

## HYDROCARBON-AIR FUEL CELL SYSTEMS

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### INTRODUCTION

In reviewing the state-of-the-art I wish to include all hydrocarbon-air system configurations. This is defined broadly to include all fuel cell systems which utilize a hydrocarbon fuel and an air oxidant. The four variations which have been under investigation at this laboratory are shown schematically in Figure 1.

### EXTERNAL REFORMER INDIRECT SYSTEM

The external reformer indirect systems are based on the use of separate hydrocarbon reformers to liberate the bound hydrogen energy of a liquid hydrocarbon fuel. Hydrogen produced from hydrocarbons by the conventional steam reforming process has been of commercial importance for some time. Only recently, however, has emphasis been placed on simplification and miniaturization of these process plants to become compact hydrogen generators for fuel cell systems. The first hydrogen generators for fuel cell systems which were constructed over the last few years using natural gas, methanol, or JP-4 as the fuel were quite bulky and heavy because they utilized largely state-of-the-art, off-the-shelf type process components. These hydrogen generators, themselves, weighed between 100 and 200 lbs/KW equivalent of hydrogen produced. In one instance, with the Engelhard reformer fabricated under contract to USAERDL, a special fuel and water pump and air blowers were developed to greatly reduce the weight and the electrical power consumed by these auxiliaries. Only recently has emphasis been placed on the design of very lightweight systems. Based on hydrogen reformer systems which are still at the design (Contract DA-44-009-AMC-967(T) with Pratt and Whitney Aircraft) or very early development stage, it is estimated that about 40-45 lbs/KW must be assigned to this major component.

A second major component of an indirect system is the hydrogen-air fuel cell stack or module. Based on electrode performances of greater than 200 amps per square foot at 0.8 volts per single cell, this component should have a weight of 15-20 lbs per KW for a 28 volt stack in the 2-10 KW size range.

A third major component for an a.c. fuel cell powerplant is the combination voltage regulator and inverter. Recent experience with hardware procured by USAERDL indicates that inverter weights are within the range of 10-15 lbs/KW of net a.c. output. By adding together the weights of these major components it is evident that only about 20 to 30 lbs/KW are allowable for the auxiliaries if a

power density of 100-110 lbs/KW is to be obtained for a total a.c. output, fuel cell powerplant. A power density of 100 lbs/KW is roughly that obtained with conventional engine generators.

Therefore, for a fuel cell powerplant to be weight competitive, a major emphasis must be placed on process simplification. Major weight reduction is best achieved by elimination of unneeded components. To cite one example, in an Army fuel cell powerplant for operation in the field, adequate moisture must be reclaimed for use in the steam reformer to avoid the need for makeup water. In the present Allis Chalmers 5 KW system (USAERDL Contract DA-44-009-AMC-240(T)), Figure 2, part of this moisture is reclaimed from the air exhaust, but the major portion comes from the evaporation and condensation in an air stream of water removed from a circulating KOH stream. This requires that a water removal plate be included next to each hydrogen electrode in each single cell to allow the excess moisture to come in contact with and dilute the circulating KOH. In this system part of the water is reclaimed also from the reformer combustion exhaust.

In a much simplified system now being studied (Contract DA-44-009-AMC-967(T) with Pratt and Whitney Aircraft) all of the moisture from the cell is removed in the air exhaust which is used as the combustion air for the reformer burner. A single condenser is therefore all that would be required to condense the required water from the burner exhaust. This simplification would eliminate two condensers, blowers, valves and piping as well as simplifying the cell stack construction.

Future wide application of indirect systems will be dependent on research to achieve greatly improved current densities and to protect the reformer catalyst from the sulfur impurities found in presently available liquid hydrocarbon fuels. Research now in progress indicates that current densities several times the 200 ASF at 0.8 V, which is now state-of-the-art, may be achieved in hydrogen-air cells with very low or no platinum metal content of the electrodes. Likewise, research studies indicate that the "guard catalyst", renewable cartridge, technique may be applicable to protect the compact hydrogen generator catalyst from excessive degradation due to sulfur impurities.

#### INDIRECT ACID ELECTROLYTE SYSTEMS

The description and weight predictions already given are based on a pure hydrogen alkaline electrolyte system which involves a major weight penalty due to the inclusion of a scrubber to remove the small amounts of carbon dioxide present in the incoming air and for a hydrogen diffusion membrane purification system. For an indirect system based on an acid electrolyte hydrogen-air fuel cell module, the carbon dioxide scrubber would not be required and also the possibility exists that an impure hydrogen contaminated with small or moderate amounts of carbon monoxide, may be utilized directly. The attractiveness of the acid electrolyte system, however, depends largely on the power density which can be achieved in the hydrogen-air cell stack and the efficiency with which hydrogen and air can be electrochemically converted in the acid electrolyte system. Because of the

significant system simplifications, research emphasis is being placed on electrode structures and electrocatalysts for the anodic oxidation of hydrogen-carbon monoxide mixtures with air. Under Contract DA-44-009-AMC-479(T) with General Electric a tungsten oxide-platinum black electrocatalyst system has shown high activity for this mixture. Using very thin electrodes and lightweight plastic cell components and a circulating electrolyte coolant, a module of comparable power density to that of an alkaline system may be achieved even with the lower voltages of the acid electrolyte single cell.

#### INTERNAL REFORMER INDIRECT SYSTEM

The principal disadvantages of an external reformer are the need to operate the reformer at temperatures of about 1400°F to produce significant quantities of hydrogen, and the need to control the hydrogen production rate to match exactly the fuel requirements of the cell at all times. The internal reforming cell developed by Pratt and Whitney (Contract DA-44-009-AMC-756(T) for operation with hydrocarbons and air may overcome some of these problems. In this cell, the hydrocarbon-steam reaction occurs in a catalyst bed which is in direct contact with the fuel cell anode. With a concentrated potassium hydroxide electrolyte the cell can be operated at 500°F, at which the equilibrium for hydrocarbon-steam reactions is such that only a small percentage of hydrogen is produced. However, as the fuel cell anode consumes the hydrogen by diffusion through the silver-palladium anode, the equilibrium is shifted so that it is possible to convert a high proportion of the fuel to hydrogen and to utilize this hydrogen in the anode reaction. This type of cell can be more efficient since the endothermic reform reaction takes its heat requirement directly from the waste heat of the cell. Such a system is largely self-controlling since hydrogen is produced only as fast as it is required by the anode.

The status of this system and its ability to utilize hydrocarbon fuels will be discussed in detail in another paper in this symposium.

The principal research problem is to find the optimum reforming catalyst. The catalyst should have very high activity (fast kinetics for the hydrocarbon to hydrogen reaction) at 500°F and be stable for long term operation. The commercially available reforming catalysts designed for higher temperature (1500°F) operation are not necessarily the best for this lower temperature reforming. Serious catalyst activity decay problems have been encountered. The relative attractiveness of the internal reforming hydrocarbon-air system will depend largely on what improvements are possible in the long term stability of the reformer catalysts.

#### PARTIAL OXIDATION OF LIQUID FUELS AND MOLTEN CARBONATE FUEL CELLS

The air partial oxidation of liquid hydrocarbon fuels is insensitive to the fuel type or the amounts of sulfur found in military fuels. Under Contract DA-44-009-AMC-54(T) (Texas Instruments), marine white gasoline, JP-4, kerosene, Number 2 diesel fuel, and CITE engine fuel, ranging in sulfur content from 30 ppm to 3,200 ppm, were successfully converted to electrical power in a partial

oxidation molten carbonate fuel cell system. The unpurified product of partial oxidation is utilized directly in the molten carbonate fuel cell. The sulfur is carried into the anode as hydrogen sulfide but does not adversely affect performance. The molten carbonate electrolyte system, Figure 3, due to its higher temperature of operation tends to be more rugged and heavier than competing systems. The auxiliaries are simplified; no liquid water must be condensed and the stacks can probably be air cooled. The cell stack in this case represents about 50% of the total weight. This means that the current densities which can be achieved are a very important factor in determining the total weight of the system. Today 30 watts/sq ft is routinely achievable and 40-60 watts/sq ft can most likely be achieved by minor engineering improvements. Power densities of greater than 100 watts/sq ft are required, however, if the molten carbonate system is to be competitive in the 3-10 KW power range. Significantly more research emphasis must be placed on understanding the electrode limitations with this mixed fuel and air and the design and testing of more active electrode structures.

#### DIRECT OXIDATION

The status of direct oxidation hydrocarbon fuel cell research and preliminary engineering is being ably discussed by others in this symposium. I wish to add to this only by stressing two major points.

Tremendous progress has been made over the last several years in anodically oxidizing hydrocarbon fuels at an electrode. Whereas, three years ago the ability to oxidize saturated hydrocarbons at lower temperature (150-200°C) and atmospheric pressure was questioned, today 10-15 watts/sq ft with n-octane can be routinely obtained with electrodes with useful lives of over 1000 hours. Twenty watts/sq ft is a legitimate goal for this year. The current density at a cell voltage of 0.5 to 0.6 volts, however, must be greatly increased for a direct oxidation system to become attractive. A several fold increase in current density must be achieved while at the same time greatly reducing the platinum content of the electrodes. The progress has been very encouraging but a tremendous amount of research must still be devoted to understanding the complex nature of hydrocarbon anodic oxidation.

Most of the work to date has been done on pure single component hydrocarbon fuels. Work now in progress is determining the tolerance of electrodes to olefinic, naphthalenic and aromatic components. The future "fuel cell fuel" may not be what we burn in our automobiles today, but economics dictate that it will be a multi-component fuel which can be produced from a petroleum refinery. Greater research emphasis must be placed on the direct oxidation of raffinates and other complex fuel mixtures.

#### CONCLUSIONS

Indirect hydrocarbon fuel cell systems are closest to the hardware stage but require additional research to simplify auxiliary systems, to increase current densities with less costly electrodes, and to protect reformers

from the effect of sulfur impurities present in liquid hydrocarbon fuels. An internal reformer system can achieve major efficiency and control advantages if present research aimed at long life low temperature reformer catalysts is successful. Major current density gains are required for the molten carbonate system to be competitive for portable power plants. Tremendous progress has been made with direct oxidation but much higher current densities must be achieved with multi-component fuels for a practical system.

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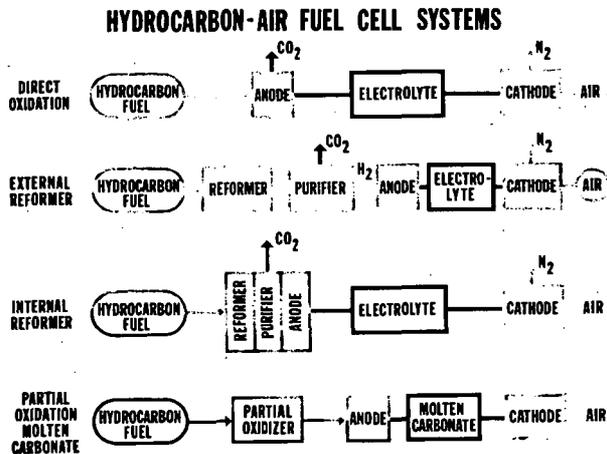


Fig. 1.-ALTERNATIVE HYDROCARBON-AIR FUEL CELL SYSTEMS

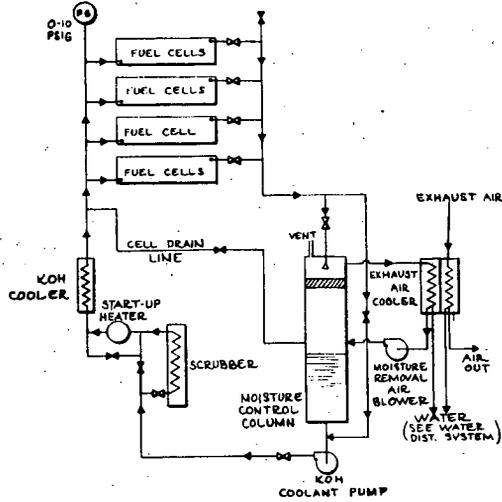


Fig. 2.-MOISTURE SUBSYSTEM

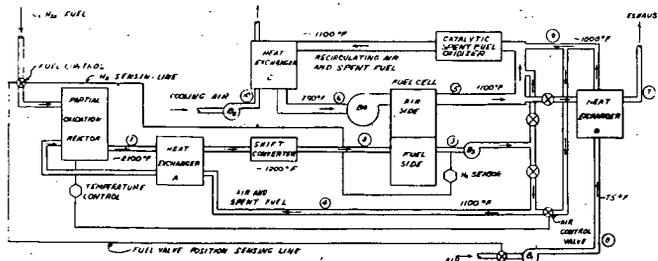


Fig. 3.-PARTIAL OXIDATION-MOLTEN CARBONATE SYSTEM