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DEVELOPMENT OF PARTIAL OXIDIZER/REFORMER
FOR PAFC POWER PLANTS

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report documents the development of a methanol partial oxidation reformer designed to provide hydrogen to a 3 kW Phosphoric Acid Fuel Cell Powerplant. The partial oxidation reformer operates on neat methanol and utilizes the fuel cell cathode exhaust stream as the oxidant. | | |

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Summary

A 24 month program was carried out which contained four development areas:

- System design analysis
- Catalyst activity, kinetics and mechanism
- Single tube and subscale tests
- Reactor design and subscale verification

Partial oxidation of methanol was chosen as the simplest system for achieving a neat methanol reformer. This will not be the most effective but it will be the simplest. A system of this type might also be adapted for other fuels such as desulfurized diesel and JP-4. The choice of the system most appropriate for a given application requires detailed system analyses for all expected operating conditions. For the present study simplicity and proof of concept were most important. Typical fuel cell operating conditions of 50% cathode utilization were used during the testing of the final reformer design. This design utilizes the cathode exhaust for partial oxidation of methanol.

The reformer performs the partial oxidation and reforming separately using two different catalysts. The partial oxidation section also incorporates a wick vaporizer. When the platinum catalyst chosen for the partial oxidizer was initially tested the activity was extremely high. In fact, significant conversion to hydrogen was achieved. The spiralled platinized metal monolith combined with the wick vaporizer produced a very effective low pressure drop partial oxidizer. The kinetics of the partial oxidation reaction were so rapid in this section that little benefit would have been achieved in this initial design phase by doing any additional development of the partial oxidation section. Emphasis was, therefore, placed on evaluating methanol reforming. A kinetic expression was developed and new mechanistic information was obtained which showed the formation of dimethylether as a side product and zinc aluminate formation in the catalyst. These discoveries did not limit further

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development of the system. Component testing in single tube reactors and subscale reactors culminated in a low pressure drop design (2.5 inches of H₂O) of a full scale 3kW partial oxidation reactor. The reactor was tested for start-up within 17 minutes from room temperature and endurance tested for 300 hours.

Preface

This effort was conducted under the direction of Dr. Larry G. Christner and Mr. George Steinfeld with advisory support from Dr. B. Baker, Dr. H. Maru and Mr. S. Abens.

Material and energy balances and systems evaluations were conducted by Mr. Dhilip Patel and Dr. Hossein Ghezeli- Ayagh. Test operations including fabrication, component assembly, gas analysis and data acquisition were conducted by Mr. S. Koehler.

Drafting and drawings were done by C. DeCarvalho and C. Hunt. Word processing and layout were done by M. Shanley and J. Muehlfeld.

The cooperation and support of all the above people is appreciated and acknowledged in carrying out this effort.

The U.S. Army Belvoir R&D Center Project Manager was Lavon Joyce.



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1. INTRODUCTION

Methanol fueled phosphoric acid fuel cells has represented a major activity of Belvoir R&D Center development projects. Among these is a 6.3 Project at Energy Research Corporation (ERC), directed toward 3 and 5 kW power units. The basic systems operate well, but require the use of a methanol/water premixed fuel. ERC evaluated the overall fuel cell system and determined that it was possible to build a fuel cell power unit, which required only methanol as the fuel. Eliminating the need for the water would greatly enhance logistic support for this system within the military. Furthermore, the elimination of water may result in low temperature characteristics and faster start up for the power units. Water storage or water accumulation for premix systems or water recovery systems has the potential for freezing and requires additional heat to raise steam. These requirements affect the low temperature characteristics of the standard reforming systems. Use of air during start-up of the partial oxidizer/reformer may raise the temperature of the system quickly and provide hydrogen immediately.

Recently, work in the fuel processing of methanol and hydrocarbon fuels has focused on various system approaches to allow operation without an external water supply. These approaches utilize anode and/or cathode off gases to supply water and oxygen. Although the primary purpose of using the fuel cell gases is to provide water for steam reforming, cathode gases which contain oxygen can be used to provide heat. Methanol does not require oxygen for an effective carbon-free steam reforming even at very low steam to methanol ratios, but combustion of cathode gas oxygen and methanol can provide heating inside the partial oxidation reformer rather than the usual external heat provided by a burner.

There are two basic technologies for conventional steam reforming for hydrogen production; 1) cracking, and 2) partial oxidation. There are several variations of these two basic

types. Sometimes these variations are categorized as separate & distinct types, but we considered them as falling within the two general classifications. A list of these variations is given below:

- 1) Cracking
 - a) Straight thermal cracking
 - b) Thermal cracking with gas clean-up
 - carbon monoxide separation
 - carbon monoxide methanation
 - c) Catalytic cracking
 - d) Catalytic cracking with gas clean-up
 - e) Combinations of the above systems

- 2) Partial Oxidation
 - a) Standard partial oxidation (fuel plus air)
 - b) Partial oxidation with gas clean-up
 - c) Combined cracking and partial oxidation
 - d) Partial oxidation with water insertion (auto thermal reaction)
 - e) Partial oxidation with fuel cell cathode and/or anode exit water containing feeds
 - f) The above systems operated adiabatically
 - g) The above systems operated with external temperature control.

Each of these systems requires less water than the conventional steam reforming units but most have deficiencies which limit their applicability to fuel cell systems. Although partial oxidation does provide a means of operation with a variety of pure and impure fuels, it does require the presence of water to lower the concentration of carbon monoxide. One method of obtaining the water is injecting cathode and/or anode off gas into the partial oxidation reactor. This process is simple, and requires no external water.

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A considerable amount of work has been supported by government agencies in the development of reformed methanol systems. Automotive applications research by Los Alamos, NASA Lewis Research Center, Solar Energy Research Institute, Institute of Gas Technology, and the Jet Propulsion Laboratories have focused on standard steam reforming and cracking for hydrogen production. Recently, Energy Research Corporation has evaluated various forms of partial oxidation. The basic conclusion has been that these systems are viable, but require some development to meet the demands of specific applications. This program was designed to investigate those development areas required prior to building an effective neat methanol reformer for a 3 kW power unit.

A 24 month program was carried out which contained four developmental areas:

- System design analysis
- Catalyst activity, kinetics and mechanism
- Single tube and subscale tests
- Reactor design and subscale verification

Partial oxidation was chosen as the simplest system for achieving a neat methanol reformer. However, a number of variations were evaluated to different degrees before choosing a single system for further development. The initial selection of a partial oxidation catalyst produced an extremely active catalyst and, therefore, a very limited development time was allotted to it. Although methanol reforming had been studied previously, additional analyses were deemed necessary to provide an effective basis for a reactor design. After obtaining sufficient activity and kinetic information, single tube and subscale tests were performed to provide limited design data. This information was used to design, build and test a partial oxidizer/reformer which produced sufficient hydrogen for a power unit of at least 3 kW net power.

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2. INVESTIGATION AND DISCUSSION

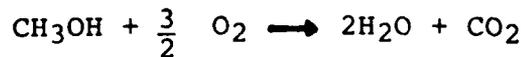
2.1 System Design Analysis

Due to the necessity of integrating the fuel processor with the fuel cell stack, a systems analysis was conducted to study available options; their advantages and their disadvantages. Because the reformer is normally coupled to at least one of the stack exhaust gases, several options are available in integrating a reformer with a fuel cell stack. The objective is to develop a system configuration which can run on neat methanol with maximum efficiency and minimum complexity. Some form of partial oxidation of methanol was identified as an attractive means of generating water in-situ. The following systems were evaluated in this program.

1. Partial oxidation using cathode exhaust and a conventional air fired anode gas burner.
2. Recycle of anode and cathode gas burner exhaust (partial oxidation during transients).
3. Partial oxidation with cathode recycle and no burner.
4. Partial oxidation with ambient air and no burner.

Figure 2.1 illustrates configurations for each of these systems.

System 1 is an extension of the conventional reformer system with the addition of a cathode exhaust recycle. The unutilized oxygen in the cathode exhaust serves to partially oxidize methanol according to the following reaction:



In addition, the moisture in the cathode exhaust also serves to provide the water requirement for the reformer. The desired steam/methanol ratio in the reformer can then be obtained by controlling the amount of cathode exhaust recycled to the reformer. By recirculating diluent N_2 & CO_2 into the reformer, the hydrogen in the fuel gas leaving the reformer is diluted. The net result is a loss of efficiency. A plot of the relative efficiency of

this partial oxidation system as compared to conventional reforming (Figure 2.2) indicates that an optimum exists at a cathode utilization of 80%. At this point, the partial oxidation system can achieve 89% of the efficiency of the standard reformer. A penalty of 11% is being attributed to operation on neat methanol, and is due to the dilution of hydrogen in the fuel stream.

System No. 2 utilizes reformer burner exhaust to recycle moisture to the reformer. Strictly speaking, this is not a partial oxidation system because oxygen in the burner exhaust should be very low and, therefore, methanol fuel will not be oxidized to form water. The moisture required for reforming is formed by combustion of H_2 in the reformer burner. A portion of the burner exhaust is then recycled to the reformer. This type of system takes advantage of the moisture generated in the stack, and recycles it without condensing and revaporizing the water. This was the system chosen for development in Contract No. DAAK70-84-C-0099, under which a fuel processor was developed. There is, however, an aspect of this system which relies on the partial oxidation of methanol. The start-up and transient operation will result in partial oxidation because start-up will require the combustion of methanol with air. Transients will also result in partial oxidation during the load-increase mode. In this case, as anode exhaust is depleted of hydrogen by a load increase in the stack, there will be unconverted oxygen in the burner exhaust, which will serve to partially oxidize methanol and boost the reformer output to handle the increased load. Although the optimum partial oxidation system was calculated at 80% cathode utilization, this is not considered a practical operating point at this time.

System No. 3 is equivalent to system No. 1 when the anode exhaust burner is removed and the CH_3OH /Cathode exhaust oxidizer is shown external to the reformer. This modification results in less excess heat in the reformer. The amount of excess heat depends on the utilization of the H_2 and O_2 in the fuel cell

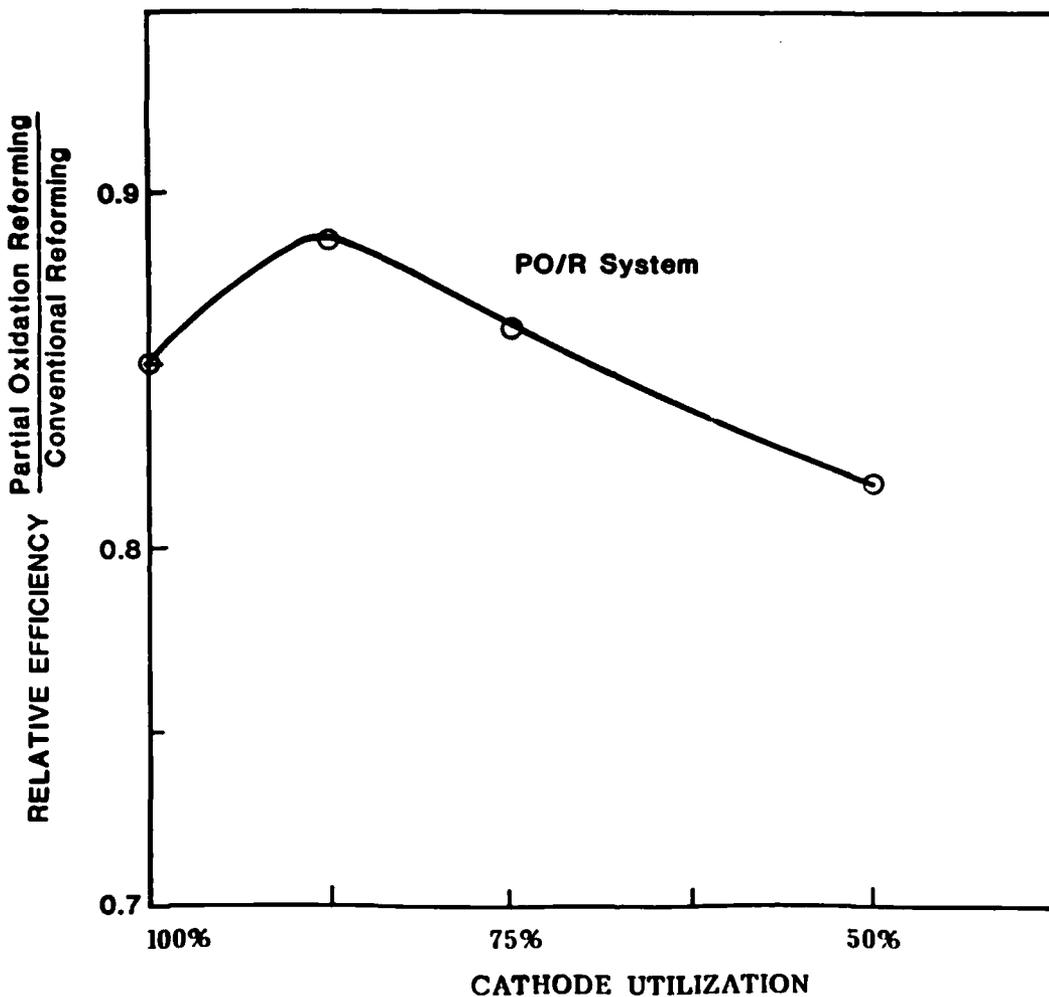


FIGURE 2.2 Relative Efficiency of Partial Oxidation Reformer Compared to Conventional Reformer

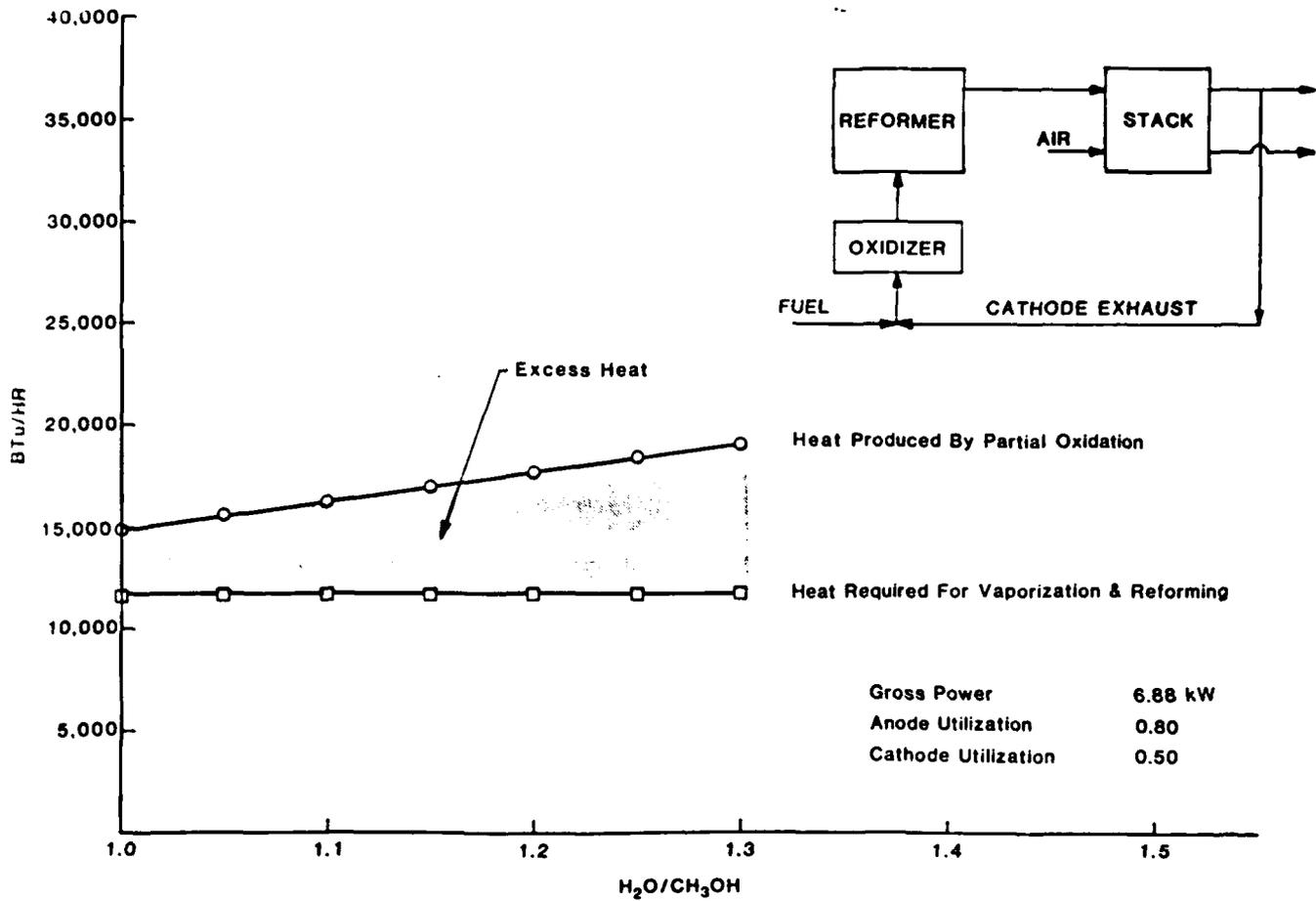
stack. Without burning anode exhaust gas, cathode utilizations of 50% to 67% provide sufficient oxygen for the partial oxidation to produce heat for reforming, vaporization and some excess heat. Above 67% cathode utilization some additional heat would be required from anode combustion. Figures 2.3 to 2.5 illustrate the heat balance for system no. 3 at cathode utilizations of 0.50 to 0.67.

System No. 4 is obtained when air is substituted for cathode exhaust as the oxidant. Since air contains less moisture than cathode exhaust, more oxygen is required for partial oxidation with air to achieve an equal H_2O/CH_3OH ratio. The result is that the excess heat generated is much greater for partial oxidation with air. Figure 2.6 illustrates this excess heat. This magnitude of excess heat is not desirable under normal operating conditions, but is suitable during start-up.

For the purpose of further testing, System No. 1 was originally chosen to represent conditions under which a partial oxidation/reformer system might operate. The condition chosen for testing purposes was a cathode utilization of 67%, yielding the following gas composition at the inlet of the partial oxidizer:

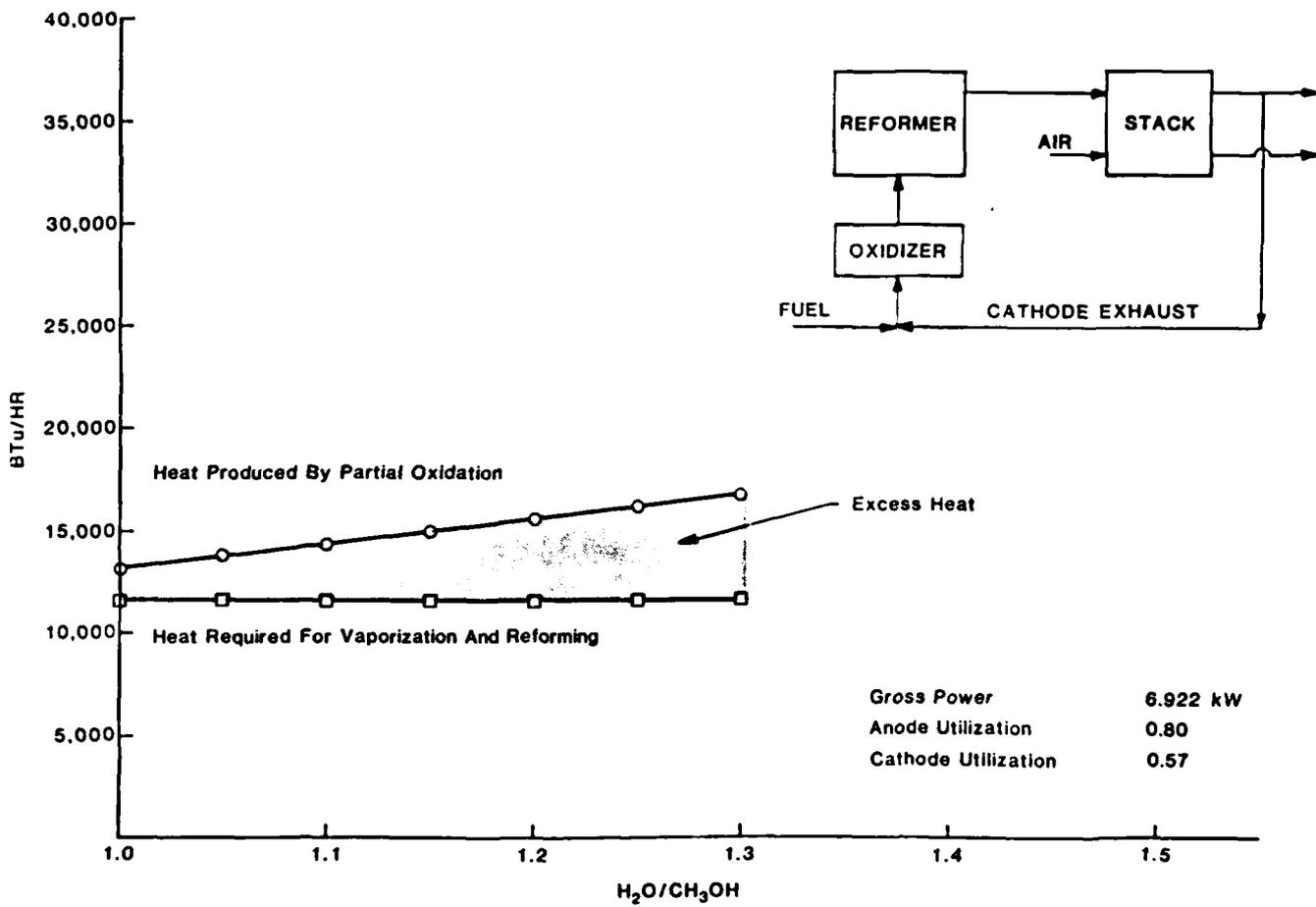
| | <u>mole %</u> |
|----------|---------------|
| CH_3OH | 24 |
| N_2 | 57 |
| O_2 | 5 |
| H_2O | 14 |

After complete oxygen combustion, the steam to carbon ratio at the reformer inlet was calculated to be 1.0, a more near term, practical cathode utilization of 67% was chosen for the design basis. Although this is not the optimum 80% cathode utilization, it is considered achievable in a real system using existing technology. Having made this choice to accommodate the existing stack technology, the anode gas burner is not necessary for heat and the system configuration becomes System No. 1 without the



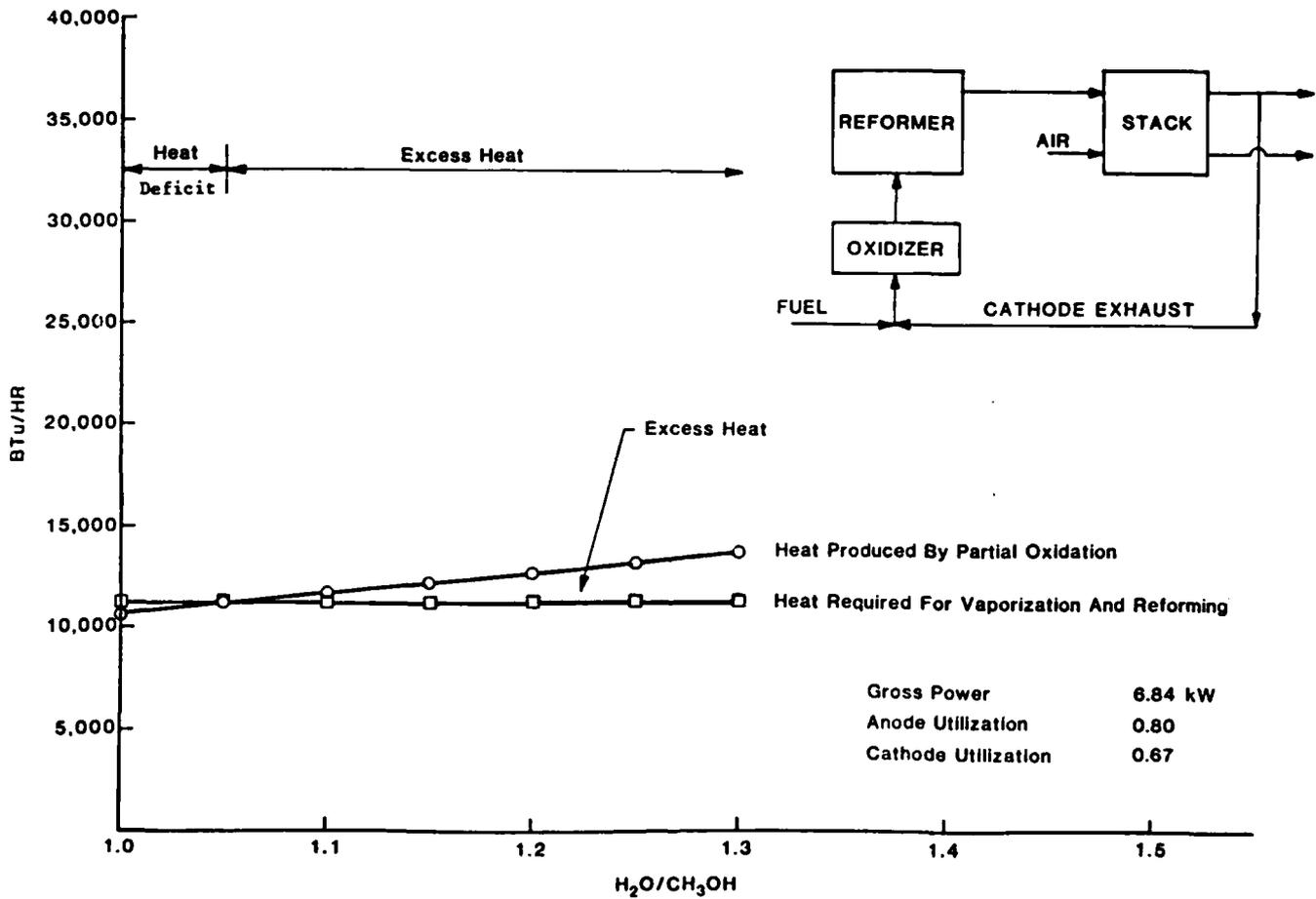
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FIGURE 2.3 Fuel Processor Heat Balance



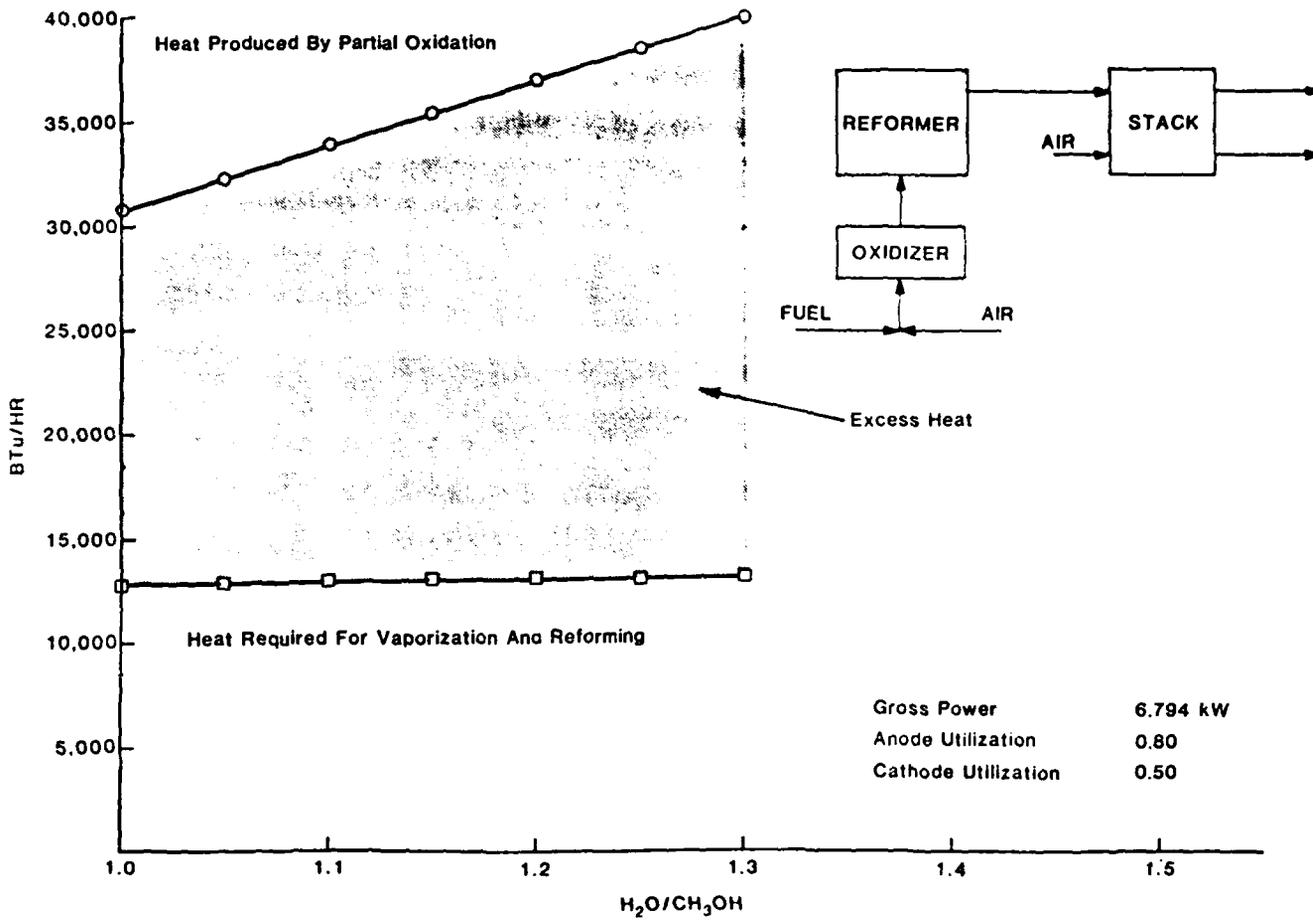
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FIGURE 2.4 Fuel Processor Heat Balance



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FIGURE 2.5 Fuel Processor Heat Balance



LD497

FIGURE 2.6 Fuel Processor Heat Balance for System No. 4 Utilizing Air as Oxidant

anode gas burner which is the same as system no. 3. This is due to the fact that as cathode utilization is decreased, additional oxygen becomes available for the partial oxidation of methanol, until sufficient heat is generated for the reforming by partial oxidation and no burner is required. As cathode utilization is increased to the optimum of 80% the combustion of anode exhaust becomes necessary to provide sufficient heat for reforming and start-up.

Much of the preliminary testing was conducted using the gas composition shown above. In later stages of the reactor development, a cathode gas composition corresponding to 50% utilization was chosen for testing.

2.2 Catalyst Activity, Kinetics and Mechanisms

A survey of the published literature revealed a considerable range of activity, kinetics, and mechanistic information (1 - 11) on hydrogen production from methanol. In 1983, H. Kobayashi et. al. (1) demonstrated the variability observed among a broad range of catalyst supports, copper loading, active copper surface areas, and catalyst calcination temperatures. Each of these factors was shown to affect the activity, activation energy, and product gas composition. Thus, it was not surprising to find a rather broad range of values for activity and activation energy in the literature. A selected summary of this data is shown in Table 2.1. Kobayashi et. al. (1, 2) pointed out in their studies that catalysts with copper surface areas above 100 m²/g showed the most variability. As might be expected, various methods of catalyst reduction employed by different investigators produce different copper surface areas. The time and conditions of operation typically result in varying degrees of metallic particle sintering and thereby alter the catalyst surface area.

It seemed apparent that the catalyst chosen for the present study would have to be characterized under the conditions anticipated for the partial oxidizer/reformer. This character-

TABLE 2.1
REFORMING KINETIC MODELS USED BY VARIOUS INVESTIGATORS

| MODEL | PARAMETER DEFINITIONS AND VALUES | CATALYST | REF |
|---|--|----------------------------|----------------|
| 1. Pseudo - First - Order $k = \text{WHSV} \ln \left(\frac{1}{1-x} \right)$ | <p>k = reaction constant x = methanol conversion WSHV = weight hourly space velocity</p> | UCI-T2107 | Pre-sent Study |
| 2. Power Law $r = k p_M^m p_W^n p_{\text{Total}}^l$ | <p>η = effectiveness factor k = reaction constant = $Ae^{-E/RT}$ p_M = methanol partial pressure p_W = water partial pressure p_{Total} = total system pressure</p> | UCI-T2107 | Pre-sent Study |
| 3. Langmuir - Hinshelwood Kinetics $r = \frac{1}{A+B} \frac{b_M^0 e^{-E_M/RT} p_M^0 + b_W^0 e^{-E_W/RT} p_W^0}{1 + b_M^0 e^{-E_M/RT} p_M^0 + b_W^0 e^{-E_W/RT} p_W^0}$ | <p>η = effectiveness factor $k_M^0 = 6.429 \times 10^9 \text{ mol h}^{-1} \text{ g atom}^{-1}$ $b_M^0 = 1.563 \times 10^{-2} \text{ atm}^{-1}$ $b_W^0 = 6.315 \times 10^{-4} \text{ atm}^{-1}$</p> | BASF low temperature shift | (5) |
| 4. Second order in Methanol and Water $k_{\text{obs}} = \text{WHSV} \ln \left[\frac{M-X_A}{M(1-X_A)} \right]$ | <p>C_{A0} = initial methanol conc. M = water/methanol ratio X = methanol conversion k = reaction constant WSHV = weight hourly space velocity</p> | ICI 52-1 | (1) |

ization was as complete as possible within the limitations of the program.

Previous studies reported in the literature (3, 4) and ERC programs DAAK-53-76-C-0118 and DAAK70-79-C-0249 had shown that Catalyst T2107 (United Catalyst, Inc.) is a very effective steam reforming catalyst and is equal to or better than other commercial copper catalysts such as UCI G66B, ICI 52-1, and BASF K3-10. Therefore, UCI T2107 was utilized throughout this program. A typical chemical analysis provided by the vendor is shown in Table 2.2. The catalyst was tested as 1/8 inch X 1/8 inch pellets and as the 14 to 16 Tyler mesh fraction of crushed material.

Effective partial oxidation requires a low temperature combustion catalyst. Previous ERC reformer programs have employed a platinum coated metal monolith catalyst prepared by Johnson Matthey Co. This monolith is a one inch wide corrugated stainless steel sheet coated with platinum black that can be wound into a right circular cylinder or twisted into a spiral.

Each of the catalysts was tested in a one inch diameter tubular reactor. A schematic drawing of the reactor is shown in Figure 2.7 and a photograph of the complete test facility is shown in Figure 2.8. A typical analysis of the methanol used for this program is shown in Table 2.3. Although it is a reagent grade methanol, there are a number of impurities. A very important impurity is the chloride. Copper catalysts are poisoned by chloride and the zinc oxide support provides some protection. The chloride in our methanol was identified as methylchloride. Other impurities were below our chromatographic detection limits and were identified by mass spectroscopy.

Initial testing of the platinum monolith was performed using a gas composition of 0.248 CH₃OH, 0.734 H₂ and 0.018 O₂. Using a very high flow rate of 62.5 liters per minute to keep the conversion down, the catalyst was very active at 250°F. Later testing of the reactor showed that combustion occurs spon-

TABLE 2.2
CATALYST PROPERTIES

SPECIALTY CATALYST

Catalyst Type T-2107
 Catalyst Form Tablets
 Catalyst Size 1/8" x 1/8"

| <u>Chemical Composition</u> | <u>Weight% (Oxide Basis)</u> |
|----------------------------------|------------------------------|
| CuO* | 43 ± 4 |
| ZnO* | 20 |
| Al ₂ O ₃ * | 30 |
| Cr ₂ O ₃ * | 3.2 ± 0.4 |
| C | 1/3 |
| S* | <0.05 |

Physical Properties

- A. Bulk Density, lbs./Cu.Ft.* 70 ± 5
- B. Surface Area, m²/g* 130 ± 30
- C. Pore Volume, cc/g 0.25 - 0.35
- D. Crush Strength, lbs. DWL* 10 minimum

* Properties normally measured by UCT Quality Control.

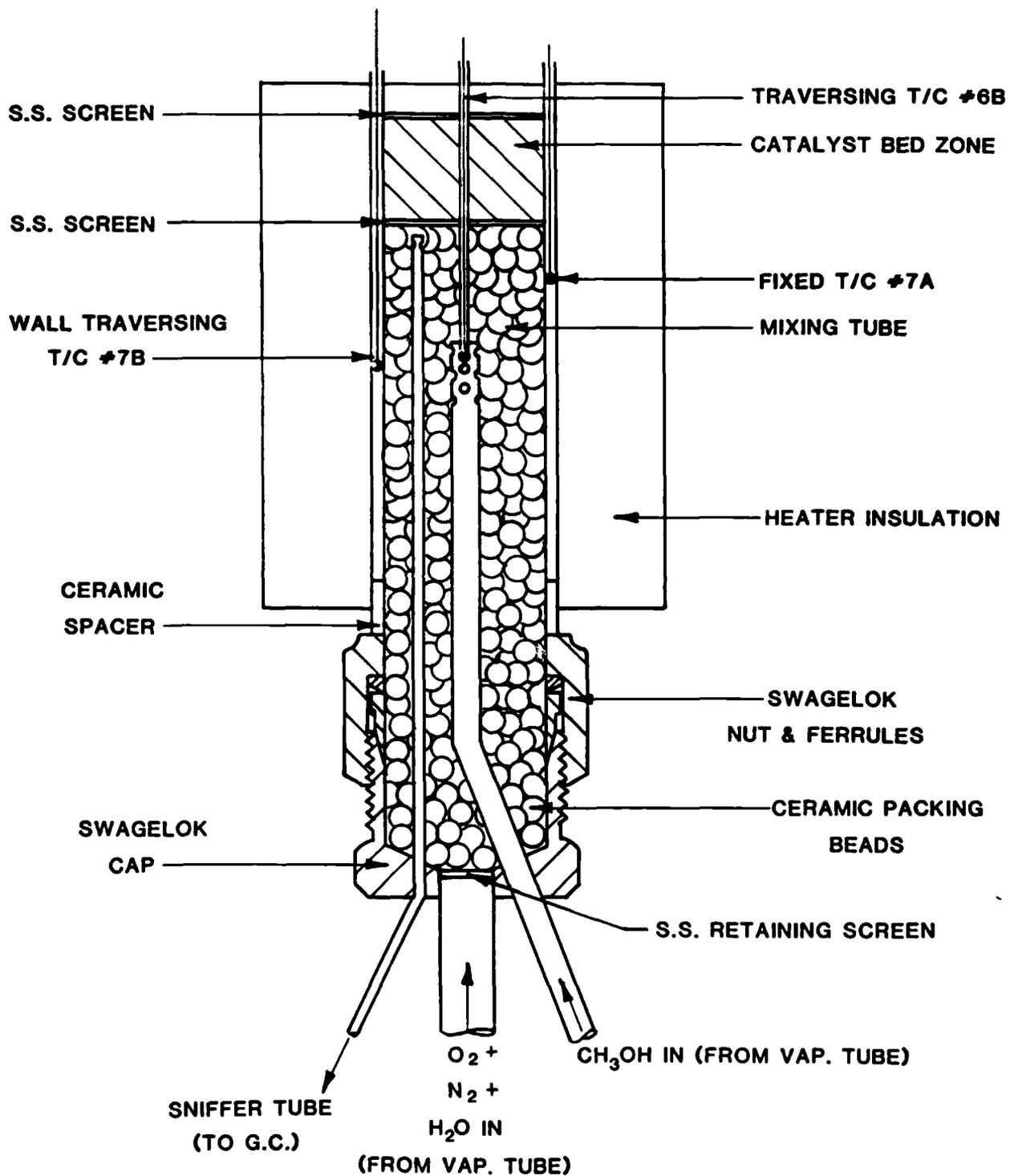
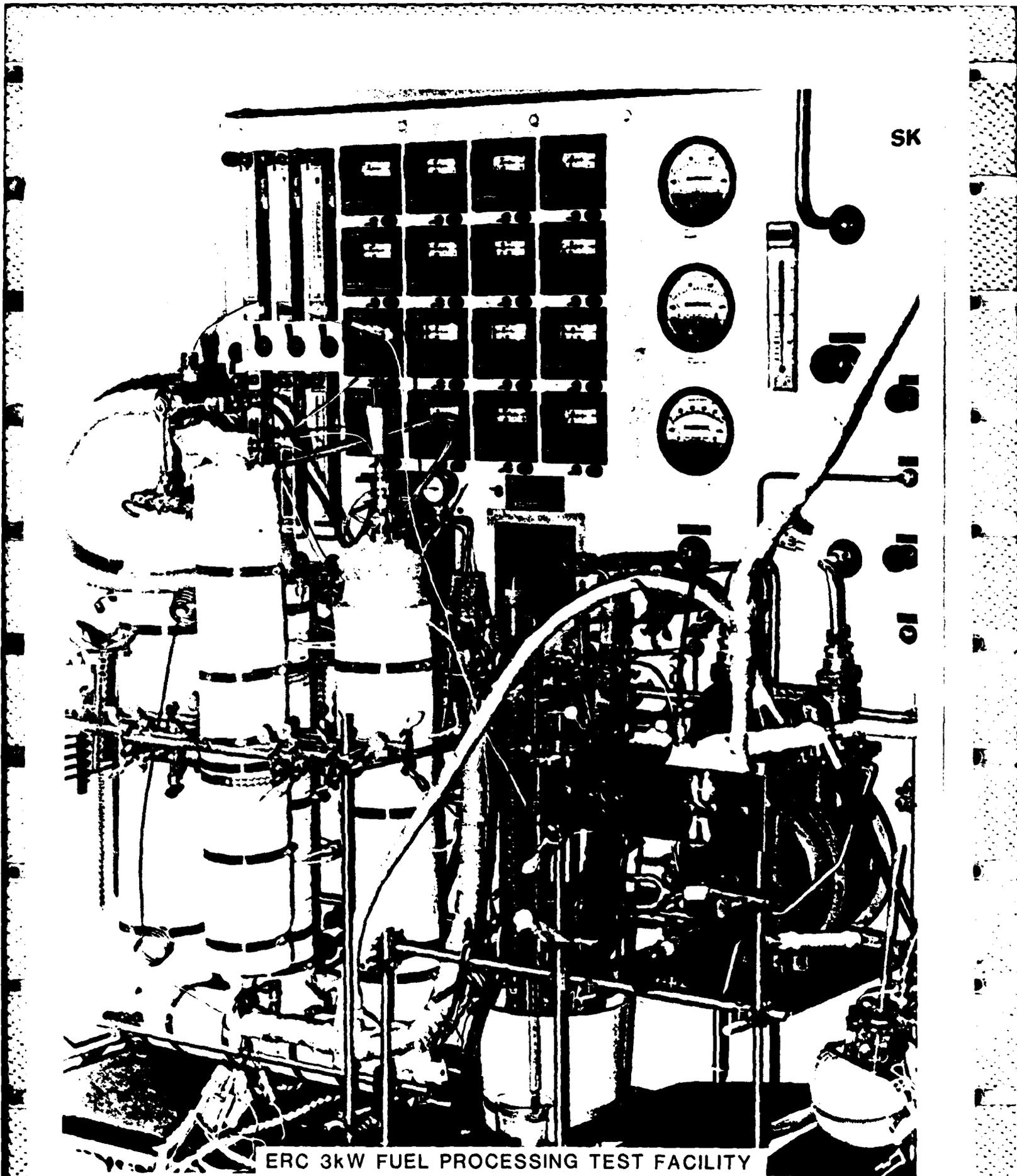


FIGURE 2.7 Reactor Tube Entrance



ERC 3kW FUEL PROCESSING TEST FACILITY

TABLE 2.3

METHANOL USED FOR TESTING OF T2107 CATALYST

Manufacturer: Ashland Chemical Co., Columbus, Ohio 43210

Distributor: KEM Chemical Corp., Mt. Vernon, New York

Description: M-368 Reagent A.C.S.
Absolute, Low in Acetone

Specifications:

| | |
|--|-----------------|
| CH ₃ OH | F.W. = 32.04 |
| Maximum Limits of Impurities Meets A.C.S. Specifications | |
| Appearance - | PACST |
| Assay (CH ₃ OH) - | 99.8 |
| Color (APHA) - | 0.1 Max. |
| Water (H ₂ O) - | 0.1 |
| Residue after evaporation - | 0.001 |
| Solubility in water - | PACST |
| Acetone, Aldehydes (as Acetone) - | PACST |
| Titrateable Acid - | 0.0003 Meq./dl. |
| Titrateable Base - | 0.0002 Meq./dl. |
| Substances darkened by | |
| Sulfuric Acid - | PACST |
| Substances reducing | |
| Permanganate - | PACST |
| Nonphotochemically Reactive | |

Methanol
Methyl Alcohol
CH₃OH

Analysis

| | |
|--|--|
| Methanol weight % | 99.85 minimum |
| Aldehydes weight % | 0.002 maximum |
| Hydrocarbons | passes test 4.3.3.6 in Federal Specification O-M-2303 |
| Nonvolatiles weight % | 0.001 maximum |
| Acidity weight % as acetic acid | 0.003 |
| Alkalinity weight % as NH ₃ | 0.003 |
| Color APHA (Pt-Co scale) | not darker than 4.3.3.6 |
| Density at 20°C | 0.7918 (nominal) 0.7914-0.7922 |
| Specific gravity at 20°C/20°C | 0.7918 |
| Permanganate test (minutes) at 25°C | 10 |
| Acid equivalent weight % | 0.001 maximum |
| Alkalinity weight % | 0.001 maximum |
| Iron (ppm) | 0.01 maximum |
| Copper (ppm) | 0.01 maximum |

Properties

| | |
|-------------------------|---------------|
| Molecular weight | 32 |
| Boiling point, °C | 64.6 148.3 |
| Freezing point, °C | -97 -142.5 |
| Flash point, °F | 53 |
| Vapor density (air = 1) | 1.11 |

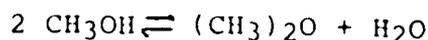
Uses

The largest use for methanol is in the manufacture of formaldehyde. It is also used in the manufacture of many other chemicals and plastics including dimethyl-terephthalate, acrylics, methyl chloride, methylene chloride, methyl amines, and plasticizers. Methanol serves as a fuel for automobiles, railroad cars and truck heaters, lamps, and boilers, as well as being a denaturant for ethanol. Methanol has excellent solvent properties and can be used as a replacement for ethanol or isopropanol in many operations.

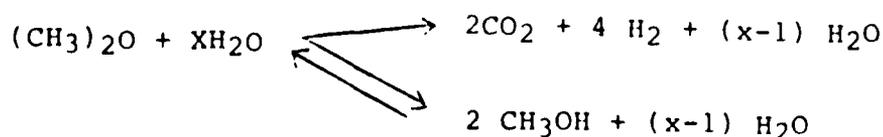
taneously at room temperature. Raising the reactor temperature with external heaters increased the conversion of methanol but also increased the formation of dimethylether and methane side products as shown in Figure 2.9. Removing the oxygen from the inlet gas demonstrated that the platinum monolith was a very good dehydration catalyst. As shown in Figure 2.10, the dehydration is significant as low as 350°F. Since the expected operating temperature is above 750°F as indicated by the temperature profiles demonstrated in Figure 2.11, dimethylether will be formed in substantial quantities.

Dimethylether must be reformed if this partial oxidizer configuration is to be effective. Dimethylether and steam were passed over a 20 gram bed of crushed T2107 catalyst at 267°C and no reaction was observed. Raising the temperature to 370°C produced a significant reaction although it produced methanol in addition to carbon dioxide and hydrogen. For a period of 42 hours the conversion to hydrogen and carbon dioxide remained about the same but the conversion to methanol steadily increased. Raising the temperature to 390°C and holding for an additional 100 hours increased the conversion stepwise to hydrogen, and the conversion to methanol steadily increased. Because of this aging phenomenon an accurate measure of the dimethylether reforming activity could not be obtained. It was not deemed necessary to pursue this aspect of the system; the ability to reform dimethylether was adequately demonstrated. The data collected lead us to the following conclusions with respect to the behavior of dimethylether:

1. Dimethylether and methanol approach equilibrium over UCI T2107 catalyst



2. Catalyst aging changes its selectivity



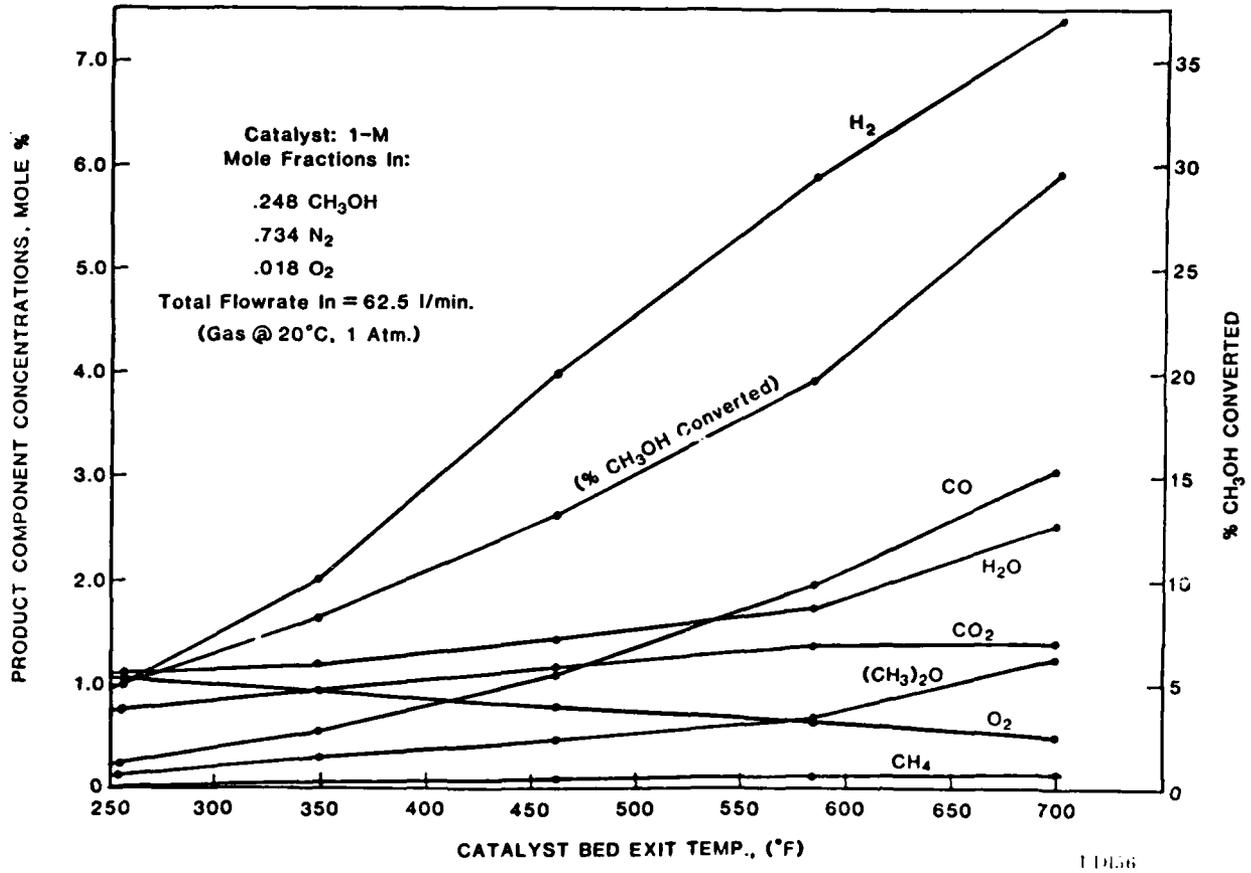
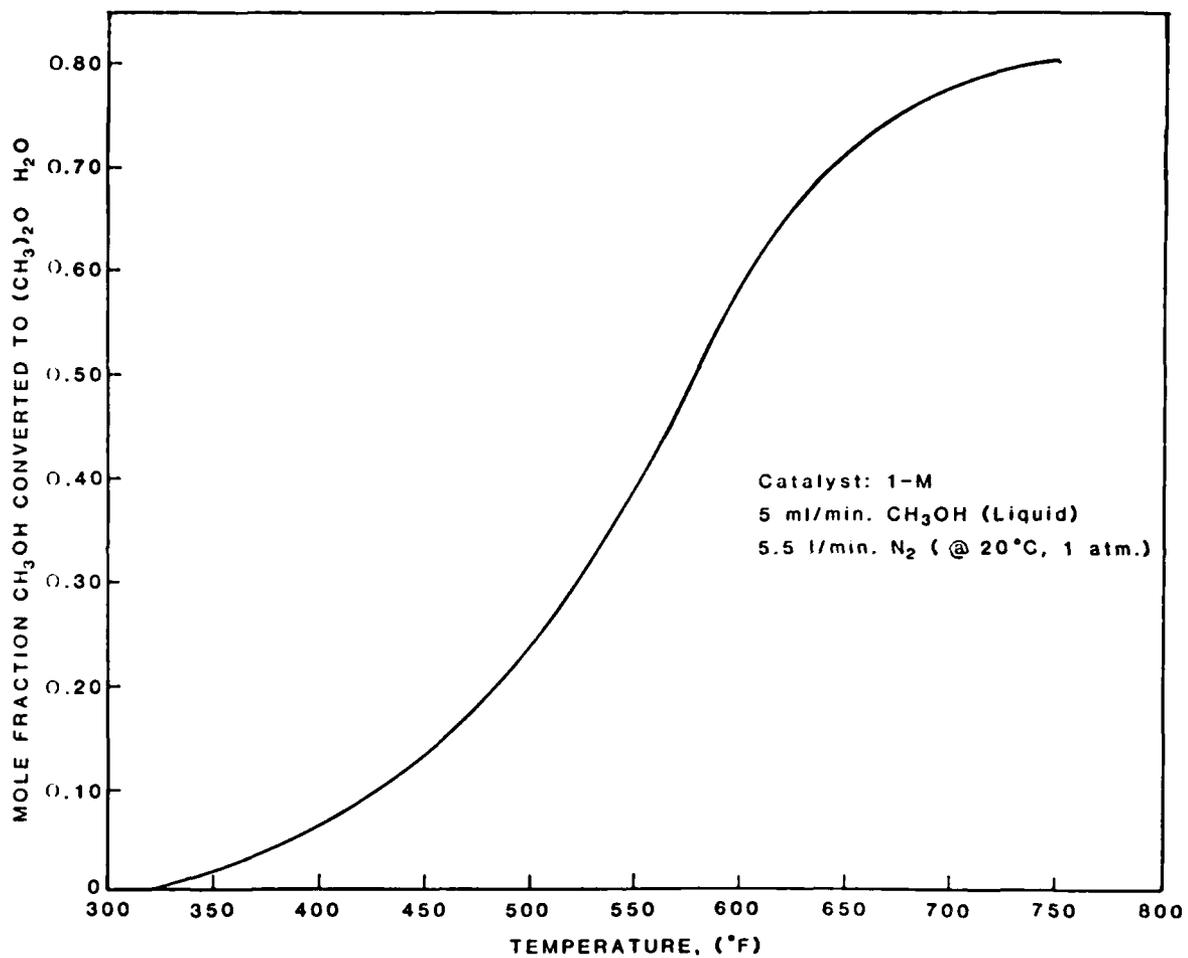
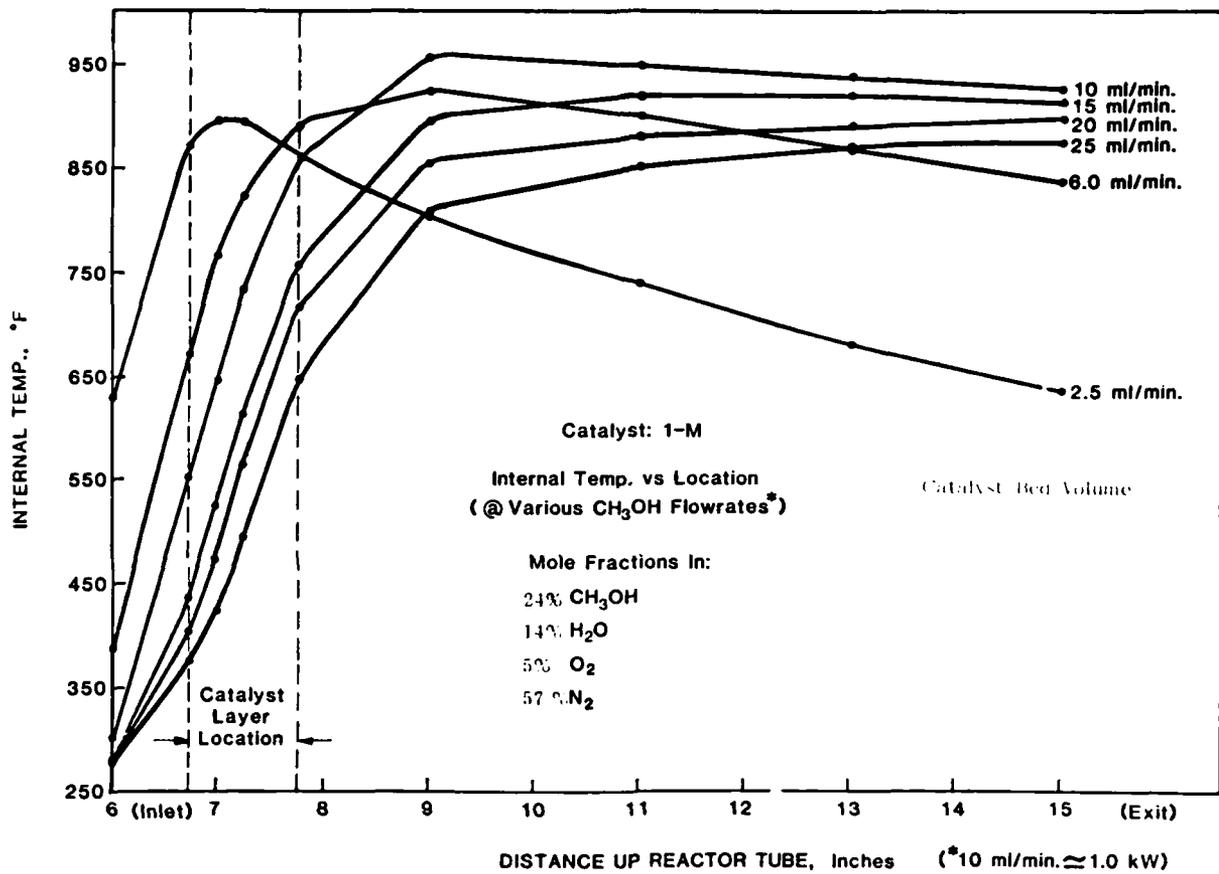


FIGURE 2.9 Effect of Temperature on Methanol Oxidation



1107

FIGURE 2.10 Dimethylether Formation from Methanol on a Pt Catalyst



1 D54

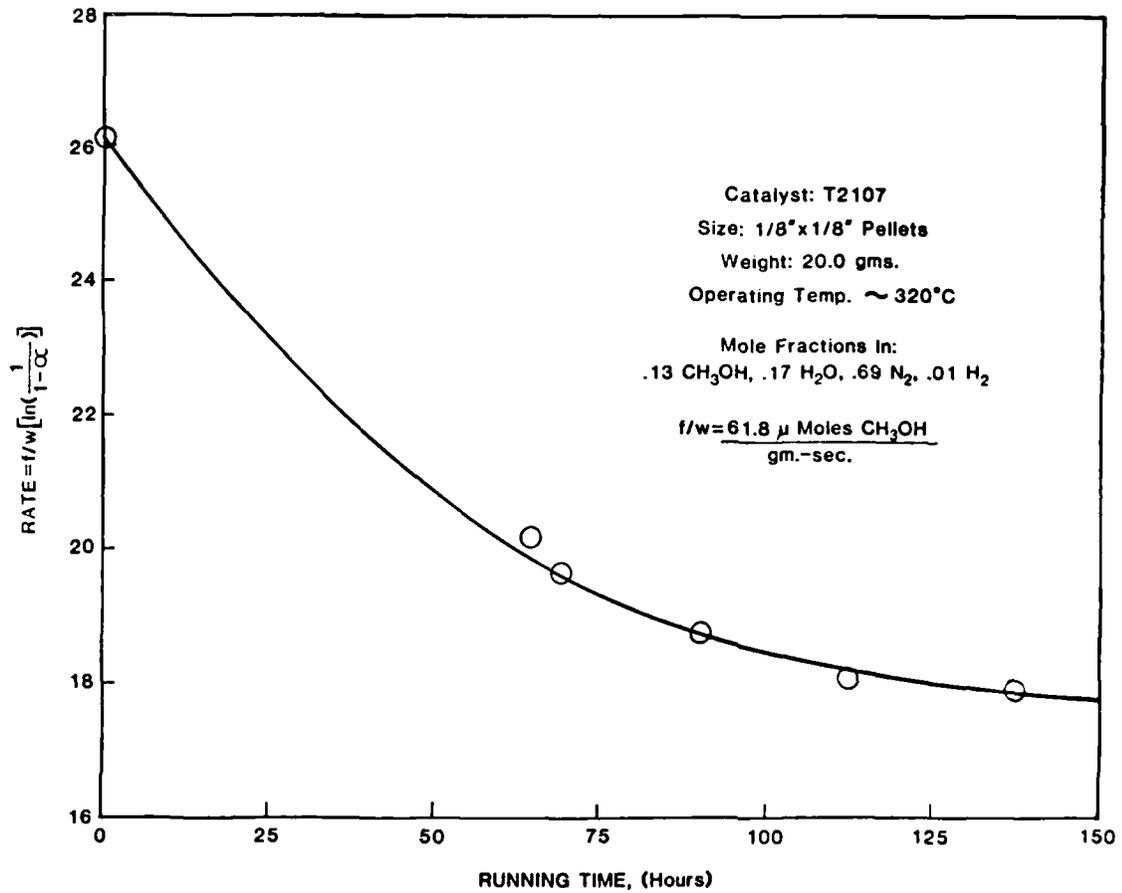
FIGURE 2.11 Reactor Temperature Profiles

3. The apparent rate for eliminating dimethylether at 390°C is given as:

$$r = 3.37 \frac{p_{(\text{CH}_3)_2\text{O}}^{0.6}}{p_{\text{H}_2}^{-0.14}}$$

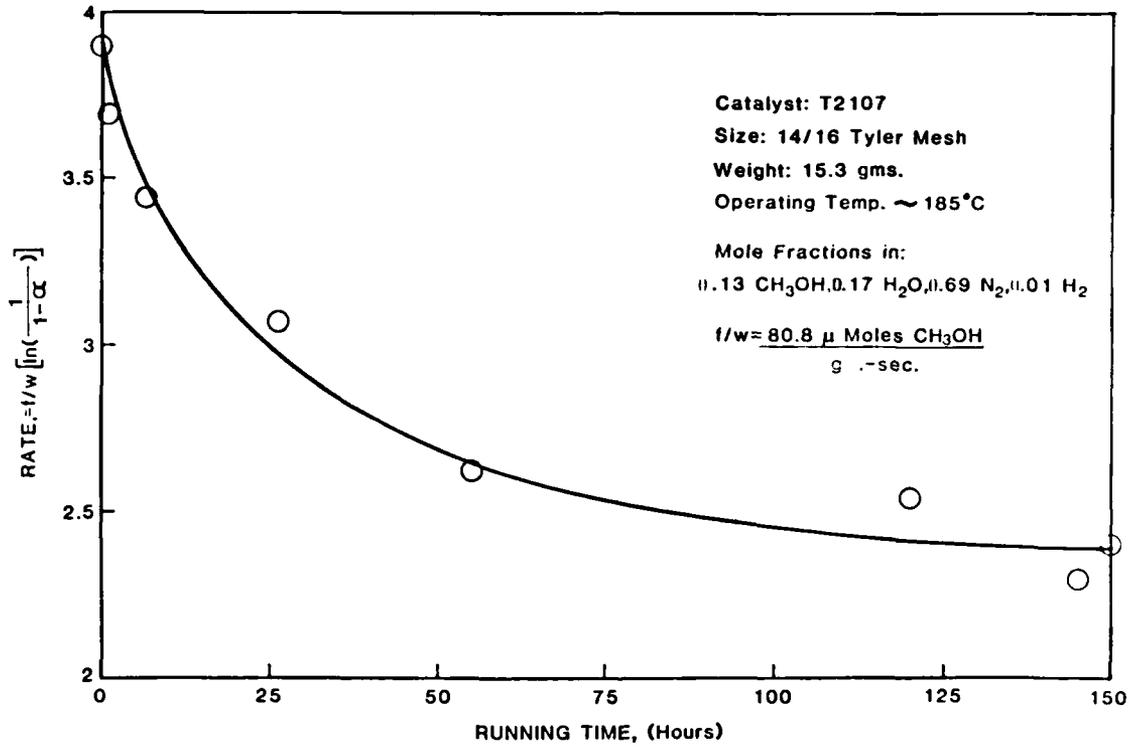
Previous methanol reforming kinetic studies (1 - 7) have resulted in different rate expressions, activities and activation energies. As Kobayashi et. al. demonstrated, the physical state of a catalyst may determine the values obtained. The physical state of a catalyst changes with operating conditions and time. During a single tube endurance run described in Section 2.3, the catalyst was observed to form zinc aluminate from the zinc oxide and aluminum oxide in the initial material. X-ray diffraction analysis also showed that the copper crystallites increased to between 290Å and 500Å, depending on their position in the bed. This conversion occurred at 399°C which is slightly higher than the anticipated temperature for the inlet to the reforming bed.

Pellets and crushed catalyst were tested in the one inch differential reactor at lower temperatures to evaluate the loss in activity with time. Figures 2.12 and 2.13 show that both pellets and crushed materials stabilize after about 125 hours of operation, irrespective of temperature and particle size. This suggests that the loss was due to copper sintering and that the sintering was not very temperature dependent in the range of 185°C to 320°C. Since its activity does change with time it is important to precondition the catalyst prior to determining the kinetic data. When this was done the change in activity as a function of temperature indicated that the activation energy was 21 kcal/mol in the diffusion-free region and 10.5 kcal/mol in the diffusion region. The typical Arrhenius plot shown in Figure 2.14 demonstrates that the 1/8 inch pellets become diffusion limited at about 180°C and the 14 to 16 Tyler mesh material becomes diffusion limited above 205°C. The normal operating temperature of the methanol steam reformers is 200°C to 300°C.



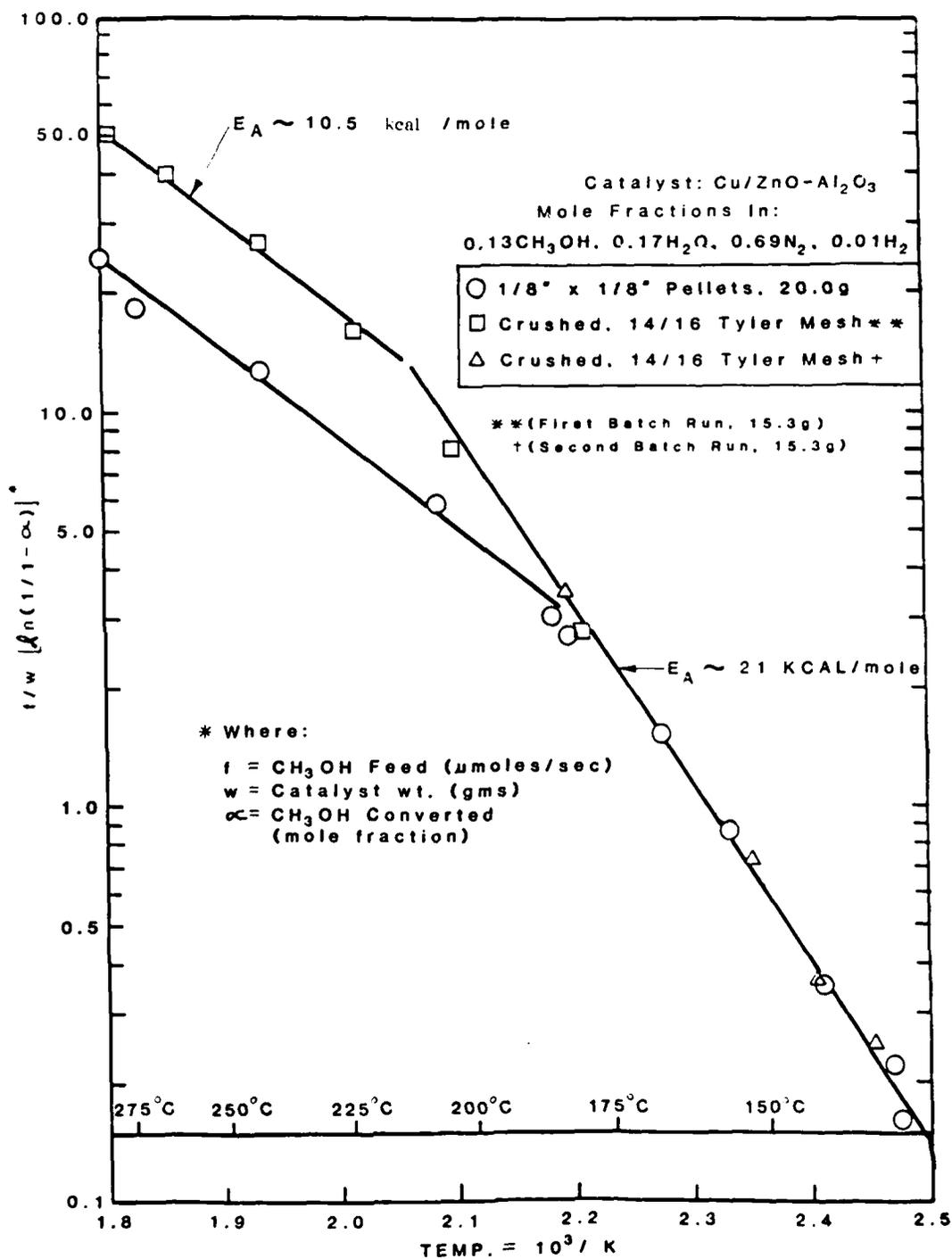
LD499

FIGURE 2.12 Aging of Catalyst Pellets



LD500

FIGURE 2.13 Aging of Crushed Catalyst



D343

FIGURE 2.14 Arrhenius Plot for Methanol Steam Reforming On A Cu/ZnO-Al₂O₃ Catalyst

This means that the reaction is definitely diffusion controlled so that the smallest possible particles should be used within the allowable pressure drop of the system. The final design took this fact into account.

Understanding the significance of changes occurring in the inlet gas composition requires definition of the kinetic parameters. After establishing the previously discussed aging and diffusion characteristics of this spectrum, kinetic experiments were performed after 100 hours of conditioning at temperatures less than 180°C. Using 15.3 grams of 14 to 16 Tyler mesh UCI T2107 catalyst in the differential reactor, a series of tests were performed with varying partial pressures of methanol and water. The data was analyzed and fit with a simple power law rate expression. The data shown in Table 2.4 resulted in the following rate expressions:

$$r = 3.9 \times 10^{-10} e^{\frac{-21,000}{RT}} P_{\text{CH}_3\text{OH}}^{0.32} P_{\text{H}_2\text{O}}^{-0.12} P_{\text{Total}}^{0.20}$$

$r = \mu$ moles CH_3OH converted/gram unreacted catalyst/sec

This rate law indicates that the steam/methanol ratio should be kept as low as possible within the constraint of the allowable carbon monoxide level exiting from the reactor. Higher levels of water will decrease the carbon monoxide level, and must be balanced against its effect on the reforming rate.

The primary activities occurring in this system are listed in Table 2.5. The system is complex, but the three areas; a) partial oxidation; b) reforming and c) shift, are dominated by their anticipated reactions. The side reactions are also significant and play an important role in the overall performance of the integrated reactor.

The partial oxidizer temperature profile indicated in Figure 2.11 showed a rapid increase in temperature in the catalyst section and beyond, with a final temperature in the 850 - 950°F

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TABLE 2.4

TYPICAL KINETIC DATA FOR REFORMING OF
METHANOL AS A FUNCTION OF GAS COMPOSITION

| <u>SAMPLE</u> | <u>PCH3OH, atm</u> | <u>PH2O, atm</u> | <u>RATE</u> |
|---------------|--------------------|------------------|-------------|
| 3 | .389 | .509 | 2.774 |
| 4 | .065 | .510 | 1.557 |
| 5 | .065 | .085 | 1.943 |
| 6 | .065 | .510 | 1.553 |
| 7 | .129 | .169 | 2.294 |
| 8 | .064 | .252 | 1.710 |
| 9 | .129 | .084 | 2.463 |
| 10 | .129 | .169 | 2.252 |
| 11 | .389 | .509 | 2.789 |
| 12 | .065 | .085 | 1.916 |
| 13 | .389 | .509 | 2.772 |
| 14 | .065 | .085 | 1.923 |
| 15 | .064 | .252 | 1.752 |

R-SQ: .996 CORR R-SQ: .995
SER: .014 SSR: >>>>

Catalyst: T2107, Crushed, 14/16 Tyler Mesh.
Data taken after ~100 hrs. run time

Temperature: 184°C

Total Pressure: 1 atm

Rate: Micromoles of CH₃OH converted/gram unreduced catalyst/sec.

TABLE 2.5

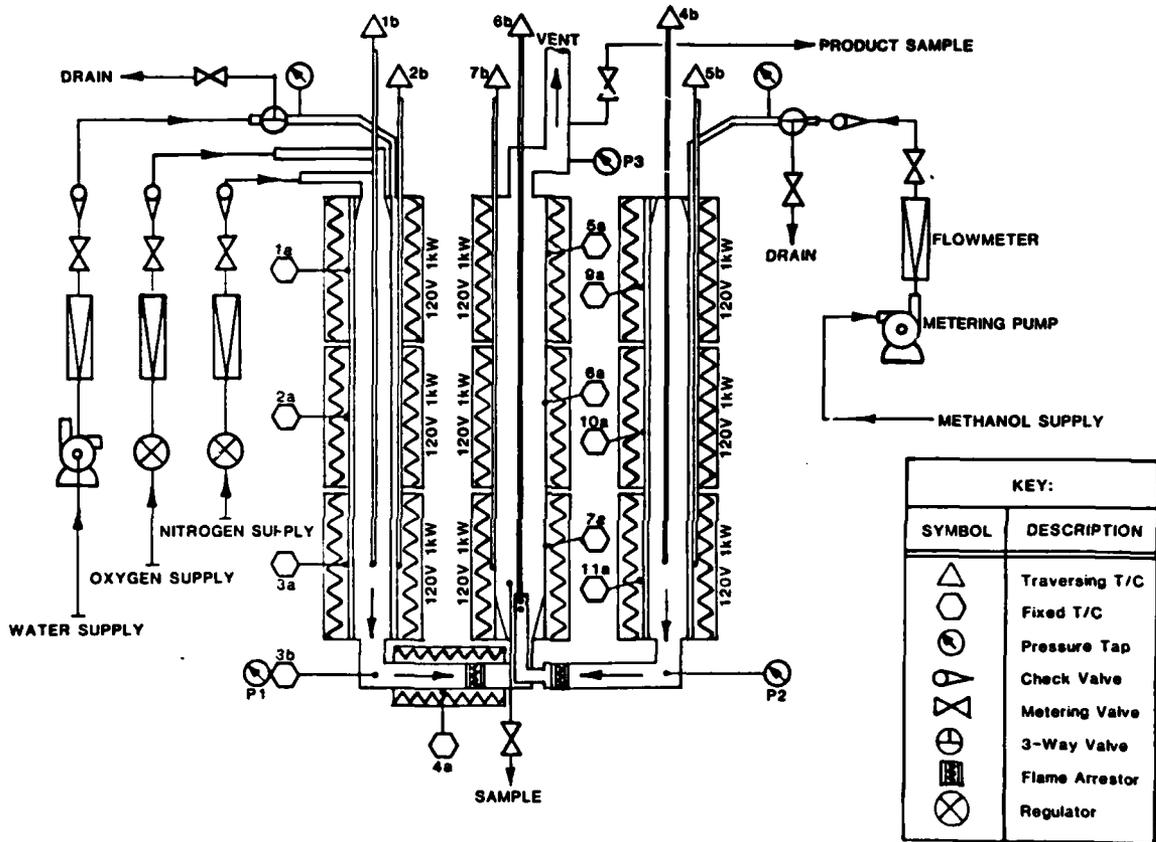
REACTIONS OCCURRING IN PARTIAL OXIDATION OF METHANOL

| | | | | | |
|----|--|----------------------|--|--|-------------------------|
| 1. | $\text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2$ | \rightarrow | $\text{CO}_2 + 2\text{H}_2\text{O}$ | $\Delta\text{H}_{298\text{K}} = -161.6 \frac{\text{kcal}}{\text{g mol}}$ | Combustion |
| 2. | CH_3OH | \rightarrow | $\text{CO} + 2\text{H}_2$ | $\Delta\text{H}_{298\text{K}} = 21.7 \frac{\text{kcal}}{\text{g mol}}$ | Decomposition |
| 3. | $\text{CH}_3\text{OH} + \text{H}_2\text{O}$ | \rightarrow | $\text{CO}_2 + 3\text{H}_2$ | $\Delta\text{H}_{298\text{K}} = 11.8 \frac{\text{kcal}}{\text{g mol}}$ | Steam Reforming |
| 4. | $\text{CH}_3\text{OH} + 2\text{CO}_2$ | \rightarrow | $3\text{CO} + 2\text{H}_2\text{O}$ | $\Delta\text{H}_{298\text{K}} = 41.3 \frac{\text{kcal}}{\text{g mol}}$ | CO_2 Reforming |
| 5. | CH_3OH | \rightleftharpoons | $\frac{1}{2}(\text{CH}_3)_2\text{O} + \frac{1}{2}\text{H}_2\text{O}$ | $\Delta\text{H}_{298\text{K}} = -2.8 \frac{\text{kcal}}{\text{g mol}}$ | Dehydration |
| 6. | $(\text{CH}_3)_2\text{O} + \text{H}_2\text{O}$ | \rightarrow | $2\text{CO} + 4\text{H}_2$ | $\Delta\text{H}_{298\text{K}} = 48.9 \frac{\text{kcal}}{\text{g mol}}$ | Reforming |
| 7. | $\text{CO} + 3\text{H}_2$ | \rightarrow | $\text{CH}_4 + \text{H}_2\text{O}$ | $\Delta\text{H}_{298\text{K}} = -49.3 \frac{\text{kcal}}{\text{g mol}}$ | Methanation |
| 8. | $\text{CO} + \text{H}_2\text{O}$ | \rightleftharpoons | $\text{CO}_2 + \text{H}_2$ | $\Delta\text{H}_{298\text{K}} = -9.9 \frac{\text{kcal}}{\text{g mol}}$ | Shift |

range. Gas compositions showed that the oxidant is almost completely utilized to partially combust methanol to CO_2 and H_2O . The heat generated serves to increase the temperature of the reactants, and promotes some decomposition and possibly some reforming of methanol. This is evident by the hydrogen detected after partial oxidation. Dimethylether is also formed and detected at low levels. The partial combustion of methanol generates H_2O and heat which in turn raises the temperature of the reactants so that, decomposition and reforming can occur in the presence of the platinum catalyst. Reforming can be accomplished with steam or CO_2 , although CO_2 reforming requires a greater degree of heat. Dimethylether can be formed by the dehydration of methanol, but can also be steam reformed to CO and H_2 at a large heat penalty. Traces of methane appear by the methanation reaction, and the shift reaction determines the changes in CO and CO_2 levels.

2.3 Subscale Single Tube Tests

A test apparatus was built to test the partial oxidation of methanol in an electrically heated reactor. Boilers for methanol and water were installed, and the test facility was set up to simulate cathode exhaust gas composition over a range of flows. A traversing thermocouple was installed for monitoring reactor temperatures. Figure 2.15 illustrates the test system. Three combinations of partial oxidation and reforming catalyst considered for the final reactor design were tested in 1 1/2 and 3 inch diameter tubes prior to the fully integrated tests which are described in section 2.4. This provided an opportunity to identify any potential problems due to high temperature gas exiting the partial oxidizer or fouling from the dimethylether and other gas constituents during extended operation on research and technical grade methanol. A scaled up version of the single tube was operated to examine temperature profiles and possible size limitations. Finally, the partial oxidation and vaporizer were tested as an integrated unit.



LD501

FIGURE 2.15 Single Tube Reactor System (1 Inch Diameter)

2.3.1 Partial Oxidation/Reforming Tests In One Inch Diameter Tube

The three catalyst configurations listed in Table 2.6 were tested to evaluate their endurance capabilities. The first test utilized the Johnson Matthey stainless steel monolith containing platinum ahead of 175 grams of United Catalyst T2107 1/8 x 1/8 inch copper catalyst. This test ran for only 48 hours before the pressure drop required that it be discontinued. Upon disassembly, the T2107 pellets were found to be severely spalled at the inlet of the bed, and normal from the middle of the bed to its end. The gas compositions and catalyst temperatures shown in Figure 2.16 revealed no abnormality. Bed temperatures were uniform from inlet to outlet. Some mechanical abrasion may have occurred but at the low flow rates used, this seemed unlikely. X-ray diffraction of material from the inlet revealed complete absence of zinc oxide and zinc aluminate. The exit had zinc oxide reflections and no zinc aluminate. Apparently, the conversion to zinc aluminate weakened and/or spalled the pellets. Most likely, mechanical action packed the material and resulted in a high pressure drop. In order to provide a back up to this potential problem for the full scale reactor, a fibrous catalyst packet was manufactured to entrap 14 to 16 Tyler mesh particles in a stainless steel fiber mat.

The second endurance test utilized a crushed 1/4 inch Engelhard 0.1% platinum on alumina, entrained in stainless steel fibers. A fiber packet of this material was substituted for the monolith catalyst. A similar fiber packet containing crushed T2107 copper catalyst was substituted for the pellet bed. A 120 hour endurance run was conducted with no pressure problems and steady conversion after the first 30 hours. Gas compositions and bed temperatures shown in Figure 2.17 indicate that the much smaller copper catalyst bed (30 grams verses 175 grams) resulted in methanol, dimethylether and oxygen exiting from the reactor. The composition was constant for the last 90 hours of the test. Apparently, these gases do not cause any significant decay

TABLE 2.6

CATALYST DESCRIPTIONS

| <u>Partial Oxidation</u> | <u>Reforming</u> | <u>Description</u> | |
|--------------------------|------------------|--|-----------------|
| I. Monolith | Pellets | Johnson Matthey Stainless Steel, 400 cpi UCI-T2107-1/8" x 1/8" pellets | 24.6cc 175 g |
| II. Fiber Packet | Fiber Packet | 14/16 Mesh Engelhard 0.1% Pt on Alumina plus Stainless Steel Fibers 14/16 Mesh, T2107 plus Stainless Steel Fibers | 8 g 30 g |
| III. Monolith | Fiber Packet | J.M., 1" wide Stainless Steel, 400 cpi 14/16 Mesh, T2107 plus Stainless Steel Fibers | 24.6cc 76 g |

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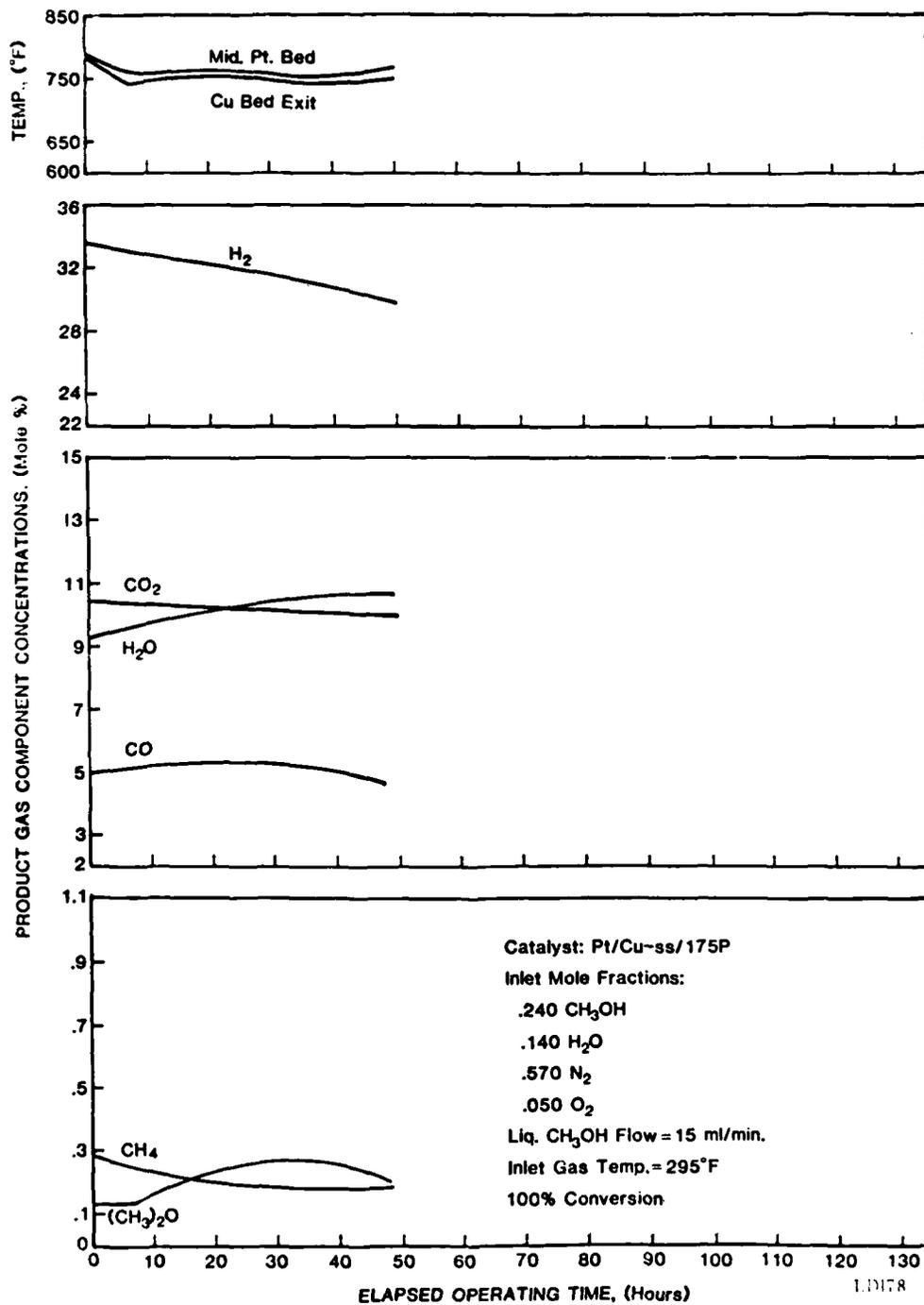
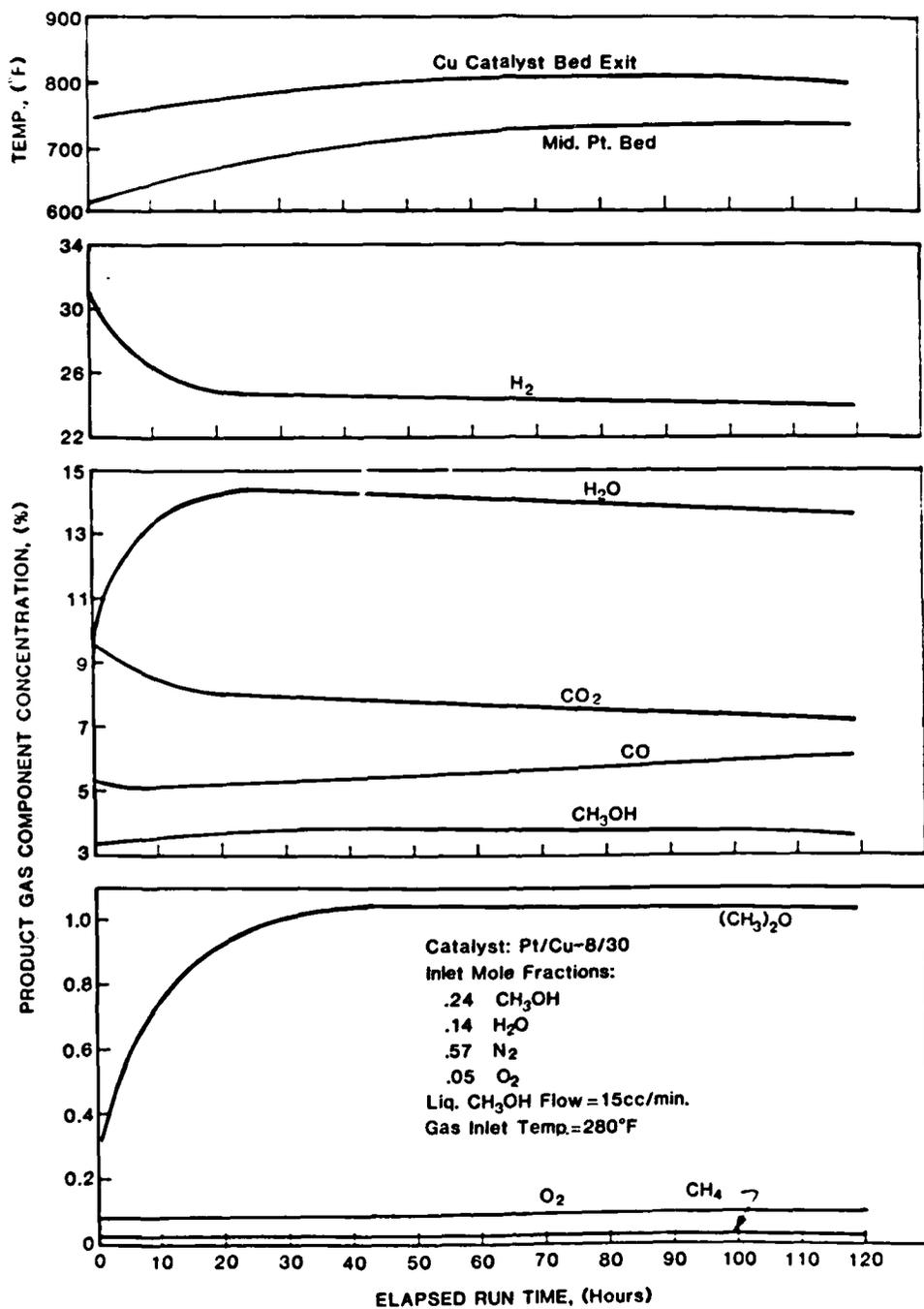


FIGURE 2.16 T2107 Pellet Tests



LD502

FIGURE 2.17 Pt Alumina and T2107 Fiber Packet Tests

beyond the particle sintering which is expected during the initial hours of operation. These results suggested that the system may operate for much longer periods.

A longer endurance test was initiated using the platinum monolith in combination with the 14/16 mesh T2107 fiber packet. The amount of catalyst and the operating conditions were chosen so that unconverted methanol would be obtained at the exit. During preliminary tests it is very important to have less than 100% conversion so that any change in conversion can be observed. During the first 145 hours of operation there was a small, gradual increase in methanol exiting from the reactor as shown in Figure 2.18. This is consistent with the expected decrease in catalyst activity during the first 100 hours. After this break-in period, the reagent grade methanol was replaced with technical grade. There was a stepwise decrease in methanol conversion which did not alter when reagent grade methanol was returned. After an extended shutdown period the reactor was started again using reagent grade methanol. A second switch was made to technical grade and back again to reagent grade. Product gas compositions changed but the methanol conversion remained constant. After a second shut down the system was restarted without any decay. Total operating time was 483 hours. The shut downs, restarts and technical grade methanol did not significantly alter the methanol conversion, however, the product gas composition was altered. This suggested that the changes occurred in the portion of the copper catalyst which was operating as a shift catalyst. These changes were not considered to be significant enough to delay testing a scaled up version of these 1 1/2 inch single tube tests.

2.3.2 Reforming Tests on Three Inch Diameter Tubes

A three inch single tube reactor was built to handle higher flows, as depicted in Figure 2.19. The partial oxidation section was heated at the top of the reactor, and the reforming/shift catalyst bed filled the remainder of the reactor.

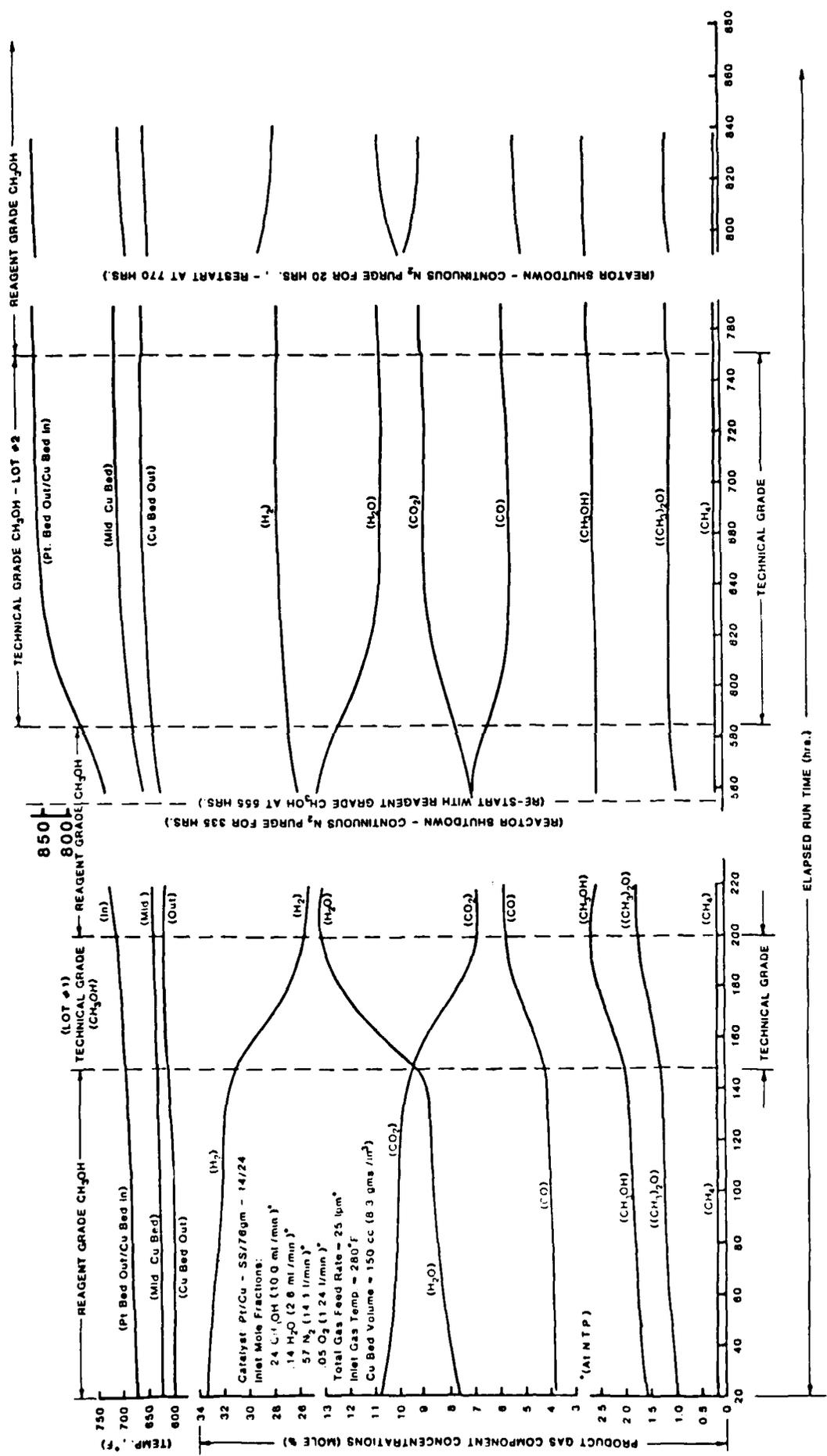


FIGURE 2.18 Reforming Technical Grade Methanol With Fiber Packets

LD230

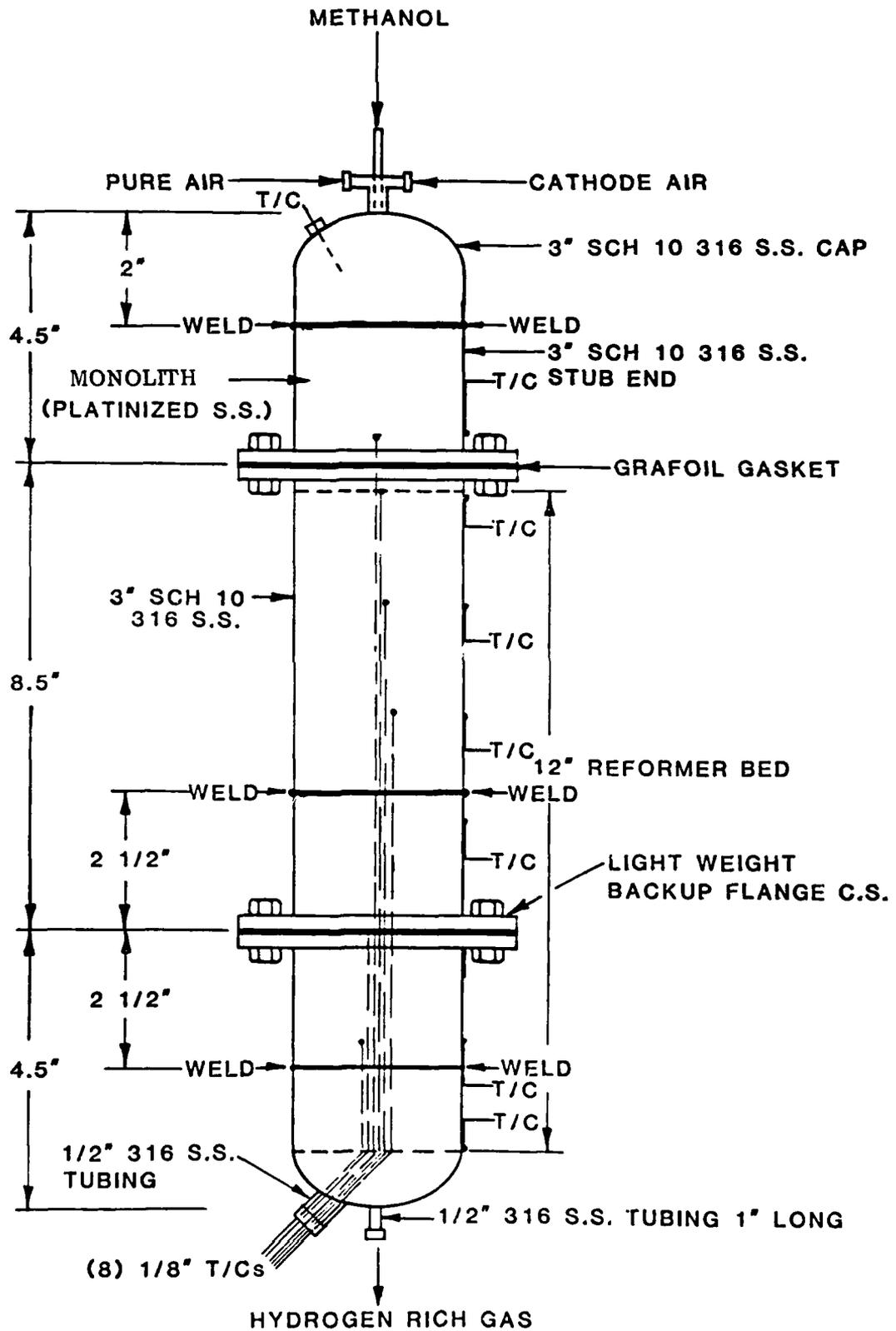


FIGURE 2.19 Single Tube Reactor System (3 In. Diameter)

Initially, no provision was made for vaporizing methanol in the reactor, so that methanol was vaporized in a separate boiler, and fed in as a vapor. Figure 2.20 illustrates the thermocouple locations. The six tests conducted on this reactor are summarized in Table 2.7. Due to the external vaporization of methanol, lower flow rates were required in order to prevent over heating. Methanol conversion of 100% was achieved at flows designed to achieve a H_2O/CH_3OH of 1.3 at the reformer inlet, using a simulated 50% cathode utilization exhaust gas. The CO level was at 5.38%, and the exit temperature was 830°F. These tests were conducted to characterize the performance of this reactor for partial-oxidation reforming. The conclusions drawn were as follows:

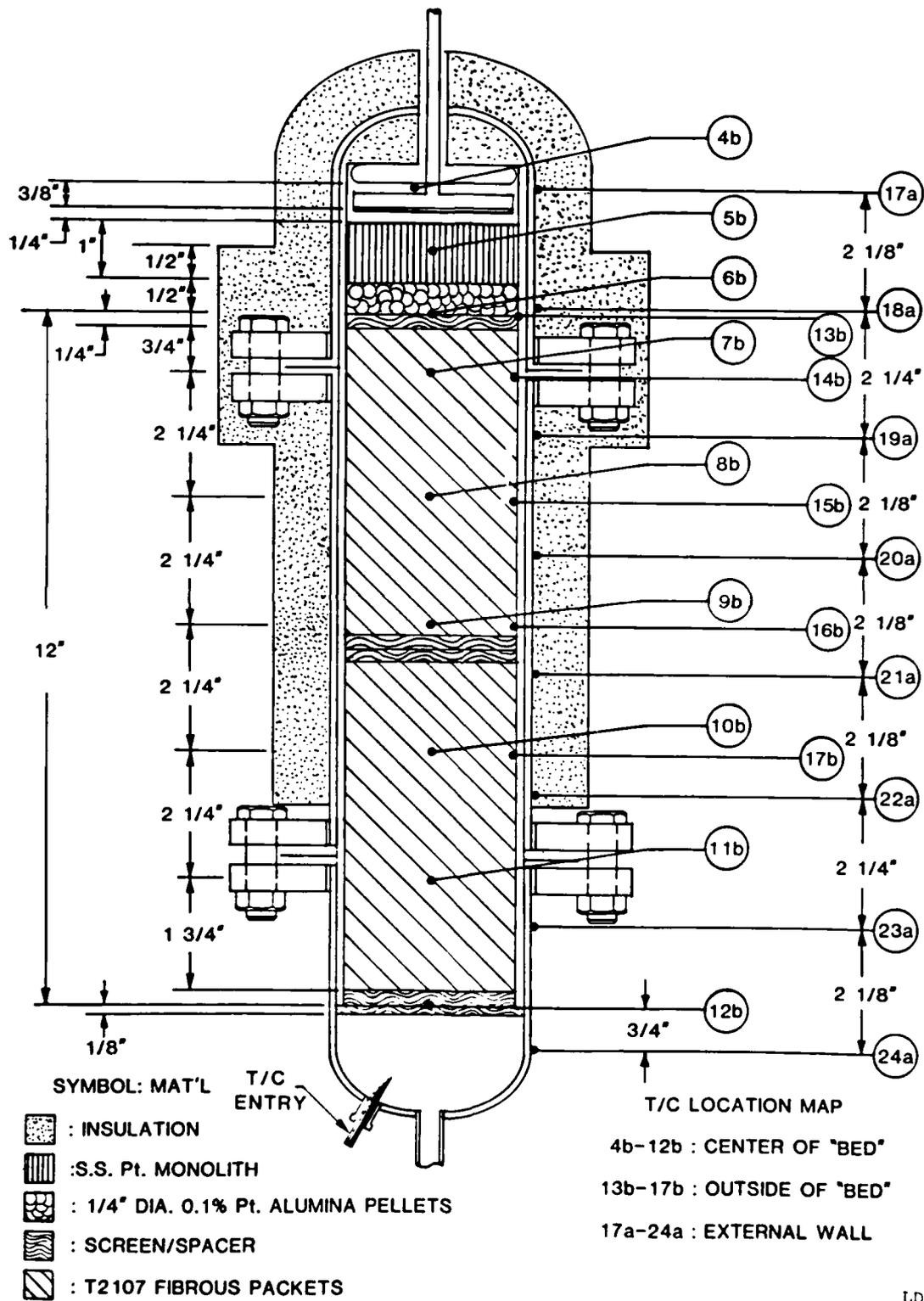
- External vaporization of methanol results in high reactor inlet temperatures as expected.
- High reactor inlet temperatures of 873 - 1640°F result in conversion rates of methanol of 97.67 - 100%. Conversion generally increased with inlet temperature.
- CO compositions of 2.29 - 5.38% were 20 - 65°F approach to equilibrium.
- Dimethylether ranged from 0.04 - 0.47% and decreased with an increasing H_2O/CH_3OH ratio.
- Vaporization of methanol must be incorporated into the reactor system, and its effect determined.

2.3.3 Integrated - Vaporization/Partial Oxidation

The partial oxidation reformer system can be considered to have three basic components:

- methanol vaporizer
- partial oxidizer
- reforming/shift

Testing in the early part of the program was carried out with vaporized methanol in order to study the partial oxidation of methanol. However, in order to incorporate the concept into a



LD507

FIGURE 2.20 3kW Partial Oxidation Reformer T/C Locations

TABLE 2.7

PARTIAL OXIDATION TESTS USING 3 INCH DIAMETER REACTOR
AND EXTERNAL METHANOL VAPORIZATION

| Test Number | Conditions* | Results |
|-------------|---|--|
| POR 001 | 4.25 kW gross flows to achieve $H_2O/CH_3OH = 1.3$ 50% cathode utilization | Temperature reached 1655°F and was climbing. Flows too high. |
| POR 002 | 2.2 kW gross flows $H_2O/CH_3OH = 1.0$ | Methanol conversion 98.9% Inlet temperature 920°F Exit CO is 2.89% |
| POR 003 | 2.2 kW gross flows $H_2O/CH_3OH = 1.1$ | Methanol conversion 97.67% Inlet temperature 873°F CO at 2.29% |
| POR 004 | 2.2 kW gross flows $H_2O/CH_3OH = 1.3$ by increasing H_2O | Methanol conversion 99.4% Inlet temperature 1050°F CO 2.62% |
| POR 005 | 2.2 kW gross flows $H_2O/CH_3OH = 1.3$ 50% cathode utilization | Methanol conversion 100% Inlet temperature 1640°F CO 5.38% |
| POR 006 | 2.2 kW gross flows $H_2O/CH_3OH = 1.5$ | Methanol conversion 99.8% Inlet temperature 1628°F CO 4.79% |

*1 kW equivalent flow is 10 cc/min of CH_3OH

partial oxidation reformer, a vaporization section was added. Since partial oxidation generates a large amount of heat, it was desirable to have the methanol vaporization in the partial oxidation zone. This also serves to moderate the maximum temperatures generated in the partial oxidation process. A vaporizer/oxidizer was constructed to simultaneously test vaporization and partial oxidation of liquid methanol with a simulated cathode exhaust. A 24 inch long, 1 1/2 inch diameter tube with a stainless steel wick lining was used with a spiralled platinum monolith filling the void volume. Figure 2.21 illustrates the geometry of the reactor.

Testing of the vaporizer/oxidizer at 2.2 kW and 3.63 kW gross flows indicated that the heat required for vaporizing moderates the temperature in the vaporizer/oxidizer and produces a maximum temperature of 800°F at mid bed. Wall temperatures of the tube indicated that the methanol is completely vaporized within approximately the first 8 inches of the 24 inch reactor. Figure 2.22 depicts the temperature profile obtained. Analysis of the exit gases indicates that 78 to 79.7% of the methanol is converted in the vaporizer/oxidizer. In addition, a small amount of CH₄ (0.21%) was detected, and dimethylether was measured at 0.55%. The overall result is that almost 80% of the methanol is converted before coming in contact with the reforming catalyst and only a small amount of methanol (4%) and (CH₃)₂O (0.55%) requires reforming. The CO level leaving the vaporizer/oxidizer is relatively high at 8.7%, and will require shifting to CO and H₂. It appears that the catalyst bed following the vaporizer/oxidizer will function more as a shift bed than as a reformer, and in this case will require more cooling than heating.

The vaporizer/oxidizer was also tested to simulate start-up using air instead of cathode exhaust for heating up the reactor. The test data indicated that air start-up resulted in 1200°F at the inlet within one minute. The rest of the reactor required longer to heat up, as shown in Figure 2.23. After

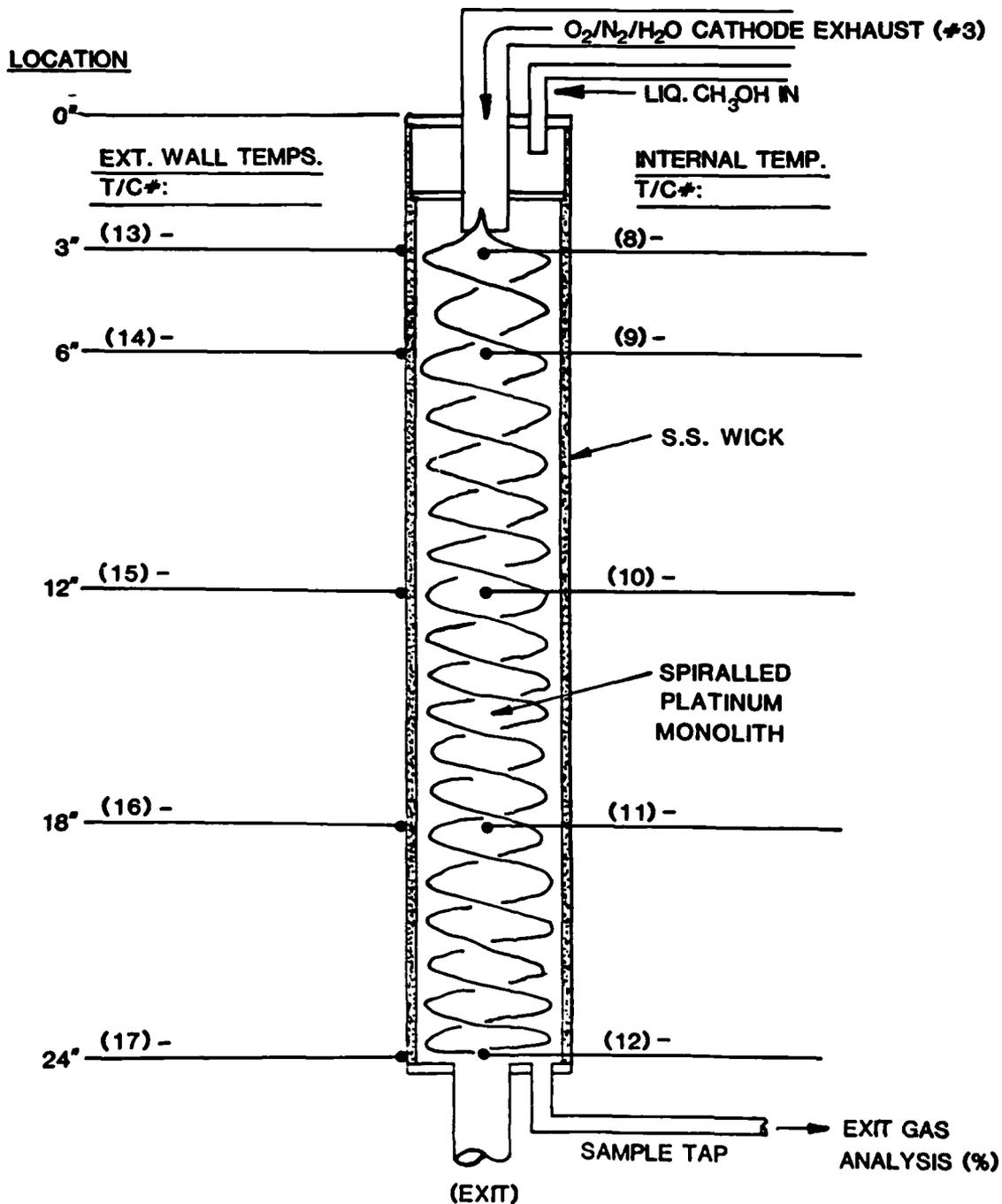


FIGURE 2.21 CH₃OH Partial Oxidizer/Vaporizer

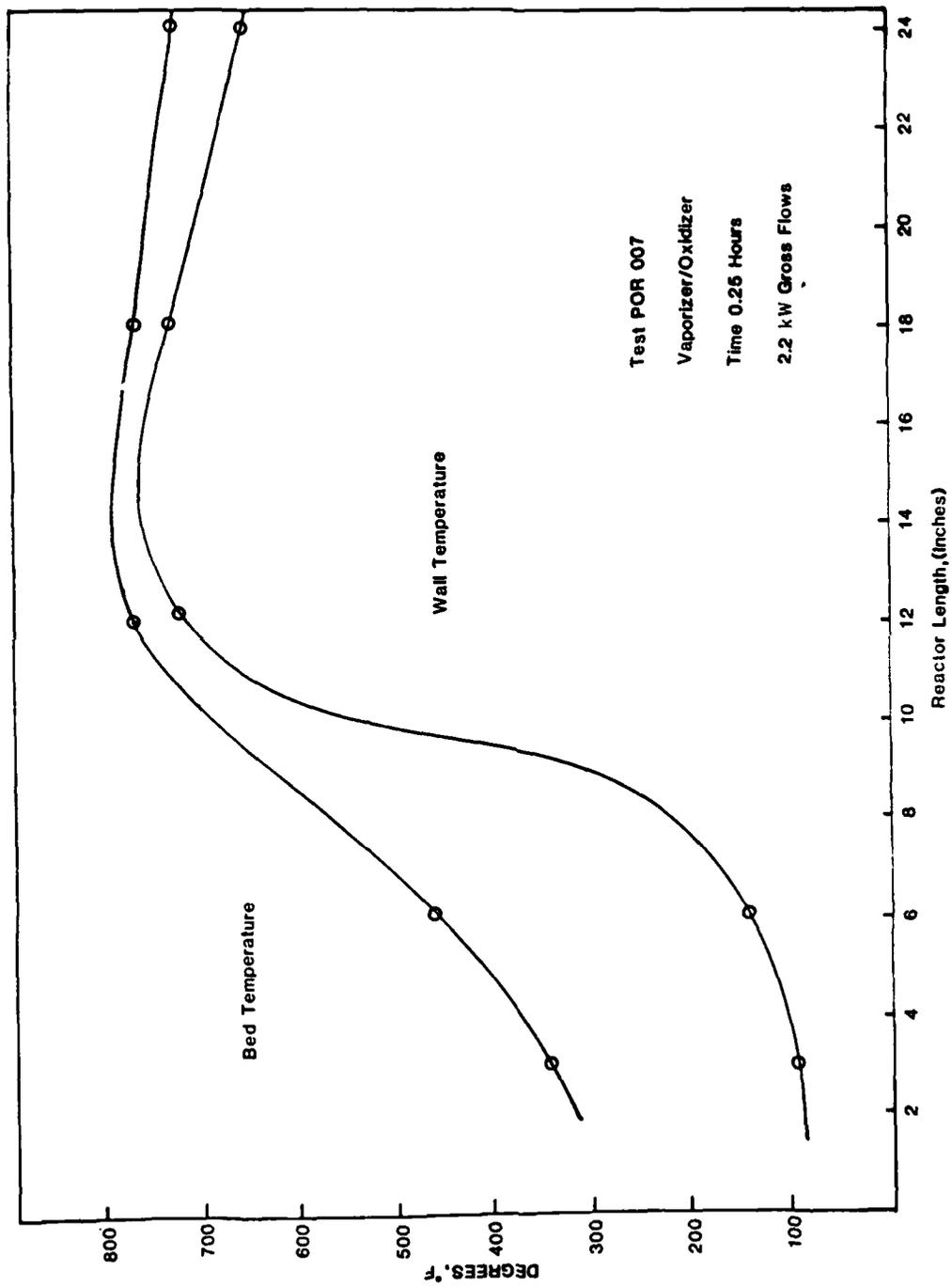
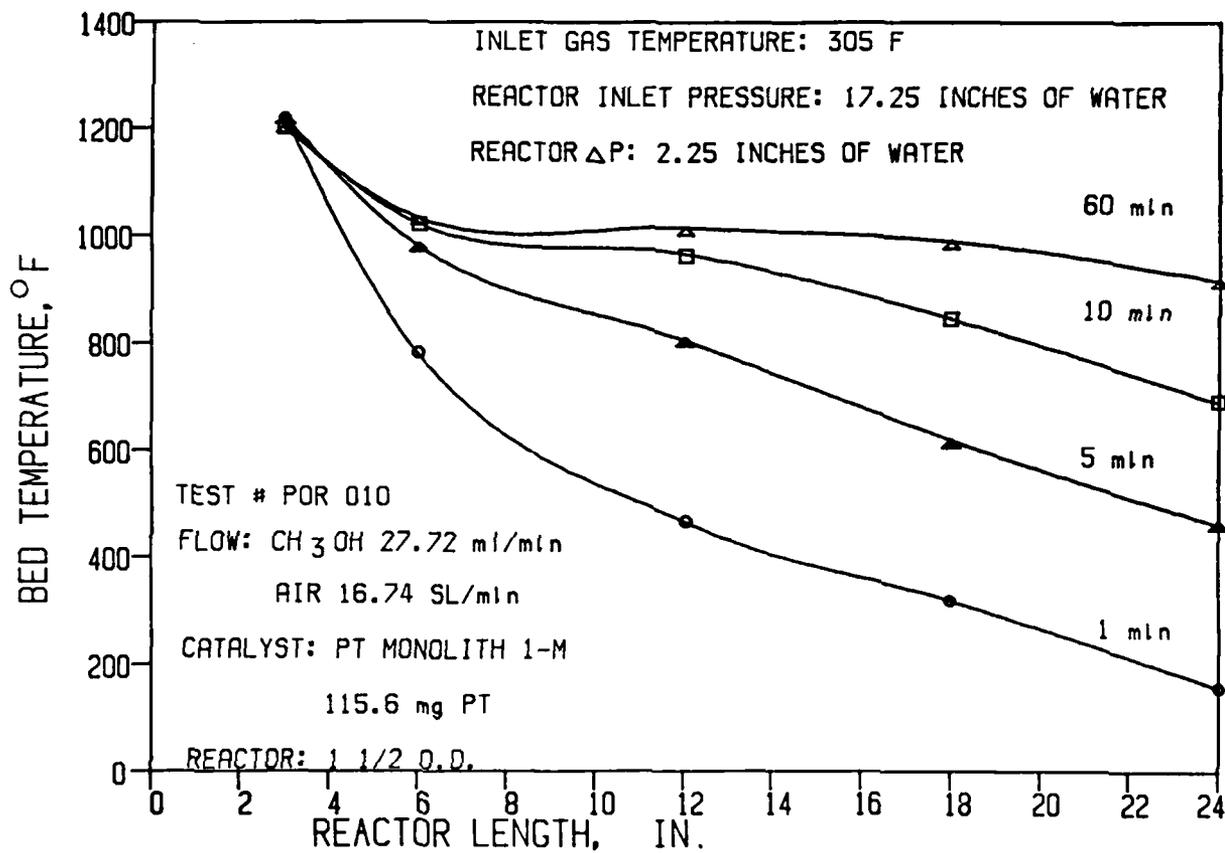


FIGURE 2.22 Vaporizer/Oxidizer Temperatures

LD317



I.D342

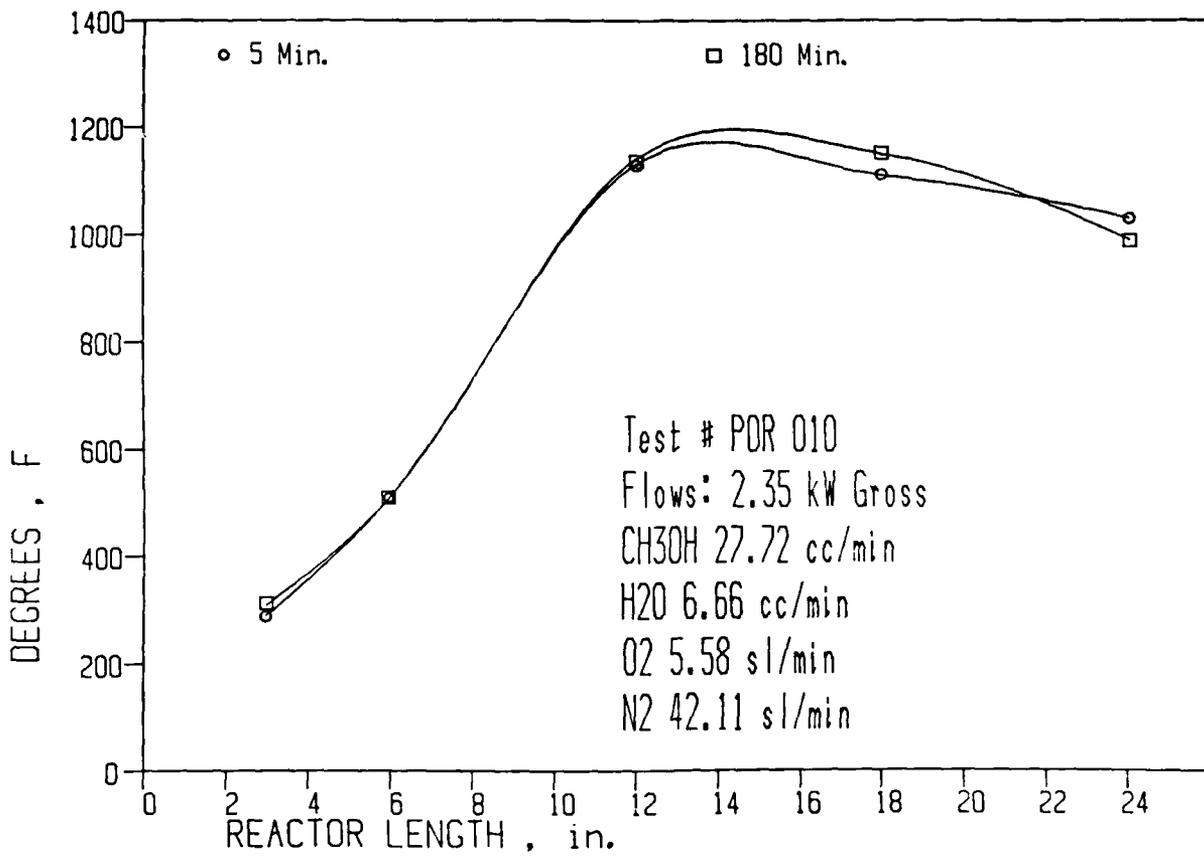
FIGURE 2.23 Start-Up Bed Temperature Profile

switching off the air and replacing it with simulated cathode exhaust gas, the temperature profile changed, as shown in Figure 2.24. The inlet cooled down to about 300°F, and higher temperatures (around 1100°F) were demonstrated in the second half of the reactor. Methanol conversion during start-up with air was 81.2% with approximately 16% hydrogen and 10% CO leaving the vaporizer/oxidizer reactor (Figure 2.25). After switching to partial oxidation conditions using cathode exhaust, the methanol conversion dropped to 54%. This was a lower conversion than obtained previously in tests without air start-up. The difference between the air start-up tests and the previous tests without air (using cathode exhaust gas) was the operating temperatures obtained. The previous testing produced temperatures of 342 - 772°F (Test POR 007) and resulted in higher methanol conversion than the air start-up in which operating temperatures were 312 - 1079°F. Apparently, the start-up procedure tested here generates a much higher inlet temperature which sustains a higher operating temperature when switching to cathode exhaust gas. The net result of the partial oxidation, and reforming and decomposition of methanol at the higher temperature was less conversion of methanol at 312 - 1079°F as compared to operation at 347 - 772°F. This suggests that the platinum catalyst operates more efficiently at the lower temperature or that the catalyst was deactivated in some way at the higher temperature.

2.4 Reactor Design and Verification Tests

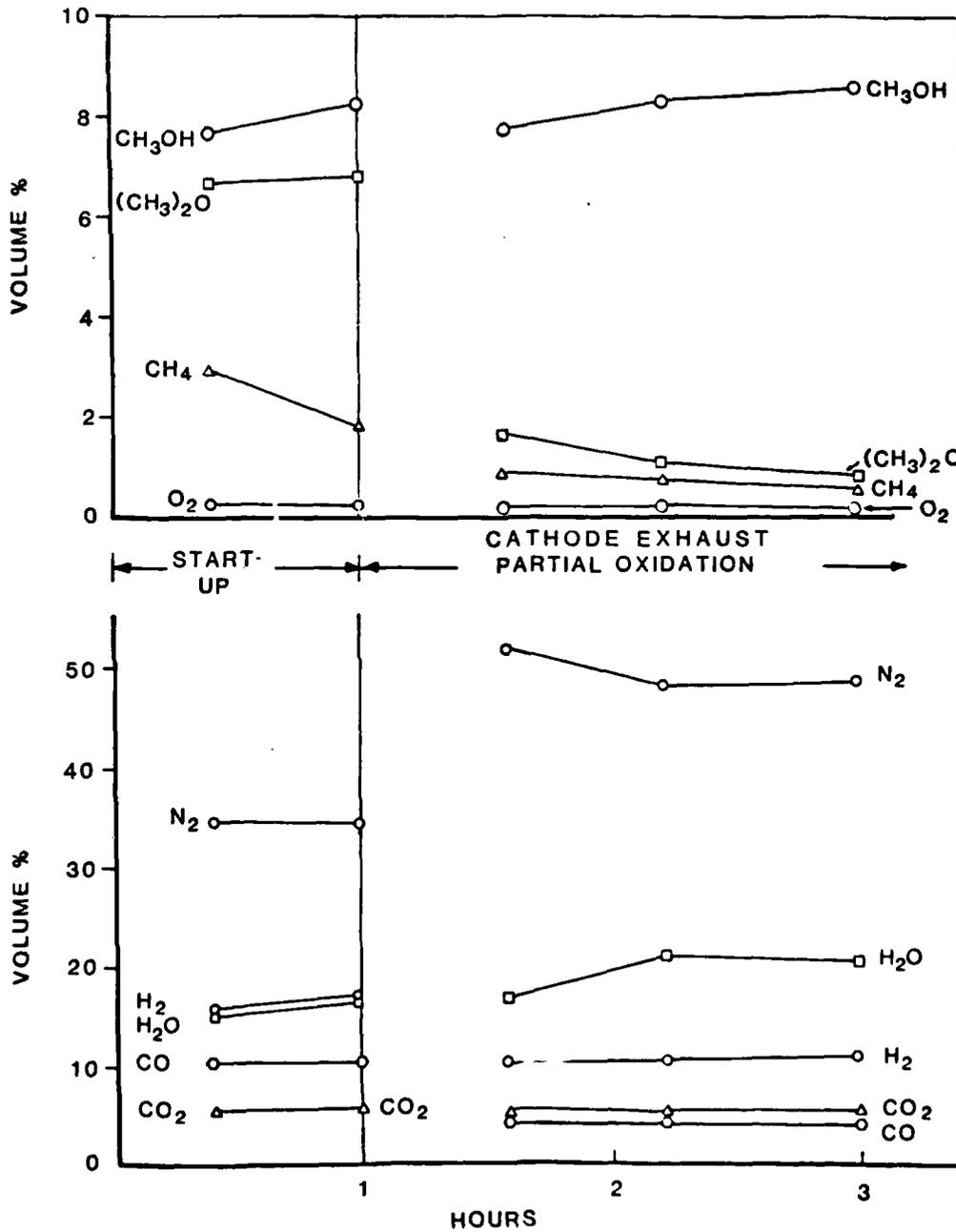
2.4.1 Preliminary Integrated Reactor Tests

Following the testing of the vaporization/oxidizer and conversion of approximately 50% of the methanol by partial oxidation, the reforming/shift catalyst section was added. Figure 2.26 depicts the reactor tested. Five tests were conducted covering a flow range from 0.78 kW to 5.5 kW gross flows. At 3.9 kW and higher flows, temperatures were high enough to obtain 100% conversion of the methanol. These temperatures were in the range of approximately 530 to 725°F. Figure 2.27 depicts



LD341

FIGURE 2.24 Bed Temperature Profile Partial Oxidation After Start-Up



T.0340

FIGURE 2.25 Test POR 010 Exit Gas Composition

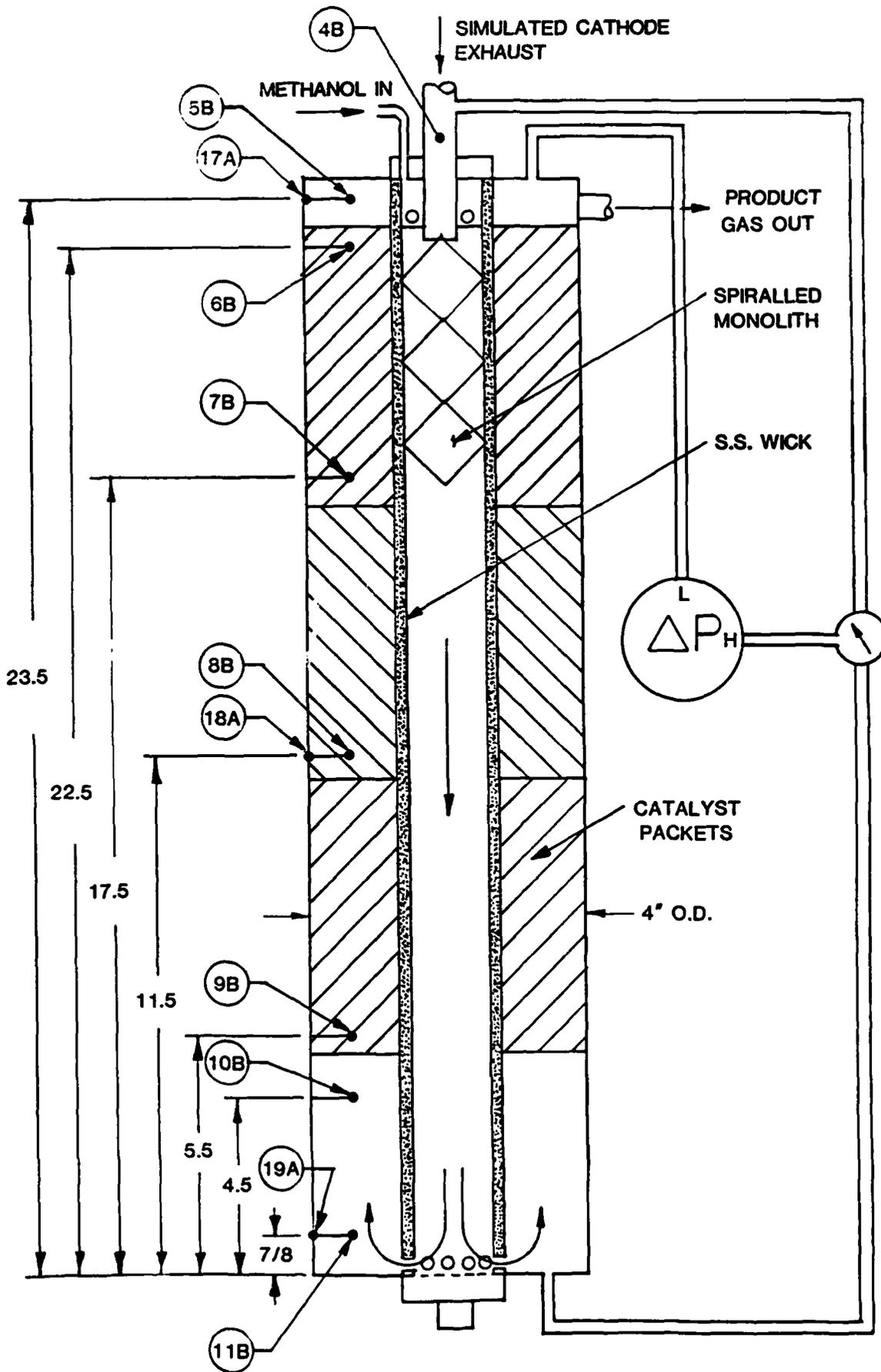


FIGURE 2.26 3kW Partial Oxidation Reformer

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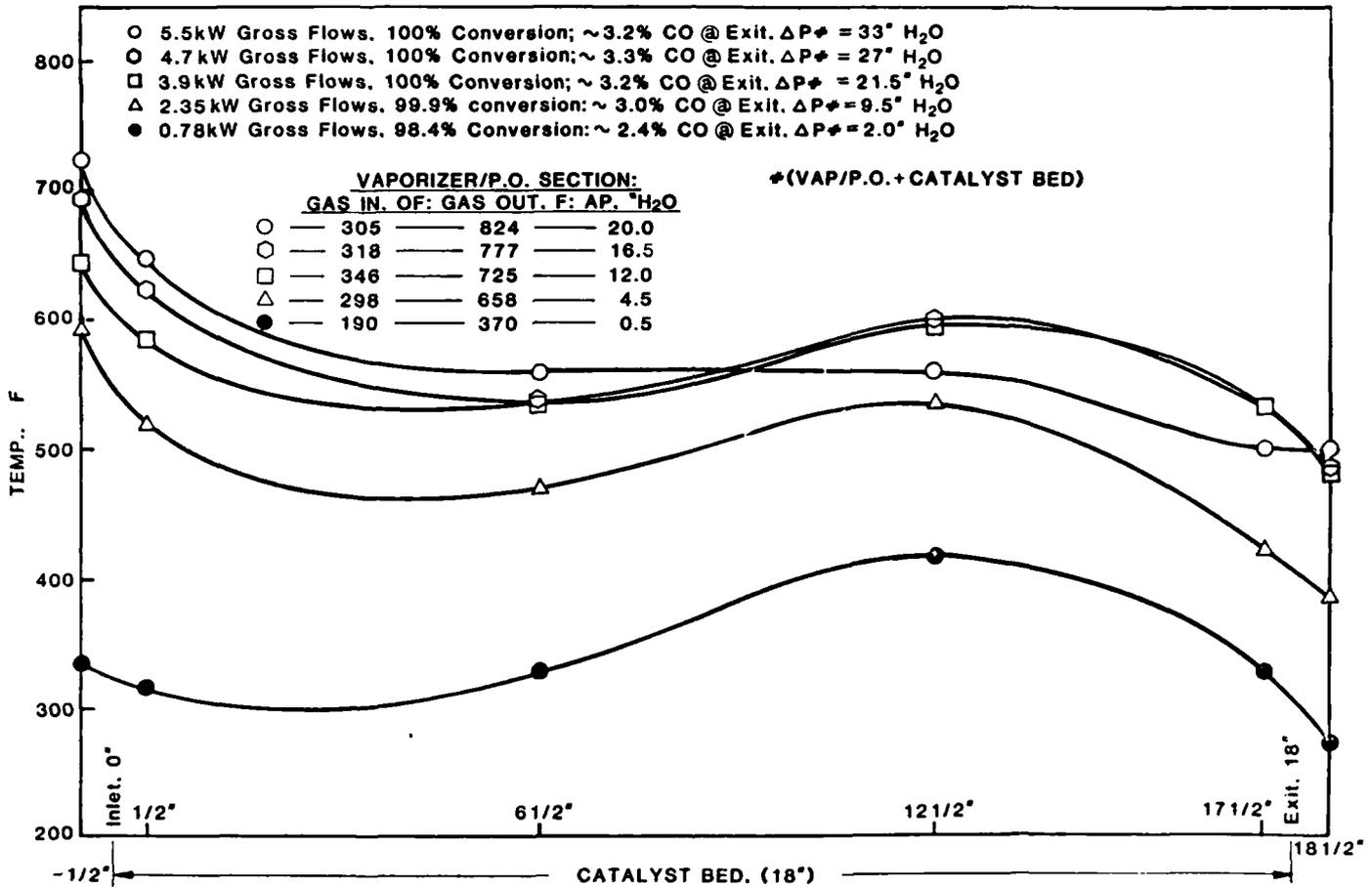
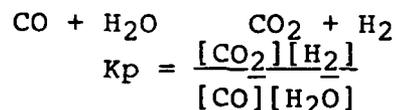


FIGURE 2.27 Temperature Profile Partial Oxidation Tests 3kW POR 012-016

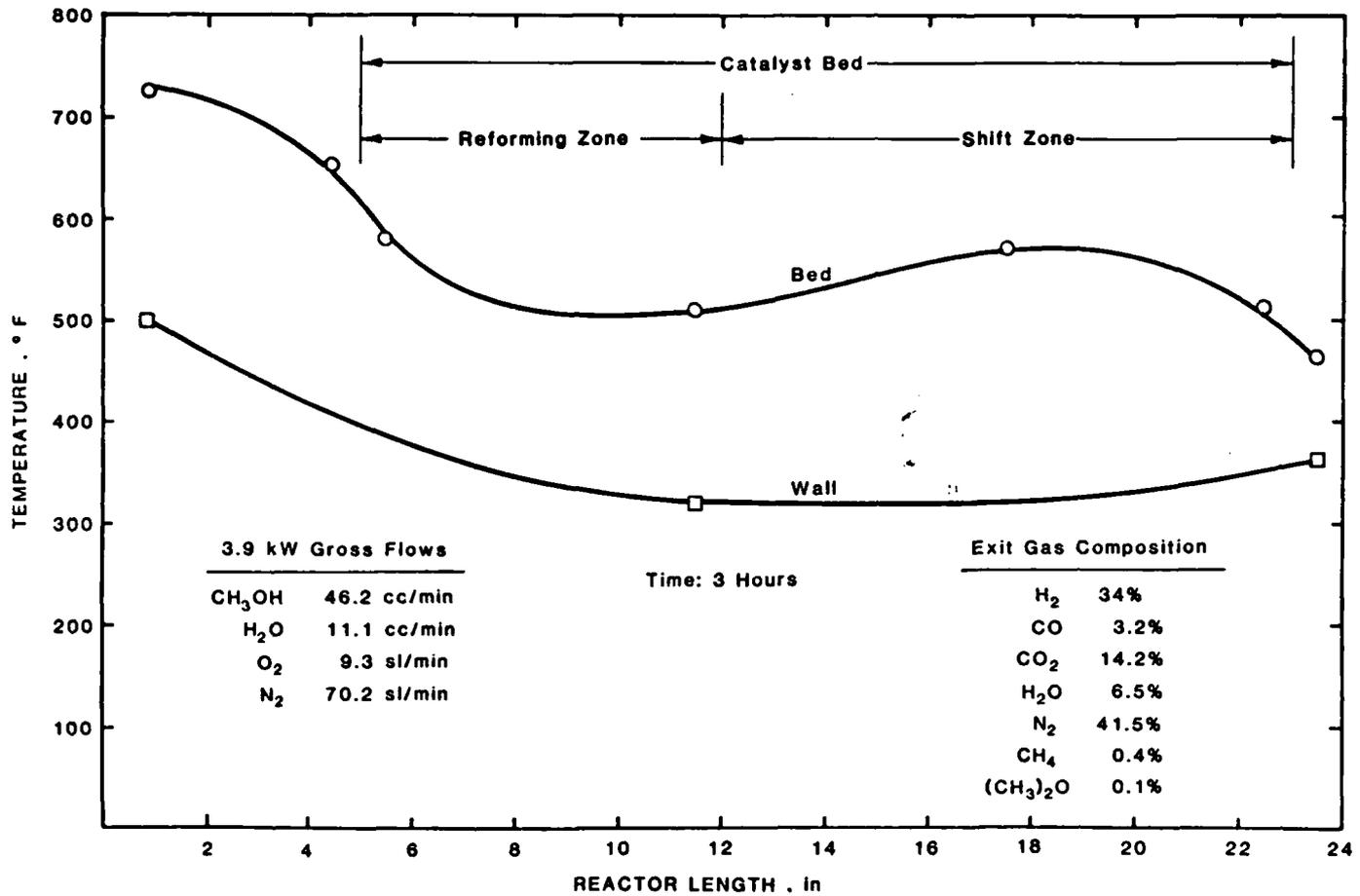
the temperature profiles and conversions obtained in these tests. The temperature profile of the catalyst bed section of the reactor indicates that an endothermic reforming zone occurs in approximately the first third of the catalyst bed, and that the last two thirds of the bed catalyzed the exothermic shift reaction. This is indicated in Figure 2.28 where the reforming zone is in the decreasing temperature region, and the shift zone is in the increasing temperature region.

Methanol conversion in the catalyst bed is 100% when temperatures in the bed are above approximately 530°F at the lowest point in the reforming zone. These temperatures were achieved at flow rates of 3.9 kW gross flows and above. When lower flows were tested, the minimum temperature in the catalyst bed dropped, and resulted in unconverted methanol leaving the reactor. The catalyst bed temperature, particularly at the exit of the reactor affects the CO concentration leaving the reactor. This is due to the effect of the CO shift equilibrium. Figure 2.29 illustrates the effect of temperature on the CO shift equilibrium constant K_p .



As the temperature increases, the equilibrium constant decreases. This has the effect of increasing the CO concentration at equilibrium. Although the gas composition leaving the catalyst bed was not at equilibrium (approach to shift equilibrium was 150°F to 300°F), the CO level leaving the catalyst bed generally increases with temperature.

An attempt was made to lower the CO level exiting from the catalyst bed by adding a small reactor at the exit of the partial oxidation reformer. It was determined that additional catalyst volume was required due to the large departure from equilibrium (150 - 300°F) measured with the existing catalyst volume of the partial oxidation reformer. An additional catalyst volume of



LD505

FIGURE 2.28 Temperature Profile Test POR 012

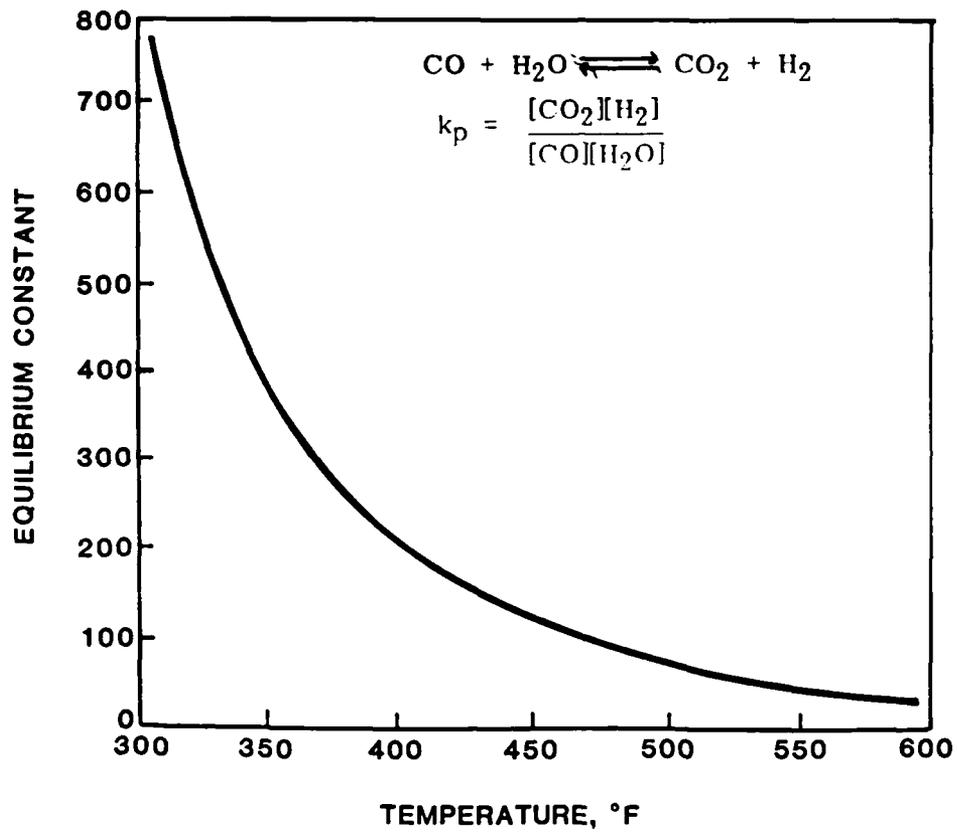


FIGURE 2.29 Equilibrium Constant for the Water Gas Shift. Reaction at Temperatures from 300°F to 600°F.

860 gm of T2107 RS pellets in the added reactor served two purposes. It allowed additional surface area for heat loss, thereby allowing the catalyst bed temperature to drop from 480 to 415°F, and it provided more catalyst volume to obtain a closer approach to a lower equilibrium level of CO. The end result was a decrease in the CO level from 3.3%, without the reactor, to 2.5% with the reactor. This level of CO was not sufficient to reach the desired level of 1% but did allow us to estimate the volume required toward optimal shift conversion.

Based on the data obtained and space velocity considerations for the additional shift reactor volume, a larger reactor was designed.

2.4.2 Reactor Design

Testing of the preliminary integrated partial oxidation reactor provided data and input for the following final 3 kW reformer design.

- The 3.2 liter catalyst volume tested was sufficient for 100% conversion of methanol, at 3 kW net flows.
- Additional catalyst volume is required to lower exit CO level below 1%.
- Vaporization and partial oxidation of methanol with simulated cathode exhaust can be carried out in the presence of a platinum catalyst, at the conditions tested. Sufficient H₂O is generated for reforming CH₃OH.
- Sufficient heat is generated to vaporize methanol and provide the heat for reforming.
- Start-up can be accomplished with air in less than 10 minutes.
- Pressure drop in the vaporizer/oxidizer is 12 to 20 inches of water.
- Pressure drop in the catalyst bed is 9 to 13 inches of water.

Design objectives were as follows:

- Maintain 100% methanol conversion
 - Reduce CO level to 1% or lower
 - Minimize over-all system pressure drop
 - Minimize over-all size and weight of reactor system
 - Maintain good start-up and transient response capabilities
-
- Reforming/Shift Catalyst Volume - Based on test data and space velocity considerations, catalyst volume was calculated to obtain a space velocity of 5000 hourly in the volume above the 3.2 liter volume tested. This resulted in a total catalyst volume of 5.6 liters.
 - Vaporizer/Partial Oxidizer Section - In order to reduce the pressure drop in this section, a larger diameter was chosen. The section was increased from a 1 1/2 to a 2 inch diameter. The amount of platinum monolith was decreased from 74.8 in² to 54.3 in². The wick vaporizer was platinized, which increased the over-all platinum loading from 115.6 mg Pt to 1.35 gm Pt. This is a factor of an 11.6 increase.

The overall geometry of the reactor allows for heat loss from both sides of the shift catalyst bed section. The reforming section of the catalyst bed is expected to be in the lower 1/3 of the bed. The reactor design for final testing is shown in Figure 2.30. Figures 2.32 and 2.33 demonstrate the test facili-

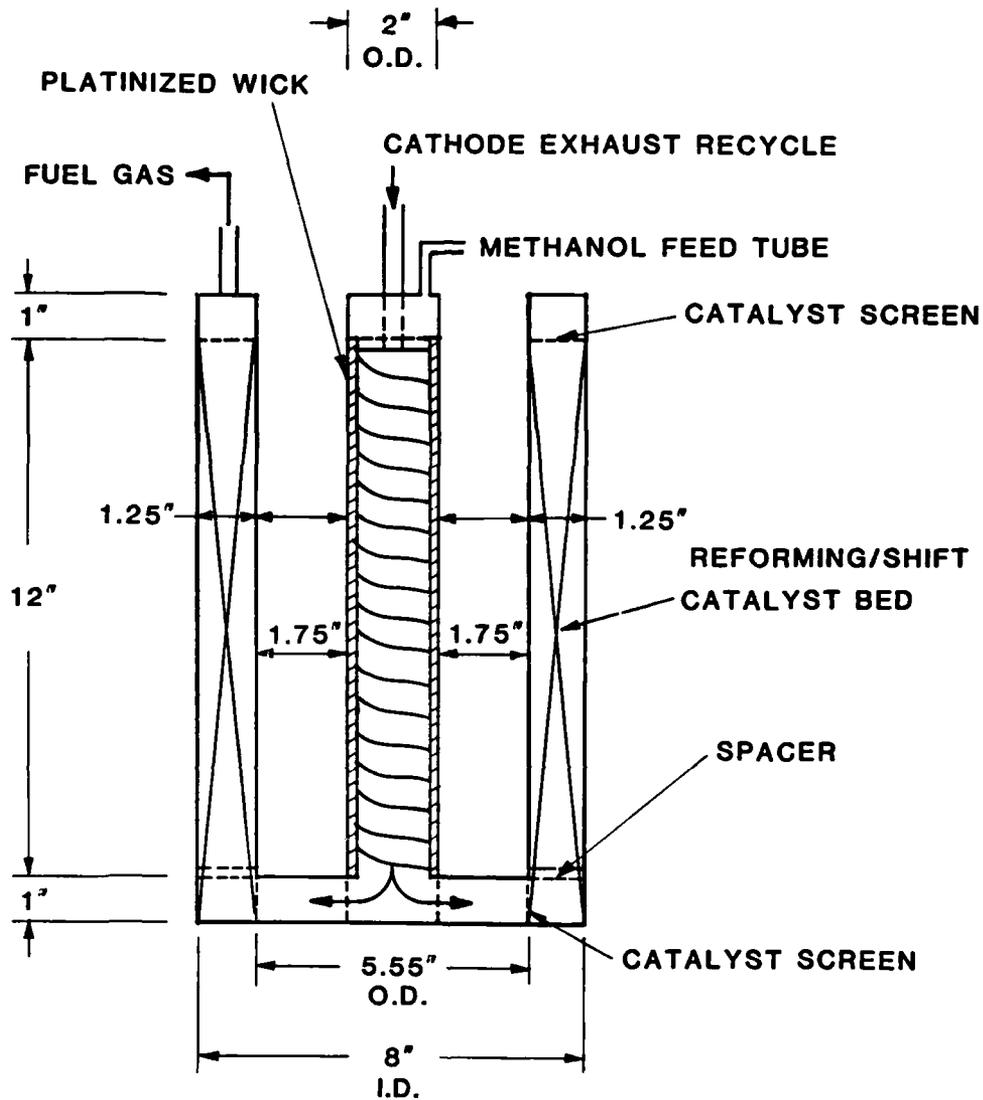
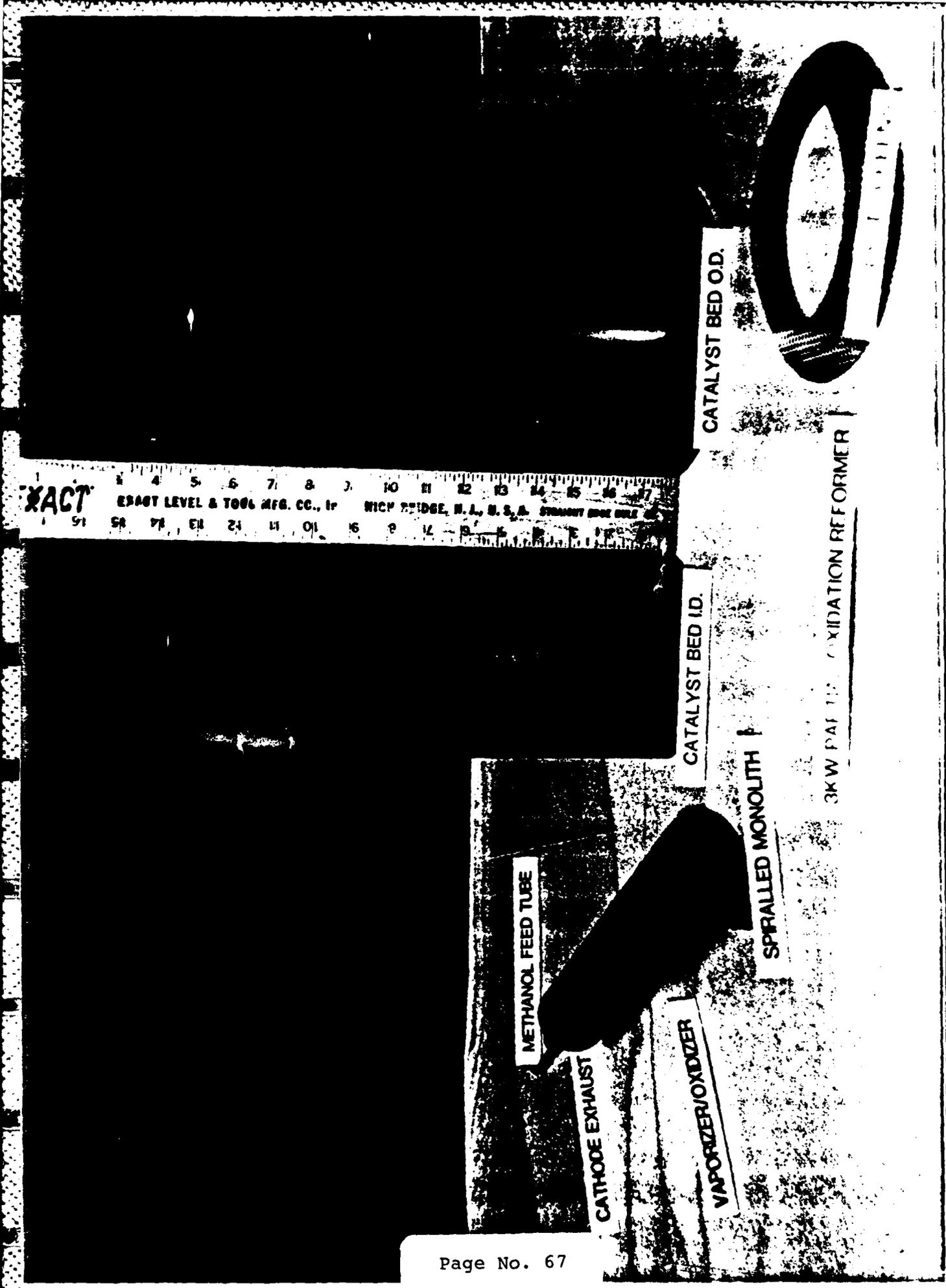


FIGURE 2.30 3kW Partial Oxidation Reformer

| | |
|-----------------------|------------------------------------|
| Catalyst Weight: | 6870 gm |
| Catalyst Bed Volume: | 5.6 liter |
| Overall Volume: | 11.53 liter (0.4 ft ³) |
| Total reactor weight: | 9,476 gm (20.27 lbs) |



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CATALYST BED O.D.

3KW PARTIAL OXIDATION REFORMER

FIGURE 2.31 3 kW Partial Oxidation Reformer

LP028

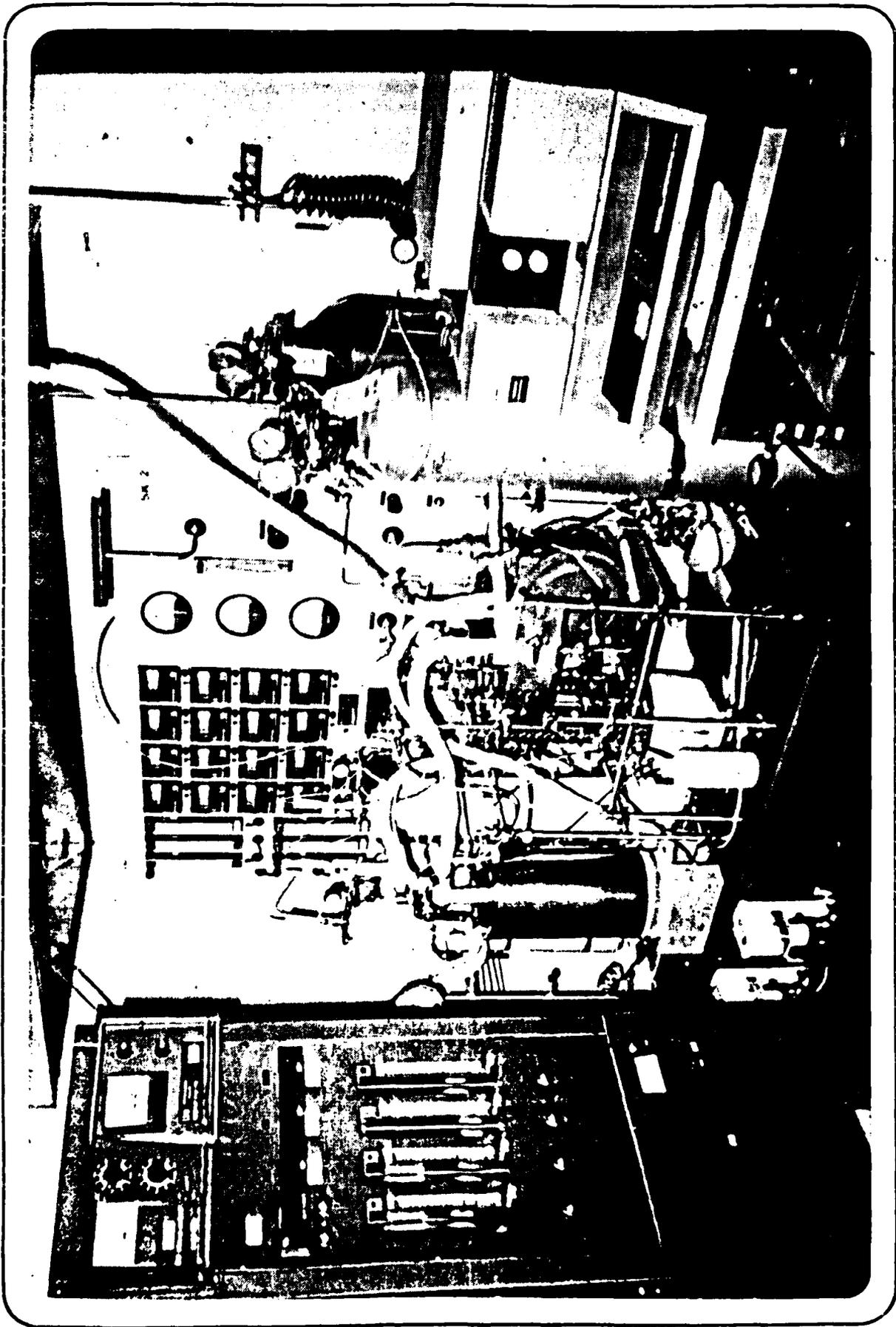


FIGURE 2.32 3 kW Partial Oxidation Reformer Test Facility During 300 Hour Endurance

LP029

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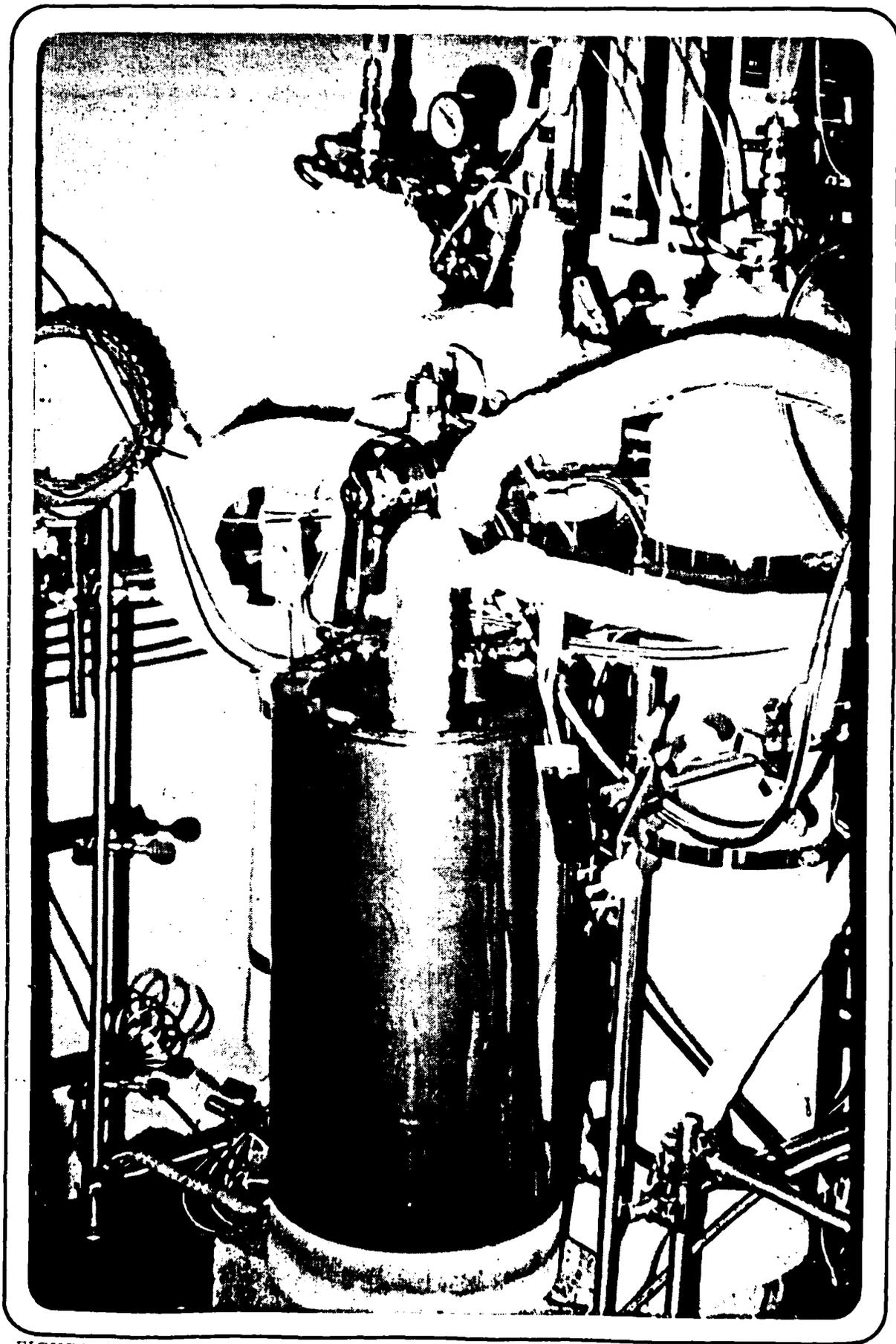


FIGURE 2.33 Partial Oxidation Reformer During 300 Hour Endurance Test LP030
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ties. A photograph of the reactor components is shown in Figure 2.31.

2.4.3 Final Reactor Design Testing and Endurance

Following fabrication of the reformer, three tests were conducted as summarized in the table below:

| <u>TEST NUMBER</u> | <u>CONDITIONS</u> | <u>CONCLUSIONS</u> |
|--------------------|---|---|
| POR 019 | 4.7 kW gross flow, N ₂ heat-up | Methanol conversion 100%. CO at exit 2.3% is higher than desired. |
| POR 020 | 4.7 kW gross flow, insulation removed, N ₂ heat-up | Methanol conversion 100%. CO at exit 2.03% is little better. |
| POR 021 | 4.7 kW gross flow, 250°F cathode recycle temperature, No insulation, Air start-up 300 hr. endurance | Completed 300 hr endurance methanol 100%. CO increased gradually from 1.44% to 1.87%. |

The two short tests conducted prior to the endurance test produced the temperature profile and gas compositions shown in Figures 2.34 and 2.35. The vaporizer temperature rises according to an "S" shaped curve, and reaches about 740°F. The difference between the vaporizer exit and catalyst bed inlet is due to heat loss, and reforming at the catalyst bed inlet. The rapid drop in catalyst bed temperature ends at about 1/3 the bed height (4 inch), at which point the shift reaction plays a more dominant role. The exothermic heat of the shift reaction, and the available surface area for heat loss results in a more gradual temperature drop to the exit of the reactor.

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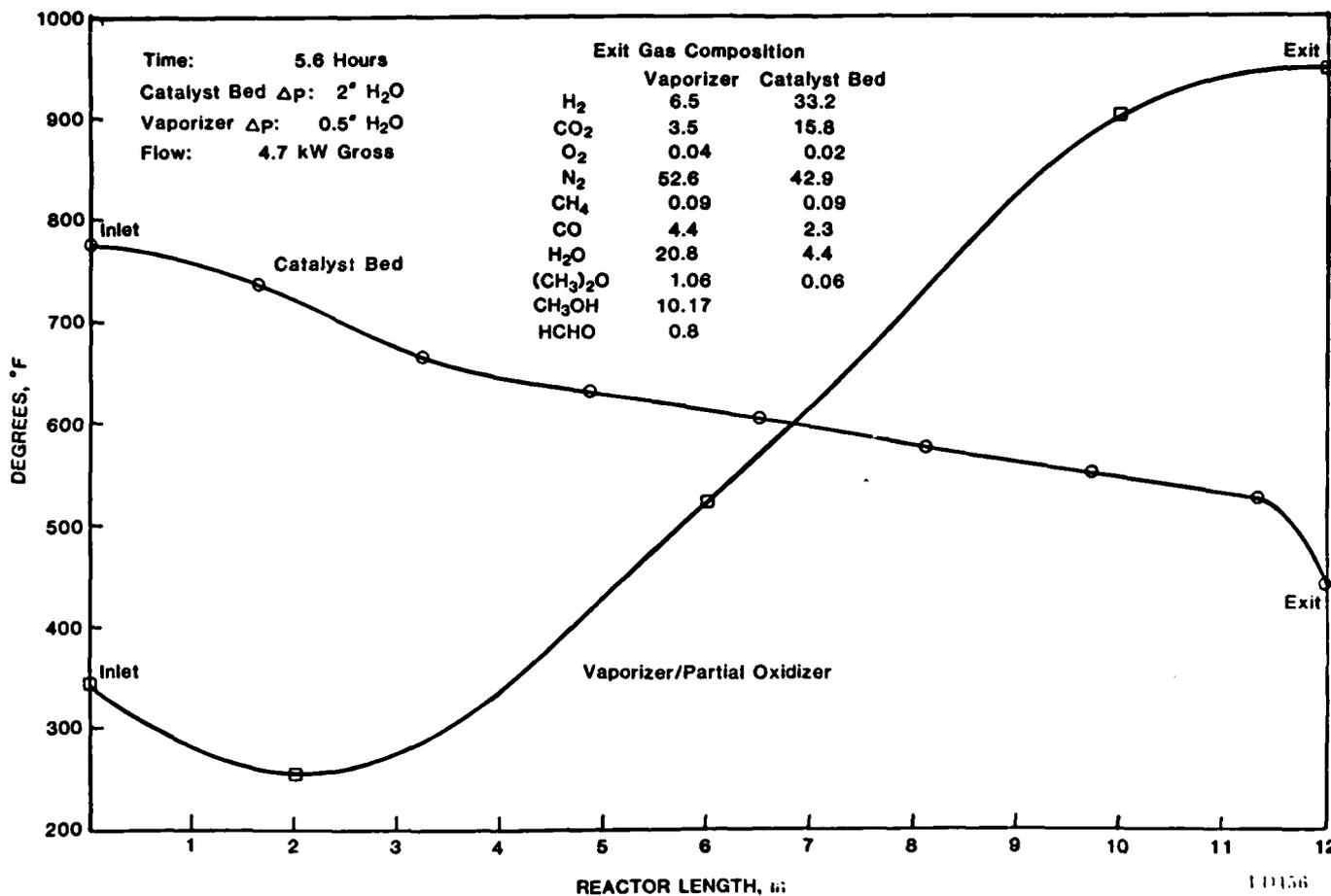


FIGURE 2.34 Temperature Profile Test POR 019

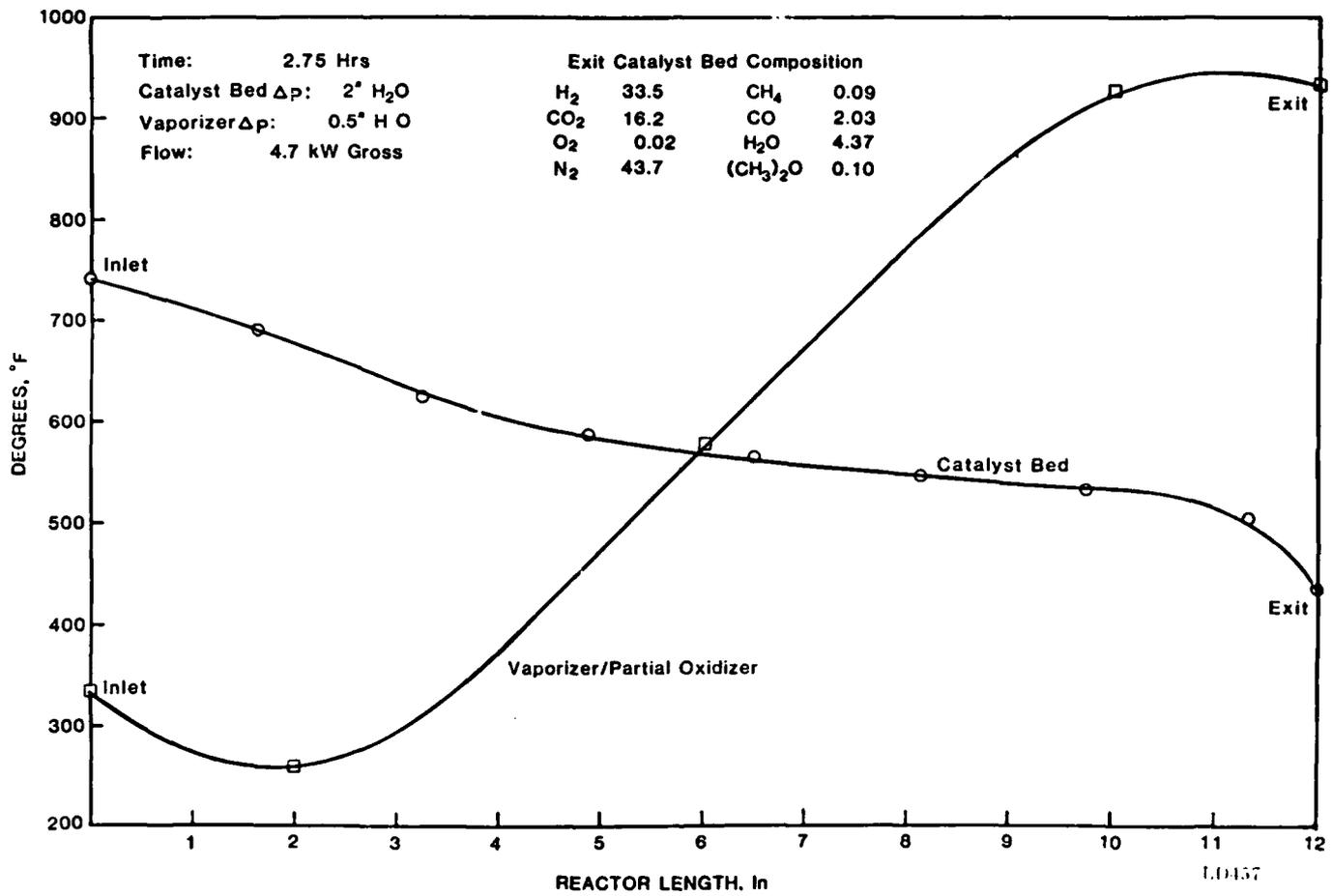


FIGURE 2.35 Temperature Profile Test POR 020

The 300 hour endurance test was conducted with a slightly cooler simulated cathode exhaust gas. The temperature was 250°F as opposed to the typical 350°F. This was done to achieve a slightly lower catalyst bed temperature. Methanol conversion was maintained at 100% throughout the test period. The CO level increased slightly during the test from 1.44% to 1.87%. This indicates a decay in shift activity, possibly due to sintering. The decay may be minimized by operation at lower temperatures and can be achieved by several methods:

- operation at higher cathode utilization
- recycling less cathode exhaust (lower H₂O/CH₃OH)
- cooling cathode exhaust prior to recycling to the reformer.

Gas analysis of the vaporizer exit and the catalyst bed exit revealed that a methanol conversion of 53.25% was achieved in the vaporizer. Dimethylether and formaldehyde were also detected at the vaporizer exit. At the catalyst bed exit no formaldehyde was detected, but dimethylether was still detected at 0.1%. This is a slightly higher level than at the vaporizer exit. Apparently, more dimethylether is made in the catalyst bed.

3. CONCLUSIONS

3.1 System Design

The Partial Oxidation/Reforming system based on cathode exhaust recycle has been demonstrated to be a viable option and operates as anticipated. The basic building blocks for a neat methanol reformer were tested and incorporated in the final reactor design provided in this report. This type of reformer and the components evaluated during this study can be used in a number of neat methanol system options as evidenced by the fact that the wick vaporizer and catalyzed wick materials were incorporated in a companion Army 5kW neat methanol reformer (contract DAAK70-84-C-0099). These components were key elements in the successful operation of the reformers tested on the present and companion program. Although the basic components may be common to many reactor designs each system option requires a different overall reactor design. The components and materials developed on this program are applicable to all of the system options.

The choice of system and reactor design depends on many variables and the priority assigned to each variable. The simplest system is less efficient than the more complex option. In addition the overall heat requirements for each potential application and the possible use of excess heat for space heating will affect the system rated efficiency. Availability and reliability can also influence the choice of the simple or complex system.

For the present study the simplest system which could utilize a fuel cell exhaust gas was chosen for evaluation to prove the viability of the concept. A simulated cathode gas was used since the exact recycle gas (anode, cathode or both) composition for any chosen system will depend on the specific application and fuel cell operating conditions. A separate study would be required to evaluate specific applications before

making a more definite choice among the system options and possible reactor designs.

3.2 Catalyst and Catalyst Configurations

The vaporizer/oxidizer is very effective and only has a 1/2 inch pressure drop. It not only functions as a vaporizer/oxidizer but converts additional methanol. In its present configuration, only 10 inch of the 12 inch length is required for complete reaction. An optimization of the catalyst loading and configuration should be able to reduce this size even further while retaining good endurance. No decay was evident during the 300 hour endurance run.

The unconverted methanol exiting from the vaporizer/oxidizer appears to be completely converted in the first 4 inches of the copper catalyst bed and the shift reaction requires the last 8 inches. Although the catalyst is one of the most effective commercially available, the exit gas does not reach equilibrium at the exit temperature of the vaporizer. Initially a 67°F approach was achieved which decayed to 119°F. This behavior demonstrates how the shift reaction controls the exit gas composition and the ultimate size of the reactor. A pressure drop of two inches for the reformer and shift bed resulted in a total pressure drop of only 2 1/2 inches. Analysis of the kinetic data for reforming showed that the reaction rate can be expressed by the following power law expression:

$$r = 3.9 \times 10^{-10} \left(e^{\frac{-21,000}{RT}} \right) p_{\text{CH}_3\text{OH}}^{0.32} p_{\text{H}_2\text{O}}^{-0.12} p_{\text{Total P}}^{0.20}$$

When pellets are used the activity is diffusion controlled with an activation energy of 10.5 kcal/mol. A fiber packet catalyst was manufactured which utilized small particles of catalyst and still retained a low pressure drop. The catalyst packing density of the 14/16 Tyler mesh particles did not reach 50% of the 1/8 inch x 1/8 inch pellets which is required to achieve equal

activity. Some additional development will be required to reach this level and possibly beyond.

3.3 Reactor Design and Operation

The reactor operated effectively for 300 hours at a gross hydrogen production level equivalent to 4.7 kW. This is more than sufficient for a powerplant with a 3 kW net power output. Overall weight is 21 lbs. and overall volume is 0.4 ft³. This is considered compact and light weight in comparison to conventional reformers. Start-up was achieved from room temperature within 17 minutes and the ease of start-up suggested that this time could be significantly reduced. With only 2.5 in. of pressure drop for the complete reformer there should be no difficulty in obtaining a cathode gas blower to supply the air required. Control interfacing will require development, but at this time there does not appear to be any large stumbling blocks. Components developed for this reactor design were instrumental in the successful operation of a 5kW neat methanol reformer on another Army contract (DAAK70-84-C-0099). The alternate system used for the 5kW reformer was a logical outgrowth from the present program and provided additional evidence that the basic concept is viable and a number of systems, as well as, reactor designs are possible. Specific applications and requirements will dictate the preferred design.

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4. RECOMMENDATIONS

4.1 Catalyst Screening and Development

The partial oxidation, reforming, and shift conversion of methanol and its products of combustion have been tested in the compact reformer design developed under this program. It is recommended that further screening and development be conducted to identify improved catalysts for the following functions:

- Lower temperature shift conversion
- Methanol decomposition
- Methanol reforming - minimizing dimethylether production
- Multifuel capability

Areas of improvement desired include:

- Increasing activity at lower temperatures
- Better selectivity to H₂ and CO production
- High activity for other fuels

An improved low temperature shift conversion catalyst is particularly desired in order to reduce catalyst volume requirements. Since shift catalysts are available from various commercial vendors, a screening process is needed to evaluate several candidates at the required conditions.

Improvements in these areas are expected to allow reduction in overall size and weight of methanol fuel processors when incorporated with extended surface heat transfer features, for more compact thermal management.

4.2 Catalyst Configurations

Low pressure drop catalyst configurations with minimum diffusion resistance were investigated under this program. Improvements in catalyst densities in these configurations can potentially result in improved catalyst activity per unit volume of reactor without increasing the pressure drop. Additional

development in this area is required to develop the technology for supporting small catalyst particles in a matrix which allows high catalyst density, low pressure drop, and good heat transfer. In addition, techniques must be developed for producing this catalyst system on a larger scale.

4.3 Reactor Designs

As more testing is conducted with the 3 kW partial oxidation reformer at a fixed set of operating conditions, more will be learned about its operating characteristics. This information can be utilized to suggest further improvements in design which can improve performance, reduce size and weight, simplify construction and possibly extend the system to multifuel capability. Further optimization of the reactor design can be carried out, with possible improvements in the following areas:

- Improvement in thermal management by extended surface for heat transfer, and enhancement of ambient air flow outside the catalyst bed annulus.
- Optimization of platinum loading and configuration of the vaporizer/oxidizer.

Prior to extending these results to new reactor designs, however, an evaluation of system options and reactor designs with respect to specific applications will be required. This effort would identify important areas of development for those applications.

4.4 Reactor Testing

Although there was significant developmental testing and endurance testing, this program did not address the area of system integration. If the reactor developed here is to be incorporated into a power system, several additional areas of testing will be required:

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- Transient response with a fuel cell
- Start-up with a fuel cell
- Cathode recycle blower and methanol fuel control integrated with a fuel cell.

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