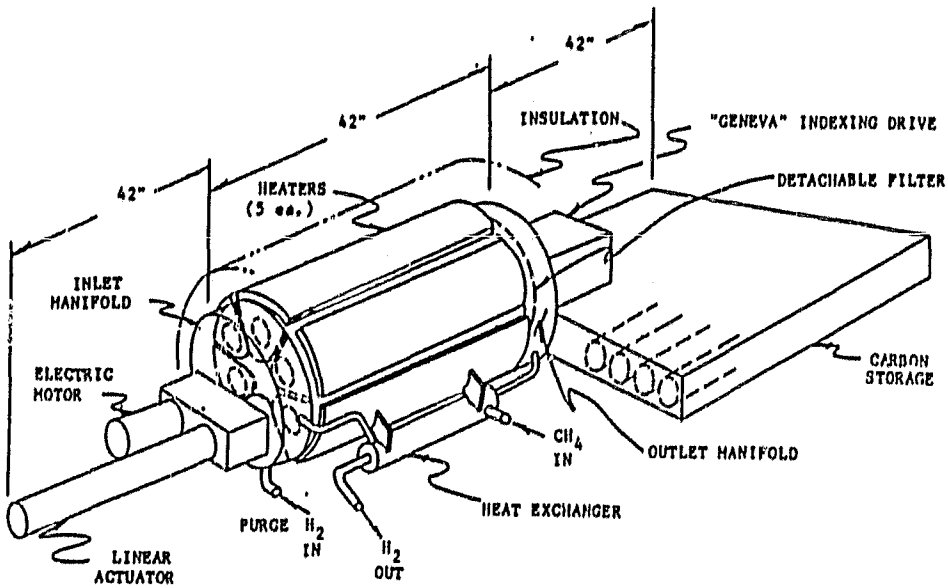


FIGURE 8
CAROUSEL TUBE REACTOR, AUTOMATIC REMOVAL

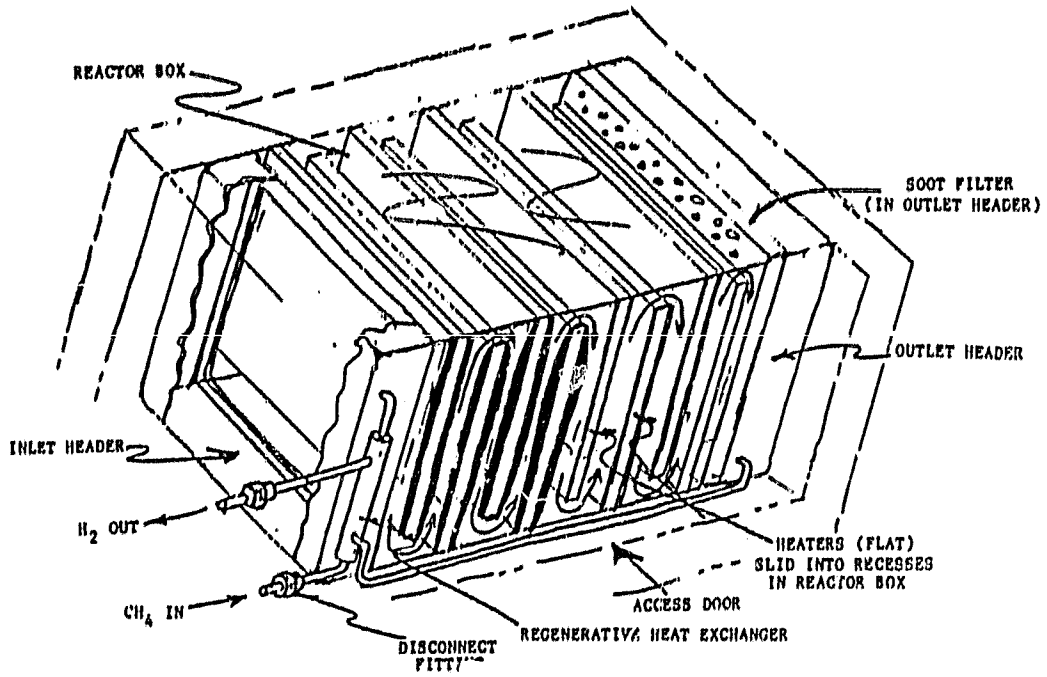


FIGURE 9
FLAT FIN STORAGE REACTOR

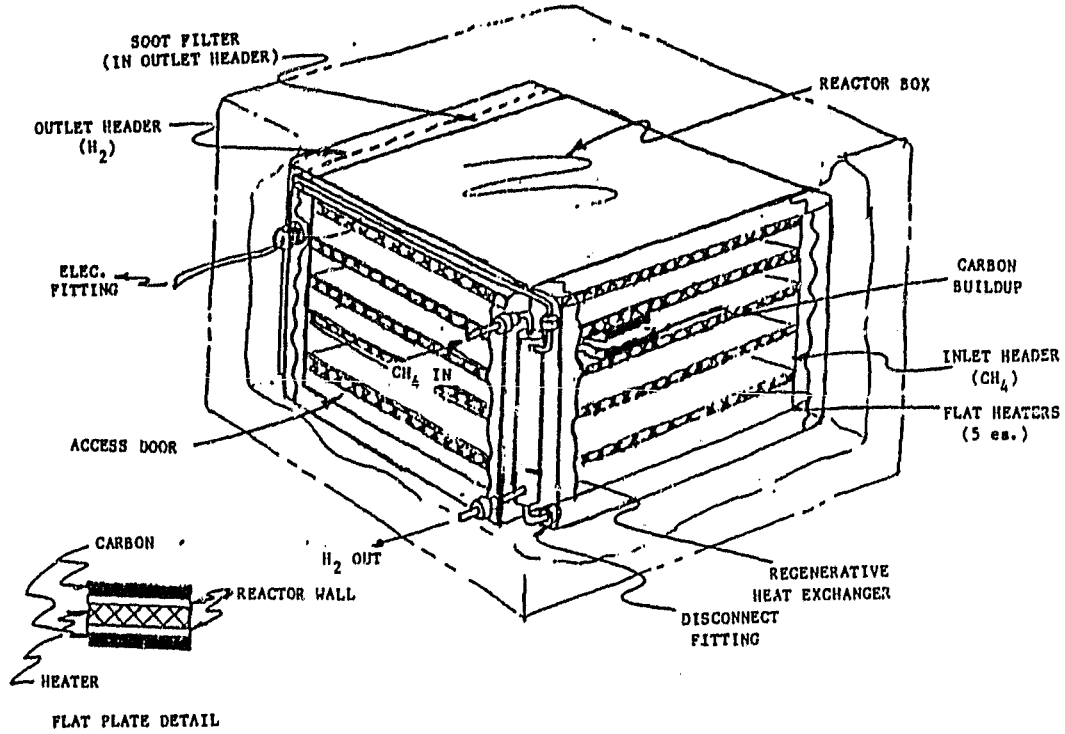


FIGURE 10
FLAT PLATE STORAGE REACTOR

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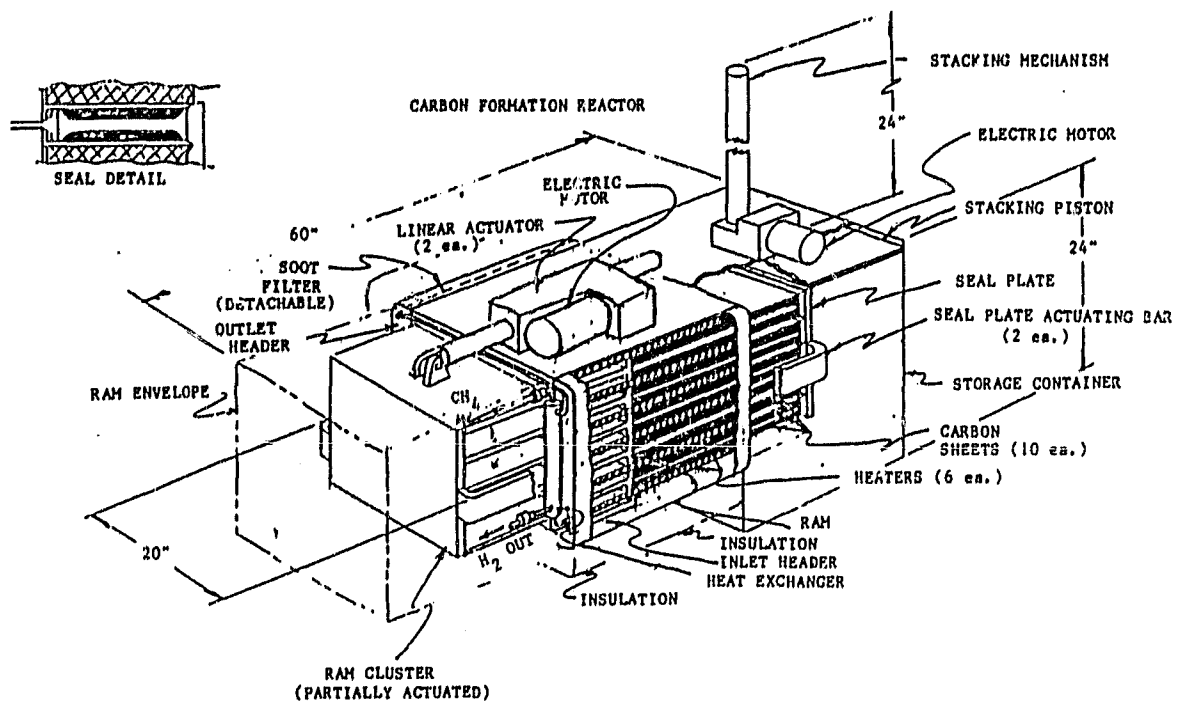


FIGURE 11
 FLAT PLATE REACTOR, AUTOMATIC REMOVAL

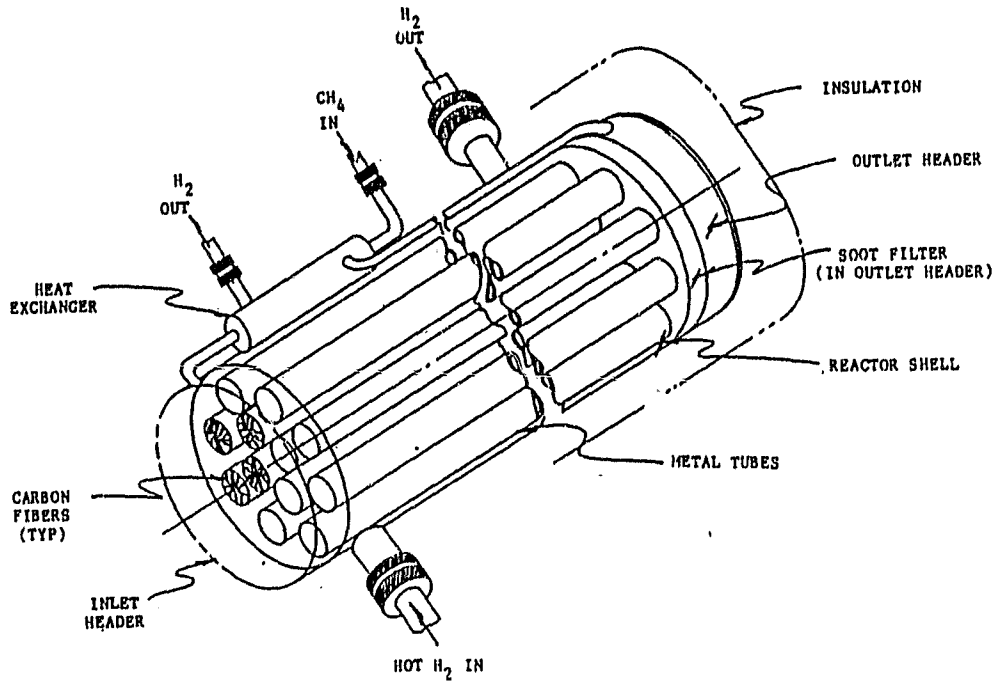


FIGURE 12
FIBERS-IN-TUBE STORAGE REACTOR

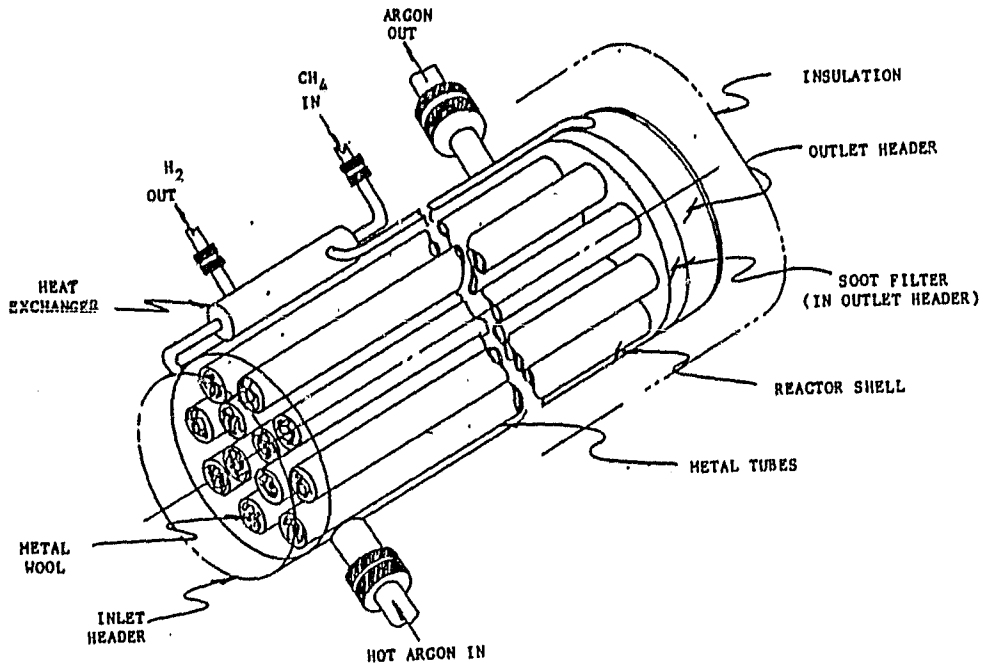


FIGURE 13
WOOL-IN-TUBE STORAGE REACTOR

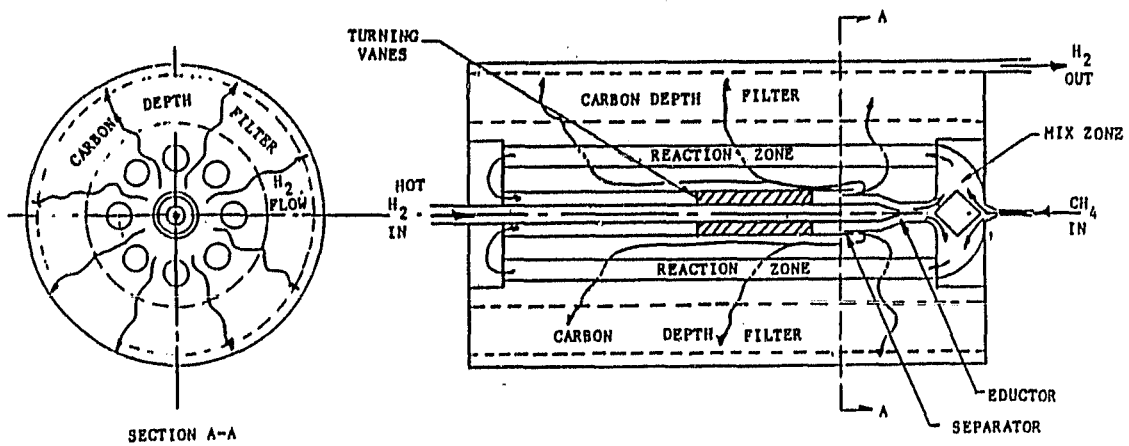


FIGURE 14
ENTRAINED PARTICLE STORAGE REACTOR

reactor packing, as fibers growing from reactor walls, and as soot collected on depth filters.

Finally, the CFR concepts are characterized by mode of heating. The carbon formation surfaces may be directly heated by electrical resistance or indirectly heated via circulation of a heat transport fluid.

Concepts Selection and Ranking

In order to select at least three of the ten CFR configuration concepts for laboratory-scale testing, a set of criteria for concept selection were defined and are presented in Table 6. Based on available data and engineering judgement, four concepts were rejected for inability to meet one or more of the absolute criteria. These concepts, the criteria not satisfied, and the reasons for rejection are listed in Table 7.

The remaining six concepts met all the absolute selection criteria and were therefore considered for laboratory-scale testing. As shown in Table 8, these six configurations cover three carbon formation concepts and three modes of carbon collection and removal.

For each of the six viable CFR concepts, estimates of consumables equivalent weight, maintenance time, development/qualification

TABLE 6

CFR CONCEPTS SELECTION CRITERIA

Absolute Criteria (Go/No-Go)

1. Performance
 - Ability to completely decompose methane to carbon and hydrogen
 - Ability to collect and transfer carbon
2. Safety
 - Combustible gas leakage (fire/explosion hazard)
 - Exposure of crew to high temperature
3. Availability/Confidence
 - Confidence in basic process
 - Availability by 1987

Primary Criteria (Relative, each rated 1-6 points)

1. Equivalent Weight of Consumables
 - Includes equivalent weight for volume of consumables
 - Consumables include carbon disposal containers and spares
2. Maintenance Time
 - Total number of life-limited components
 - Complexity of maintenance requirements
3. Development/Qualification Cost
 - Number of new technology components
 - Total number of components

Secondary Criteria (Relative, each rated 1-4 points)

1. Equivalent Weight of Fixed Hardware
 - Includes equivalent weight for power consumption, heat rejection to cabin air, and volume of fixed hardware
2. Reliability
 - Number of moving parts
 - Number of thermally life-limited components
3. Contamination
 - Potential for toxic gas production and gas leakage
 - Potential for release of carbon soot
4. Flexibility
 - Capability of off-design performance and cyclic operation
 - Capability for future improvement and optimization

TABLE 7
CFR CONCEPTS REJECTED (ABSOLUTE CRITERIA)

<u>Concept Rejected</u>	<u>Criterion Failed</u>	<u>Reason for Rejection</u>
<ul style="list-style-type: none"> ● Carousel tube reactor, automatic removal, direct heating 	<ul style="list-style-type: none"> ● Safety 	<ul style="list-style-type: none"> ● Probability of combustible gas leakage through hot reactor-tube sliding end seals
<ul style="list-style-type: none"> ● Flat-plate reactor, automatic removal direct heating 	<ul style="list-style-type: none"> ● Availability & Confidence 	<ul style="list-style-type: none"> ● Risk in development of rectangular poppet valves for hot reactor static end seals ● Probability that carbon will not detach from reactor wall as flat-plates required for automatic removal
<ul style="list-style-type: none"> ● Fibers-in-tube storage reactor, indirect heating with hydrogen 	<ul style="list-style-type: none"> ● Availability & Confidence 	<ul style="list-style-type: none"> ● Risk in optimization of basic carbon-growth process ● Risk in development of 1200 C hydrogen indirect-heating loop
<ul style="list-style-type: none"> ● Entrained-particle storage reactor, indirect heating with hydrogen 	<ul style="list-style-type: none"> ● Performance 	<ul style="list-style-type: none"> ● Basic carbon-growth process not demonstrated to date ● Probability of reaction tube clogging by carbon growth on walls ● Risk in development of 1200 C hydrogen indirect-heating loop

TABLE 8
CFR CONCEPTS SELECTED FOR DESIGN SUPPORT TESTING

<u>CFR Concept Selected</u>	<u>Carbon Formation Concept</u>	<u>Carbon Transfer Concept</u>
Tube storage reactor	Cylinder on tube inner wall	Reactor replacement
Tube reactor, manual removal	Cylinder on tube inner wall	Manual to storage bag
Tube reactor, automatic removal	Cylinder on tube inner wall	Automation to storage box
Flat-fin storage reactor	Sheet on planar wall	Reactor replacement
Flat-plate storage reactor	Sheet on planar wall	Reactor replacement
Wool-in-tube storage reactor	Coating on wool fibers	Reactor replacement

cost, fixed hardware equivalent weight, reliability, contamination potential, and flexibility were generated. All concepts were ordinally ranked for each of these selection criteria. The ranking scores were then summed to create an overall rating for each concept.

Results of ranking on the basis of primary criteria are presented in Table 9. Secondary criteria ranking are shown in Table 10. Overall ranking scores along with consumables and fixed hardware equivalent weights are listed in Table 11. The assumptions used in the estimation of equivalent weights are also noted on Table 11. A primary assumption used in the evaluation of these CFR concepts was that almost all carbon formed would be dense, hard graphite with negligible soot production.

TABLE 9
CFR CONCEPTS PRIMARY RANKING

<u>Concept Ranked</u>	<u>Consumables Egvt. Weight</u>	<u>Maintenance Time</u>	<u>Devt./Qual. Cost</u>	<u>Primary Total</u>
Tube storage reactor	4	6	6	16
Tube reactor, manual removal	6	3	3	12
Tube reactor, auto. removal	5	1	1	7
Flat-fin storage reactor	2	5	4	11
Flat-plate storage reactor	3	5	4	12
Wool-in-tube storage reactor	1	4	3	8

NOTE: Concepts ranked on a scale of 1-6, with six being best.

TABLE 10
CFR CONCEPTS SECONDARY RANKING

<u>Concept Ranked</u>	<u>Fixed Hardware Egvt. Weight</u>	<u>Reliability</u>	<u>Contamination</u>	<u>Flexibility</u>	<u>Secondary Total</u>
Tube storage reactor	2	4	4	1	11
Tube reactor, manual removal	2	3	2	1	8
Tube reactor, auto. removal	1	1	1	1	4
Flat-fin storage reactor	2	4	4	3	13
Flat-plate storage reactor	3	4	4	2	13
W601-in-tube storage reactor	1	3	3	4	11

NOTE: Concepts ranked on a scale of 1-4, with 4 being best.



TABLE 11

CFR CONCEPTS OVERALL RANKING AND PROJECTED PENALTIES

<u>Concept Ranked</u>	<u>Ranking Score</u>	<u>Consumables Eqvt. Wt., lb</u>	<u>Fixed Hardware Eqvt. Wt., lb</u>
Tube storage reactor	27	62	1300
Tube reactor, manual removal	20	16	1350
Tube reactor, auto. removal	11	46	1750
Flat- storage reactor	24	138	1440
Flat-plate storage reactor	25	103	1130
Wool-in-tube storage reactor	19	376	1830

NOTES:

- (a) Consumables Eqvt. Wt. is for 90-day resupply interval, 4-man subsystem; includes volume.
- (b) Fixed Hardware Eqvt. Wt. is for 4-man subsystem less SMR; includes volume, power, and heat rejection.
- (c) Weight equivalents are: volume 4.6 lb/ft³, power 0.8 lb/w, and heat rejection to air 0.4 lb/w.

DESIGN SUPPORT TESTING

The purpose of this second task of the CFR development program was to experimentally evaluate the selected CFR concept configurations via laboratory-scale testing. A primary goal of Design Support Testing (DST) was to determine the CFR configuration(s) that maximize dense carbon formation and minimize soot production. Since it was not a priori apparent what process configuration would achieve this end, DST was conducted in the manner of an applied research project.

First a literature search was performed to learn as much as possible about the fundamentals of pyrolytic carbon formation. Then hypotheses were formed concerning CFR configuration and appropriate reaction parameters. An experimental apparatus and procedure were then generated. Finally, experiments were performed to validate the research hypotheses and determine optimal CFR configuration/parameters.

Pyrolytic Carbon Fundamentals

Mechanism of Formation - Several reviews of solid carbon formation by thermal decomposition of methane and other hydrocarbon gases have been published (Refs. 5, 8 and 9). The most universally accepted model for hydrocarbon pyrolysis is given below and in Figure 15:

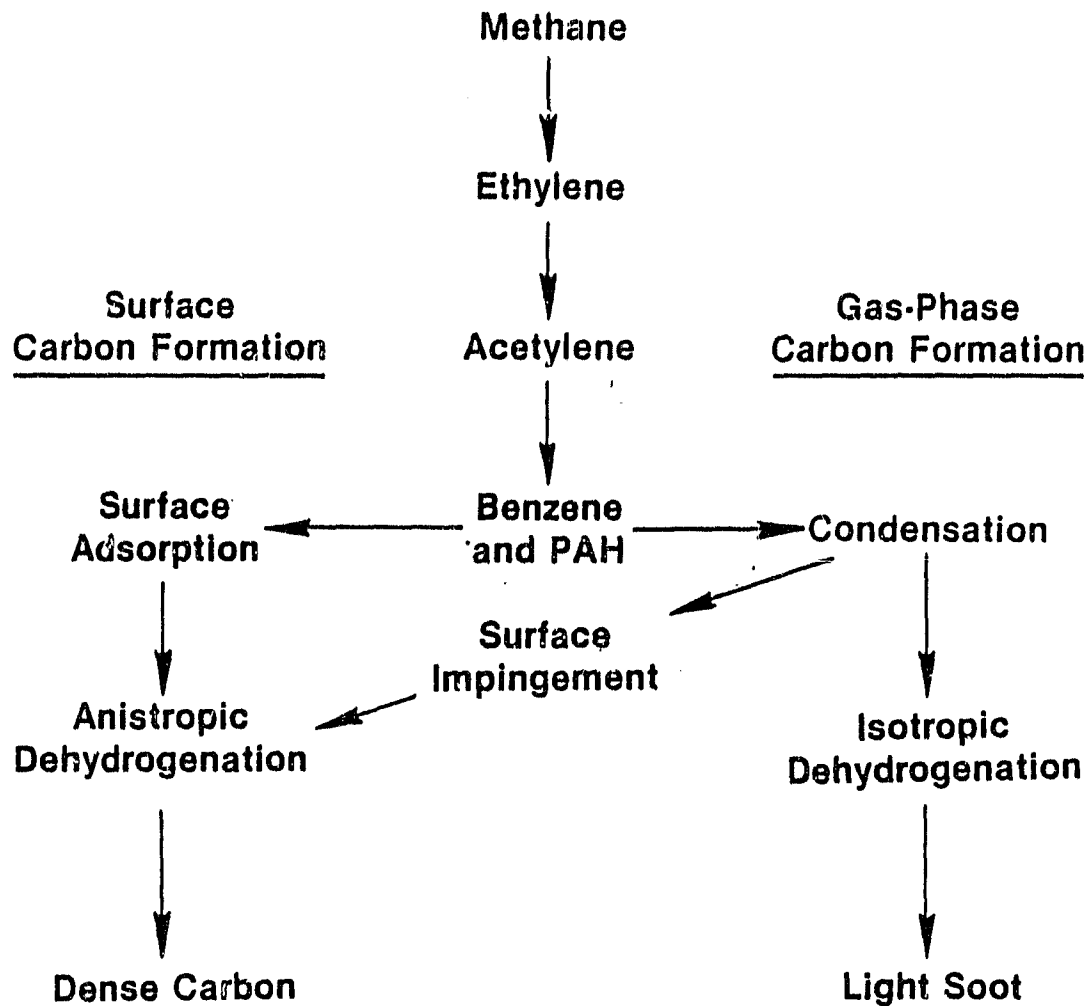


FIGURE 15
METHANE PYROLYSIS TO CARBON



- A. Polymerization of gaseous hydrocarbons and formation of aromatics;
- B. condensation in the gas-phase and surface adsorption/-impingement of polyaromatic hydrocarbons; and
- C. final dehydrogenation to carbon in the gas phase and on reactor surfaces.

The carbon black (soot) formed in the gas phase has low density (0.4 - 1.2 g/cc) and has highly disordered structure (Ref. 9). The orienting effect of reactor surfaces creates pyrolytic carbon with higher density (1.6-2.2 g/cc). Pyrolytic carbon formed on surfaces has structures varying from amorphous through turbostratic (semi-crystalline lamellar) to fully-dense graphitic (crystalline lamellar). The density of pyrolytic carbon is also dependent on temperature, exhibiting the lowest densities between 1500 C and 1900 C (Ref. 9).

Kinetics and Thermodynamics - Methane pyrolysis is a highly endothermic reaction. It requires a high temperature to obtain significant equilibrium conversion to carbon and hydrogen. Because of the stability of C₂ intermediates, gaseous hydrocarbons in equilibrium with hydrogen and carbon exhibit concentration minima of .01 to .001 bar (at one bar total pressure) between 1100 C and 1900 C (Ref. 10). These minima are the preferred conditions for spontaneous hydrocarbon pyrolysis with maximum carbon yield.

Below about 1000 C, attaining decomposition equilibrium is very slow (Ref. 10). Between 1000 and 1500 C, the rate-limiting reaction for methane pyrolysis is the polymerization (first-order) of methane to C₂ species, terminating in acetylene. Above 1500 C, the conversion of acetylene (second-order) to benzene becomes the rate-determining step. Because of the high activation energies of these controlling reactions, methane pyrolysis rate is very dependent on temperature.

Experimental Study of the Process

Configuration/Parameters Selection - Since soot forms in the gas phase and dense pyrolytic carbon is formed on reactor surfaces, more dense carbon should be formed in a reactor with a high surface-area-to-volume ratio (S/V). Pyrolysis tests (Ref. 11) in quartz tubes and quartz tubes containing ceramic or silica substrates resulted in deposition of dense carbon films in the packed tubes and soot in the empty tubes. Similar results were observed with carbon tubes and carbon fiber substrates (Ref. 11).

In order to insure that carbon could be removed from the pyrolysis reactor, the reactor wall material had to have a lower coefficient of thermal expansion than that of carbon. The wall material also had to be available in a form suitable for testing (i.e., thin-walled tubes) and capable of thermal cyclic operation at high

temperature. The only material meeting these criteria was fused quartz.

The reactor substrate chosen for evaluation was fused quartz wool, with an average fiber diameter of nine micrometers. This reactor packing material had a higher S/V than any other readily available fibrous material (for equivalent packed volume density).

From reaction kinetics, it was determined that the pyrolysis temperature had to be greater than 1000 C. Reaction equilibria suggested an appropriate temperature range of 1100-1900 C. Considering pyrolytic carbon density minima, the reaction temperature was limited to about 1400 C. Because the maximum continuous use temperature of fused quartz is about 1300 C, the temperature range chosen for the evaluation of methane pyrolysis in fused quartz tubes packed with fused quartz wool substrate was 1100-1300 C.

Apparatus and Materials - The laboratory apparatus used in the carbon formation experiments is schematically depicted in Figure 16. The apparatus is shown in Figure 17 in the lab. Pressures and flows of hydrogen, methane and purge argon from storage cylinders were controlled and monitored with pressure regulators/-gauges, rotameters, and variable orifices. Process heat was supplied by molybdenum disilicide electrical-resistance heater

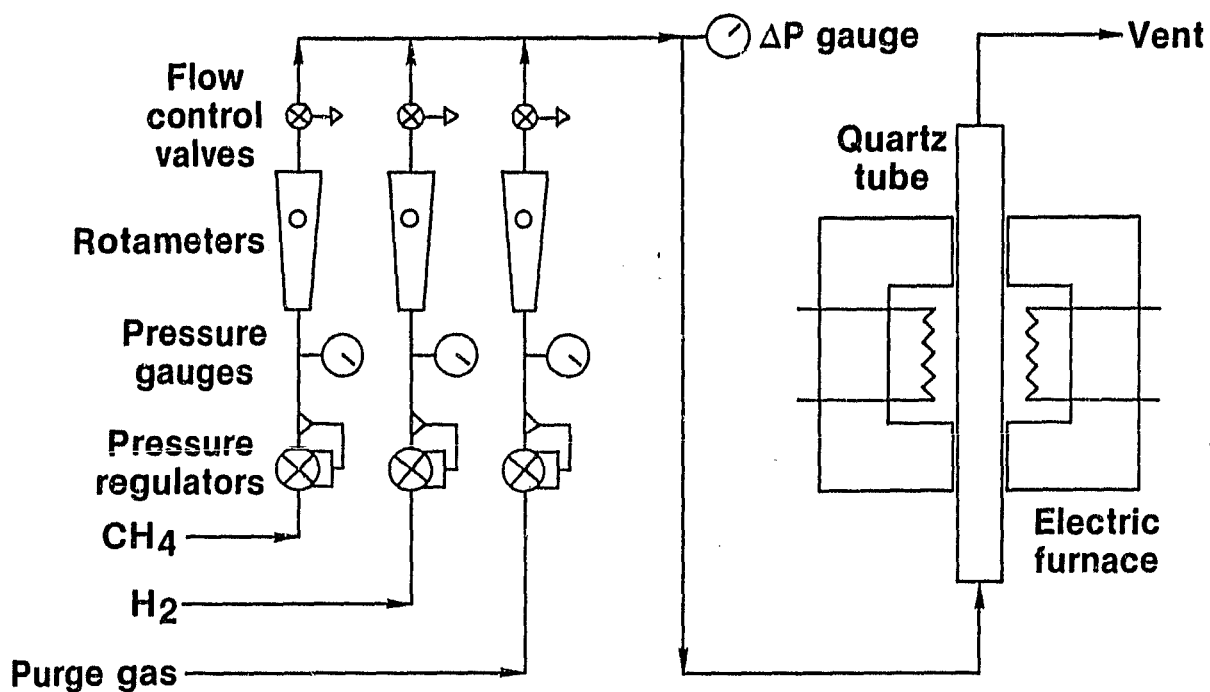
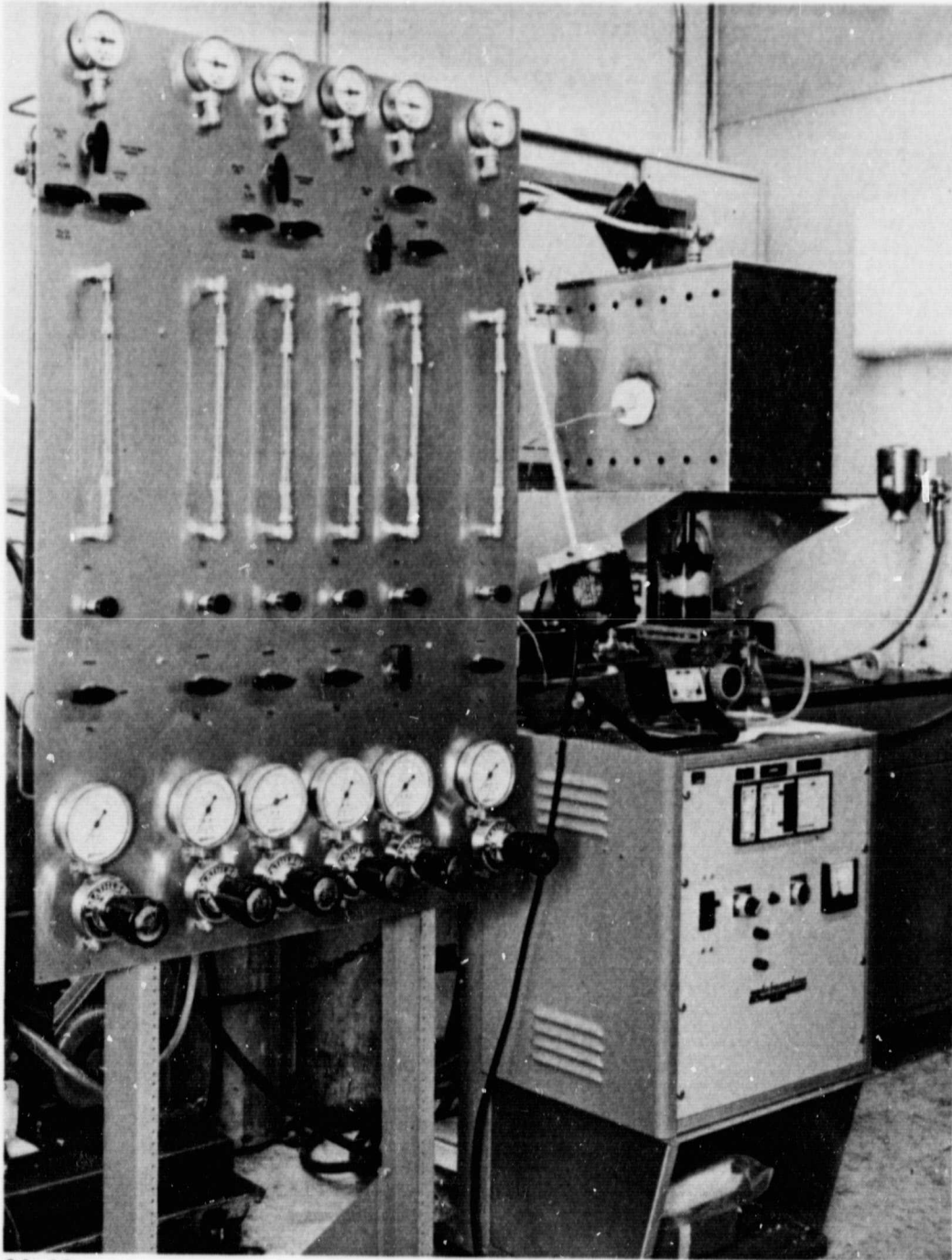


FIGURE 16
CARBON FORMATION TEST SETUP SCHEMATIC



84-98

FIGURE 17
TEST SETUP IN LAB

elements in the 10 cm high by 15 cm square heated zone of the fibrous-alumina-insulated box furnace.

Power for the heater was generated and controlled with a pulse-width-modulated power supply. Platinum-rhodium thermocouples were used to measure process temperature on the wall outer surface of the vertical reactor tubes at the midpoint of the heated zone. A fibrous filter was employed to capture any soot in the effluent from unpacked reactor tubes.

Reactor tube material used was transparent, high-purity (less than 50 ppm total impurities by weight) fused quartz. The packing and soot filter material was high-purity (less than 100 ppm total impurities by weight) fused quartz wool with nine micrometer fiber diameter. Impurities in the source methane and hydrogen were less than 300 ppm and 100 ppm by volume, respectively.

Test Procedure - Quartz reactor tubes 60 cm long were first washed with laboratory detergent and then distilled water and methanol rinses. Once dried, the tubes were handled only with lint-free linen gloves. In order to pack a tube, a 30 cm wide quartz wool mat was rolled, radially compressed, then inserted and centered in the tube. Once inserted, the quartz wool plug expanded radially to completely fill the cross-section of its

tube. Volume density of the packing was taken as the ratio of packing bulk density to actual quartz density (2.2 g/cc).

Typically, a reactor tube (and soot filter in the case of an unpacked tube) was first weighed, then vertically centered in the cold furnace and sealed with rubber inlet/outlet corks. The tube was purged with argon, heated to the test temperature, and the desired inlet gas composition (percent methane in hydrogen) and flow were established and continued for a predetermined time (usually six hours). At the end of the test run, process gas flow was stopped and the tube was purged with argon, cooled, and removed from the furnace. At the end of the run, the tube (and soot filter) were reweighed to determine the total amount of carbon formed. Conversion efficiency was calculated as the percent ratio of carbon formed to total carbon as methane input to the reactor tube.

Initial Results - Carbon deposition data for studies in unpacked 22 mm ID quartz tubes are presented in Figures 18 and 19. The gases were introduced downward to reduce tube blockage by soot. Inlet gas composition affected the conversion efficiency, increasing with increasing methane concentration. Conversion also increased with increasing temperature as would be expected by kinetics and for an endothermic reaction. The reactor residence time (gas flow rate), on the other hand, had little effect on conversion efficiency. It was concluded that a greatly

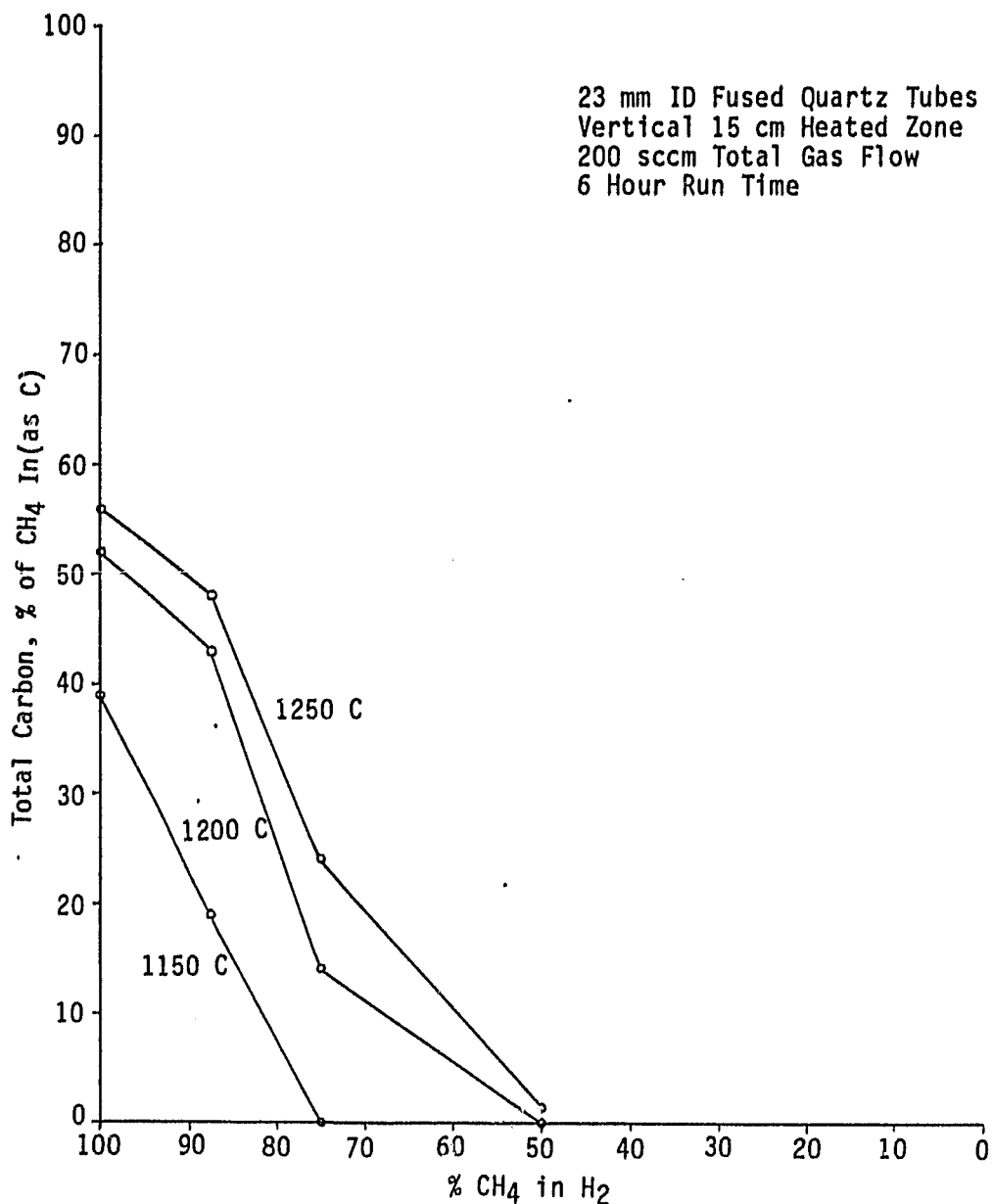


FIGURE 18
EMPTY-TUBE RESULTS: EFFECT OF HYDROGEN DILUTION

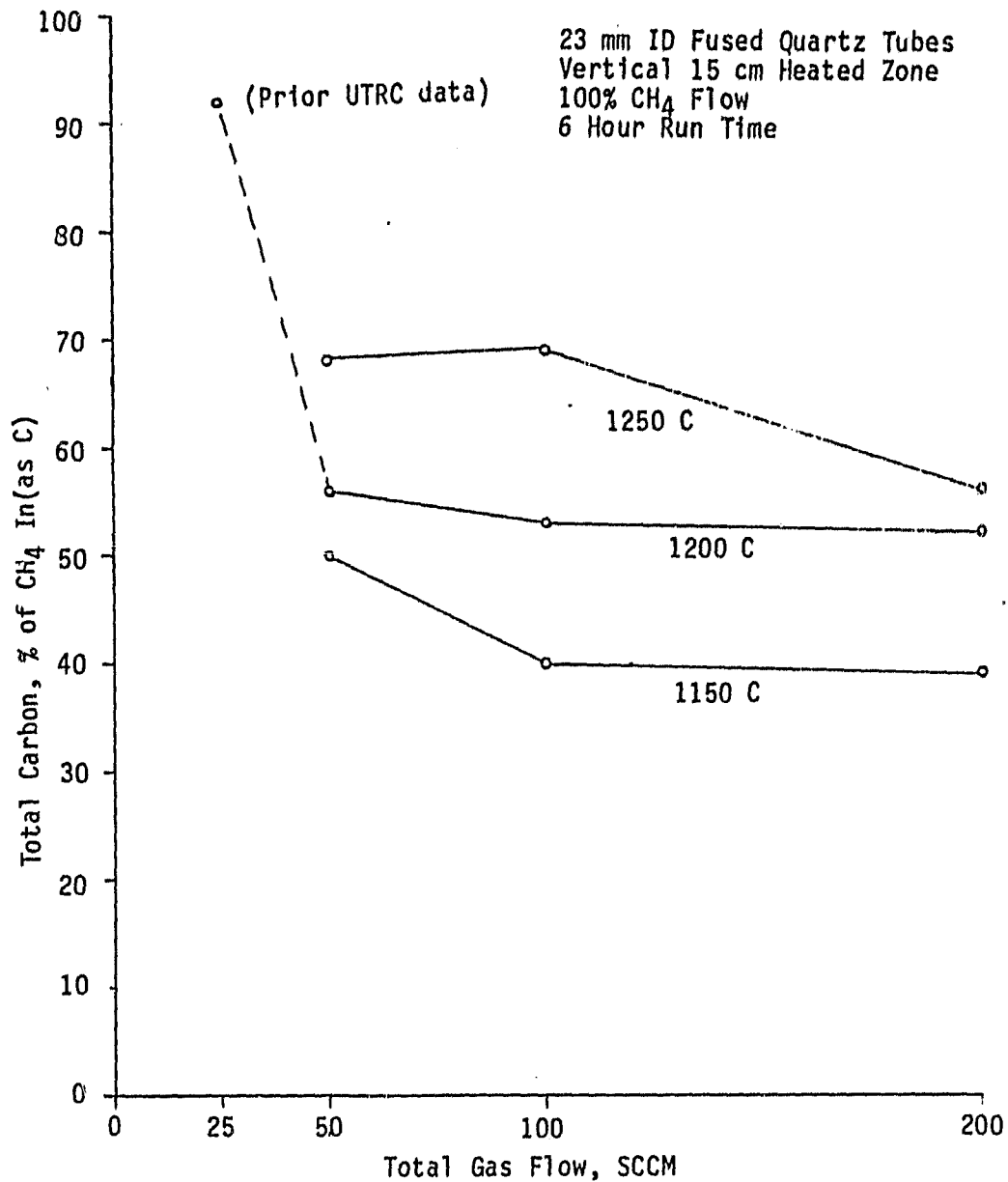


FIGURE 19
EMPTY-TUBE RESULTS: EFFECT OF FLOW RATE

Increased residence time would be required to achieve high single-pass conversion of methane to carbon in an unpacked quartz reactor.

The nature of the carbon formed in the unpacked tubes was mostly light soot, with a thin film of hard carbon formed on the inner wall of the tube in the heated zone. Flaking of the hard carbon film during cooling caused mixing of this film with soot, preventing determination of the relative weights of soot and film carbon. In some test runs, soot completely blocked the tube in the heated zone, forcing premature termination of the run.

Data for quartz wool (QW) packed 22 mm ID tube experiments are presented in Figure 20. Total inlet gas flow was directed upward in the tube at 50 sccm. Downward gas flow was not required because soot formation did not occur in these packed tube reactor hot zones. In addition, no significant difference in conversion efficiency was noted for downward versus upward gas flow. Conversion efficiency improved significantly relative to the conversion in unpacked tubes, especially at low methane concentration and high temperature. Increasing quartz wool packing density caused a smaller yet still significant increase in conversion.

All carbon was completely contained in the quartz wool; microscopic inspection revealed that carbon had coated the wool fibers

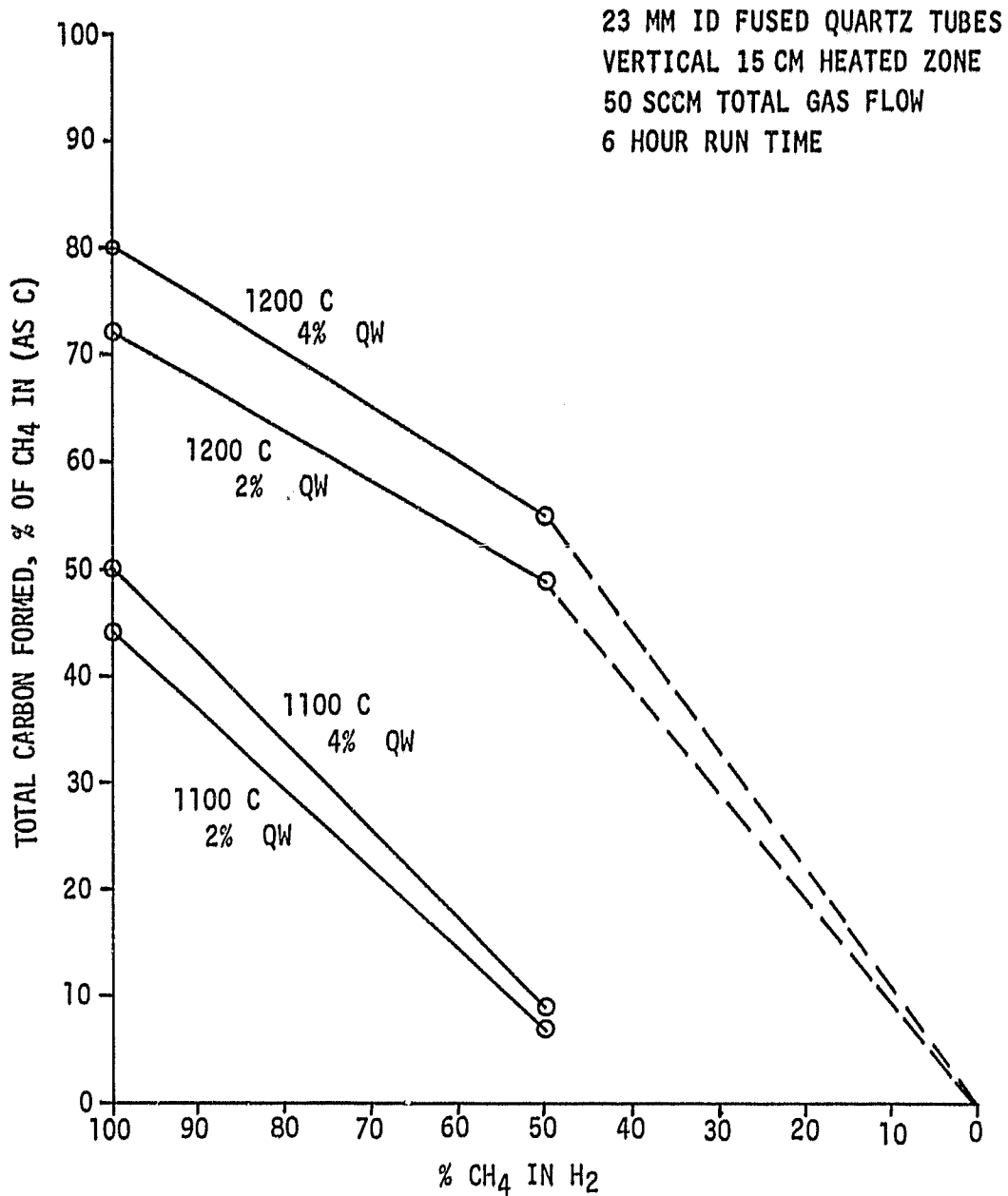


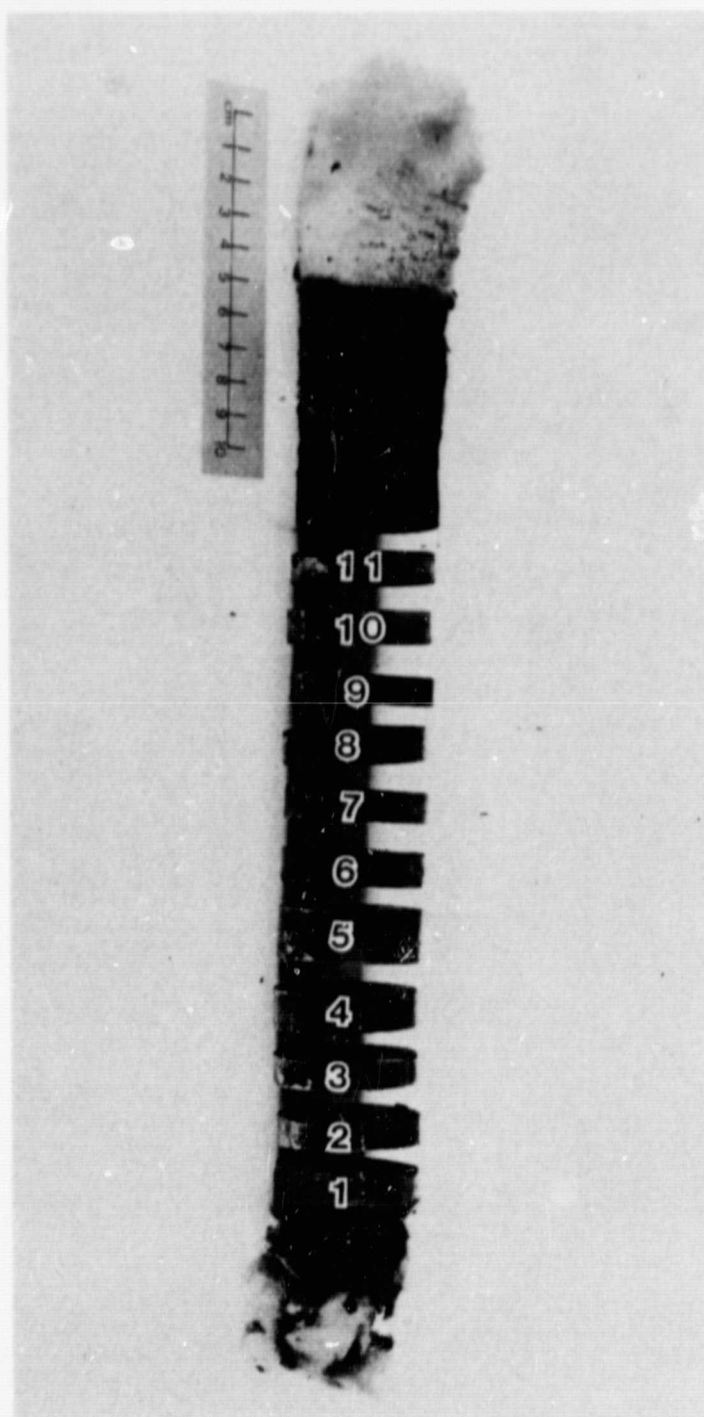
FIGURE 20
 INITIAL PACKED-TUBE RESULTS

with no evidence of soot. X-ray diffraction revealed that the carbon thus formed was semi-crystalline or turbostratic graphite of the type usually formed at temperatures of 1700 C or higher (Ref. 12). It is speculated that this result was due to the extremely smooth and amorphous nature of the quartz fiber surfaces-

Carbon density and loading capacity were determined in an extended test using a 45 mm ID quartz tube packed with two volume percent quartz wool. The experiment was run using a 1200 C temperature with a pure methane upward inlet gas flow of 100 sccm. When the pressure drop through the packing reached 0.07 bar (1.0 psi), the test was terminated at 104 hours. The weight gain was 232 g (0.51 lb) and a conversion efficiency of 74 percent was constant throughout the run.

A dense rod of carbon, which had formed in the heated zone, was easily separated from the tube after cool down. Since only traces of carbon were left on the tube wall after rod removal, the tube could have been repacked with new wool and re-used to form more carbon. This result confirmed the predicted separation of the formed carbon from the quartz tube wall due to differential contraction.

A picture of the carbon/wool rod is shown in Figure 21. The rod was cut into disks with a diamond saw and the carbon density was



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FIGURE 21
CARBON LOADING TEST SPECIMEN

determined by toluene displacement. As shown in Table 12, the carbon bulk and actual densities were quite high, averaging 1.27 g/cc (79 lb/cu ft) and 1.78 g/cc (110 lb/cu ft) respectively. The carbon disks were very hard and rigid, and were repeatedly handled without any loss of carbon.

Supplemental Testing

The initial results reported above confirm that high-surface area quartz wool packing in a quartz tube CFR produces high density carbon at appreciable formation rates at temperatures of 1100-1200 C, with the capability to remove the resulting carbon/wool rod from the reactor tube.

At this point in the CFR development program, it was decided by agreement between Hamilton Standard and NASA Johnson Space Center to extend the Design Support Testing phase of the program to explore the effects on the CFR process of higher reaction temperature, different reactor packing substrates, and catalysts.

Specifically, the reaction temperature was extended to 1400 C by using mullite (60 percent alumina, 40 percent silica) tubes, since quartz is limited to a reaction temperature of 1300 C. A rigid carbon foam called reticulated carbon (RC) was chosen as a carbon formation substrate alternative to quartz wool (QW). Two different porosities of RC were chosen for evaluation, 45 and 100

TABLE 12
CARBON LOADING TEST RESULTS

<u>LOCATION IN TUBE</u>	<u>BULK DENSITY G/CC REACTOR</u>	<u>VOLUME DENSITY PERCENT</u>	<u>ACTUAL SOLID DENSITY G/CC</u>
2	1.46	83	1.76
4	1.65	73	2.26
6	1.41	86	1.64
8	1.13	70	1.61
10	0.71	45	1.58
MEAN	1.27	71	1.78

NOTE: Tube locations numbered from inlet to outlet (low to high location numbers)

pores per inch (ppi); both had the same volume density of 3.3 percent. Finally, the Group VIII metals iron, nickel, and cobalt were tested as candidate catalysts for methane pyrolysis.

Catalyst Preparation - Each of the three metals were deposited on each of the three substrates (QW and two RC porosities) by first soaking the substrate in a saturated solution of the metal chloride at room temperature. The substrate was then drained, dried at 150 C in an oven, and the metal chloride decomposed and oxidized in air at 300 C. Finally, the metal oxide was reduced to the free metal by treating the substrate with hydrogen in a tube furnace at 300 C. A single soak in the metal chloride solution produced a two-weight-percent catalyzed substrate, while three soaks with drying/oxidation/reduction in between soaks produced a six-weight-percent catalyzed substrate.

Results With 11 mm ID Tubes - Comparison testing of tube materials, substrates, and catalysts were performed with packed 11 mm ID tubes. Results of this testing are presented in Table 13. The QW substrates were packed to the same 3.3 percent volume density as the RC substrates.

On the average, QW substrate performed better than RC substrates, catalyzed or uncatalyzed. Iron exhibited a suppressing effect on reaction rate, while nickel and cobalt enhanced the reaction rate as compared to uncatalyzed substrate. The averaged results for

TABLE 13
FINAL DST PACKED 11 MM ID TUBE TEST RESULTS (a)

Uncatalyzed Substrates

	(b)			
Fused quartz tubes		45 RC = 65	100 RC = 69	QW = 80
	(c)			
Cast mullite tubes		45 RC = 74	100 RC = 84	QW = 86

Catalyzed 100 RC Substrate (b)

2 wt % catalyst	Fe = 66	Ni = 78	Co = 78
6 wt % catalyst	Fe = 80	Ni = 87	Co = 85

Catalyzed QW Substrate (b)

2 wt % catalyst	Fe = 70	Ni = 82	Co = 83
6 wt % catalyst	Fe = 76	Ni = 79	Co = 88

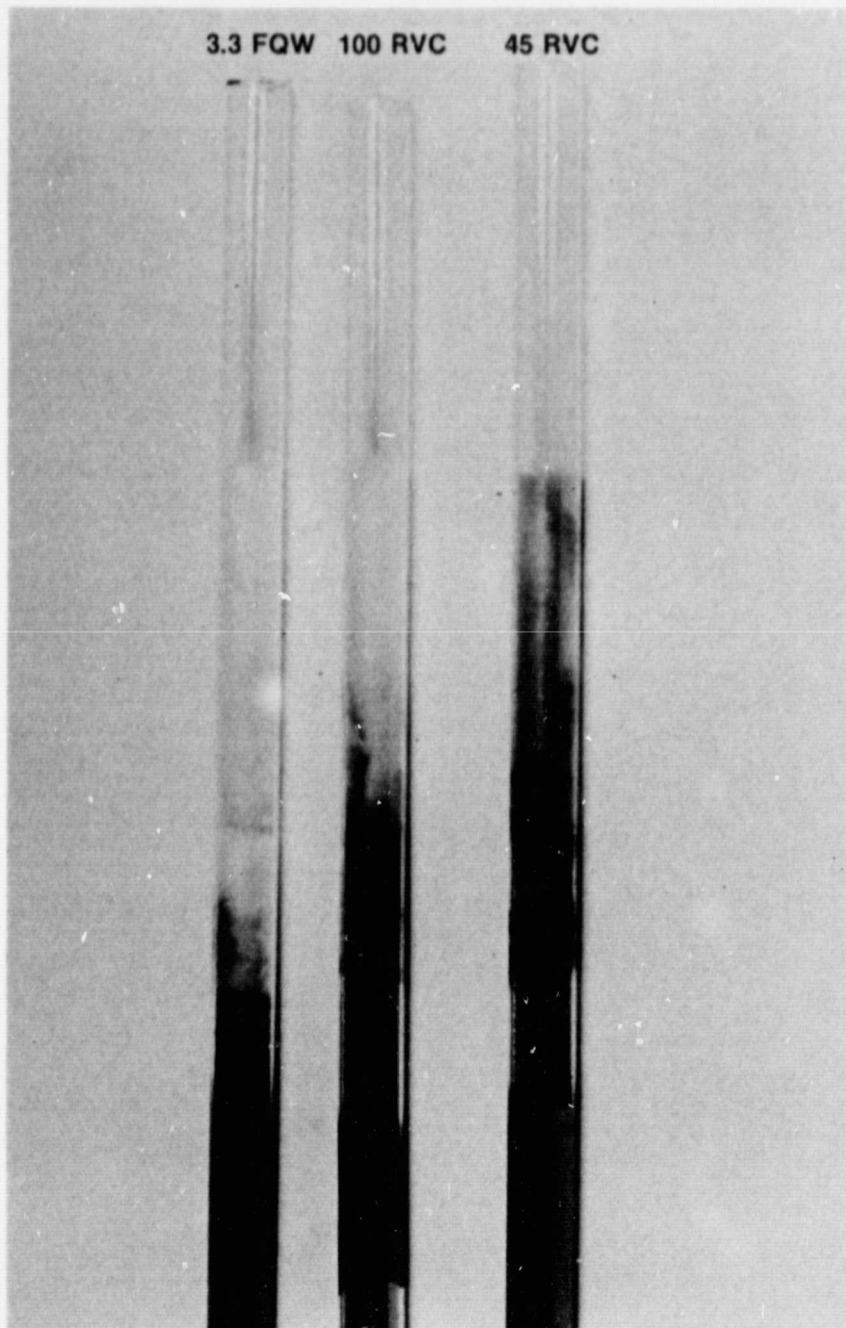
NOTES

- (a) Each data point is percent conversion of methane to carbon averaged for 4 runs: 50/100% methane-in-hydrogen and 2 different temperatures.
- (b) Run temperatures for fused quartz tubes were 1200/1300 C.
- (c) Run temperatures for cast mullite tubes were 1300/1400 C.

nickel versus cobalt were the same within experimental error. Although the averaged results for mullite tubes were higher than quartz tubes due to higher average temperature, the conversion efficiencies at the same temperature (1300 C) were actually lower for mullite than for quartz. Finally, as evident in Figure 22, a dark residue of condensed hydrocarbons contaminated the outlet end of the RC-packed tubes. This is probably due to the inability of the coarse RC to retain the hydrocarbon aerosol in the heated zone of the tubes.

Results With 45 mm ID Tubes - On the basis of initial catalyst evaluation and data from the literature (Ref. 10), nickel was chosen as the catalyst for comparison testing in 45 mm ID tubes. Tests were run with QW and RC, both catalyzed and uncatalyzed. The tubes had a 6 mm OD thermocouple tube down the middle to measure axis temperature in the heated zone.

Results of this testing are shown in Table 14. Best results were obtained with two percent uncatalyzed QW. Nickel had a much greater catalytic effect on QW substrate than on RC. The high pressure drops prompted comparison testing of QW-packed 45 mm ID tubes with and without centerline thermocouples. The results presented in Table 15 clearly show that the presence of this centerline obstruction greatly increased pressure drop, even with less carbon than in the runs without thermocouple tubes.



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FIGURE 22
CFR SUBSTRATES EFFLUENT QUALITY

TABLE 14 (a)
SUBSTRATE TESTING IN 45 MM ID QUARTZ TUBES

<u>TUBE PACKING</u>	<u>RUN TIME HOURS</u>	<u>CENTERLINE TEMPERATURE, C</u>	<u>CARBON FORMED GRAMS</u>	<u>CARBON CONVERSION PERCENT</u>	<u>FINAL ΔP PSI</u>
100 RC UNCATALYZED	161.5 (b)	1170	164	42.5	0.3
100 RC NI-CATALYZED	124.1	1165	153	51.7	6.0
1% QW UNCATALYZED	168.0	1140	193	48.1	2.7
1% QW NI-CATALYZED	113.0	1150	232	85.9	6.5
2% QW UNCATALYZED	74.7	1110	160	89.9	6.1

(a) Run conditions were 1250 C tube wall temperature and 80 scfm methane input. Runs terminated at one week or by excessive pressure drop.

(b) Run terminated due to building power failure.

TABLE 15

(a)

CARBON FORMATION IN QW-PACKED QUARTZ TUBES

<u>PACKING DENSITY VOL. %</u>	<u>TUBE WALL TEMPERATURE CENTIGRADE</u>	<u>RUN TIME HOURS</u>	<u>CONVERSION EFFICIENCY PERCENT</u>	<u>CARBON FORMED GRAMS</u>	<u>FINAL ΔP PSI</u>
1 (b)	1250	168	48	193	2.7
2 (b)	1250	75	90	160	6.0
2 (c)	1200	96	74	232	1.0
2 (c)	1100 (d)	168	43	172	0.3

NOTES: .

- (a) Runs performed with 45 mm ID tubes and 80-100 sccm methane input.
- (b) Thermocouple protection tube (6 mm OD) along 45 mm ID tube axis.
- (c) No thermocouple protection tube.
- (d) Estimated due to control/measurement offset caused by changeout of partial set of DST furnace heater elements before run.

BREADBOARD CFR DESIGN AND FABRICATION

This third task of the CFR development program comprises final CFR configuration concept selection, Breadboard CFR and test setup design, and reactor and test setup fabrication.

Final Concept Selection

Analysis of Design Support Testing data revealed that the best overall carbon formation performance was achieved with quartz wool packing in quartz tubes at 1100-1300 C. Conversion efficiencies of methane to carbon were about 45-95% over this temperature range. Dense carbon grew throughout the heated zone of the reactor tubes, with no evidence of soot; all carbon was contained in the QW packing. The carbon/packing separated easily from the reactor tubes upon cooling to ambient temperature. Average carbon bulk densities covered the range of 0.7-1.3 g/cc (44-79 lb/cu ft) in the heated zone of the reactor tubes.

Based on these results, a QW-packed tubular quartz reactor, slightly tapered to facilitate carbon/packing removal from the large end, was chosen as the final CFR geometry. The carbon collection concept selected was manual removal of the carbon/-packing tapered rod to a light plastic storage bag. The filled bag would be manually transported from the CFR location to the final storage location. Fresh CFR packing would be removed and

replaced by the used packing at the storage site. The CFR reactor tube itself is considered to be part of the ACRS fixed hardware and not a consumable item.

Breadboard Reactor Design

Projection of rate data from DST indicated that a reactor sized for up to 60 man-days (36 lb) of carbon should exhibit high conversion of up to a 6-man (4.8 lb/day) input flow rate of methane at an operating temperature of 1200-1300 C. It was therefore decided to design the Breadboard CFR for inlet methane flow rates up to the 6-man level. Reactor size was limited to 36 lb of carbon due to a microgravity manual-transport constraint of 40 lb.

A cutaway drawing of the Breadboard CFR design is presented in Figure 23. The reactor tube was 43 inch long with a 4.9 in ID at the small end and 7.9 inch ID at the large end, giving a 4 degree solid angle taper and 0.82 cubic foot total internal volume. The 25 inch heated zone, beginning 8 inches above the large end, had an internal volume of 0.48 cubic feet. With a design value of 75 lb/cubic feet for average carbon bulk density in the heated zone, the reactor was sized for a maximum of 36 pounds of carbon. Reactor aspect ratio (L/D) of 4 was chosen to be the same as for the DST 45 mm ID tubes.

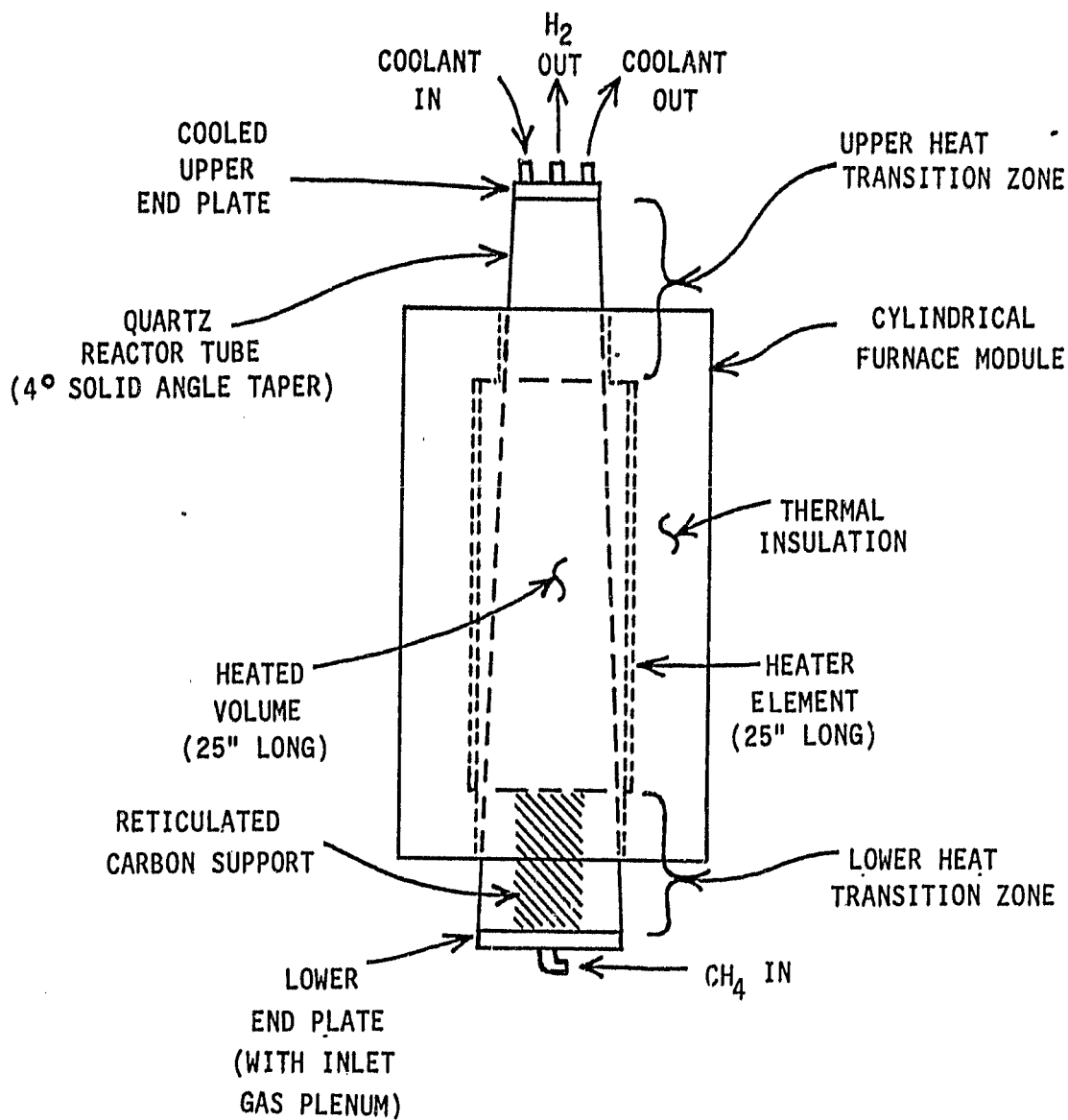


FIGURE 23
 BREADBOARD CFR CUTAWAY

The reactor is surrounded by a cylindrical furnace module with a 25 inch heating length and 4 inch thick fibrous insulation on the sides and 4 inch thick ceramic vestibules at the ends. The heater element was 40 turns of 325 mil diameter kanthal (iron-chrome-aluminum) wire capable of continuous operation at a maximum temperature of 1300 C.

The reactor tube extended 4 inches out the bottom and 8 inches out the top of the furnace module for fan cooling to protect the end seals. End seals were three turns of silicone rubber strip wrapped around and glued to the reactor tube and end plate circumferences with silicone adhesive. The lower end plate had a plenum for inlet gas distribution, while the upper end plate had a plenum for cooling water throughput. The reactor tube was completely packed with QW, except for an 8 inch long RC support for the formed carbon. End plates were fabricated from 6061-T6 aluminum for high thermal conductivity and ease of fabrication. The end plate/seal combination could withstand 250 C continuous use temperature.

Test Setup Design

The Breadboard CFR test setup is shown in Figure 24; it was attached on the back of the DST rack and utilized the same 5 KW power supply as the DST box furnace. The reactor rested on a 100

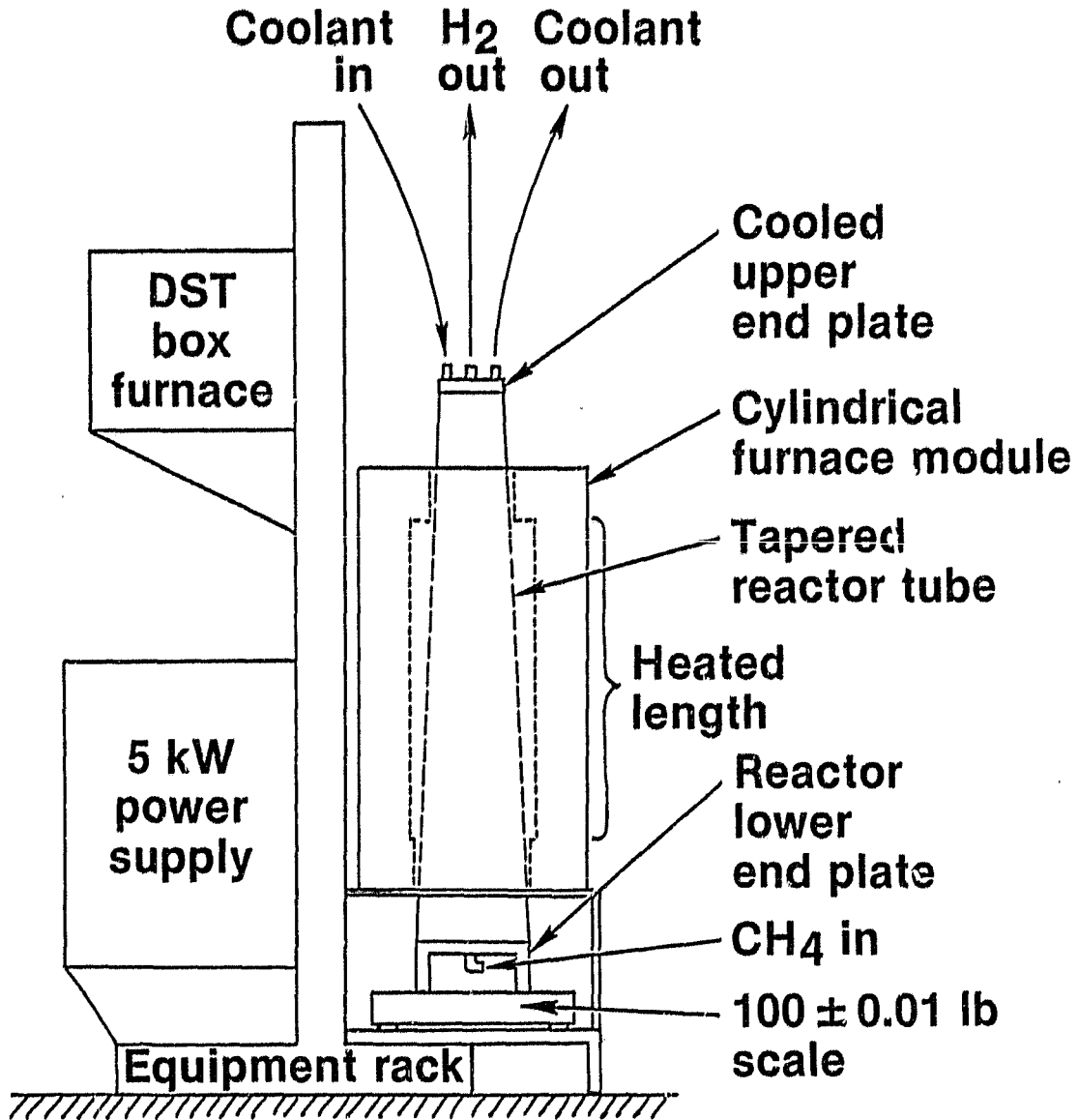


FIGURE 24
BREADBOARD CFR TEST SETUP

± 0.01 lb load scale, while the furnace module was supported separately on an aluminum shelf.

The DST gas management section (see Figures 16 and 17) was modified to provide 1-6 man (380-2280 sccm) flows of methane, hydrogen, and purge nitrogen. The rig was instrumented to interrupt heater power and combustible gas flow and initiate purge gas flow upon occurrence of heater overtemperature, under-temperature, or detection of a combustible gas leak. This allowed for the unattended continuous operation required for Breadboard CFR testing.

Reactor and Test Setup Fabrication

After approval of the Breadboard CFR design by NASA, the long-lead items (reactor tube and furnace module) were ordered from custom fabrication vendors. Reactor end plate fabrication and test setup modification were then performed. Upon receipt of the reactor tube and furnace module, the tube was packed and the Breadboard CFR assembled.

The CFR QW packing scheme is shown in Table 16. This arrangement provided 1.0 percent volume density QW in the lower third of the heated zone and 1.5 and 2.0 percent in the middle and upper thirds, respectively. Based on projections from DST tests in 45 mm ID tubes, this packing scheme would result in about 98%



TABLE 16
BREADBOARD CFR PACKING CONFIGURATION

<u>SEGMENT LENGTH, IN(a)</u>	<u>MIDPOINT DIAMETER, IN</u>	<u>VOLUME CU IN/CC</u>	<u>PACKING VOL. DENSITY, %</u>	<u>PACKING WEIGHT, GM</u>
8	5.180	169/2763	1.0	61
9	5.775	236/3864	2.0	170
9	6.405	290/4753	1.5	157
9	7.035	350/5734	1.0	126
8	7.630	366/5955	2.4(b)	234

(a) Segments listed top to bottom of reactor tube.

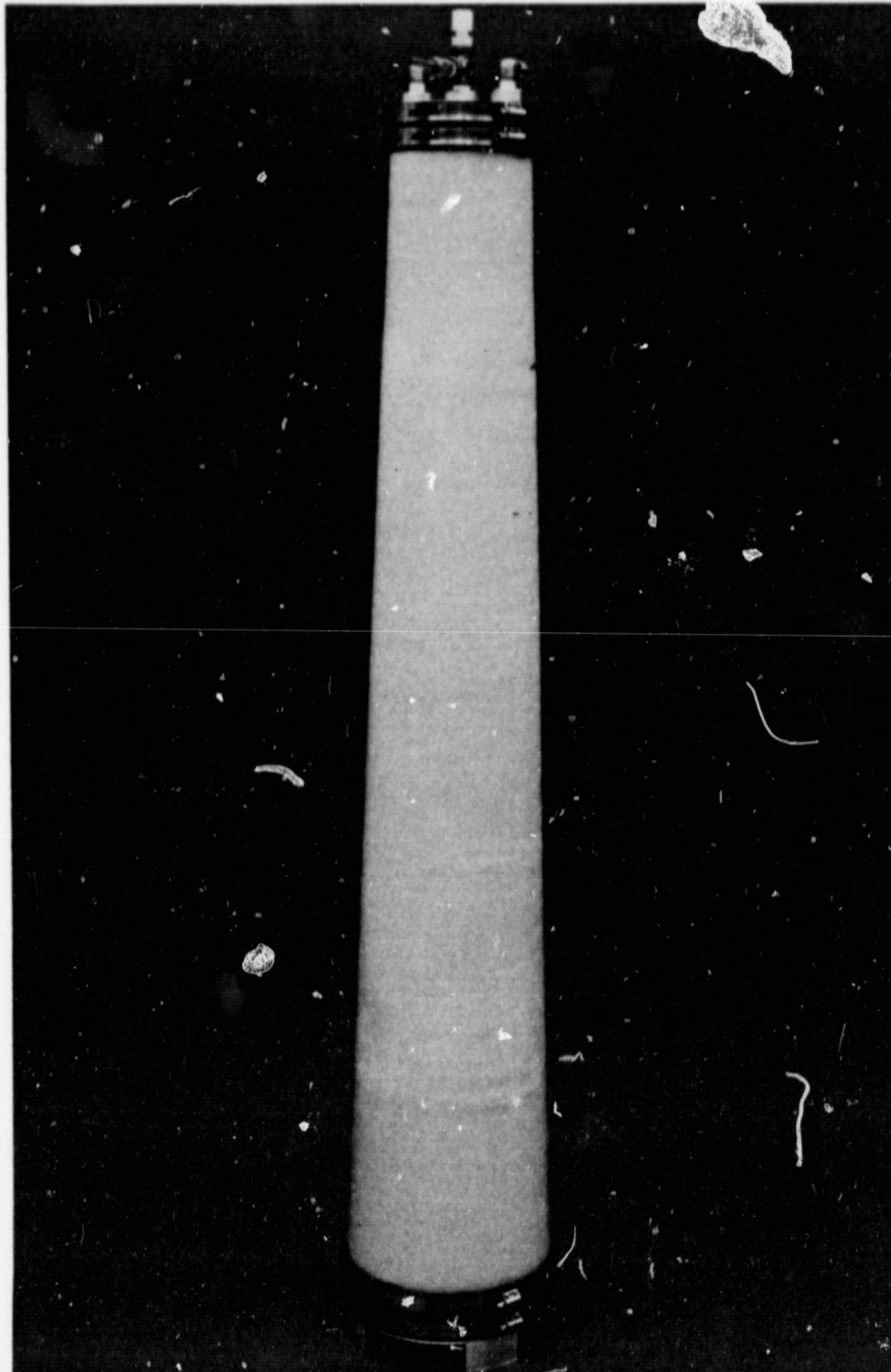
(b) Contains 6 in. dia. x 8 in. lg. RC support (100 pores per inch).

conversion of methane to carbon at a pure methane nominal inlet flow of 1140 sccm and an operating temperature of 1250 C.

After packing, the reactor end plates were attached to the tapered quartz tube. A picture of the completed reactor is shown in Figure 25. The reactor was placed on the load scale (Figure 26), the furnace module was lowered into place, and all plumbing/electrical connections were made. The completed Breadboard CFR and test setup is shown in Figure 27. Control thermocouples were inserted through the furnace module wall to contact the outer wall of the reactor tube at the vertical midpoint of the heated zone. Small fans and combustible gas detectors were mounted on the equipment rack in the vicinity of the reactor upper and lower end seals. After electrical and fluid checkout tests were satisfied, the Breadboard CFR was ready for testing.

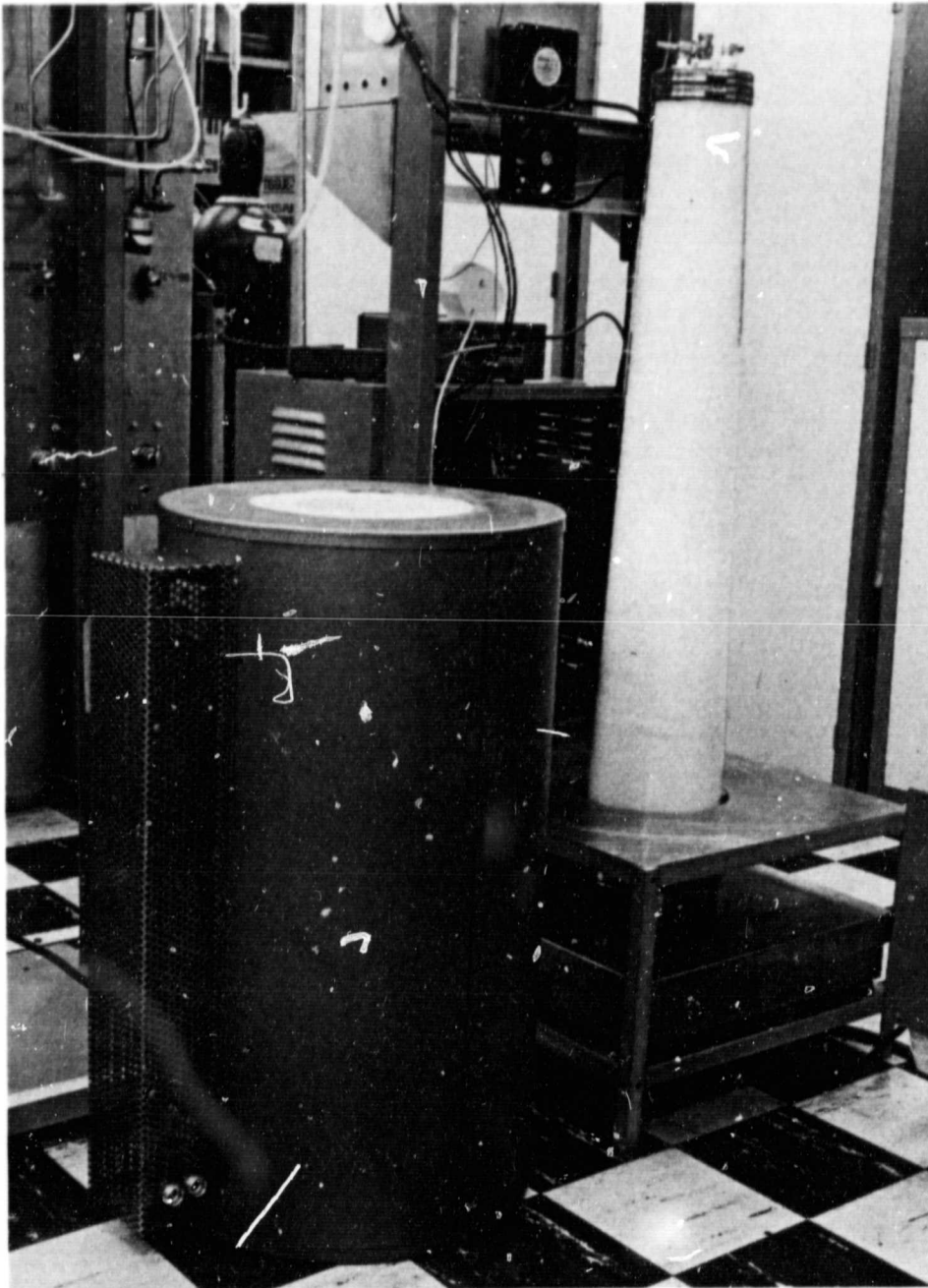


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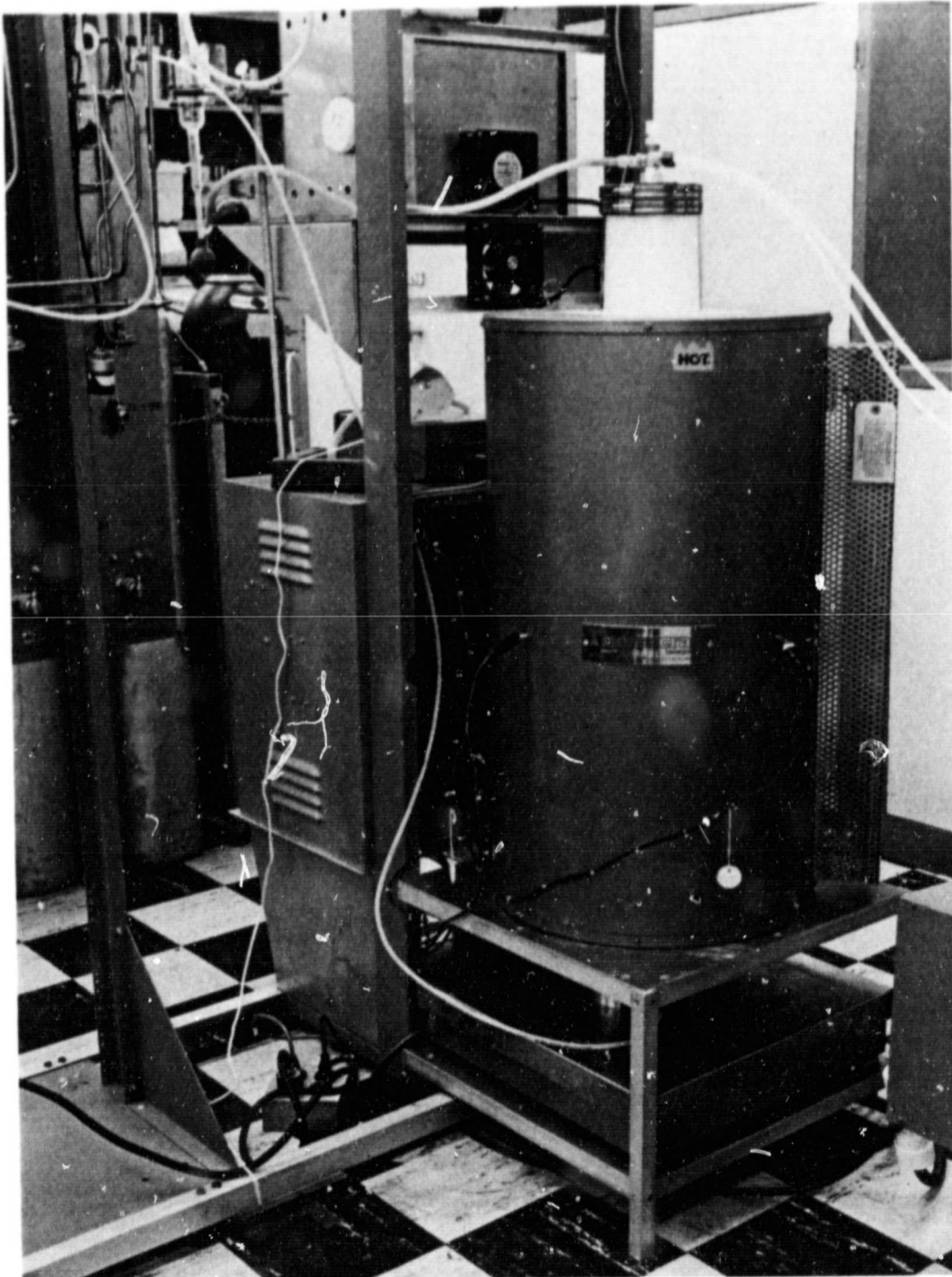
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FIGURE 25
BREADBOARD REACTOR BEFORE USE



G 67071

FIGURE 26
BREADBOARD REACTOR AND FURNACE MODULE



G 67072

FIGURE 27
ASSEMBLED BREADBOARD CFR AND TEST SETUP

BREADBOARD CFR TESTING

Breadboard CFR testing covered functionality tests, parametric testing, an extended-duration carbon loading test, and final carbon removal. Functionality tests were first performed. Once it was established that gas flows could be maintained at the required levels, the reactor was purged with hydrogen and heated.

Full-power heating time to 1300 C took four hours. End seal temperatures were below 100 C at this reactor temperature. After verification of alarm shutdown capability, the Breadboard CFR was ready for parametric testing.

Parametric Testing

The reactor was first run at a one-man (380 sccm) inlet flow rate of pure methane at a temperature of 1200 C for one day. Reactor weight gain was 0.60 lb for 100 percent conversion of methane to carbon. Subsequent 1200 C runs at 3-man and 6-man inlet flows of pure methane and 3-man inlet flow of 50 percent methane in hydrogen gave conversion of 90 percent or higher.

In order to acquire parametric data over a wide range of conversion efficiency, it was decided at this point to complete parametric testing at 1150 C and 1100 C rather than the originally-intended 1250 C and 1300 C, due to the unexpectedly high

conversions at 1200 C. Results of parametric testing are presented in Figure 28. This data has a maximum error of about two percent. At the end of seven days of parametric testing, 7.2 lb of carbon had formed, with no detectable pressure drop through the reactor. It is readily apparent from the data that dilution of inlet methane with hydrogen significantly decreases conversion efficiency.

Carbon Loading Test

It was decided to run the carbon loading test at 1150 C and 3-man (1140 sccm) inlet flow of pure methane, the midpoint of the nine pure methane parametric tests. As carbon loading proceeded, reactor weight gain was measured each day. Conversion efficiency remained quite constant throughout the loading test, varying between 88 and 92 percent (1.58-1.66 lb/day of carbon).

Reactor pressure drop became detectable during the 15th day of Breadboard CFR testing (8th day of carbon loading test). As shown in Figure 29, pressure drop rose exponentially until the carbon loading test was terminated at 6.7 psi pressure drop at the end of the 19th day of Breadboard CFR testing. A total of 25.7 lb of carbon was formed in the 1.65 lb of packing, resulting in 15.6 lb of carbon formed per pound of reactor packing.

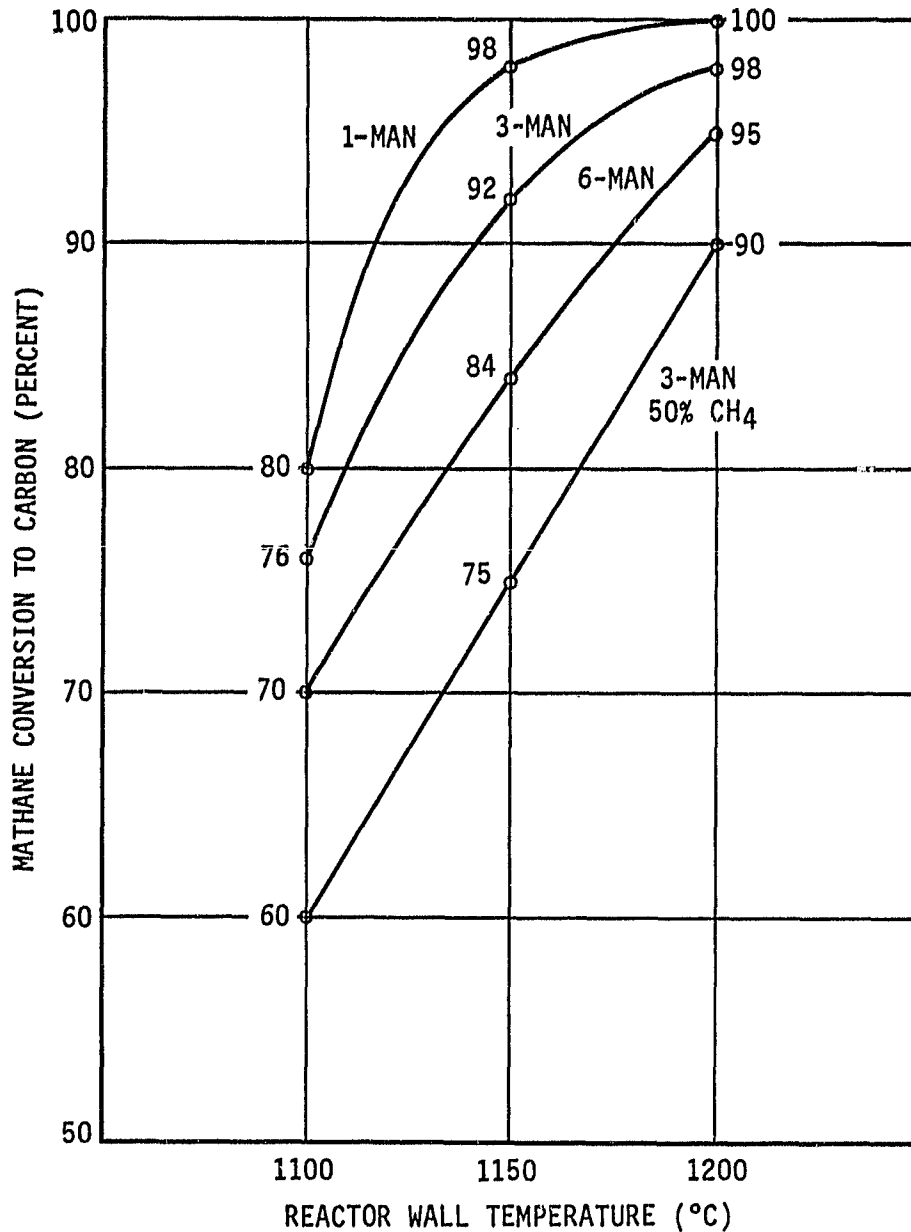


FIGURE 28
BREADBOARD CFR PARAMETRIC PERFORMANCE

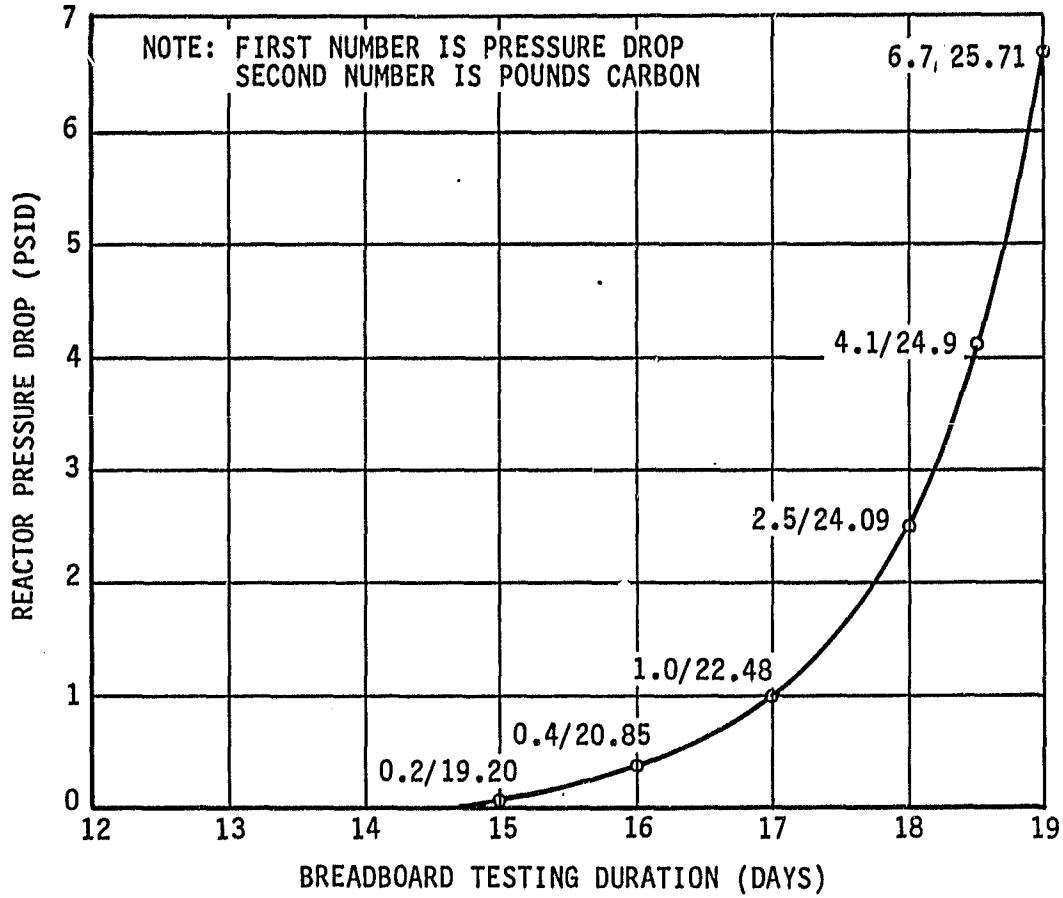


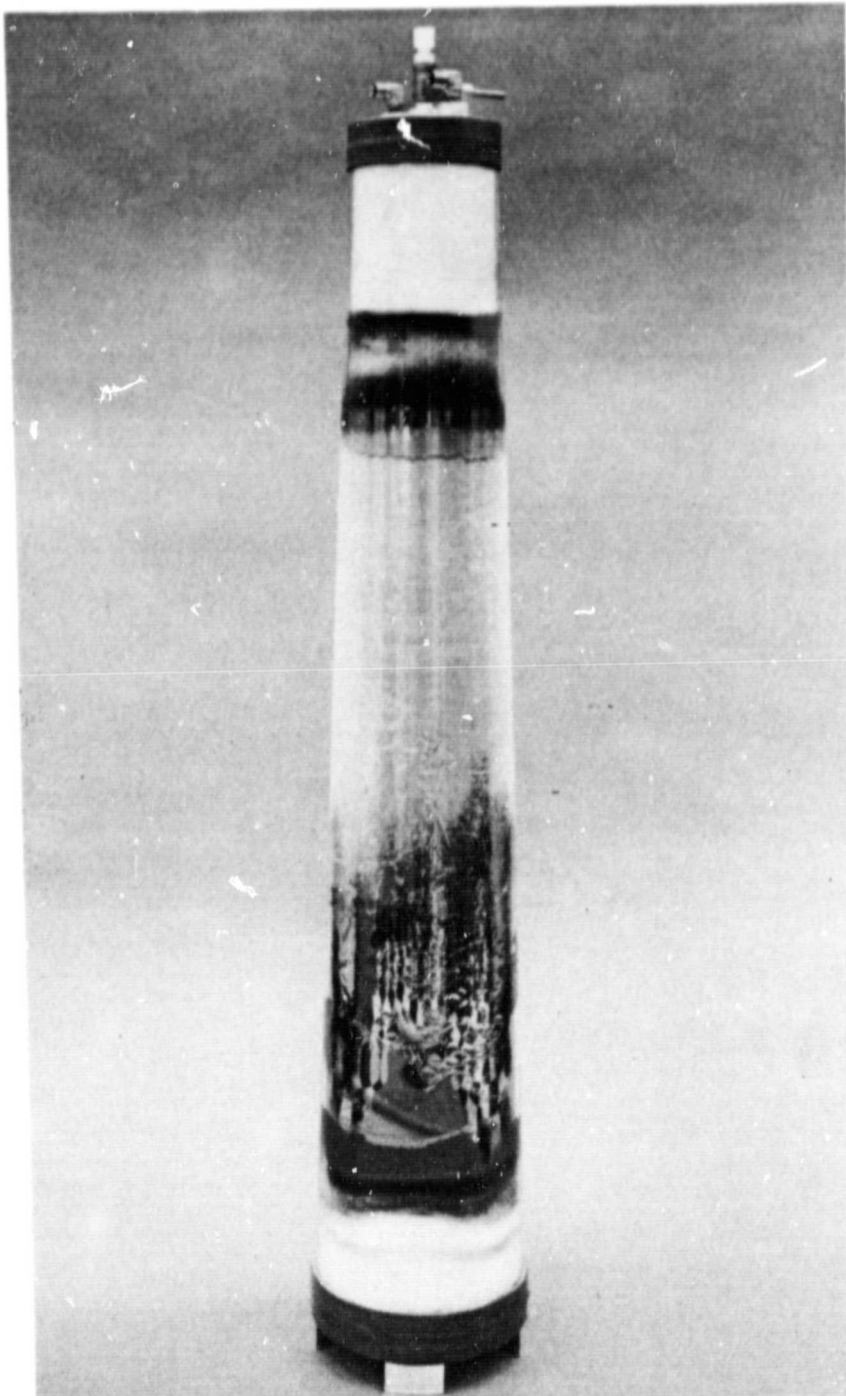
FIGURE 29
BREADBOARD CFR PRESSURE DROP HISTORY

The reactor was then purged with nitrogen, cooled, and removed from the test setup. As evident in Figure 30, the quartz tube retained its original shape throughout testing. A slight haze of devitrified quartz appears on the tube outer surface in the upper half of the heated zone. Spatial termination of carbon growth was quite sharp, especially at the upper end. No condensed hydrocarbons appeared in the white wool in the heat transition zones. No deterioration of the silicone end seals was evident.

Carbon Removal

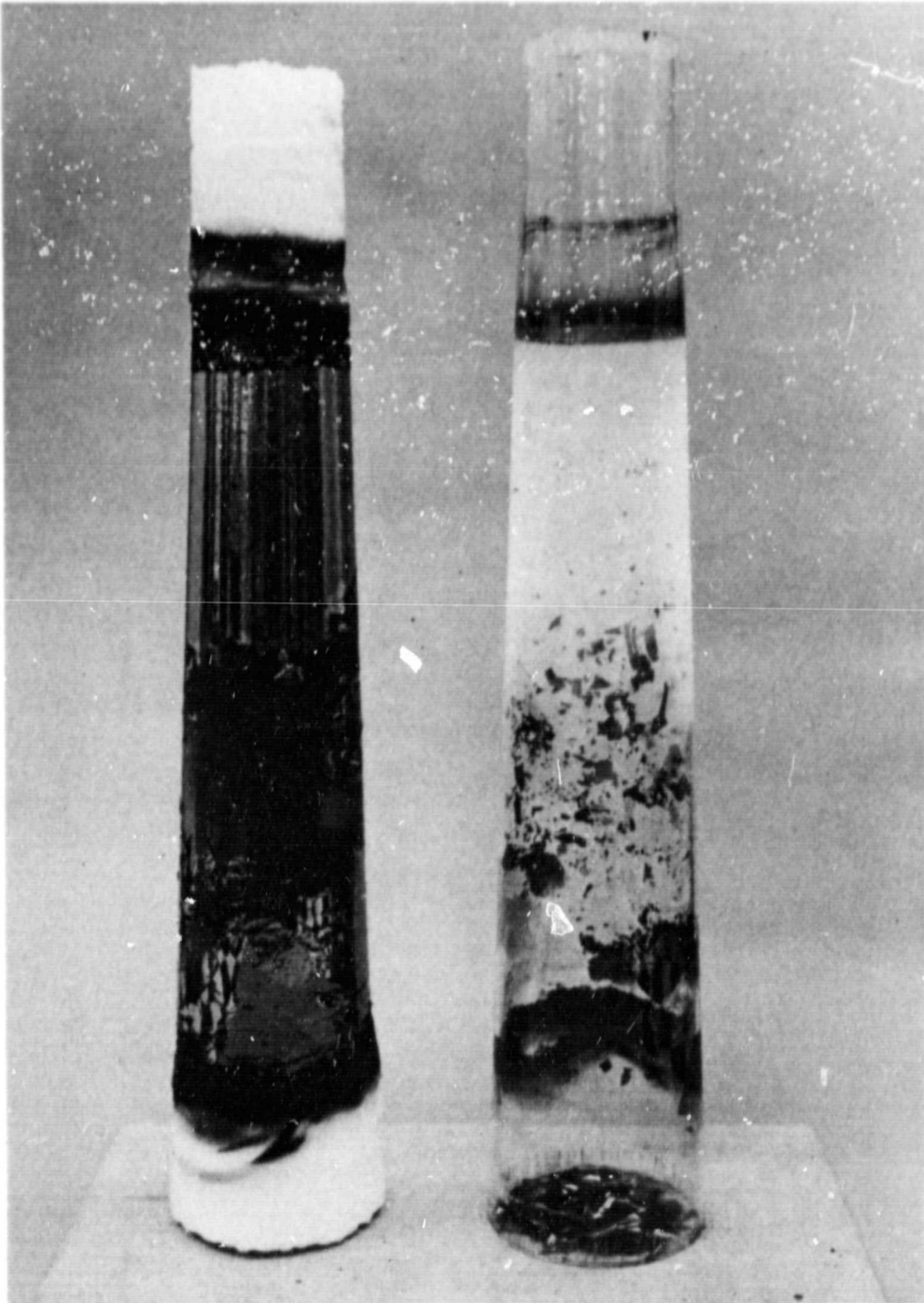
Even before removal of the reactor end seals and plates, the carbon/wool rod was observed to slide freely about a centimeter back and forth within the tube. After removal of the end seals and plates, the carbon/wool rod slid easily from the tube.

As shown in Figure 31, the carbon/wool rod was free standing. The carbon body formed in the heated zone was quite hard and rigid. Film carbon had adhered to the inner wall of the tube in several places and was removed by gentle brushing. During the somewhat rough handling of the tube during removal of the glued-on end seals, some of the shiny film of carbon on the surface of the carbon rod was flaked off; this carbon is evident at the bottom of the empty tube in Figure 31.



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FIGURE 30
BREADBOARD REACTOR AFTER USE



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FIGURE 31
CARBON ROD AND REACTOR TUBE

These minor problems with cleanliness of carbon/wool removal from the CFR reactor tube could probably be solved by (1) gentle removal of the carbon rod made possible by an optimized end closure and (2) application of a high-temperature release agent (such as finely-divided boron nitride powder) to the tube inner wall before packing insertion.

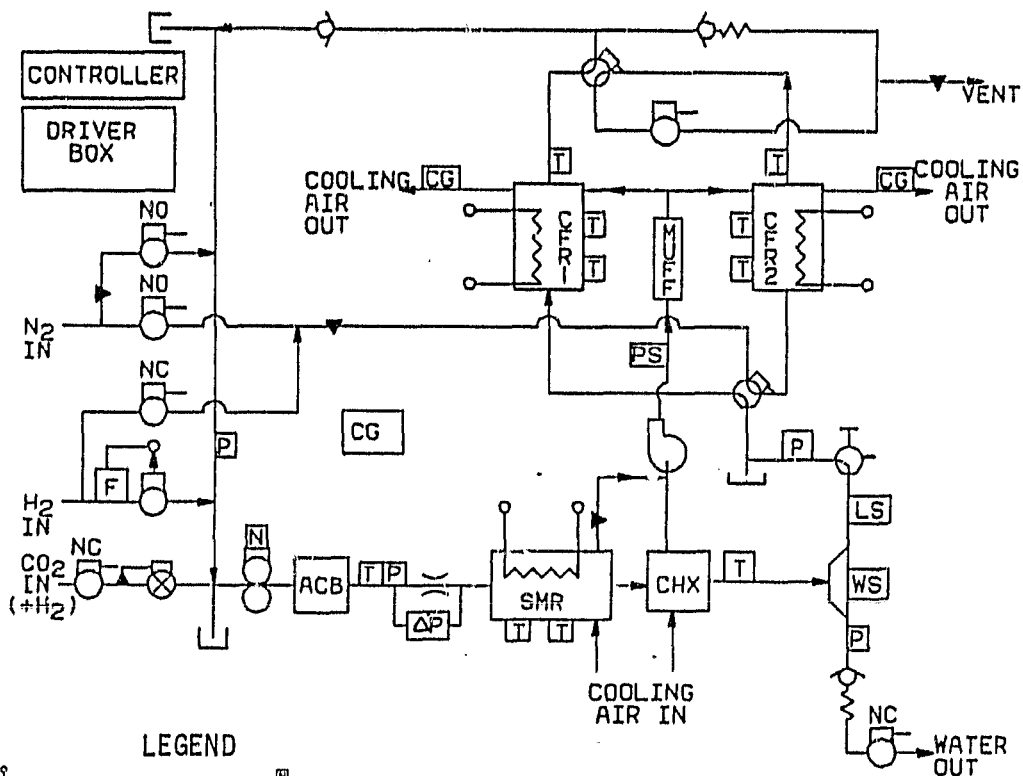
Future development of the CFR should address these problems. Also, further work should include analysis of carbon density distribution in the CFR and optimization of QW packing density distribution in order to maximize overall carbon bulk density and minimize reactor pressure drop.

SABATIER/CFR INTEGRATION CONCEPT

The final task of the CFR development program was study of SMR and CFR integration into an ACRS preliminary concept. The ACRS consists essentially of the SMR, two CFR reactors and furnaces for continuous operation, and associated fluid-handling components.

Description of Integration Concept

A schematic of the proposed ACRS is presented in Figure 32. Carbon dioxide (and hydrogen, depending on the CO₂ concentrator) enters the subsystem through a pressure regulator and a variable speed pump which maintains gas flow into the subsystem and around the recycle loop. Additional hydrogen is added as required to maintain a H₂/CO₂ stoichiometric ratio (4:1) at the inlet to the SMR. The carbon dioxide and hydrogen mixture enters the SMR through a charcoal filter which protects the reactor from potential trace amounts of contaminant carryover from an upstream electrochemical carbon dioxide concentrator or the electrolysis subsystem. The mixture then passes to the reactor where it is converted to water vapor and methane. The water vapor and methane then flow to the air cooled condenser, where the water vapor is condensed from the gas stream. Condensed water is then removed from the gas stream by a centrifugal water separator which pumps the water out of the ACRS.



LEGEND

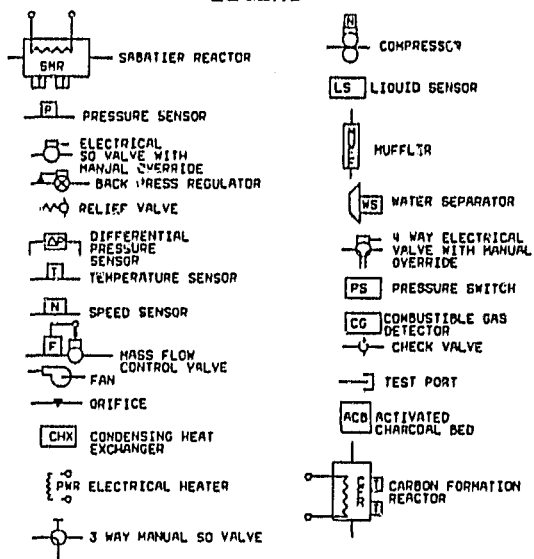


FIGURE 32
 PROPOSED ACRS SCHEMATIC

The remaining gas, which is almost all methane, is fed into one of the two CFRs, where it is heated. The methane is decomposed to carbon and deposited on a fused quartz wool substrate in the CFR.

The hydrogen is cooled as it leaves the CFR and is returned to the SMR inlet and mixed with the incoming carbon dioxide. When the CFR becomes full of carbon, as determined by pressure drop, the flow can be switched to a preheated second parallel reactor. The filled reactor is purged and allowed to cool down. After cool down, the carbon-impregnated quartz wool rod is removed from the CFR and new quartz wool packing installed.

The proper 4-to-1 hydrogen to carbon dioxide molar ratio at the SMR inlet is sensed by an "analytical carburetor" consisting of temperature, pressure, venturi differential pressure, and compressor speed (and therefore volumetric flow rate) sensors. Data from these sensors is used to calculate the molecular weight of the SMR inlet gas. Hydrogen flow into the ACRS is controlled to maintain the required molecular weight of 10.4 at the SMR inlet.

The remaining ACRS components are for controlling purge gas (nitrogen and hydrogen) into and out of the system and venting excess gas from the recycle loop in the case of excessive pressure in the loop.

A drawing of the ACRS packaging scheme is shown in Figure 33. The SMR and all fluid-handling components are located between the two vertical CFRs. A cutaway drawing of the CFR is presented in Figure 34. The heated zone of the quartz reactor tube is the same size and shape as the Breadboard CFR. The lower end closure is constructed of machinable ceramics with hot gas seals. Effluent cooling occurs in a quartz heat exchanger integral with the quartz tube. Furnace insulation consists of evacuated multifoil radiation/conduction shields wrapped around a ceramic support tube.

Performance Projections

The ACRS is intended to convert carbon dioxide and hydrogen to carbon and water at a nominal 3-man rate (1.8 lb/day of carbon) on a continuous basis. Each CFR is sized for 15 days, or 27 lbs, of carbon storage.

Performance projection for a preprototype 3-man ACRS are presented in Table 17. Most of the fixed hardware penalties (power/weight/-volume) are attributable to the CFR furnaces and associated thermal insulation. Consumables penalties are very reasonable, which for long-duration missions, such as Space Station, are more important than fixed hardware penalties in determining life-cycle cost.

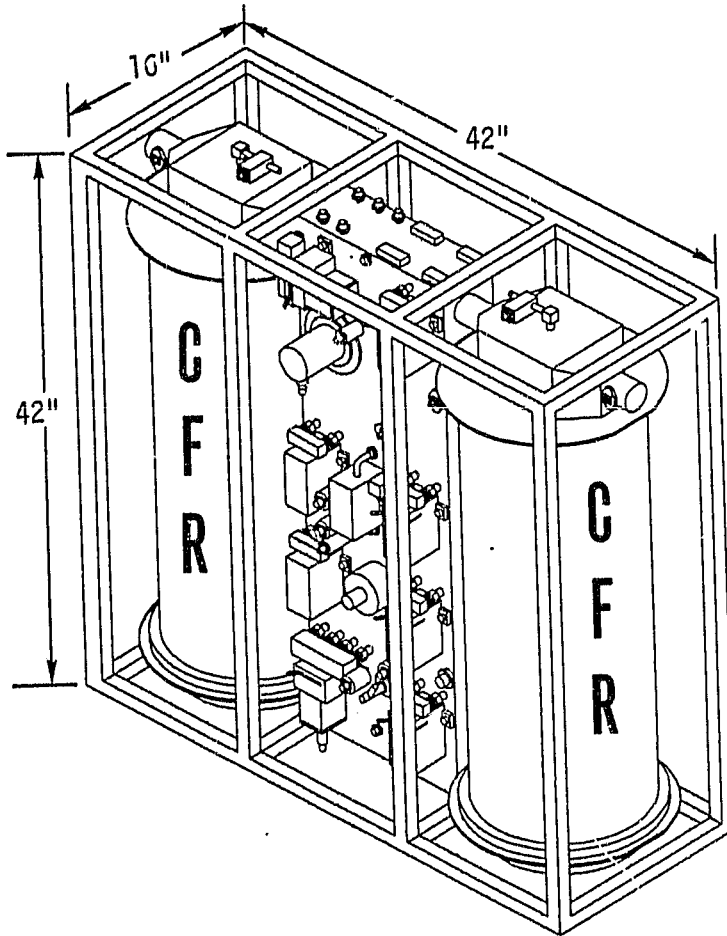


FIGURE 33
ACRS PACKAGING SCHEME

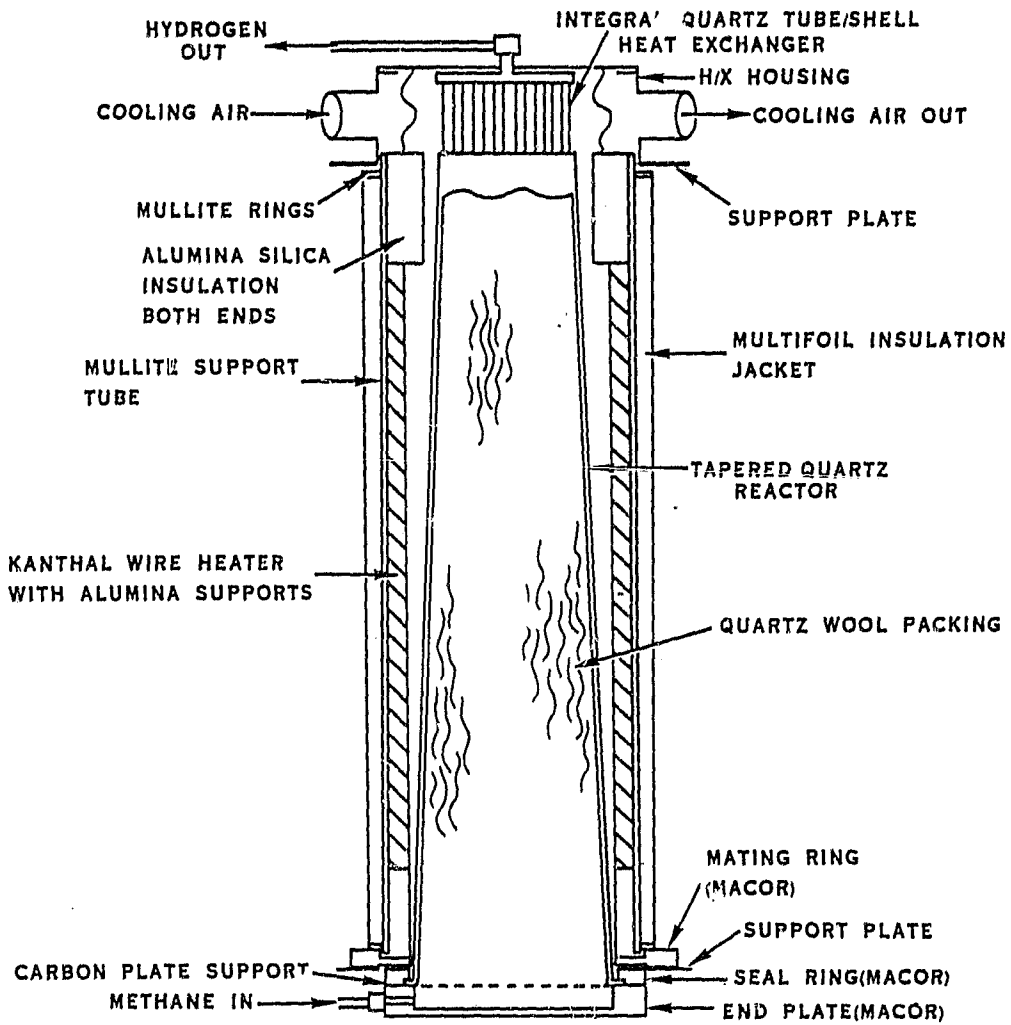


FIGURE 34
 CFR WITH MULTI-FOIL -INSULATED FURNACE

TABLE 17

PREPROTOTYPE 3-MAN ACRS PROJECTED PERFORMANCE

FIXED HARDWARE VOLUME, FT ³	16.3
FIXED HARDWARE WEIGHT, LB	400
POWER REQUIRED, W	400
CONSUMABLES WEIGHT, LB IN 90 DAYS	10.0
CONSUMABLES VOLUME, FT ³ IN 90 DAYS	4.8
CARBON TRANSPORT EPISODES IN 90 DAYS	6

CONCLUSIONS

Hard, dense carbon formation can be maximized and soot production eliminated by pyrolysis of methane on high-surface-area reactor packing. This fact supports the condensation theory of pyrolytic carbon formation from gaseous hydrocarbons.

A quartz-tube CFR utilizing quartz wool packing allows carbon removal and therefore re-use of the reactor, reducing consumables penalties for carbon formation and storage to very low values (15-20 lbs of carbon per pound of consumables).

A quartz-wool packed CFR can achieve high (greater than 90 percent) single-pass conversion of methane to carbon. Hydrogen dilution of the inlet methane significantly reduces the conversion efficiency.

Catalysis of methane pyrolysis with iron, nickel, or cobalt, at least at the levels used in this study, does not significantly improve CFR performance.

Breadboard CFR performance and ACRS performance projections show that an integrated SMR-CFR carbon dioxide reduction subsystem is a viable option for management of metabolic carbon on long-duration space missions.

RECOMMENDATIONS

Optimize CFR configuration parameters (size, shape, temperature, quartz wool fiber size, and packing density distribution) for maximal conversion efficiency and carbon density.

Develop hot gas seals, multifoil insulation, and reactor end seals optimized for minimal heat leakage yet ease of access for carbon removal.

Design, develop, and test a 3-6 man preprototype ACRS to evaluate SMR-CFR integrated performance in a spacecraft-compatible configuration.

Test subscale CFR on a Shuttle flight to determine the effects of microgravity on pyrolysis reaction and heat transfer rates.

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