

A COMPARISON BETWEEN EXTERNAL AND INTERNAL REFORMING METHANOL FUEL CELL SYSTEMS

Nigel I. Palmer, B. Lieberman and M. A. Vertes

Leesona Moos Laboratories
Division of Leesona Corporation
Great Neck, New York

INTRODUCTION

With the results of several years work in many laboratories now available, it is possible to compare the rather limited number of fuel cell systems capable of operating on carbonaceous fuels. Although many of the approaches are conceptually simple, it must be conceded that none meet the original objectives of ultra-high efficiency and system simplicity. Because of this, it may be misleading to base comparisons only on the characteristics of the central component, i.e., the fuel cell. The object of this paper is to compare designs for two complete 6 kw fuel cell systems operating on methanol and air.

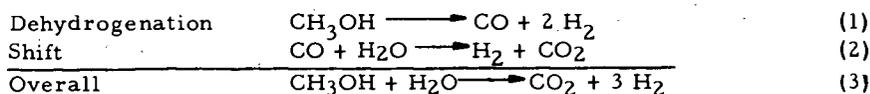
Figure 1 illustrates the basic system options that are available. The direct anodic oxidation approach remains conceptually the most attractive. However, unsolved problems of catalyst cost and stability, corrosion and electrochemical efficiency have so far prevented it entering a development stage. The remaining approaches may all be termed 'indirect' in that the anodic oxidation step involves hydrogen produced from the fuel in a previous stage. System (2), using an acid electrolyte cell retains some of the problems of the direct system; namely, materials and catalyst stability in acid, plus poisoning by trace amounts of carbon monoxide. System (3) which is undoubtedly the most developed, retains the advantages of a basic electrolyte cell by prepurifying the hydrogen -- usually with a palladium/silver diffuser. A variation of this system combining the last two stages by the use of palladium/silver anodes (System 4) has been described by Chodosh and Oswin.⁽¹⁾ More recently, Vertes and Hartner have described an alternative approach⁽²⁾ originally developed at Leesona Moos Laboratories in which the reforming, purification and anodic oxidation steps are integrated within the anode structure (System 5). This is referred to as an 'integral reforming' or 'internal reforming' fuel cell system.

In principle all the systems shown are capable of operating on any carbonaceous fuel. Methanol, however, offers several advantages for fuel cell use, and the systems compared have been designed for this fuel. Significant factors determining this choice were:

1. The favorable thermodynamics of methanol reforming at relatively low temperature.
2. The favorable kinetics and catalyst stability obtained for the methanol reforming reaction.
3. The complete miscibility of methanol and water with resultant simplification of system design.
4. The availability of relatively cheap, high purity methanol.

INTERNAL REFORMING PRINCIPLES

Before discussing the overall systems, it will be necessary to describe briefly the operating principles of the internal reforming electrodes. Figure 2 illustrates the sequential steps involved. An equimolar mixture of methanol and water is vaporized and passed through a catalyst bed contained in a thin plenum chamber behind the palladium/silver membrane. Here dehydrogenation of the methanol occurs first, followed by shift conversion of the resultant carbon monoxide.



Hydrogen from this reaction zone diffuses through the palladium-silver membrane to the electrolyte side where it is anodically oxidized. The 75% palladium/25% silver membrane, 1 mil thick, activated with palladium black⁽³⁾ imposes no restraint on the reaction and limiting currents exceeding 1 amp/cm² have been obtained. The electrolyte employed can in principle be either acid or base, but 85% KOH has been preferred because of its lower vapor pressure, lower corrosion, and the higher performance obtained.

The overall reforming reaction is endothermic. In this system the necessary heat can be supplied directly by the waste heat produced in the cell by entropy and polarization losses. Various side reactions such as the methanation reaction can be suppressed by proper selection of the catalyst. Best results have been obtained using a mixed oxide type catalyst. It may be observed here that because of the physical separation of catalyst from electrolyte, optimization of the catalyst is substantially easier than for a direct oxidation anode. Thermodynamically, conversion to hydrogen is 99% complete at 160°C. The lower temperature limit for operation is established at about this point by kinetic considerations. A higher operating limit of 300°C is established by electrolyte and materials limitations within the cell itself. Selection of the optimum operating temperature requires an analysis of several other interrelated factors and is discussed in a later section on system design.

SYSTEM EFFICIENCIES

The primary reason for using a fuel cell is the high efficiency of energy conversion, although account must be taken of other factors such as weight, volume, capital cost, etc. The priority of these will be determined by the requirements of a particular application.

The net thermal efficiencies of both fuel cell systems can be expressed as functions of the same set of component efficiencies; however, the interrelations and limits of these component efficiencies are quite different for the two cases. Figure 3 shows the location of the points of energy loss - expressed as efficiencies.

The efficiencies considered are:

$$\text{Net system efficiency } \eta_N = \frac{\text{Net electrical energy delivered}}{\text{Heating value of CH}_3\text{OH supplied}}$$

$$\text{Conversion efficiency } \eta_C = \frac{\text{H}_2 \text{ produced in the reformer}}{\text{H}_2 \text{ stoichiometrically available from CH}_3\text{OH/H}_2\text{O}}$$

$$\text{Heat exchange efficiency } \eta_E = \frac{\text{Heat supplied}}{\text{Heat available}}$$

$$\text{Utilization efficiency } \eta_U = \frac{\text{H}_2 \text{ anodically consumed}}{\text{Total H}_2 \text{ produced}}$$

$$\text{Cell thermal efficiency } \eta_T = \frac{\text{Gross electrical energy produced}}{\text{Heating value of H}_2 \text{ consumed}}$$

$$\text{Auxiliaries efficiency } \eta_A = \frac{\text{Net electrical energy delivered}}{\text{Gross electrical energy produced}}$$

Evidently, defined in this way the net system efficiency is expressed as a product of the component efficiencies.

$$\eta_N = \frac{3 \Delta H_{\text{ox}}'}{\Delta H_{\text{ox}}''} \cdot \eta_C \cdot \eta_U \cdot \eta_T \cdot \eta_A \quad (4)$$

where: $\Delta H_{\text{ox}}'$ = lower heating value of H₂ (at cell temperature)
 $\Delta H_{\text{ox}}''$ = lower heating value of CH₃OH (at room temperature)

At any steady operation condition, a state of thermal neutrality must be obtained for the system.

Case I. External Reforming System. The requirement of thermal neutrality is achieved in this system by oxidizing the purge gases from the hydrogen extractor and supplying the heat produced to the reformer. Provision must also be made for removing the cell waste heat which in this system is not utilized. Writing a simplified energy balance for the system,

$$\eta_C \Delta H_R + \Delta H_V = \eta_E \left[(1 - \eta_U) 3 \eta_C \Delta H_{\text{ox}}' + (1 - \eta_C) \Delta H_{\text{ox}}'' \right] \quad (5)$$

where: ΔH_R = heat required to reform methanol, Kcals/g. mole
 ΔH_V = heat to vaporize and superheat methanol and water, Kcals/g. mole

Considering the components of efficiency: The conversion efficiency η_C will have a theoretical limit established by the thermodynamics of reactions (1) and (2). This exceeds 0.99 at 200°C. In practice however, the primary limitation results from kinetic factors, i. e., need to minimize the reformer volume. With external reforming this restriction is not serious and values for η_C as high as 0.95 may be obtained. The cell efficiency η_T has a theoretical limit imposed by the cell entropy losses (approximately 0.9) and a practical limit determined by a tradeoff between the capital cost and operating cost. Since the cell waste heat is not utilized, thermal balance requirements do not impose an additional limit. The auxiliaries efficiency η_A can theoretically approach 1.0 for a simple system; in practice it will be as low as 0.7 in small systems, rising to higher values as the gross power level increases.

The H₂ utilization efficiency η_U has a theoretical limit in external reforming systems, imposed by the need to supply reformer heat. This limit will be determined by the conversion efficiency and the heat exchange efficiency between the catalytic burner and the reformer. The interrelationship between η_U , η_C and η_E is given in equation (5) and is shown graphically in Figure 4. For a given conversion level and heat exchange efficiency, the value of η_U in this graph represents the maximum utilization possible for thermal balance.

Table 1 shows the effect of component efficiencies on the system net thermal efficiency. Three cases are considered; the first refers to ultimate theoretical limits assuming complete reversibility of each component, the second refers to probable practical limits that may be approached, and the third gives state-of-the-art values employed in the present designs. In the second case a limiting operating voltage of 1.0 V is assumed.

Table 1. External Reforming System - Component Efficiencies

Efficiencies		Theoretical Limit	Practical Limit	Present Design (State of the Art)
Conversion	η_C	1.0	0.95	0.91
Cell	η_T	0.9	0.75	0.62
Auxiliaries	η_A	1.0	0.95	0.83
Heat Exchange	η_E	1.0	0.80	0.70
Utilization	η_U	0.78	0.77	0.76
Net	η_N	0.80	0.51	0.40

Case II. Internal Reforming System. Considering now the internal reforming system, it is evident that the same expression (5) for net efficiencies must hold. However, the expression for thermal neutrality is quite different since heat is now supplied by the cell:

$$\eta_C \Delta H_R + \Delta H_V = 3 \eta_C \eta_U \eta_E' (1 - \eta_T) \Delta H_{Ox}' \quad (6)$$

The cell thermal efficiency may be expressed in terms of operating voltage (E):

$$\eta_T = \frac{2 E F}{\Delta H_{Ox}'} \quad (7)$$

Substituting this into equation (6), an expression is obtained relating the conditions for thermoneutrality to the cell voltage:

$$\eta_C \Delta H_R + \Delta H_V = 3 \eta_C \eta_U \eta_E' [\Delta H_{Ox}' - 2FE] \quad (8)$$

The heat exchange efficiency term η_E' is defined essentially as before, but has components which themselves must be optimized for thermal balance;

$$i. e. \eta_E' = \frac{\text{heat produced} - \text{losses to air} - \text{losses to surroundings}}{\text{heat produced}}$$

As in the previous system, no theoretical limits exist for η_C . Because of cell temperature, size, and heat transfer considerations, however, the practical limit for η_C may be lower for internal reforming systems. This is due, it must be emphasized, to kinetic rather than thermodynamic considerations. It may be mentioned at this point that where thermodynamic limitations do apparently occur, as for example with hydrocarbons, they may in practice be circumvented. This results from hydrogen extraction through the membrane,

distorting the equilibrium until complete conversion has occurred. This is discussed more fully elsewhere. (4) (5) With the catalysts currently used at LML, a limit of about 0.9 is obtained for methanol. η_U has no theoretical limit in this system, but a practical limit of 0.97 is probably realistic. η_A tends to be higher for the internal reforming system because of the fewer auxiliaries and simplified controls. Unlike the previous case, η_T is theoretically limited by the requirement of thermal neutrality. Equation (6) shows how this is related to η_C , η_U , and η_E . Figure 5 shows this relationship graphically and indicates that adequate heat is available from the cell even at low heat exchange values. The apparent excess of heat, however, is balanced by losses from the cell which may impose a heat deficit. This is shown in Figure 6, which presents the components of heat balance around the internal reforming cell as a function of gross power output. The heat requirements for reforming are given for the theoretical limit of 100% conversion.

Allowing for heat input to the reformer plus losses to the cathode air streams and to the surroundings, a small heat deficit occurs. This can then be balanced by some form of heat exchange. Two possible schemes considered are: (a) inlet air to outlet air exchange to reduce air cooling; (b) outlet air to inlet methanol to reduce the vaporization load. Alternatively, if η_C is below 0.9, catalytic combustion of the residual fuel in the cell exhaust may be used, e.g., for fuel vaporization. This is the scheme employed in the present design study.

Table 2 shows values for component efficiencies equivalent to those presented in Table 1 for the external reforming system. Note that the heat exchange efficiency η_E is determined by assuming a recovery exchanger efficiency of 75% for the non-utilized cell heat losses. It can be seen that higher overall system efficiencies may be anticipated for the internal reforming system at all levels of development.

Table 2. Internal Reforming System - Component Efficiencies

	<u>Efficiencies</u>	<u>Theoretical Limit</u>	<u>Practical Limit</u>	<u>Present Design (State of the Art)</u>
Conversion	η_C	1.0	0.91	0.84
Cell	η_T	0.73	0.69	0.64
Auxiliaries	η_A	1.0	0.95	0.86
Heat Exchange	η_E	1.0	0.90	0.69
H ₂ Utilization	η_U	<u>1.0</u>	<u>0.97</u>	<u>0.95</u>
Net	η_N	0.83	0.66	0.50

6 KW DESIGN STUDIES

To permit a realistic comparison of the two approaches to be made, design studies of two complete 6kw systems have been made. The normal operating output of 6kw (net) was selected as being appropriate for probable initial commercial applications. The complete systems described have not yet been built, although extensive testing of the components and major sub-systems has been proceeding since 1962. As an example, Figure 7 shows a typical internal reforming bicell composed of two 5" x 5" anodes and a single porous nickel bicathode. Figure 8 shows an experimental 0.5 kw

multicell stack with associated instrumentation.

a. External Reforming: Figure 9 shows a simplified schematic of the external reforming system. Methanol/water is pumped to the reformer where it is first vaporized and then catalytically reformed. The reformer is operated at a temperature of 300°C, a pressure of 75 psig, and a space velocity of 1200 IHSV, † with heat supplied by catalytic oxidation of the extractor purge gases. Product gases, largely H₂ and CO₂ are purified in a palladium/silver diffuser containing 8 ft² of 1 mil foil and maintained at 300°C by the hot gases from the burner. The fuel cell employed operates at 75°C with circulated 5N KOH electrolyte. Both anode and cathode are lightweight "Teflon" †† TFE-fluorocarbon resin bonded electrodes operating at 1 psig differential pressure. In the present system, platinum activation is used but cheaper catalysts are under development. Figure 10 shows the current-voltage characteristic for the cell. Electrolyte-water concentration and temperature are controlled in separate subsystems through which the electrolyte is circulated. The cell module contains a total of 189 cells with a total electrode area of 64 ft² providing a gross power of 7 kw at normal operating load. The net thermal efficiency of the system at operating load is 40%. System specific weight and volume are 97 lbs/kw and 1.1 ft³/kw respectively.

Table 3 summarizes the weights and volumes of the major components.

Table 3. 6 kw External Reforming System - Component Parameters

<u>Component</u>	<u>Weight (lbs)</u>	<u>Volume (ft³)</u>
Fuel Cell	130	1.7
Reformer	61	0.77
Extractor	65	0.53
Battery	87	0.75
Miscellaneous Auxiliaries	<u>239</u>	<u>3.1</u>
Total System -----	582	6.85

b. Internal Reforming: Figure 11 shows a schematic of the internal reforming system. As discussed previously, thermal balance is achieved in the system by catalytic combustion of the cell exhaust gases to vaporize and superheat the methanol/water feed. The thermodynamic and kinetic factors involved in optimization of the cell operating temperature have already been mentioned. Other factors which must be considered are the requirements of heat transfer to the reaction zone and the need to minimize cell volume. As cell temperature is increased, the catalyst activity increases permitting a higher space velocity and thus a thinner catalyst bed for the same conversion level. This also results in increased heat transfer. Analysis of the present system indicated an optimum operating temperature of 225°C. Temperature control of the system is achieved by circulating oil through jackets around the cells. Water of reaction is removed from the cathodes via the excess air on a self-regulating basis. The air is scrubbed before entering the cells to prevent carbonate formation. Figure 12 shows the voltage-current characteristic for the cells. Operating point at rated load is 210 amps/ft² at 0.8 V. 121 cells

 † IHSV is the ideal hydrogen space velocity defined as the volume of hydrogen produced by stoichiometric conversion of the fuel supplied per hour divided by the reactor volume.

†† A DuPont registered trademark.

with a total area of 40 ft² provide a gross normal operating power of 7 kw. System net thermal efficiency at this operating point is 50%. Specific weight and volumes are 80 lbs/kw and 0.57 ft³/kw respectively. Weights and volumes of the major components are summarized in Table 4.

Table 4. 6 kw Internal Reforming System - Component Parameters

<u>Component</u>	<u>Weight (lbs)</u>	<u>Volume (ft³)</u>
Fuel Cell	284	1.5
Battery	87	0.75
Miscellaneous Auxiliaries	109	1.2
Total System ---	480	3.45

OVERLOAD AND CONTROL

The cell operating point is determined by the maximum overload required in a particular operation. In many applications, particularly electro-mechanical, the overload may be high but of relatively short duration. Under such conditions, an optimum for capital cost and size may be obtained by a hybrid combination of fuel cell and secondary battery. This battery supplies transient overloads and is automatically recharged by the fuel cell. The fuel cell itself may then be scaled to satisfy the integrated power requirement (i. e., total kwh/time) while operating at near peak power densities. This approach has been incorporated in both of the present system designs. It may be noted that a battery will in any case be required to provide the start-up power necessary for indirect systems. The battery capacity will be determined by either the overload requirements or the start-up demands. In the present design, lead acid batteries have been specified to provide 5:1 overload capability.

It is impossible in the present discussion to analyze the system controls in detail; however, some of the factors affecting response to varying loads should be mentioned. In a simple hydrogen/oxygen cell supplied from high pressure tanks, response is limited only by gas flow and regulator operation and is therefore quite rapid. With an indirect system, however, the change in load must be transmitted to each of the previous stages. Depending on the capacity and response of these stages, serious control lags may develop. To provide a smoother response, a small hydrogen surge tank has been incorporated in the external reforming design.

The control problem is minimized in the internal reforming system because of the closer integration of the reaction stages. In addition, the high hydrogen capacity of the palladium/silver membrane provides an effective surge capacity corresponding to approximately 6 coulombs/cm². This is roughly two orders of magnitude higher than for a platinum activated electrode.

CONCLUSIONS

An analysis of the various factors presented indicates that a selection between the external and internal reforming systems will depend largely on the requirements of the particular application. It has been shown that substantially higher system efficiencies are possible with internal reforming. This will be

obtained however at the expense of a higher capital cost resulting from the higher palladium content and more expensive materials of construction used in the system. Because of the fewer auxiliaries, the volume of the internal reforming system is substantially smaller, though system weights are similar. The superior response characteristics of this system may be important in variable load applications.

Considering future development, the efficiency of the external reforming system can be improved mainly by increasing cell operating voltages. On the other hand, to further improve the efficiency of the internal reforming system will require development of more active catalysts. This is particularly necessary if operation is to be extended to the use of hydrocarbon fuels. Capital cost reduction will require the use of thinner palladium membranes and higher operating cell current densities. Work along these lines is in progress.

REFERENCES

- (1) H. G. Oswin and S. M. Chodosh, "Fuel Cell Systems," Advances in Chemistry Series 47, p. 61 (1965).
- (2) A. J. Hartner and M. A. Vertes, London A. I. Ch. E. - I. Ch. E. Meeting, June 1965.
- (3) S. M. Chodosh and H. G. Oswin, Brussels Fuel Cell Symposium, June 1965.
- (4) M. A. Vertes and A. J. Hartner, Brussels Fuel Cell Symposium, June 1965.
- (5) D. P. Gregory, Present Symposium, ACS, September 1965.

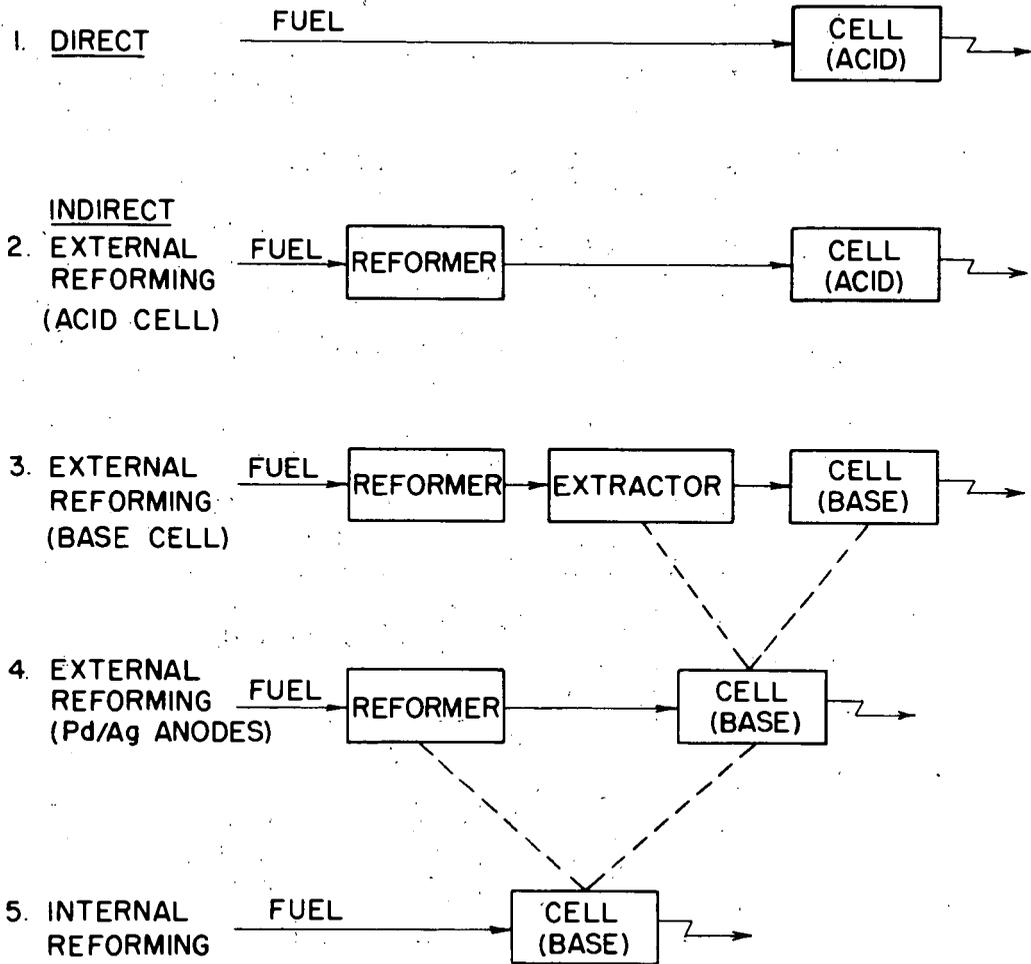


FIG. 1 CARBONACEOUS FUEL CELL SYSTEM OPTIONS

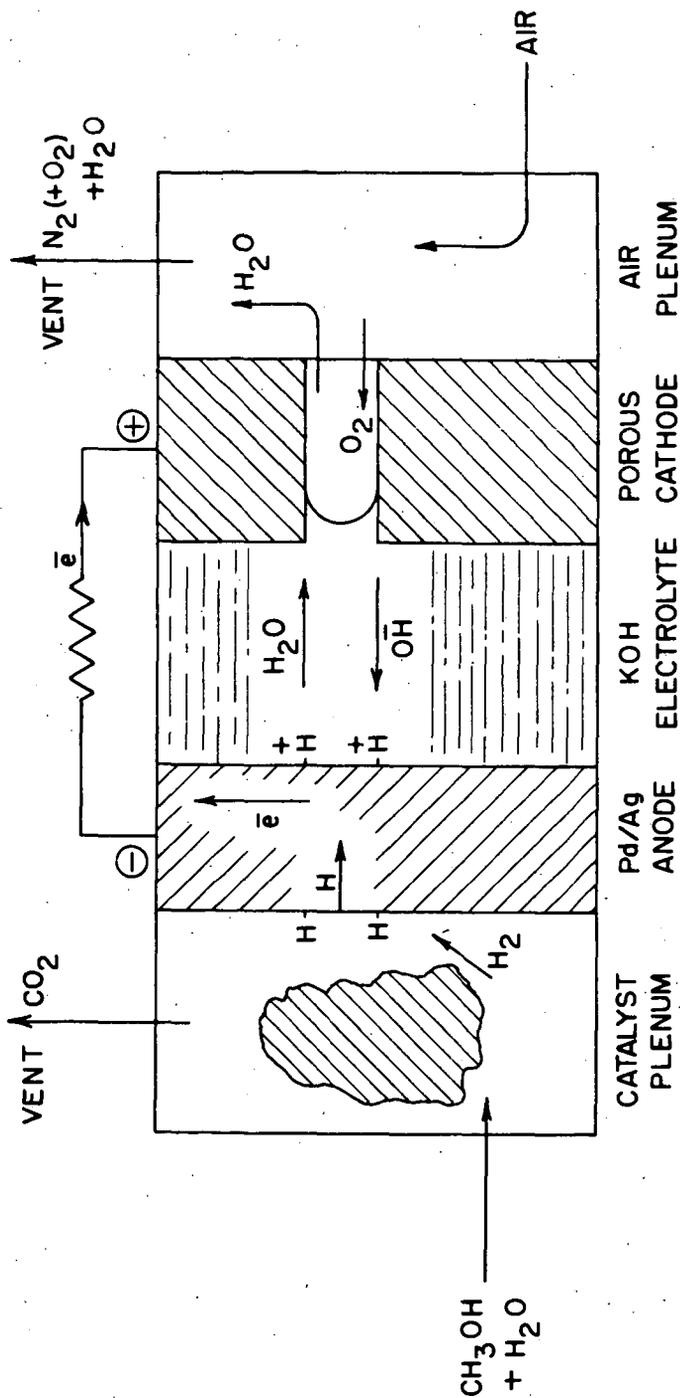
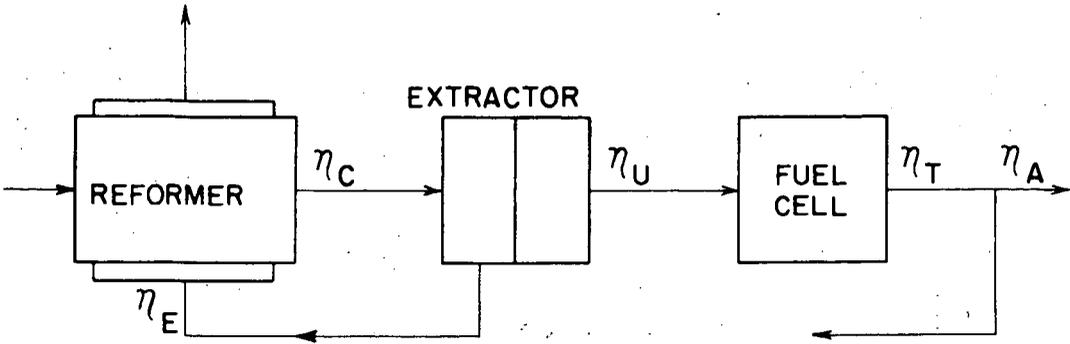
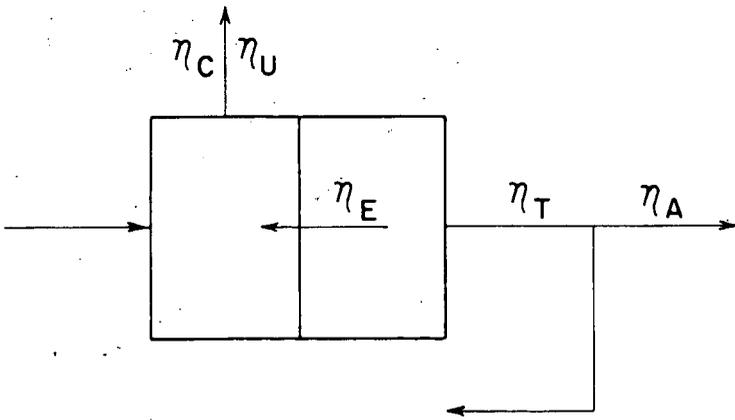


FIG. 2 OPERATING PRINCIPLE OF INTERNAL REFORMING CELL



(a) EXTERNAL REFORMING



(b) INTERNAL REFORMING

FIG. 3 ANALYSIS OF SYSTEM EFFICIENCIES

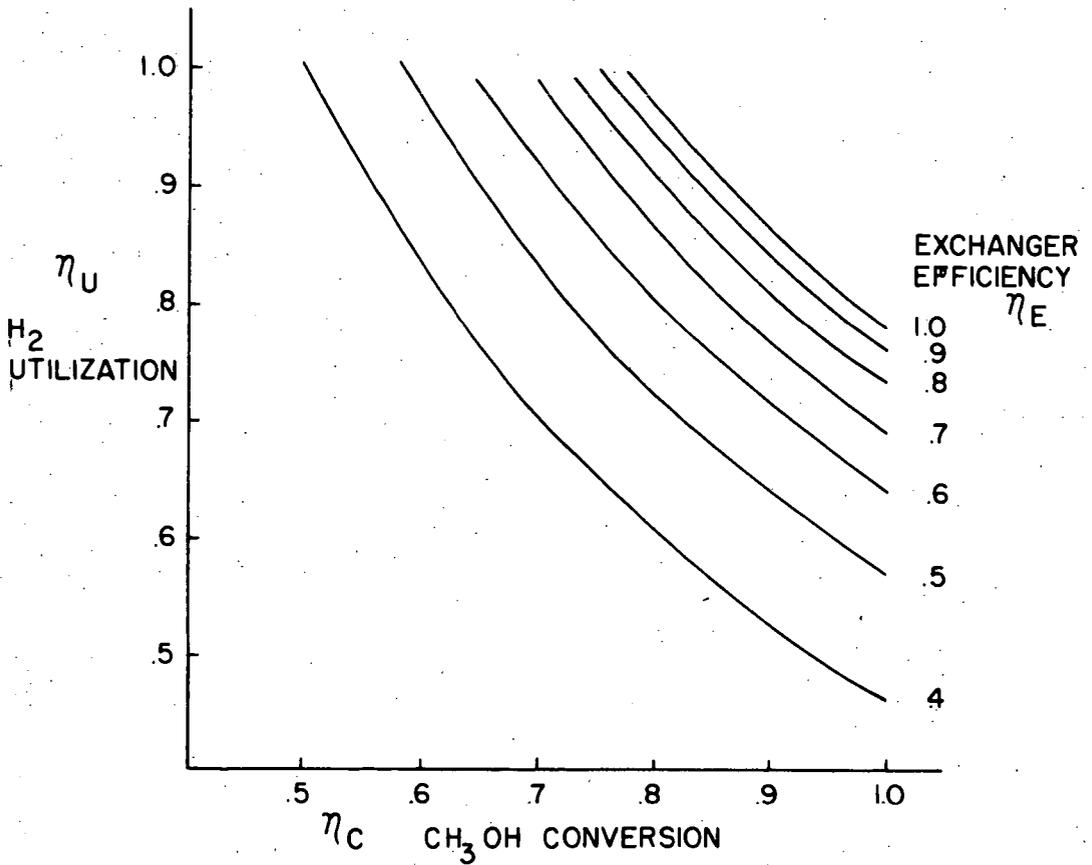


FIG. 4 CONDITIONS FOR THERMAL NEUTRALITY FOR EXTERNAL REFORMING SYSTEM

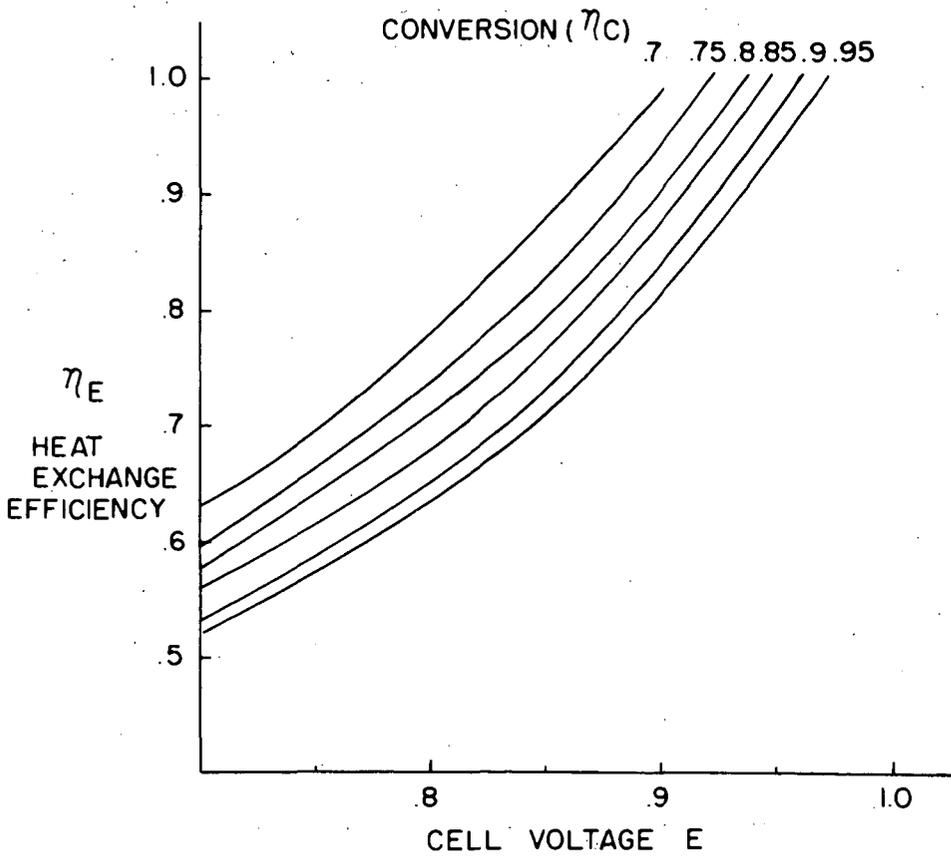


FIG. 5 CONDITIONS FOR THERMAL NEUTRALITY FOR INTERNAL REFORMING SYSTEM

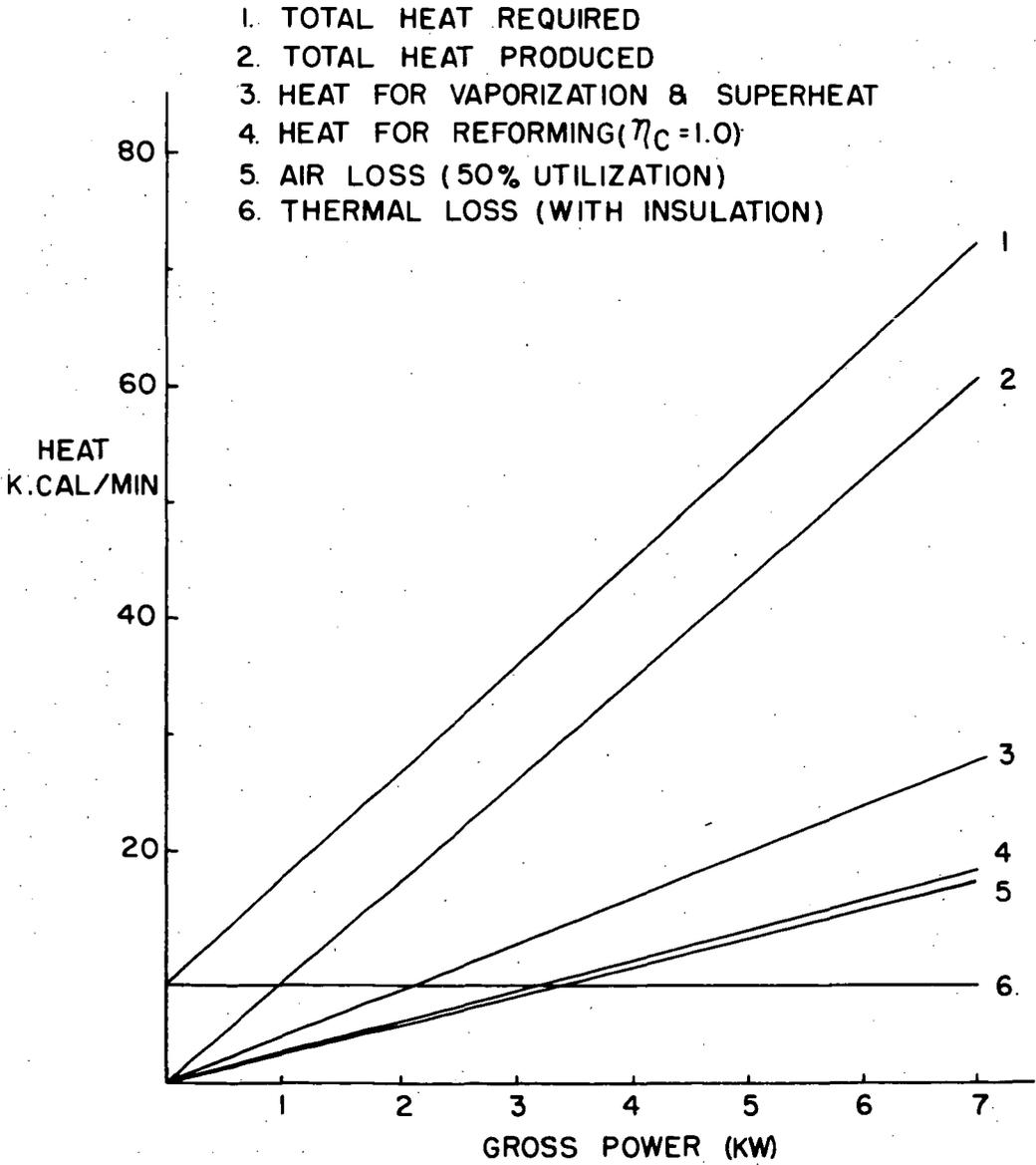


FIG. 6 HEAT BALANCE FOR INTERNAL REFORMING SYSTEM

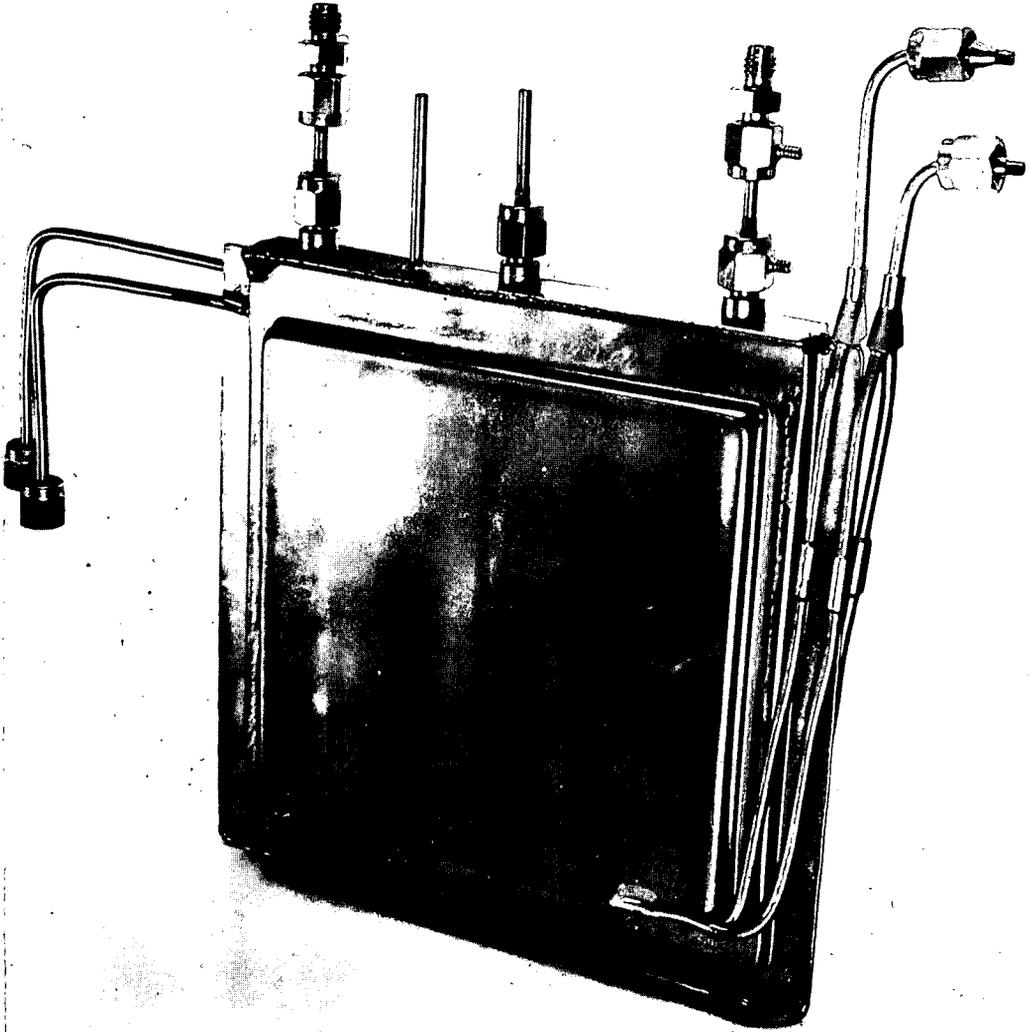


FIG. 7 METHANOL / AIR FUEL CELL

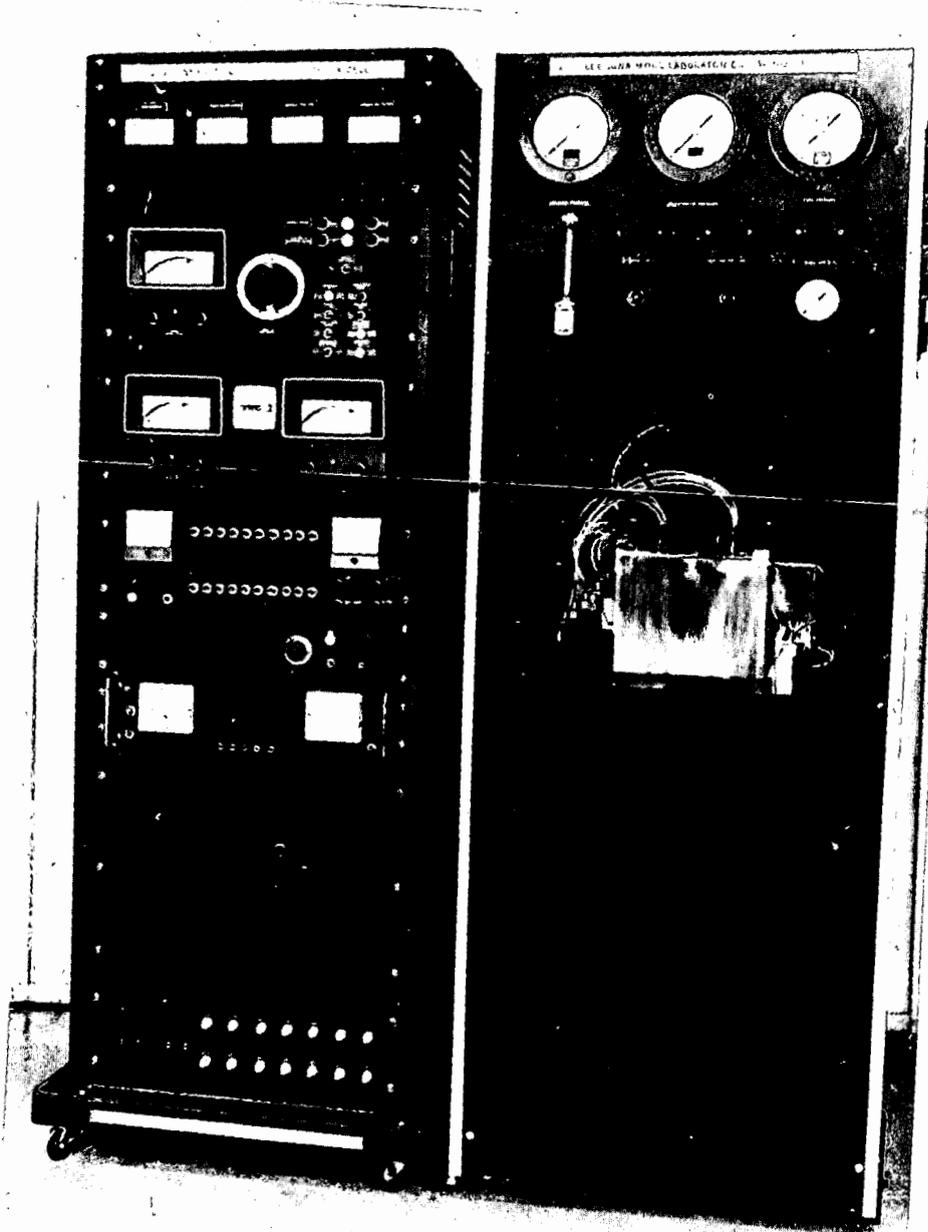


FIG. 8 EXPERIMENTAL 0.5KW INTERNAL REFORMING SYSTEM

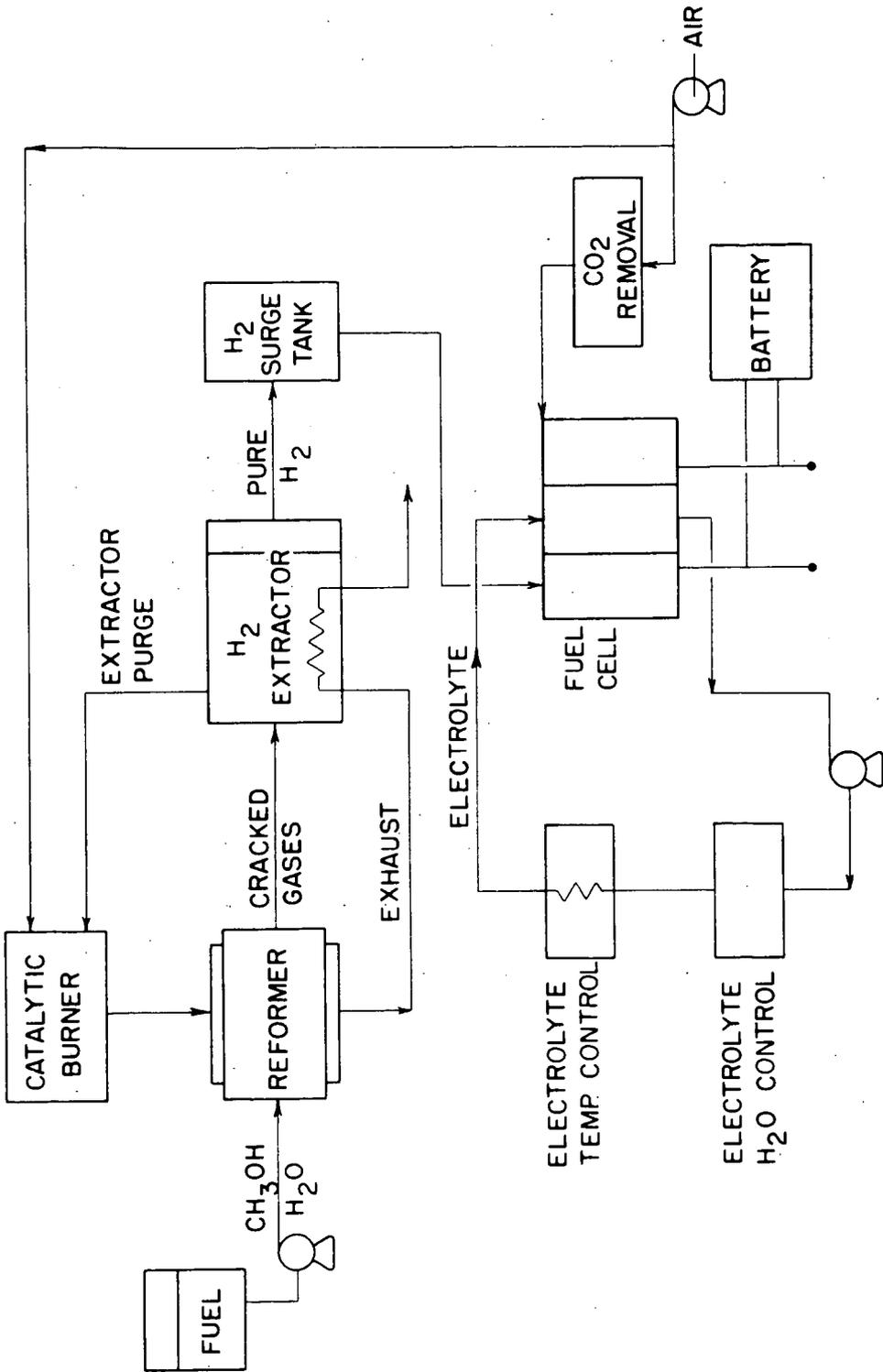


FIG. 9 SCHEMATIC OF EXTERNAL REFORMING METHANOL FUEL CELL

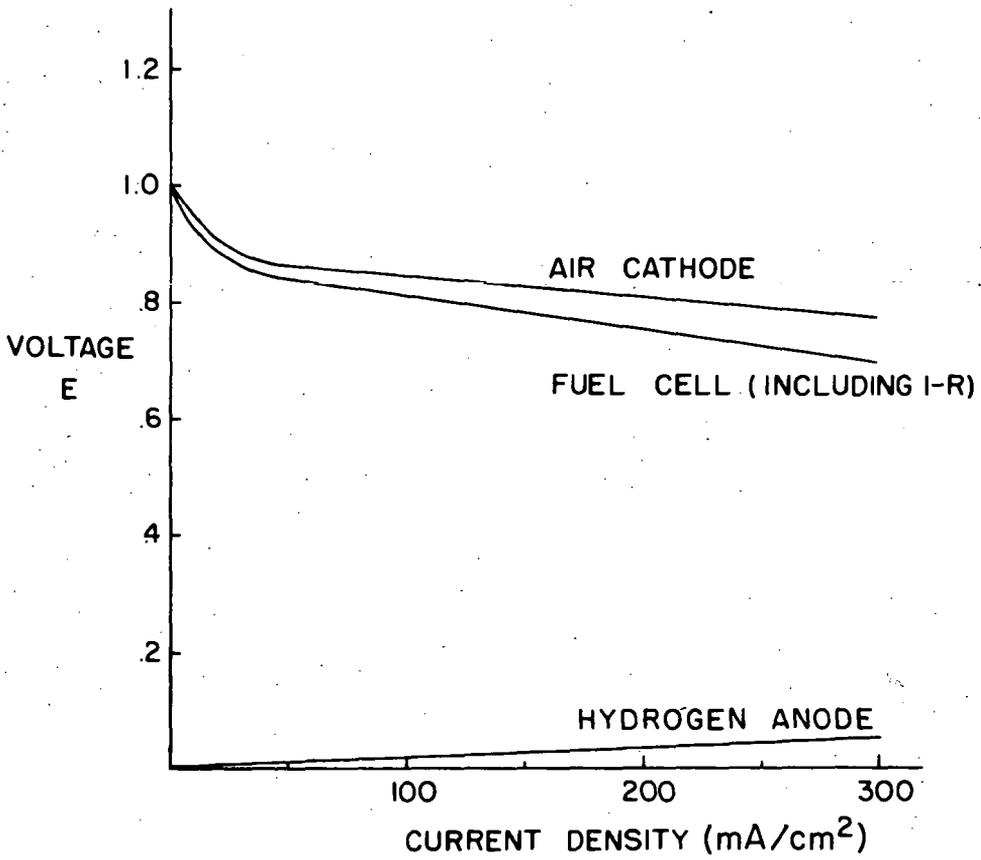


FIG. 10 E/I CHARACTERISTICS - HYDROGEN/AIR CELL

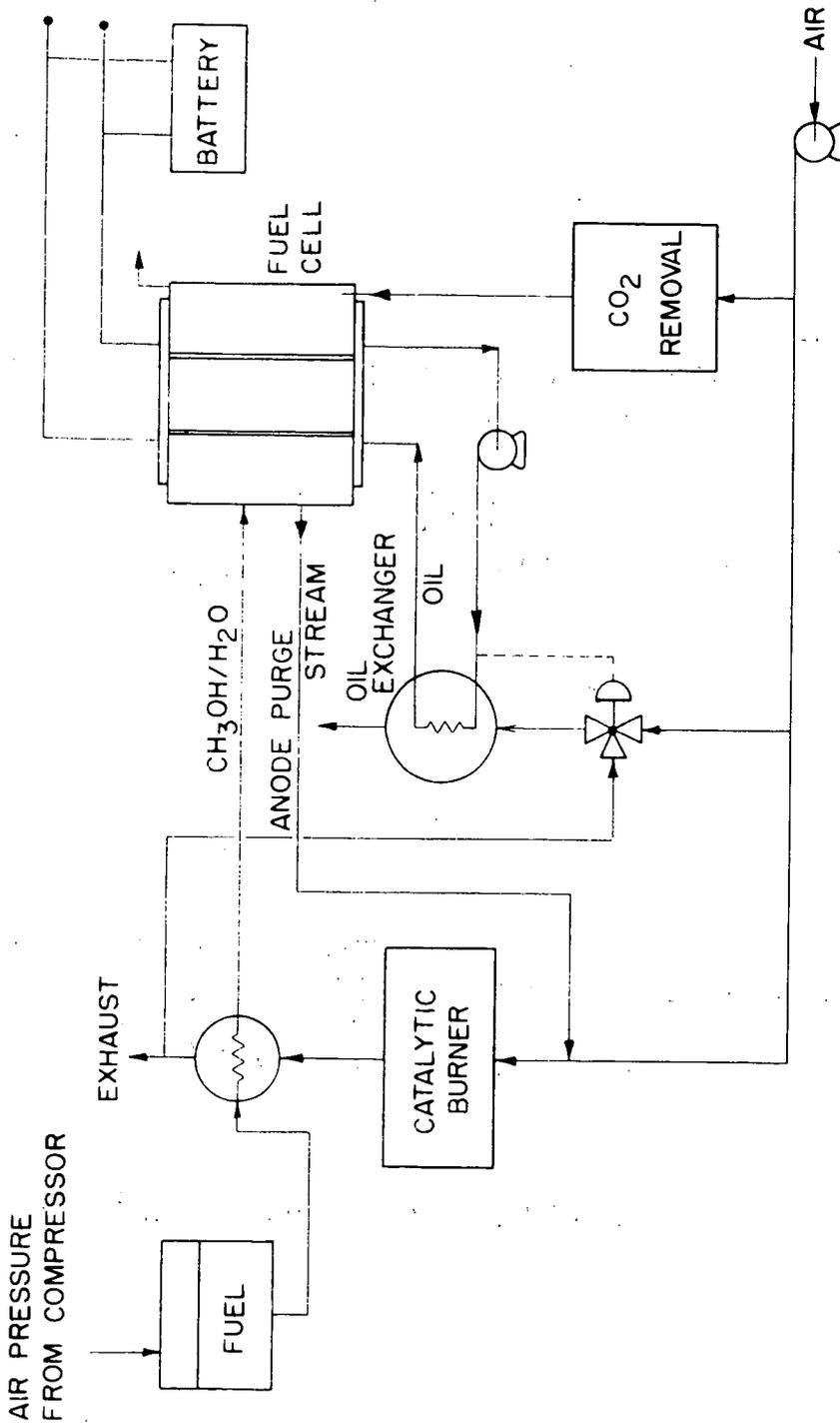


FIG. II SCHEMATIC OF INTERNAL REFORMING METHANOL FUEL CELL

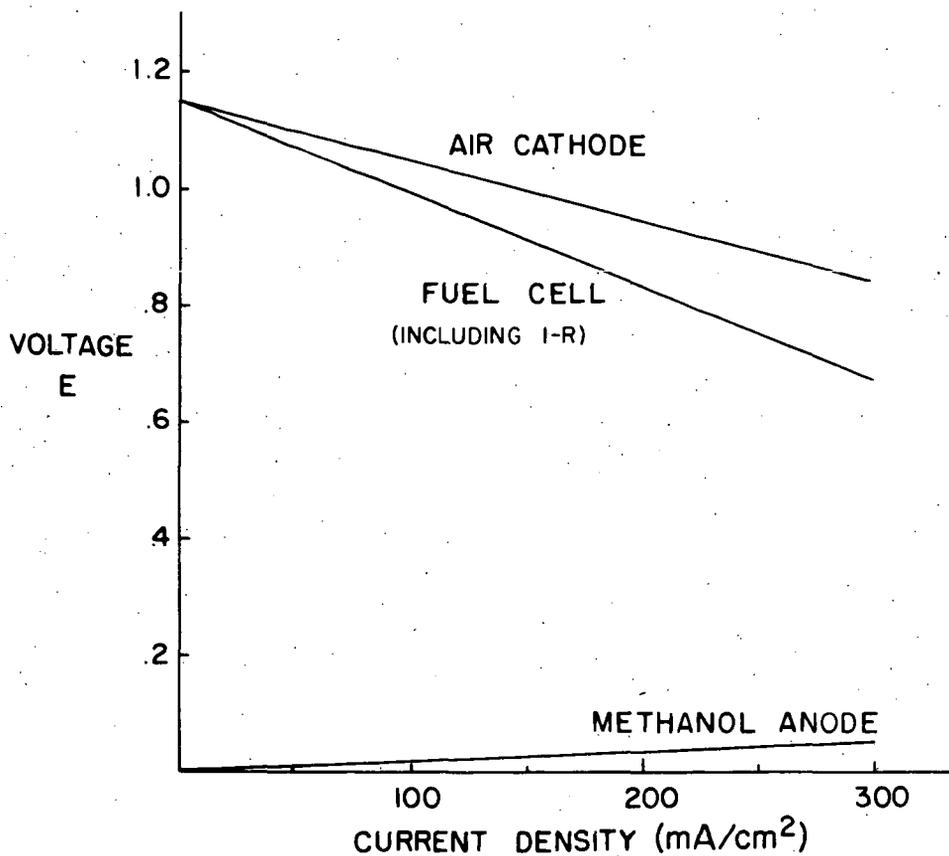


FIG. 12 E/I CHARACTERISTICS-METHANOL/AIR CELL