

THE DIRECT PRODUCTION OF METHANE  
FROM HEAVY HYDROCARBONS AND STEAM

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## 1.0 INTRODUCTION

During the past several years, much concern and interest has been focused on the so-called single-reactor concept for making substitute natural gas (SNG) from coal. In principle, this concept proposes to charge coal and steam as well as catalysts, if necessary, into a single reactor to generate a gas that contains methane as the primary combustible constituent. Diluents such as acid gases could be removed during the process to yield a product gas of high methane concentration that would not require external methanation. This single-reactor concept is generally referred to as The Direct Production of Hydrocarbons (Methane) from Coal-Steam Systems method or, more simply, as the "Wyoming Concept."

The initial concept was developed at the University of Wyoming and has been supported by the Office of Coal Research (OCR) at the University of Wyoming under Contract 14-01-0001-1196.

About 1 year ago our Process Engineering Group developed process flowsheets and approximate costs for erecting and operating equivalent sized plants using different technologies to produce medium (300-500) and high (1000) Btu gas. The results of this study suggested that, if coal could be gasified to methane directly by using steam in the process, such a concept would have a definite economic advantage over other gasification technologies presently being developed.

To substantiate our Process Engineering calculations, a limited experimental program was initiated to assess the technical feasibility of the concept. This paper summarizes the results of that program.

## 2.0 BACKGROUND

As a company, Babcock and Wilcox has been interested in coal gasification for over 20 years. Our accomplishments range from the construction of an oxygen-blown gasifier for the DuPont Company in the mid 1950's to the current construction of the BIGAS gasifier that will be built at Homer City, Pennsylvania.

So that the reader will understand our rating of product gas quality, we will identify a low Btu gas as one that produces 80-150 Btu/scf, a medium Btu gas as one that produces 300-500 Btu/scf, and a high Btu gas as one that could serve as a pipeline gas (i.e., ~1000 Btu/scf). The difference between low and medium Btu gas stems from the use of air or oxygen as the blowing medium. The major difference is that nitrogen is present as a diluent in the low Btu gas. Nitrogen, of course, is not readily removed from the product gas.

Medium Btu gas, after the removal of acid gases, consists primarily of hydrogen ( $H_2$ ) and carbon monoxide (CO) with a heating value of 320 Btu/scf. In addition, depending on the specific gasification process, a medium Btu gas may contain a low concentration of higher hydrocarbon gases for a heating value in excess of 320 Btu/scf.

In the production of high Btu gas, methane is generated in several ways. Two important routes for its production are as follows:

- During the gasification step by pyrolysis of the coal and/or hydrogasification of the volatile matter.
- By reaction of the H<sub>2</sub> and CO externally on the surface of the catalyst to form CH<sub>4</sub> (methanation).

In terms of gasification efficiency (i.e., Btu content of coal converted to Btu's as methane), the first route is preferred. For example, if char is first gasified to CO and H<sub>2</sub> and then reacted to form methane via the second path, the gasification efficiency is 69%, assuming cold reactants and an end point theoretical temperature in the gasifier of 1500°F. If, on the other hand, methane can be coupled to the gasification process so that  $2.453 C + 2H_2O + 0.453 O_2 = CH_4 + 1.453 CO_2$  (also starting with cold reactants and winding up at 1500°F), then the theoretical gasification efficiency is close to 90%.

## 2.1 PREVIOUS WORK

Development effort on the direct methanation process reported in the literature consisted primarily of batch-type tests at the bench scale level. The published results suggest that the following experimental procedure would provide the best approach to the problem (see references).

Coal was first mixed with caustic (K<sub>2</sub>CO<sub>3</sub>), then charged to the upstream part of a small (~1/2-inch ID) reactor 6 feet in length. A nickel methanation catalyst was either placed downstream or intimately mixed with the coal and caustic. After electrical resistance heaters heated the system to test temperature, water (or steam) was fed to react or gasify the coal. Off gas volume was measured and periodically analyzed. Typical test conditions were as follows:

Temperature, °F	1200 - 1400
Pressure, psig	Atmospheric - 800
Coal Weight, gm	125
K <sub>2</sub> CO <sub>3</sub> Weight, gm	15
Ni Methanation Catalyst Weight, gm	50 - 100
H <sub>2</sub> O Rate, ml/hr	4 - 8

## 2.2 LIMITATIONS

During the review of published results on gasification and the methanation catalyst state-of-the-art conducted before initiating our experimental program, we identified several potential limitations that could severely limit successful application of the concept. These limitations are discussed below.

### 2.2.1 Methanation Catalyst Life

Major concern centers on the anticipated "life" of the expensive nickel methanation catalyst. This catalyst sells for about \$3.00 per pound. Scaling the previous batch tests, that is, gasifying 125 pounds of carbon consuming 100 pounds of catalyst, indicates a projected catalyst cost of about \$150 per 1000 scf of methane produced. If we assume repeated 7-1/2 hour cycles intermittently charging fresh char, the nickel catalyst must last for 15 months to drive catalyst cost down to \$.10 per 1000 scf of methane produced.

The environment surrounding the nickel methanation catalyst is extremely harsh. Operation at 1200°F represents a temperature significantly higher than that normally used in methanating H<sub>2</sub> and CO. In addition, the possible effects of the sulfur, ash,

and coke forming entities on the life expectancy of the nickel catalyst are not currently known. Our concern for the life of the catalyst therefore relates to the following areas:

- Sintering of the catalyst at high temperatures
- Sulfur poisoning
- Deactivation by coking and ash

#### 2.2.2 Low Throughput - Batch

Using the published results as a basis for estimating coal throughput per unit of catalyst, the low weight hourly space velocity (WHSV) -  $\text{WHSV} = 125 \text{ lb coal}/100 \text{ lb Ni catalyst}/7.4 \text{ hrs} = 0.17$  - may limit application of the concept, even with a durable long-life catalyst.

The concept, as tested, involves batch operation with intermittent charging of the coal catalyst mix. Scaling up the batch operation to plants with capacities of  $250 \times 10^6$  scf-SNG per day seems unrealistic. Demonstration of continuous operation (continuous charging of hydrocarbon) is paramount to the success of the concept.

The low coal throughput rate may be due to the fact that the endothermic carbon-steam reaction to CO and H<sub>2</sub> does not occur at a rapid rate, even catalyzed with K<sub>2</sub>CO<sub>3</sub> at 1200 to 1400°F. On the other hand, a temperature of 1200°F represents a higher than optimum temperature for methanation. The overall concept settles for a tradeoff at temperatures below that desirable for rapid gasification but higher than that desired for good methanation.

### 3.0 OBJECTIVE

The focal point of the experiments was the demonstration of long methanation catalyst "life" in the direct production of methane from coal (or coal-like hydrocarbons) with steam in a continuous reactor. Pursuant to our major aim, catalysts were also surveyed at 1200°F to find the "best" catalyst to methanate CO and H<sub>2</sub> - some in the presence of sulfur.

### 4.0 EXPERIMENTAL EQUIPMENT - PROCEDURE

#### 4.1 METHANATION CATALYSTS - 1200°F

The apparatus used to test methanation catalysts at 1200°F is sketched in Figure 1. The reaction consisted of a 1-inch ID Vycor tube filled, normally, with 4 inches of catalyst. Space velocities ranged from 250 to 2000, while the H<sub>2</sub> to CO ratio was also varied from 4:1 to 1.6:1. Hydrogen sulfide, when used, ranged from 0.5 to 2.0 volume percent.

Existing gases were dried and passed through a Fisher Gas Partitioner, which is capable of analyzing H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO and CO<sub>2</sub>. The methane yield was determined from a chromatograph by using the peak height technique. Calibration samples were run periodically to check for shifts in peak height.

#### 4.2 DIRECT PRODUCTION OF METHANE

The apparatus used in this phase is shown in Figures 2 and 3. Two Lapp pumps were used to force the feedstock and/or water at elevated pressures into the reactor. The reactor shown in Figure 3 is 4 feet long and has a 1-inch ID. It is designed to withstand temperatures of 1500°F and pressures of 1000 psig. The catalyst bed is placed in the middle of the reactor and heated to the desired temperature by a Lindberg

furnace. The temperature is monitored by three thermocouples located in the thermo-well inside the reactor. The product gas passes through a motor valve which allows the pressure to be controlled.

The pressure is recorded and controlled by a Taylor Fulscope Recorder Controller. Provisions have also been made to introduce gases under pressure with controlled flow. The product gas from the reactor is sampled periodically from a water trap and passed through a Fisher Gas Partitioner which determines the methane yield. The remainder of the product gas, less the small amount used for the chromatograph, passes through a wet test meter which measures the amount of gas produced.

Several fail-safe devices are incorporated into the system. If the temperature within the reactor rises above a predetermined level, the complete system shuts down. Sensors monitor reactor pressure so that either too high an upstream pressure or too low a downstream pressure shuts down the complete system. This system is designed for a one-man operation with the possibility of unattended, continuous operation, if necessary.

#### 4.3 FEEDSTOCKS

During the direct production of methane phase of the testing, a number of different feedstocks were tried. Direct injection of coal under pressure was not considered feasible in our small laboratory reactor, so further batch tests were conducted using char. During these tests samples of char were mixed with catalysts, placed in the reactor and steamed at specific temperatures and pressures.

To evaluate the feasibility of continuous operation, feedstocks were chosen that could be continuously injected into the reactor. Four feedstocks that could be continuously added with steam to the reactor were coal tar, benzene, No. 2 fuel oil, and anthracene oil. Anthracene oil was chosen for further testing because of its ease in handling and its similarity in composition to coal, especially its H/C ratio (see Table 1).

#### 4.4 CATALYSTS

Of the 55 different catalysts tested, 10 were commercially available methanation catalysts and 45 were laboratory-prepared catalysts using accepted catalyst preparation techniques. Catalysts were prepared by impregnation, ion exchange, and decomposition. Many different promoters and combinations of promoters were examined. All prepared catalysts were calcined at 1200°F and activated using the standard activation procedure. Commercial catalysts were activated using the manufacturers' recommended procedure (see 5.0).

### 5.0 RESULTS

#### 5.1 METHANATION CATALYST SURVEY

Table 2 provides a selected list of catalysts tested and their methane yields at a  $H_2$  to CO ratio of 3 to 1 under varying conditions of space velocity and  $H_2S$ . We observed that the nickel (Ni) promoted catalysts lost activity as the catalyst bed was sulfided. Other metal catalysts were tried; however, except for platinum (Pt), each was poisoned by the  $H_2S$  in the gas feedstock. Moreover, as the space velocity was increased, the methane yield decreased for these other catalysts.

All tests were run at atmospheric conditions, and most were short-term tests ranging from 6 to 8 hours. The platinum catalysts showed no decrease in reactivity as a function of time and  $H_2S$  concentration, but all the other catalysts decreased as

the time of the test with  $H_2S$  was extended. The Norton, low surface area support is very resistant to high temperatures and should be considered an excellent support for high temperature-high pressure work.

## 5.2 DIRECT PRODUCTION OF METHANE

A data sheet of selected results is provided in Table 3. The temperatures, pressures, feedstock, catalyst, product gas produced, and weight of methane produced are tabulated. Our yield data was evaluated by integrating under the curve. An example of one of our curves appears in Figure 4. The first four tests were run so that we could determine the base for each feedstock and better understand the catalyst performance. These tests ranged in length from 1 to 30 hours, although a number of the tests were terminated because plugs formed in the reactor.

One problem was to determine the best way to introduce the alkali material needed to enhance gasification. In previous experiments, 200 grams of lignite coal with and without  $K_2CO_3$  were steamed at a water rate of 65 ml/hr. Assuming the stoichiometry to be  $2C + 3H_2O = 3H_2 + CO + CO_2$ , the theoretical yield would be 35 scf gas/lb  $H_2O$ . In the experiments without  $K_2CO_3$ , 7.1 scf gas/lb  $H_2O$  was produced for a 20% theoretical yield, whereas 25 grams of  $K_2CO_3$  gave 25.0 scf gas/lb  $H_2O$ , or a 71% theoretical yield. Therefore,  $K_2CO_3$  is obviously needed to accelerate the gasification reaction. Three methods for introducing  $K_2CO_3$  were tried in our continuous testing program. One method involved the direct addition of  $K_2CO_3$  to the feedstock before injection into the reactor. A second method tried the direct impregnation of  $K_2CO_3$  into the catalyst used for methanation. The last method added activated alumina impregnated with  $K_2CO_3$  to the methanation catalyst bed. The first method proved to be the best procedure.

From the results in Table 4, several general conclusions were drawn. In all experiments, the feedstock conversion decreased as a function of time; therefore, the gas production decreased. The catalyst activity also decreased as a function of time; therefore, the methane yield decreased (Figure 4). A number of the catalysts used were found to be regenerable after an oxidation and reduction scheme, but the decreases in feedstock conversion and methane yield were again observed.

Two possible explanations for the decrease in methane yield have been suggested. One is that the metallic nickel surface, which forms the active site for methane production, has been deactivated by the formation of nickel carbide ( $Ni_3C$ ). The second possibility is that amorphous carbon formed during the reaction plugs the catalyst surface and prevents the  $H_2$  and  $CO$  gas mixture from making contact with the active nickel. With the low sulfur feeds no detection of sulfur poisoning of the nickel catalyst has been observed at the conditions established in our tests.

## 6.0 CONCLUSIONS

### 6.1 METHANATION CATALYST SURVEY AT 1200°F

Of the 55 catalysts examined, the nickel (Ni) promoted catalyst provided the best activity for the production of methane from a hydrogen and carbon monoxide gas mixture. We also found that all nickel-promoted catalysts were deactivated when a gas containing  $H_2S$  was passed over the bed. Other metal-promoted catalysts were examined and, except for platinum (Pt), each was poisoned by the  $H_2S$  in the gas feedstock. The major drawback to using the platinum-promoted catalyst is its high cost. It is our opinion that the conventional methanation catalysts are not suitable for operation at these conditions (1200°F and  $H_2S$ ) and that further catalyst development in this area is needed.

### 6.2 DIRECT PRODUCTION OF METHANE

In the direct conversion of hydrocarbon feedstocks to methane, we have observed, in all cases, a decrease in both gas production and methane yield as the test continued.

This decrease was attributed to catalyst instability at the established operating conditions. We tried a number of different hydrocarbon feedstocks, except coal, and all our data have revealed the same results. A number of different catalysts were tried, and all showed that carbon deposition ( $\text{Ni}_3\text{C}$ ) on the active surface deactivated the catalyst. We feel that the heart of this concept is the catalyst. Before successful operation on a continuous basis is achieved, a better catalyst system must be developed.

#### REFERENCES

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3. Willson, W. G., Sealock, L. J., Jr., Hoodmaker, F. C., Hoffman, R. W., Cox, J. L., and Stinson, D. L., Preprints, Div. of Fuel Chem., 18, No. 2, 29-41, (1973).
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TABLE 1  
FEEDSTOCK COMPOSITIONS

	<u>Coal Tar</u>	<u>#2 Fuel Oil</u>	<u>Benzene</u>	<u>Anthracene Oil</u>	<u>Char</u>
BTU	16,340	19,400	17,986	16,680	13,960
H	5.5	12.7	7.7	6.0	1.0
C	90.9	86.7	92.3	91.6	80.0
N	0.83	--	--	.54	--
S	0.7	.4	--	.5	.4
Ash	.29	--	--	.02	13.9

TABLE 2  
% METHANE

Temperature, °F (One Atm)	1200	1200	1200	1200	1200
Space Velocity	250	1000	250	1000	250
H <sub>2</sub> S Volume, %	2	2	2	2	2
<u>Catalyst</u>					
Katalco 41-7					3
Katalco 11-3		13	6→2		
Houdry-Topsoe		13			
Harshaw Ni-0104T	20	20	20→5	20→4	
Harshaw Ni-0104T + 6% Mo			8→4		
Harshaw Ni-0104T + 5% Th			8→5		
Harshaw Zn-0308T	ND	ND	ND	ND	ND
Harshaw Cr-0103T	3%	ND	3	1	
Harshaw Al-1602T + 14% Ni, 7% Mo			8		
Harshaw Al-1602T + 14% Ni, 7% Mo + 13% K <sub>2</sub> CO <sub>3</sub>			4	5	
Harshaw Al-0104T + 7% Ni			7		
Harshaw Al-0104T + 5% Sn					
Harshaw Al-0104T + 5% Pd			ND		
Harshaw Al-0104T + 5% Co + 5% Cs	10→4		<1		
Harshaw Al-0104T + 15% Ni			10→0		
Harshaw Al-0104T + Ni, 6% Mo, 5% Ba			5		
Harshaw Al-0104T + Ni, 6% Mo, 5% Ba			14→2		
Harshaw Al-0104T + 7% Ni*			19→3		
Harshaw Al-0104T + 7% Ni, 6% Mo, 5% Ba*	17→12		19→2		
Harshaw Al-0104T + WO <sub>3</sub>			<1		
Harshaw Al-0104T + 5% <sup>3</sup> Pt			12→10		
Engelhard RD 150 Pt			11	3	
Engelhard RD 150 Pt + 5% Ba			8		
Catalysts and Chemicals Inc. C11-2-03			<1	<1	
Catalysts and Chemicals Inc. C13-4-04			<1	<1	
Union Carbide 13X + Ni			11→1		
Norton Zeolon + Ni			16→ND		
Norton Zeolon + Ni + Ba			18→3		
Norton SA-101 + Ni, Al Slurry			16→1		
Norton SA-101 + Na, Al Slurry + Mo + Ba	16→14		16→2		
Norton SA-101 + WO <sub>3</sub>			<1		

\*Added H<sub>2</sub>S after bed had reached 1200°F  
ND - None Detected

TABLE 3

SELECTED DATA SHEET

Test No.	Temp. (°F)	Pressure (PSIG)	Time Of Test (Hr)	Catalyst	Feedstock	Total Grams Of Carbon In	Product Gas Vol. (Cu Ft)	Wt. Of Methane (Grams)
1A	1200	1000	5.50	Norton SA-101	#2 Fuel Oil	290	4.38	50.40
B	1200	1000	4.50	Norton SA-101	Coal Tar	280	2.45	19.00
C	1200	1000	2.50	Norton SA-101	Benzene	172	.26	.50
D	1200	1000	3.00	Norton SA-101	Anthracene Oil	181	.88	6.97
2	1200	1000	4.75	Ni-0104T	Coal Tar	340	1.68	23.20
3	1200	1000	8.75	Norton SA-101-A	Coal Tar	170	1.56	23.90
5	1200	1000	11.50	Norton SA-101-B	#2 Fuel Oil	460	15.99	163.90
6	1200	1000	6.00	Norton SA-101-B	#2 Fuel Oil	583	9.94	91.40
9	1200	1000	10.00	Ni-3210T	Anthracene Oil	212	2.11	5.16
10	1200	500	2.00	RD-150 Pt	Anthracene Oil	254	1.83	6.46
11	1200	500	2.50	C11-2-03	Anthracene Oil	170	1.61	11.37
12	1200	500	2.00	Ni-3210T	Anthracene Oil	78	2.64	28.88
18	1200	1000	5.75	Ni-3210T	Char	80	2.17	17.26
20	1200	1000	4.60	IFT Ni + Ru	Char	80	1.28	3.54
21	1200	1000	5.00	Ni-3210T	Char	80	2.00	8.42

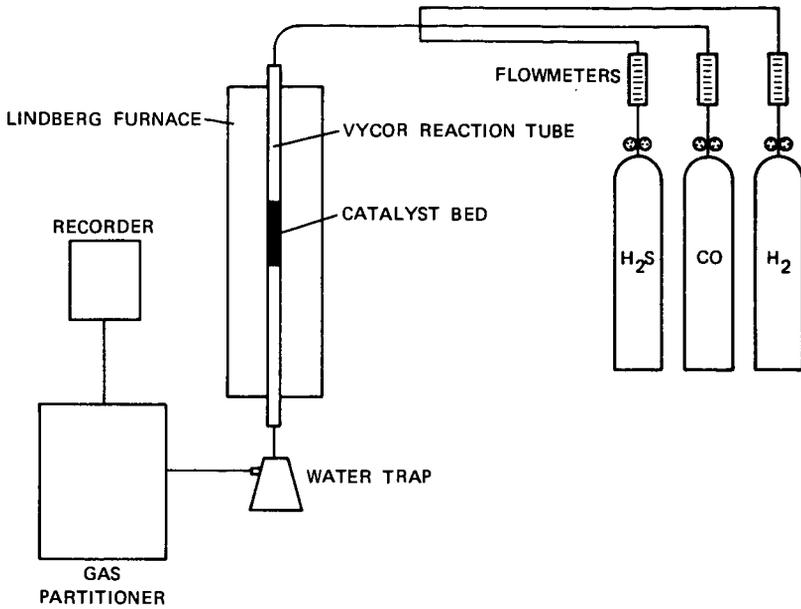


FIGURE 1 CATALYST TESTING APPARATUS

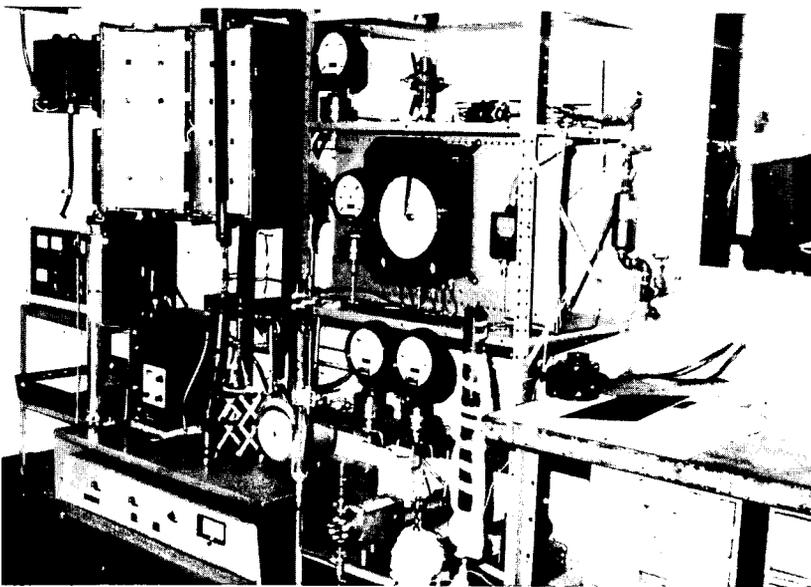


FIGURE 2 ADVANCED GASIFICATION APPARATUS

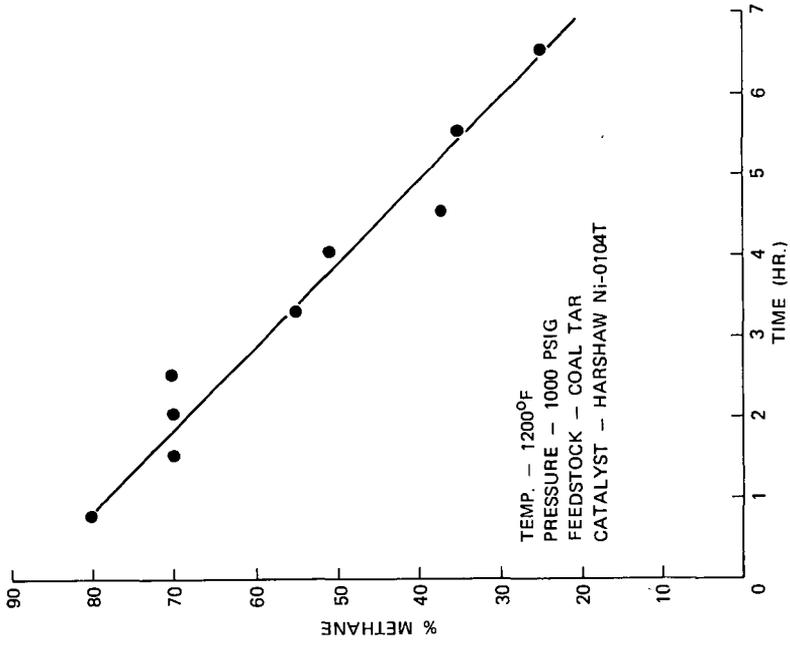


FIGURE 4 % METHANE VERSUS TIME

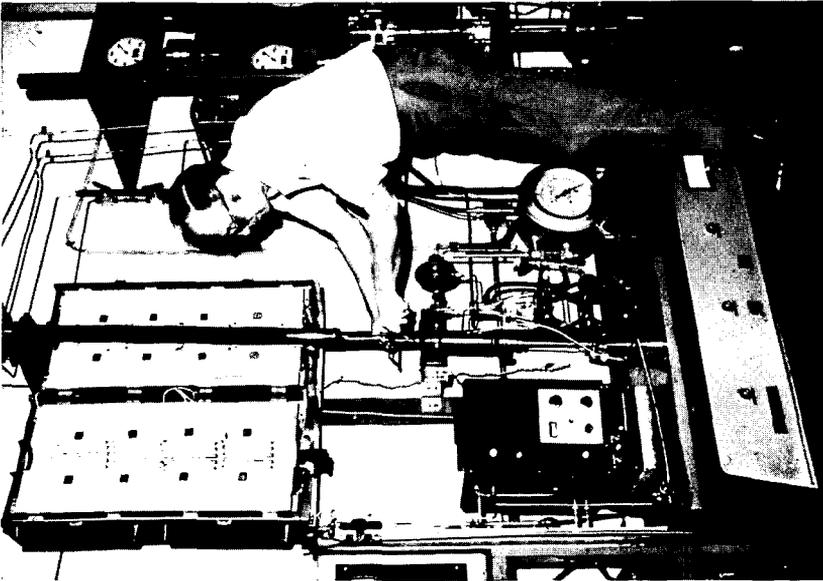


FIGURE 3 HIGH PRESSURE-HIGH TEMPERATURE REACTOR