DOE/MC/26040-3529
(DE94000054)
Distribution Category UC-109

Novel Hydrogen Separation Device Development For Coal Gasification System Applications

Final Report

Work Performed Under Contract No.: DE-AC21-89MC26040

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Energy Research Corporation
3 Great Pasture Road
Danbury, Connecticut 06813

August 1993

ACKNOWLEDGEMENTS

This effort was conducted by Energy Research Corporation (ERC) in collaboration with Fluor Daniel under the direction of the U.S.Department of Energy Morgantown Energy Technology Center (DOE/METC). The DOE/METC project managers were Mr. Richard Johnson and Dr. Venkat Venkataraman.

Fluor Daniel conducted the systems analysis. The Fluor project manager was Jacob T. Jacob, and the principle investigators were Harold Sandler and A.L. Tanner. Energy Research Corporation was the project coordinator and conducted the experimental testing and theoretical modeling. ERC participants included Dr. Mohammad Farooque, A. Kush, Marge Gaylord and Thomas Rostrup-Nielsen. The contributions of all participants is gratefully acknowledged.

EXECUTIVE SUMMARY

This study was undertaken for the development of a novel Electrochemical Hydrogen Separator (EHS) technology for low-cost hydrogen separation from coal derived gases. Design and operating parameter testing was performed using subscale cells (25 cm^2). High H_2 purity, >99%, is one of the main features of the EHS. It was found that N_2, CO_2 and CH_4 behave as equivalent inerts; EHS performance is not affected by the balance of feed gas containing these components. This product purity level is not sacrificed by increased H_2 recovery. CO, however, does adversely affect EHS performance and therefore feed stream pretreatment is recommended. Low levels of H_2S and NH_3 were added to the feed gas stream and it was verified that these impurities did not affect EHS performance.

Task 2 demonstrated the scale-up to full size multi-cell module operation while maintaining a stable energy requirement. A 10-cell full-size module (1050 cm^2 cell active area) was operated for over 3,800 hours and gave a stable baseline performance.

Several applications for the EHS were investigated. The most economically attractive systems incorporating an EHS contain low pressure, dilute hydrogen streams, such as coal gasification carbonate fuel cell systems, hydrogen plant purification and fluid catalytic cracker units. In addition, secondary hydrogen recovery from PSA or membrane tailstreams using an EHS may increase overall system efficiency.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. PROJECT OBJECTIVE

The objective of this project is to develop an electrochemical hydrogen separation device for cost-effective hydrogen recovery from coal derived gases. The potential applications are high purity hydrogen recovery from oxygen and air blown gasifiers as well as hydrogen-lean streams such as carbonate fuel cell anode exhaust.

In this program, the effect of design and operating parameters (i.e., pressure, temperature, H_2 recovery and electrochemical catalyst loading) on electrochemical hydrogen separator (EHS) performance were characterized in single subscale cells (25 cm^2 active area) and used to develop a mathematical model. Scale-up, (1050 cm^2) multi-cell stack operation was also demonstrated. An analysis of potential applications was made which compared the EHS with existing separation systems.

2. TECHNICAL BACKGROUND

The EHS is an electrochemical hydrogen separation device based on the uniquely reversible nature of hydrogen oxidation-reduction reactions in electrochemical systems. The design is an offshoot of phosphoric acid fuel cell (PAFC) development. EHS operating principle and hardware concept are shown in Figure 1.

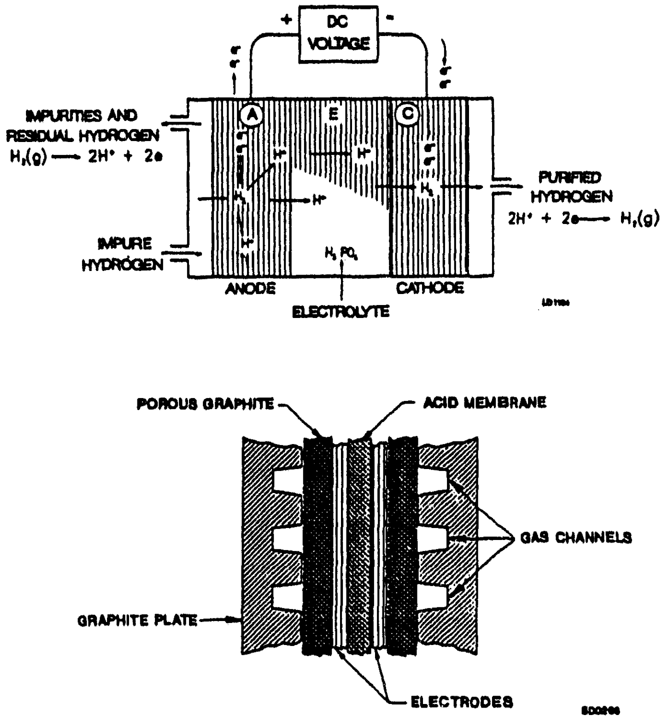


FIGURE 1. SCHEMATIC OF AN ELECTRO-CHEMICAL SEPARATION DEVICE: The Highly Reversible Hydrogen Oxidation-Reduction Reactions are Utilized for Efficient Hydrogen Separation Employing Cheap Carbon-Based PAFC Technology

Hydrogen from the impure hydrogen stream is oxidized to H^+ ions, transported through a cation transport electrolyte membrane under an applied electric field and discharged in a pure hydrogen state on the cathode. (The cation transfer electrolyte membrane also provides a barrier between the feed and product gases.)

Although any proton transfer electrolyte can be used, the phosphoric acid based system offers a unique advantage because of its operating temperature of ~200°C, which closely matches the gas exiting the water-shift reactor (~250°C).

Hydrogen-containing streams in coal gasification systems have large carbon monoxide contents. For efficient hydrogen recovery, most of the CO must be converted to hydrogen by the low temperature water-shift reaction (Figure 2). The residual CO has a very minor effect on the operation of the EHS.

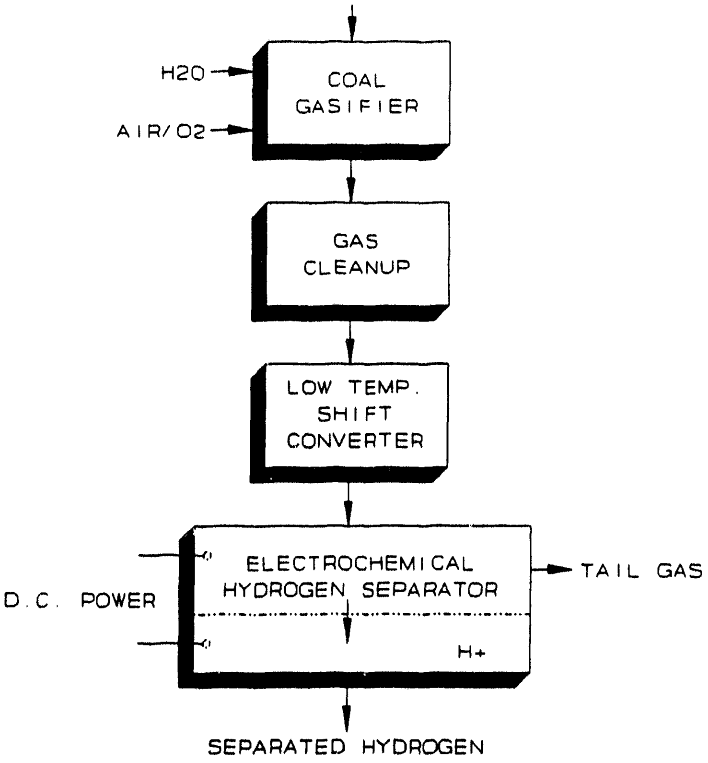


Figure 2. SCHEMATIC OF BULK SEPARATION FROM COAL GASIFIER STREAMS

Advanced coal gasification and gas separation technology offer an important pathway to the clean utilization of coal resources in the United States. Hydrogen is used today as a major chemical feed stock and is expected to play an ever-increasing role in the future. Thus, the separation technology for recovering hydrogen from coal gasification processes containing 20 to 60% H_2 is greatly needed.

Commercial and developmental processes known today can be grouped into the following process types:

- Solvent systems based on selective absorption
- Pressure swing absorption in a packed sorbent bed
- Cryogenic methods
- Semipermeable membranes

These processes operate at moderate to low temperatures and require high pressures. None of these processes are considered very economical for hydrogen-lean streams as encountered in coal gasification (20% hydrogen in air blown) systems. This presents the need for novel concepts to efficiently achieve bulk separation of gases at moderate to high temperatures (100° to 700°C).

The electrochemical hydrogen separation device, under development at ERC, has several attractive features as follows:

- The operating temperature (~200°C) is compatible with product gas from low temperature shift reactors.

- Atmospheric as well as elevated pressure can be used, and there is no pressure loss in the system; product H_2 is available at the feed stream pressure.

- Recovery of 90% H_2 from feed streams containing less than 10% hydrogen is feasible.

- The product H_2 purity is >99% (dry basis) and is virtually independent of H_2 concentration in the feed gas.

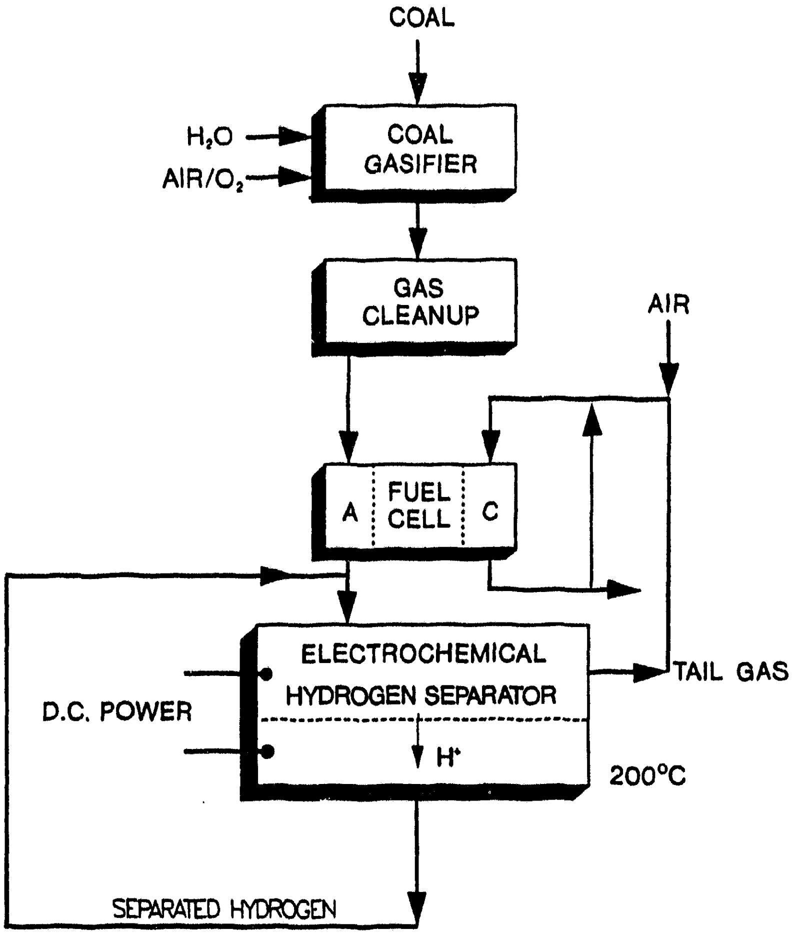
- The EHS operates in a continuous manner; no equipment regeneration is required.

- Low energy cost: Depending upon the operating conditions, the energy requirement varies between 2 and 6 kWh/1000 SCF of recovered hydrogen.

Studies under DOE/METC contract DE-AC01-87MC23274 have indicated that by using the EHS, unreacted hydrogen from the carbonate fuel cell anode exhaust can be economically recovered and recycled as shown in Figure 3. The projected energy efficiency of a carbonate fuel cell power plant containing an EHS is increased from 54% to 60% based on the lower heating value of natural gas.

3. PROJECT DESCRIPTION

To accomplish the program objective, the work was broken down into three tasks. In Task 1, the effects of design and operating parameters on EHS performance were evaluated using single subscale (25 cm^2) cells. A mathematical performance model was developed for design calculations. Task 2 involved the demonstration of scale-up, multi-cell operation and product quality. The EHS system was compared with a competing separation technology in Task 3.



LD1153a

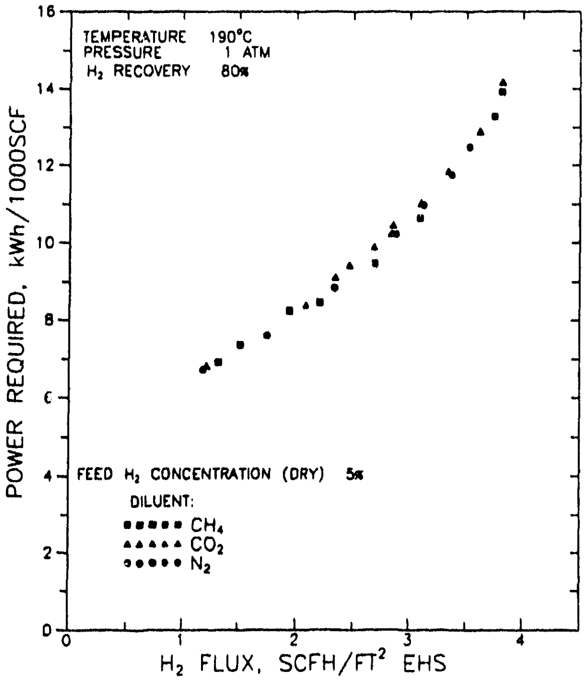
Figure 3. CARBONATE FUEL CELL SYSTEM CONCEPT: H_2 Recovery from Carbonate Fuel Cell Anode Exhaust Improves Plant Efficiency

3.1 DESIGN AND OPERATING PARAMETER EVALUATION

The design and operating parameters (temperature, pressure, membrane thickness, electrode Pt content, H_2 feed content, feed gas impurities, current density, and hydrogen recovery) evaluated in Task 1 are presented in Table 1. It was established that EHS performance is not affected by the balance of the feed gas, whether CH_4, N_2, or CO_2 (Figure 4). This is an important feature of the EHS because, unlike other separation devices, EHS product hydrogen purity and recovery are independent of the relative concentrations of other major components in the feed gas. The EHS can be used with air or oxygen blown gasifier exhaust (with a typical dry composition range of 30-60% H_2, 1-45% N_2, 24-35% CO_2, 1-4% CH_4), as well as methane producing gasifiers (with an approximate dry composition of 26% H_2, 18% N_2, 29% CO_2, 27% CH_4). It was also verified that the EHS is capable of recovering 90% H_2 with a purity of greater than 99% from low hydrogen concentration streams

Table I. TASK 1 EHS DESIGN PARAMETERS AND EVALUATION RANGES

PARAMETER	RANGE	UNIT
TEMPERATURE	190 200 220	°C
PRESSURE	1 THROUGH 10	Atm
MEMBRANE THICKNESS	0.2 THROUGH 0.4	mm
ANODE Pt CONTENT	0.2 THROUGH 0.55	mg Pt/cm^2
CATHODE Pt CONTENT	0.2 THROUGH 0.55	mg Pt/cm^2
H_2 FEED CONCENTRATION	5 10 30 60	mole %
FEED GAS IMPURITIES, (H_2S, NH_3)	3 TO 10	ppm
CURRENT DENSITY	UP TO 400	mA/cm^2
HYDROGEN RECOVERY	UP TO 90	%



JF0025

Figure 4. EHS PERFORMANCE WITH VARIOUS DILUENTS: 80% Recovery is Feasible with Dilute H_2 Containing Streams; CH_4, CO_2, and N_2 Behave as Equivalent Inerts.

such as carbonate fuel cell anode exhaust. This product purity increases with rate of recovery which signifies that high product hydrogen purity is not sacrificed by high hydrogen recovery (Figure 5).

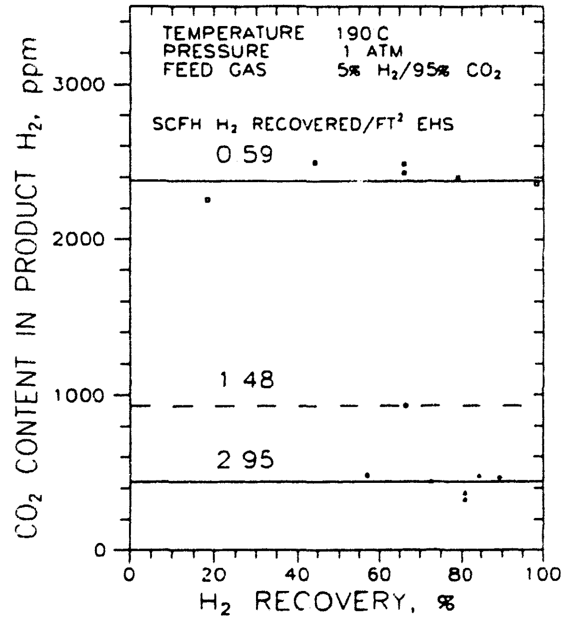


Figure 5a. PRODUCT PURITY vs. H_2 RECOVERY

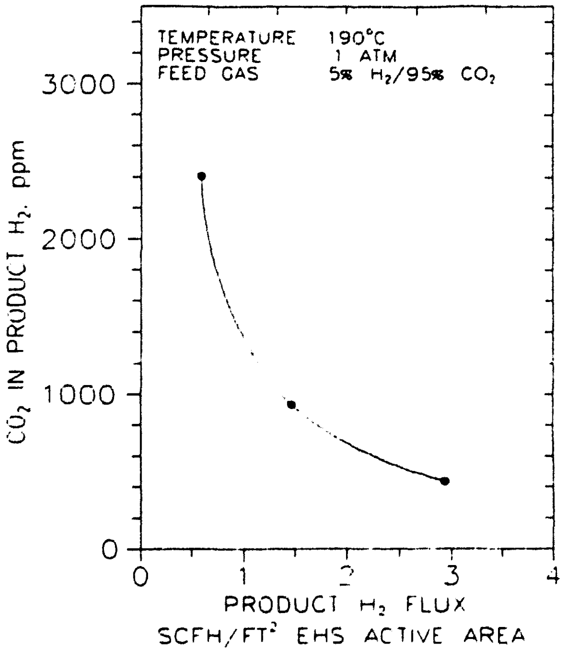


Figure 5b. PRODUCT PURITY vs. FLUX

H_2 Product Purity Increases With H_2 Recovery Rate

EHS performance is affected by the presence of CO in the feed stream and is dependant on H_2 and CO content as well as the H_2 recovery (Figure 6). This effect is greater with low H_2 concentrations which indicates that pretreatment to reduce CO content in the feed gas is beneficial to the EHS system.

Several design parameters of the EHS were investigated. It was determined that lowering the electrode platinum content from 0.5 to 0.26 mg Pt/cm^2 did not affect EHS energy requirement. This results in a reduction of EHS capital cost. The EHS membrane produces a resistive power demand which increases proportionally with membrane thickness. It was established that the membrane remains effective at a thickness in the range of 0.2-0.3 mm and therefore reduces the resistive energy demand.

A mathematical model was developed to predict EHS power consumption for gases containing as low as 5% hydrogen. This model fits well with experimental data as shown in Figure 7. A well-developed model is an essential tool for plant design calculations and economic analysis.

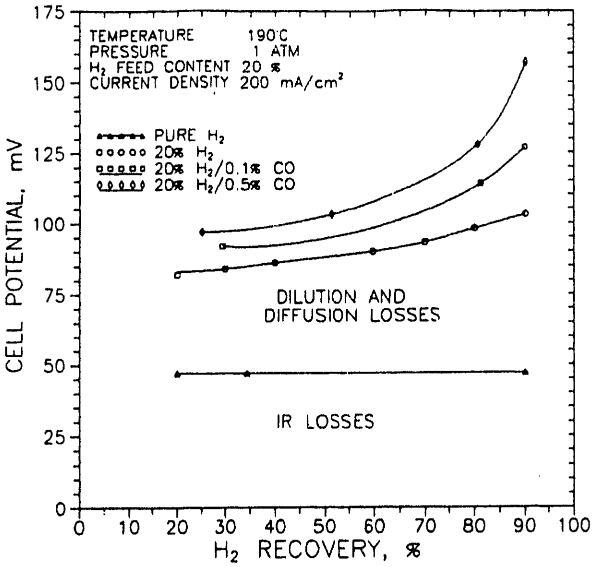


Figure 6. EFFECT OF CO FEED CONTENT ON EHS POWER
CO Feed Content and H_2 Recovery Increase Power Demand

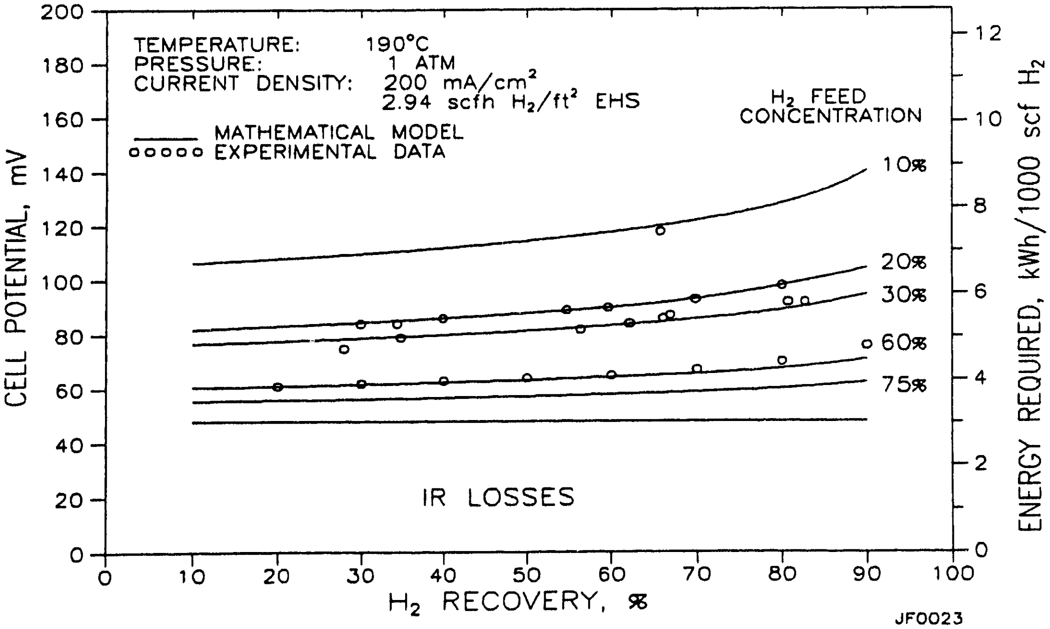


Figure 7. ESTIMATED PERFORMANCE FOR EHS
The Mathematical Model is in Good Agreement with EHS Experimental Results in a Range of H_2 Concentrations

EHS performance at various pressures was evaluated using several feed streams (Figure 8). Increasing operating pressure above atmospheric may reduce the electrical resistance of the EHS

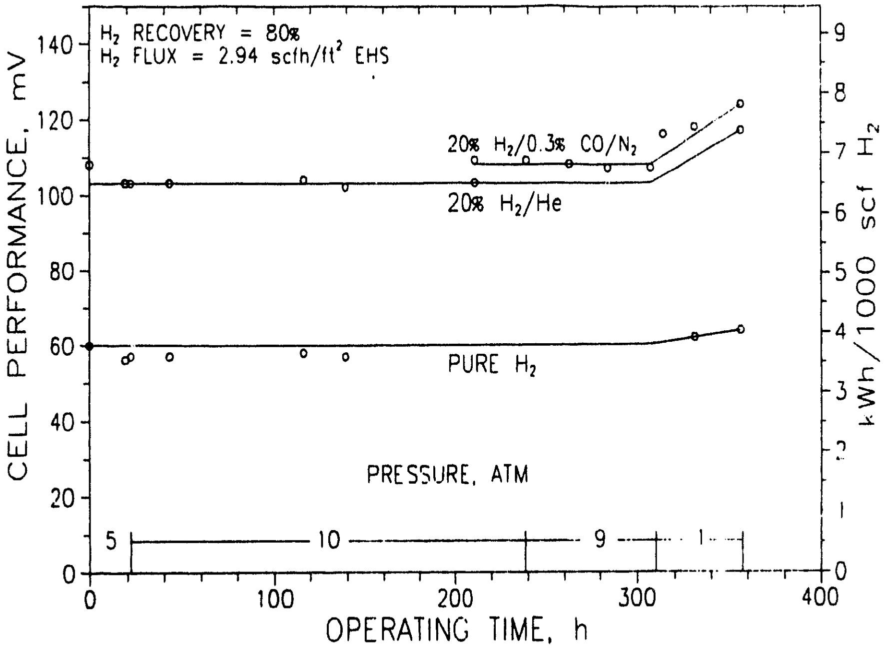


Figure 8. EHS PERFORMANCE AT VARIOUS PRESSURES
EHS Performance is Not Affected by Pressure

and therefore show an initial decrease in required energy. Varying the pressure above one atmosphere does not affect the EHS energy demand.

The effect of temperature on EHS energy consumption was established. As expected, the power demand decreases as operating temperature increases (Figure 9). This is an important attribute of the EHS system because it operates at temperatures closely matching that of the gas exiting the water gas shift reactor and also adds versatility to the EHS operating system.

Studies were also conducted using feed streams containing trace quantities of NH_3 and H_2S. Research conducted on PAFC operating conditions has established that these impurities adversely affect fuel cell performance. As trace quantities of these components may be present in coal gasifier product streams, their effect on EHS performance was investigated.

Hydrogen sulfide is present in coal gasifier streams in concentrations ranging from 200 to <1 ppm, depending on the gas cleanup systems employed. Previous work by Ross established that phosphoric acid fuel cells can tolerate 10 ppm H_2S in CO-containing fuels without performance degradation, however rapid cell failure occurs if the H_2S concentration is increased to 47 ppm.

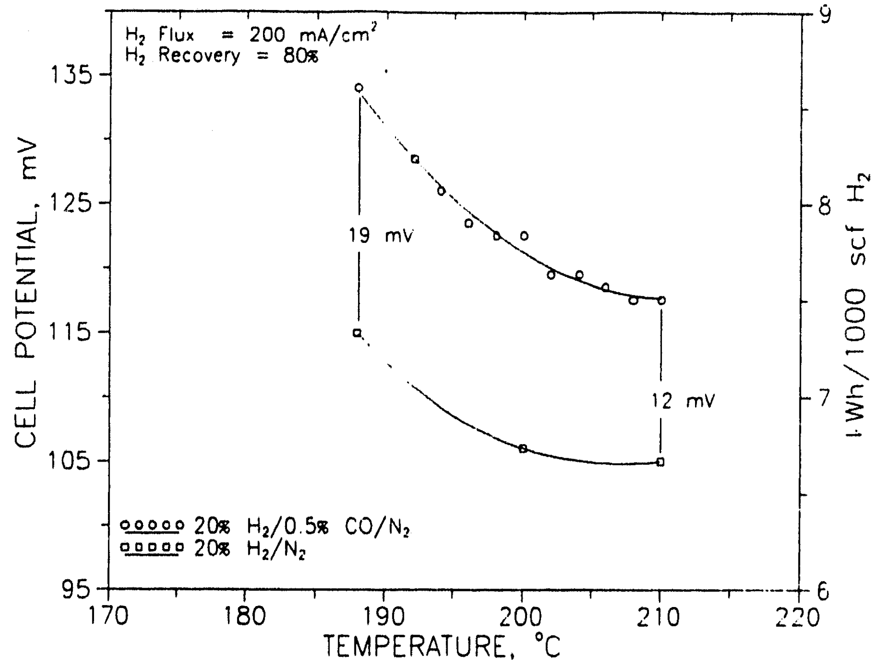


Figure 9. EFFECT OF TEMPERATURE ON EHS PERFORMANCE
Increasing the Operating Temperature Decreases EHS Power Requirement

The sulfur tolerance of the EHS was investigated using a variety of feed compositions containing up to 10 ppm H_2S. The results, listed in Table II, verify that EHS performance is not affected by low levels of H_2S, and there is no synergistic effect of H_2S and CO at these low impurity levels. EHS performance remained stable at various H_2 flux using the H_2S/CO feed stream as shown in Figure 10.

Table II. Comparison of EHS Performance Using H_2S Containing Feed

Feed Composition	Neat H_2		32% H_2/0.23% CO	
H_2S Concentration, ppm	10	0	2	0
Energy Required, mV	66	67	121	121

The presence of H_2S in the feed stream will affect the purity of the product hydrogen stream. H_2S was detected in the product hydrogen stream; this is due to the high solubility of the H_2S in the electrolyte.

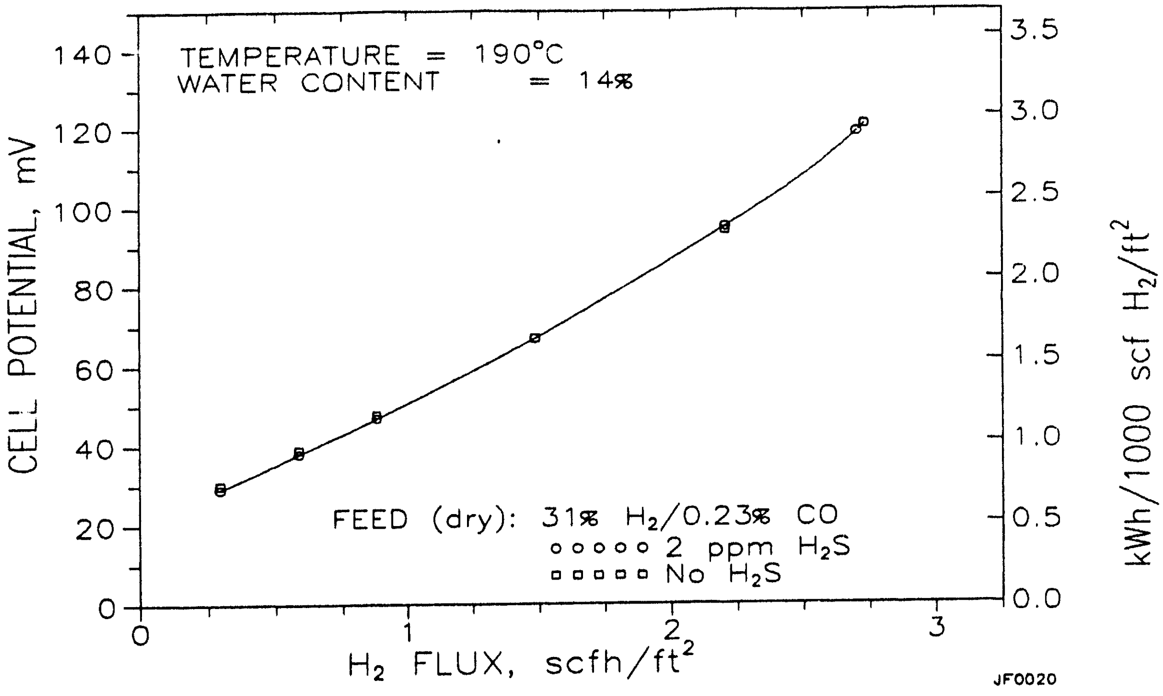


Figure 10 EHS Performance at Various H_2 Using H_2S/CO Containing Feed

The effect of ammonia in EHS feed gas on the energy requirement was also investigated. PAFC studies have shown that performance losses occur with trace levels of ammonia-containing feed. The majority of the performance losses are attributed to a reduction in the rate of O_2 reduction on the cathode catalyst. At EHS operating conditions, there is no oxidant supplied and therefore this is not a problem. However ammonia reacts with the phosphoric acid to form ammonium dihydrogen phosphate. This decreases the conductivity of the electrolyte and may therefore decrease cell performance. This effect is greatest at high acid concentrations and, as the EHS typically operates at high acid concentrations, NH_3-containing fuel may lead to some performance loss in the EHS.

The effect on EHS performance of NH_3-containing fuel was investigated in subscale cell tests. Two feed gases were tested, one containing 2.6 ppm NH_3/23% H_2 and the other a straight hydrogen stream with 10 ppm NH_3. As shown in Figure 11, the EHS performance did not change due to the addition of NH_3. Stable performance was observed in the short term stability tests conducted with the different NH_3 concentration feed gases.

Long-term stable EHS operation in subscale cells has been demonstrated. A subscale EHS cell operated for over 4,400 hours on a variety of feeds and at stringent operating conditions (Figure 12). The energy requirement remained stable throughout its

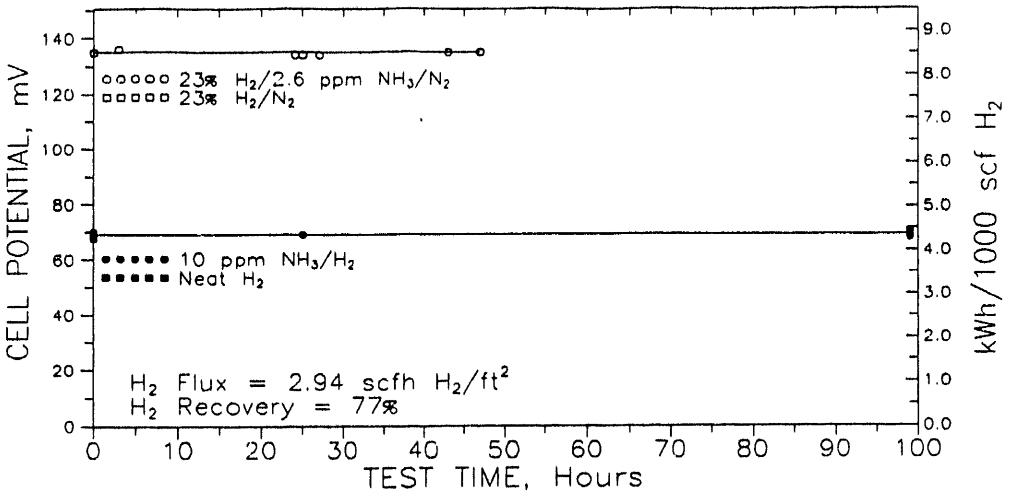


Figure 11. EHS PERFORMANCE WITH AMMONIA CONTAINING FEED
There is No Change in Performance Due to the Presence of NH_3

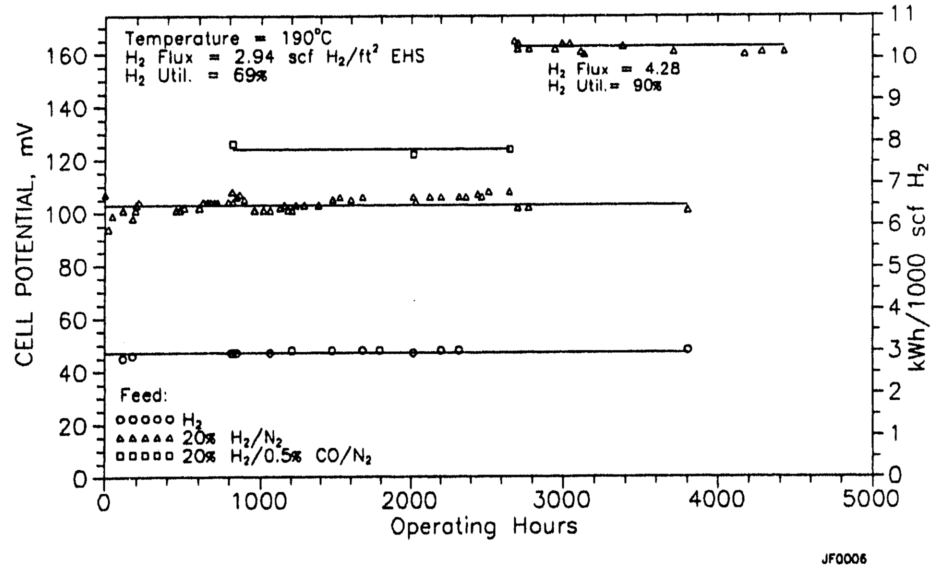


Figure 12. STABLE LONG-TERM PERFORMANCE DEMONSTRATED
EHS Performance Stability In Subscale-Cells Demonstrated at Increased H_2 Flux and Recovery

operating life, illustrating the continuous operability of the EHS concept.

3.2 MULTI-CELL MODULE OPERATION

The scale-up capability of the EHS was demonstrated in Task 2 through the testing of a ten-cell module. The module concept is shown in Figure 13, and a photograph of the tested module is shown in Figure 14. The feed gas to the module passes through a manifold supplying each cell simultaneously. The electric current of the module is set up so each cell is connected in series. The active area of each cell is approximately 1060 cm^2 as compared with the 25 cm^2 area of the subscale cells used in Task 1.

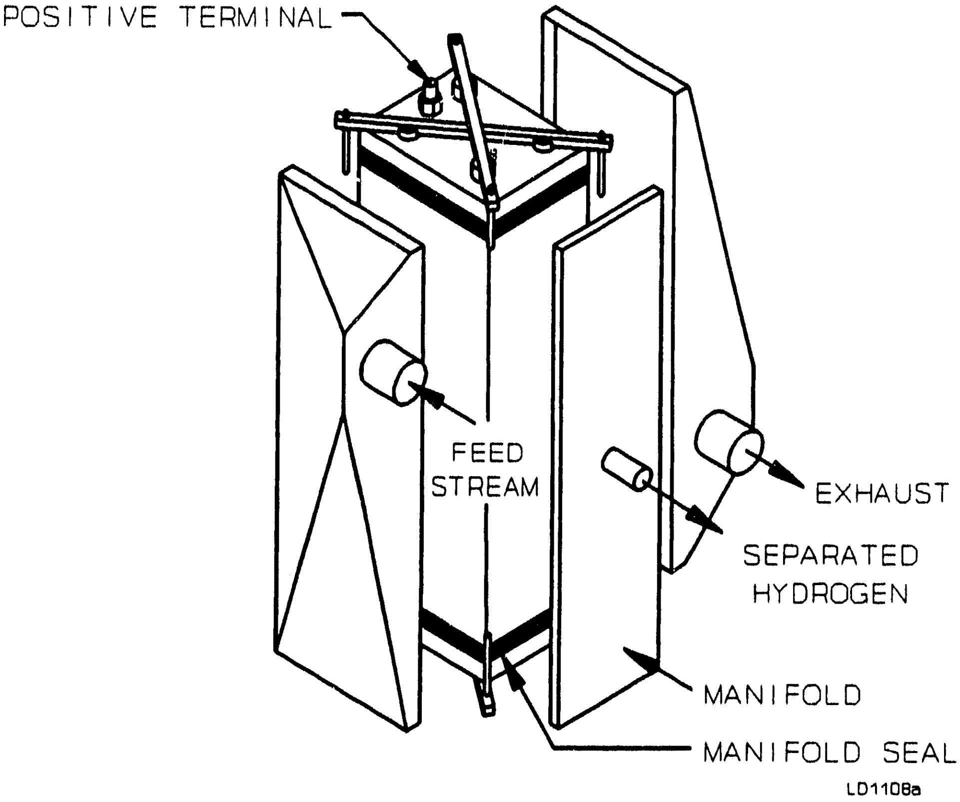


Figure 13. 10-CELL EHS MODULE CONCEPT
The Cells are Stacked Together to Form a Module

The conclusions obtained in Task 1 of this program were used in the EHS module construction and operation. As it was established in Task 1 that EHS performance was not affected by lowering the platinum content of the electrodes, the module electrode platinum content is 0.26 mg/cm^2 (compared with 0.55 mg/cm^2). To reduce resistive losses, the matrix thickness was reduced to 0.2 mm (from 0.4 mm).

The conditions for the module operation are listed in Table III. The module was operated for a total of 3,840 hours. Module

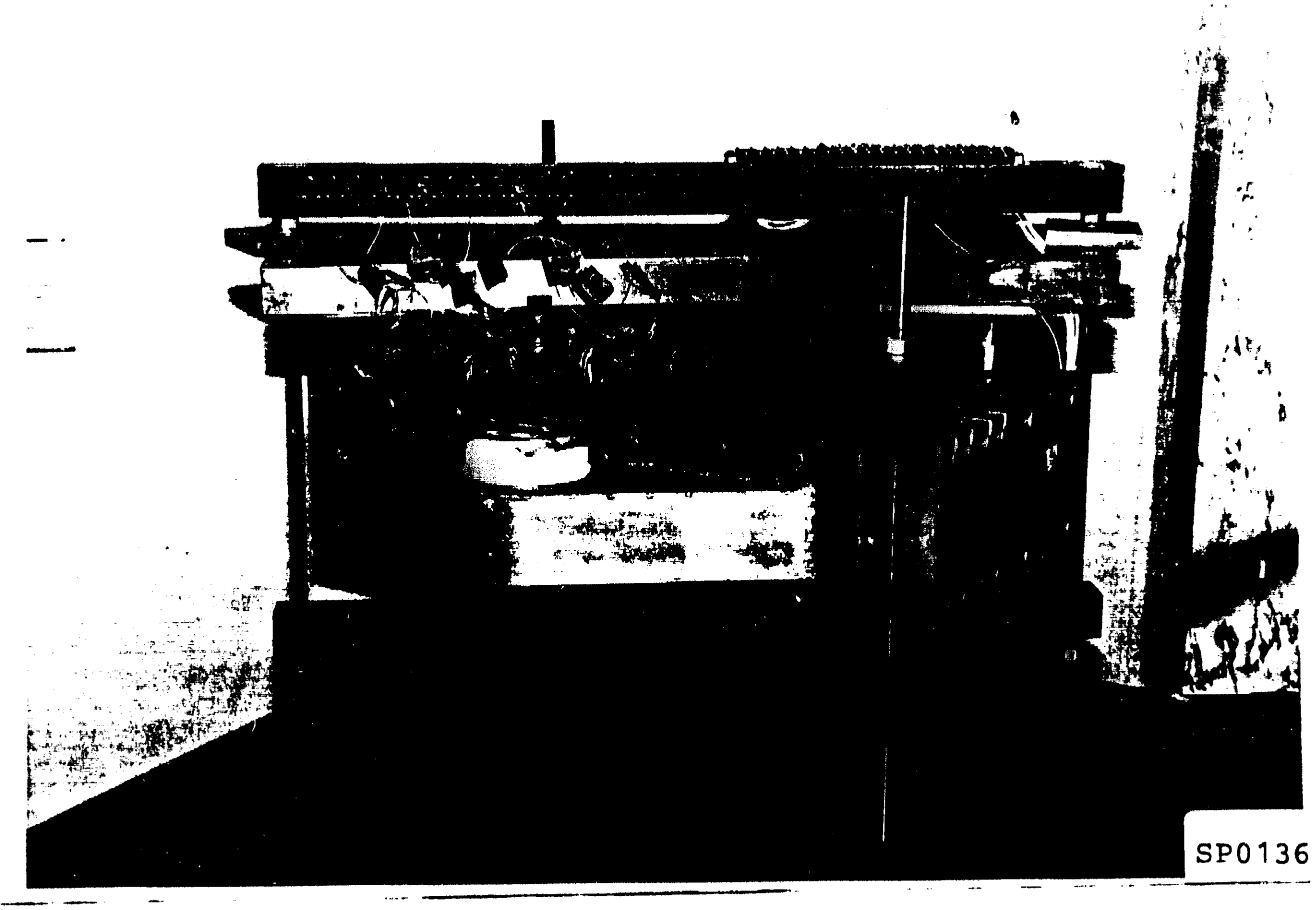


Figure 14. EHS TESTED MODULE
The 10-Cell Test Module was Constructed with 1.1 ft^2 Cells

III. The module was operated for a total of 3,840 hours. Module performance is shown in Figure 15. The stable baseline performance obtained illustrates the scale-up capability of the EHS without any adverse affect on energy requirement.

At the conclusion of the test run the module was removed from the test facility. Each cell was taken apart and characterized with respect to plate and electrode integrity. The flow channels of the plate were examined for gas flow blockages. Blockages may form due to excessive electrolyte "flooding" the channel or particulate contaminates from the feed stream depositing in the channels. The

Table III EHS MODULE OPERATING PARAMETERS

PARAMETER	SETPOINT
TEMPERATURE	165-180°C
PRESSURE	1 ATM
CURRENT DENSITY	200 mA/cm^2
FEED HUMIDITY	20-30%
H_2 FEED CONCENTRATION	33%
H_2 RECOVERY	66%

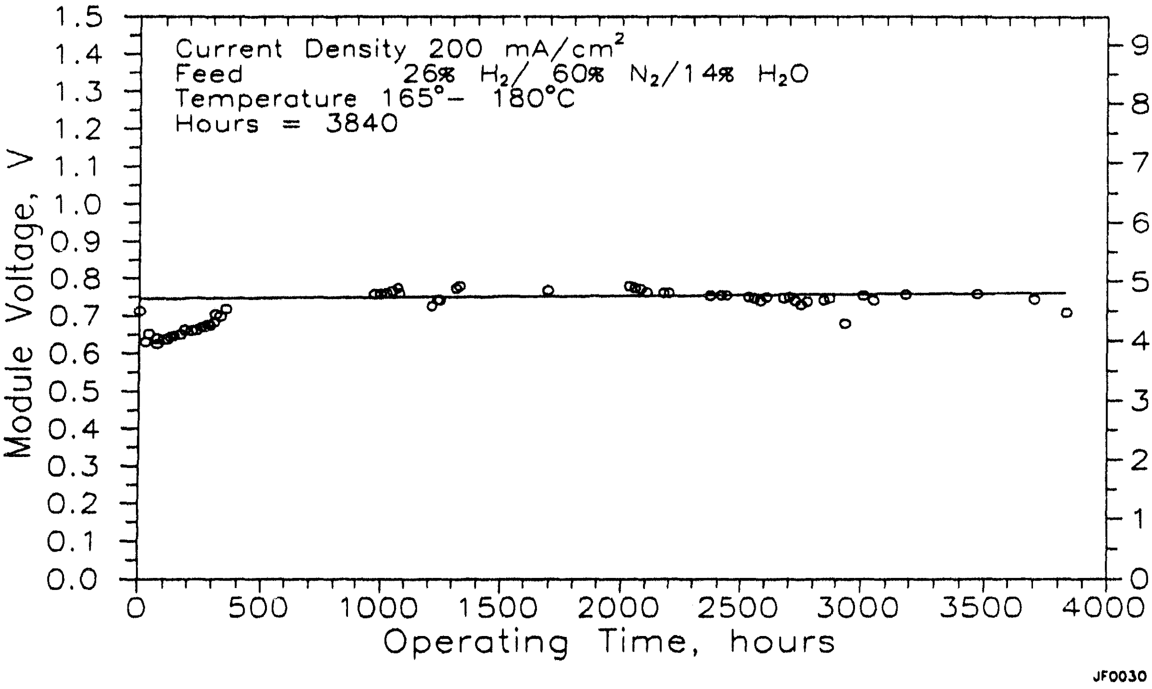


Figure 15 EHS MODULE PERFORMANCE
Stable operation of the EHS 10-Cell Module was illustrated for over 3,800 hours.

stream is not evenly distributed throughout the cell as a result of blocked channels. The flow channels of all the cells remained clear and therefore maintained uniform hydrogen distribution.

3.3 SYSTEMS ANALYSIS

A comparison of the EHS concept with commercial hydrogen recovery/purification processes was conducted to determine the economic potential of EHS systems and their applicability in industry. The results from the previous tasks indicate that the attractiveness of EHS systems is greatest with low and moderate pressure gas streams consisting primarily of hydrogen, water, carbon dioxide, nitrogen, methane and higher hydrocarbons, particularly where high purity hydrogen at feed pressure is required. Furthermore, the economics of the EHS system will depend on the capital and operating costs associated with feed pretreatment, particularly with respect to carbon monoxide and hydrogen sulfide removal as well as humidification.

The potential of EHS systems in several hydrogen purification and recovery applications is discussed below. An EHS system suitable for each application is described, including feed pretreatment and product hydrogen treatment facilities. For those applications where commercial technologies are currently in use, factors affecting the relative attractiveness of the EHS system are discussed.

EHS Applications in Coal Gasification Plants

Bulk Hydrogen Recovery/Purification

Recovery of hydrogen in coal gasification plants is probably limited to ammonia synthesis plants and applications where hydrogen can be shipped "across the fence" to a hydrogen purchaser, such as an adjacent refinery or chemicals complex. The carbon monoxide shift/solvent based CO_2 removal/catalytic methanation process is generally considered the best hydrogen purification technology for this application. This process is advantageous because sulfur compounds, carbon dioxide and other syngas impurities (HCN, formic acid, etc.) are removed by the gas treating solvent, a high recovery of 96-99 percent is achieved which minimizes the size of the gasification plant, and the product hydrogen is essentially free of carbon dioxide and carbon monoxide, both poisons for ammonia synthesis catalysts.

In comparison, the use of EHS systems for bulk hydrogen recovery and/or purification in coal gasification plants is not expected to be competitive. The syngas would still need to be shifted in two or more stages to lower the carbon monoxide content below 1% and a solvent based acid gas removal process would still be required to remove sulfur and other impurities. In addition, methanation of the product hydrogen would also be necessary to minimize carbon oxide impurities. Hydrogen recovery would be reduced to ~90% and therefore a larger gasification plant would be required as well as a use for the EHS tail gas identified. Furthermore, the feed gas would have to be remoisturized prior to being fed to the EHS system.

Applications in Carbonate Fuel Cell Power Plants

Coal Gasification Carbonate Fuel Cell Power Plant

Carbonate fuel cell power plants fueled with coal-derived syngas may benefit from using the EHS. A schematic of this application is shown in Figure 16. The spent fuel leaving the fuel cell anodes typically contains up to 5% unconverted hydrogen and carbon monoxide. In this application, the spent fuel would be cooled, passed through a low temperature shift reactor to maximize hydrogen content and minimize carbon monoxide content, and fed to the EHS. Since the feed gas cleanup requirements for carbonate fuel cells exceed those of the EHS, no additional pretreatment of the fuel cell exhaust is necessary. The product hydrogen from the EHS is recycled back to the fuel cell anode inlet to raise the fuel cell's hydrogen conversion rate, thereby increasing the plant's power production and generation efficiency.

This concept was evaluated in a recent study (Sandler, et. al., 1992) and the results indicated that an EHS can be used to improve the power plant generation efficiency of coal gasification carbonate fuel cell power plants by more than ten percent. The cost of electricity, however, is not significantly reduced due to the increase in capital cost.

Catalytic Coal Gasification Carbonate Fuel Cell Power Plant

Studies performed under DOE/METC Contract No. DE-AC21-90MC27227 investigated integrated catalytic coal gasification carbonate fuel cell power generation systems. The objective in this program was to optimize catalytic coal gasifier conditions to improve carbonate fuel cell performance. Early in the program two design approaches for the integrated power plant were compared, the "High Methane" approach and the "High Hydrogen" approach (Figure 17).

In the "High Methane" approach, the gasifier is operated at high pressure to promote methane production. The gasifier effluent is cooled, cleaned and expanded, and then fed to atmospheric carbonate fuel cells. The anode exhaust from the fuel cells is fed through a shift reactor to increase hydrogen content and lower carbon monoxide content, and then fed to an EHS. The hydrogen rich product stream from the EHS is recompressed and recycled back to the gasifier while the tail gas stream is combusted and fed to the fuel cell cathode.

In the "High Hydrogen" approach the gasifier operates at low pressure to promote hydrogen production. After the gasifier effluent has been shifted and cleaned, carbon dioxide is separated via an amine unit and fed to the carbonate fuel cell cathode. The remainder of the gas is fed to the fuel cell anode. All of the fuel cell anode exhaust is recycled back to the gasifier.

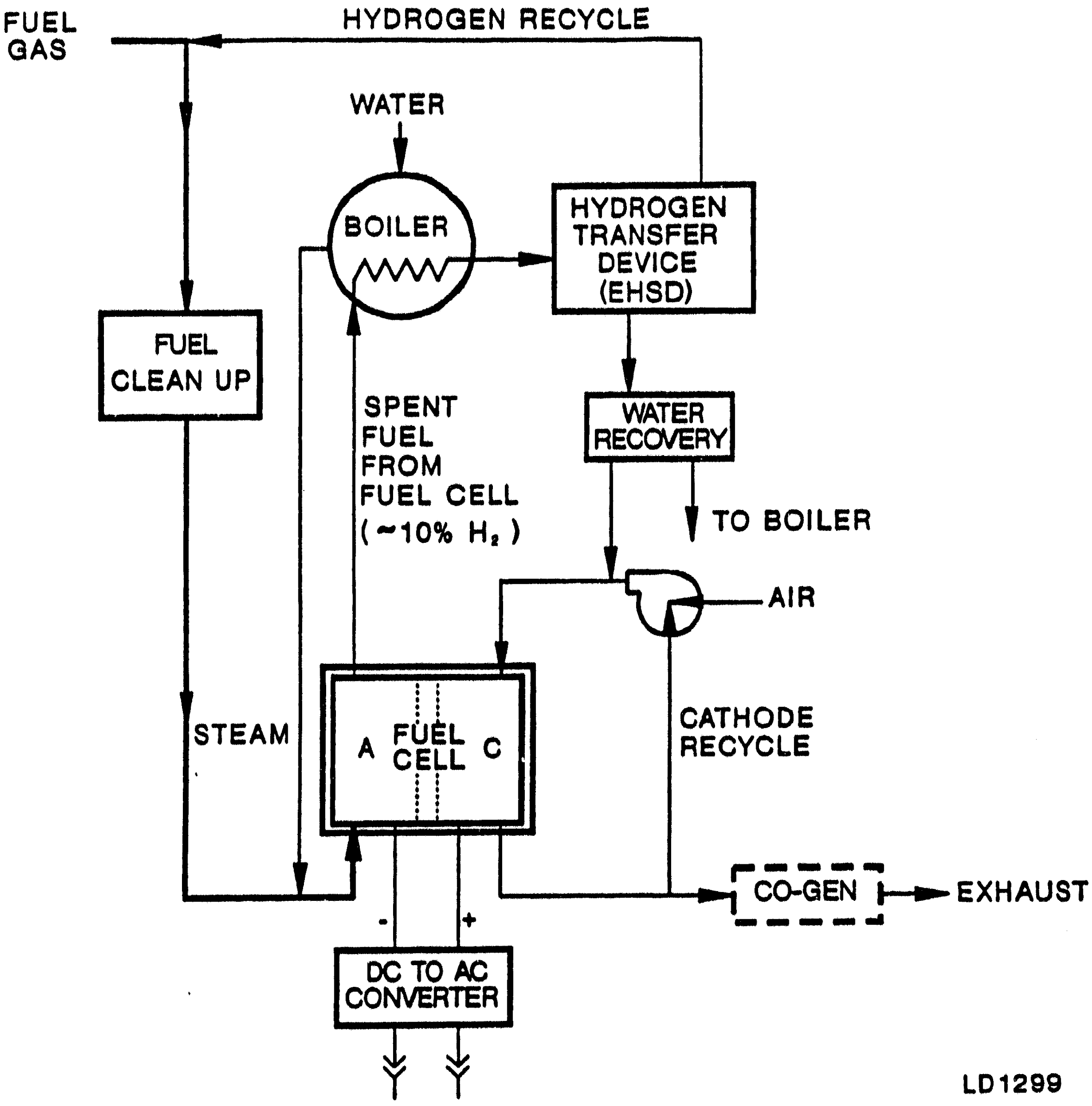
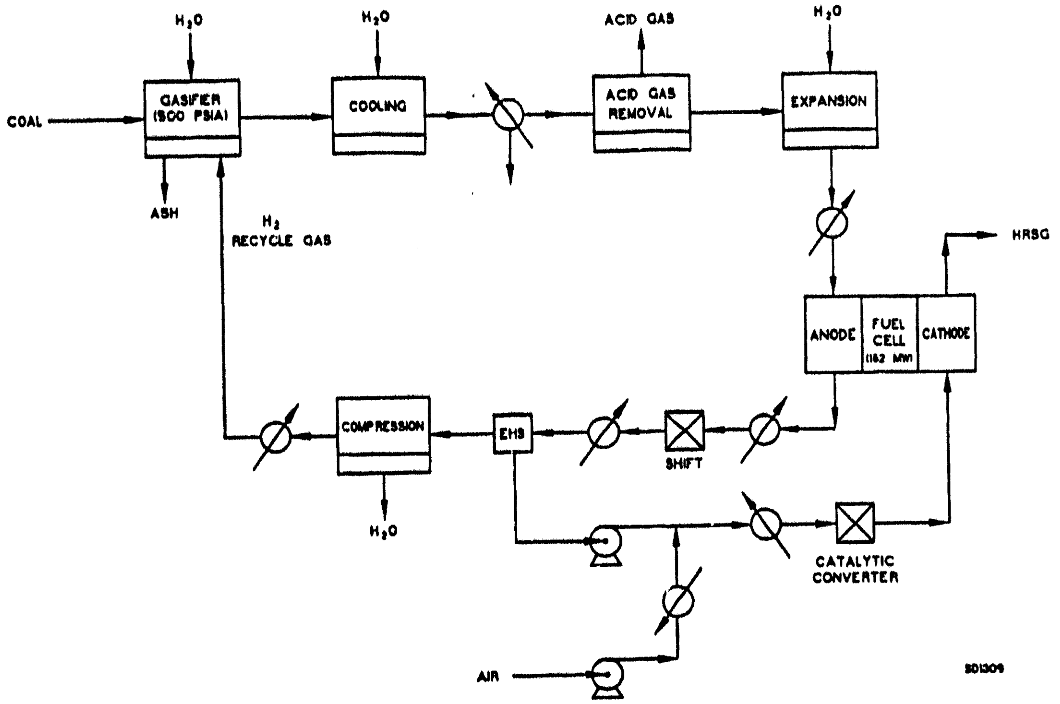
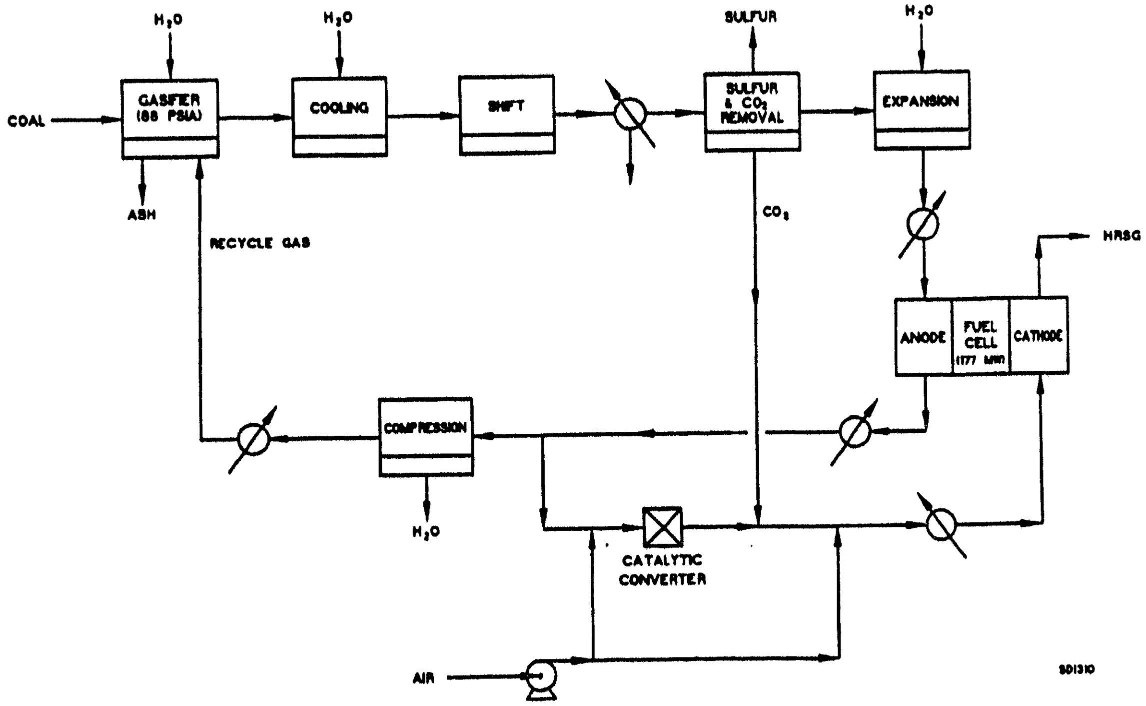


FIGURE 16. SCHEMATIC OF HYDROGEN SEPARATION FROM CARBONATE FUEL CELL EXHAUST



a. Approach Utilizing the Recycle H_2 from the Fuel Cell to the Gasifier



b. Approach Utilizing a CO_2 Scrubber

FIGURE 17. CATALYTIC GASIFICATION CARBONATE FUEL CELL POWER SYSTEMS
The Approach with an EHS Results in a Higher System Efficiency

The "High Hydrogen" approach requires a 55% higher coal feed rate to provide power for the CO_2 separation unit and to increase the fuel value of the recycled anode exhaust. The heat rate obtained for this approach was about 40% higher and the capital cost was approximately 42% greater than the "High Methane" approach.

EHS Applications in Petrochemical Plants and Refineries

Hydrogen purification and recovery in petrochemical plants and refineries is achieved by many established commercial processes. The optimum choice is dictated in each case by the suitability of the hydrogen recovery process to the feed conditions and the purity and pressure requirements of the hydrogen consumer.

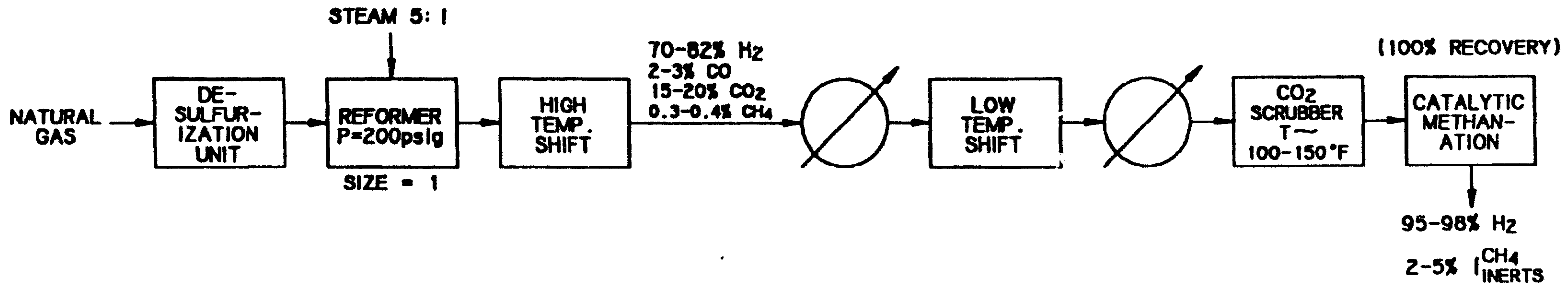
Hydrogen Purification in a Hydrogen Plant

Hydrogen plants employing steam reforming of natural gas (or light hydrocarbons) are used throughout the world to provide a purified hydrogen gas for hydroprocessing applications in refineries and petrochemical plants. The hydrocarbon feed is desulfurized, reformed, and passed through high temperature shift reactors. The composition of the effluent gas on a dry basis is approximately 70-82% hydrogen, 2-3% carbon monoxide, 15-20% carbon dioxide, and 0.3-0.4% methane. Further purification of the hydrogen is achieved by one of two conventional means.

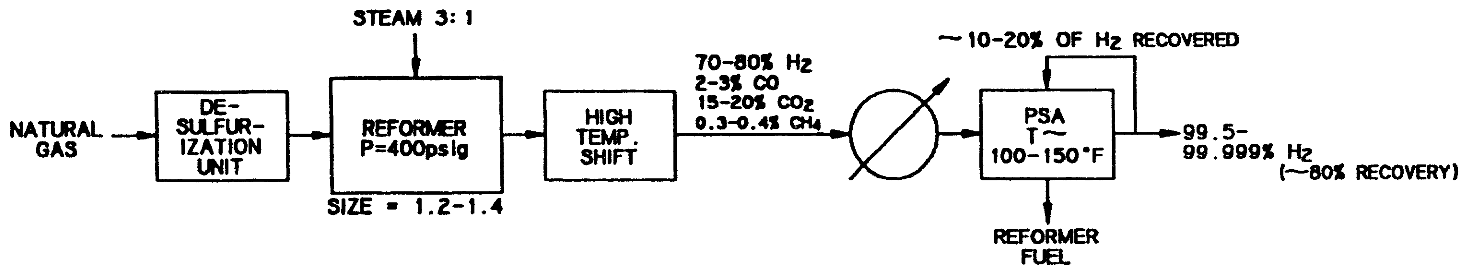
In the traditional approach, shown in Figure 18a, an ambient temperature CO_2 scrubber followed by a catalytic, methanation unit produce a 95-98% pure hydrogen stream. A steam to carbon ratio of about 5:1 is required in the reformer to achieve high purity product, and the reformer is operated at about 200 psig.

The second, more contemporary approach, shown in Figure 18b, uses a PSA to produce a 99.5-99.999% hydrogen stream. The high temperature shift effluent gas must be cooled to ambient temperature prior to entering the PSA unit. Since this process achieves a hydrogen recovery of only 80-92%, a larger reformer is required for a given hydrogen capacity. The reformer must also be designed to operate at approximately 400 psig to optimize the PSA unit operation, further increasing its cost. The PSA purge gases are burned as part of fuel for the reformer. Because the hydrogen product purity is essentially insensitive to the amount of unconverted methane, the reformer can operate at lower steam to carbon ratios, typically 3:1.

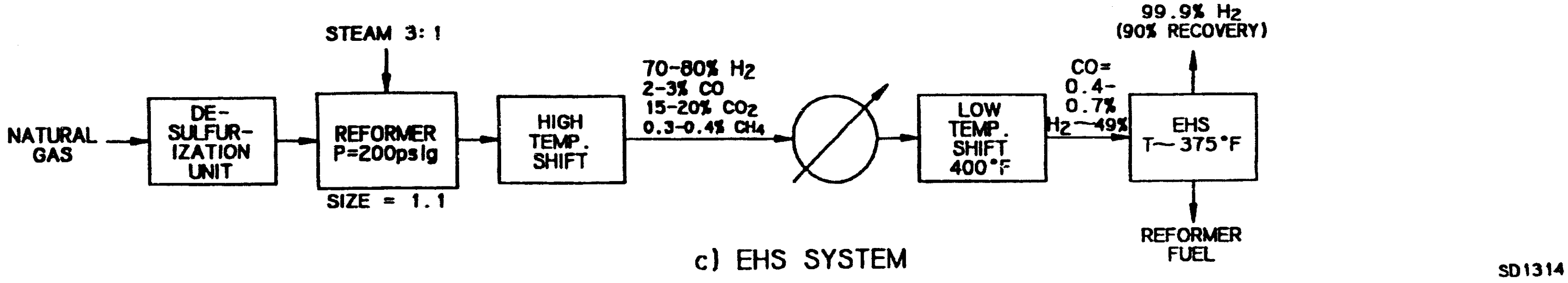
A hydrogen purification process using an EHS is depicted in Figure 18c. EHS systems are well suited for purifying the reformer effluent stream. In the process configuration for this application, the high temperature shift effluent gas is fed to a low temperature shift reactor to reduce the carbon monoxide level to 0.4-0.7% (dry basis), and then fed to the EHS. The EHS operates at a higher temperature than PSA or membrane separation and



a) TRADITIONAL



b) CONTEMPORARY



c) EHS SYSTEM

FIGURE 18. HYDROGEN RECOVERY SYSTEM FROM CARBONATE FUEL CELLS
The EHS can Recover Hydrogen from Carbonate Fuel Cell Anode Exhaust

therefore the overall heat exchange and low level heat rejection for this configuration is less than the contemporary or tradition approach. Since EHS hydrogen recovery is economically limited to ~90%, a reformer capacity similar to the PSA configuration is required. However, the reformer cost is lower for the EHS configuration due to the lower reformer pressure rating. The steam to carbon ratio in the reformer would be similar to the PSA configuration (3:1) as opposed to the higher ratio used in the membrane configuration (5:1).

Hydrogen Recovery From FCCU Offgas

Large quantities of offgas from fluid catalytic cracker units (FCCU) contain hydrogen at concentrations typically too low to economically recover, so it is generally let down to the plant's fuel gas system. This offgas typically contains ~15% hydrogen and is available at 180-250 psig and 60-120°F. The other major offgas components are nitrogen, carbon dioxide, hydrogen sulfide, and paraffinic hydrocarbons and olefins up to C_4.

Special circumstances have sometimes justified hydrogen recovery from FCCU offgas, particularly as a retrofit or in plant debottlenecking situations. For example, the cryogenic process has been used occasionally if the offgas flow rate is large and if olefins or other hydrocarbons in the gas are valuable enough to warrant their recovery. Cryogenic separation of the offgas produces a hydrogen stream at 90-95% purity and a mixed stream containing higher hydrocarbons. This approach requires compression of the offgas to 250-400 psig. Membrane separation has also been used if a low purity (80-90%) hydrogen stream is required at low pressure (100-250 psig), however compression of the offgas to 400+ psig is required. Hydrogen recovery by either of these two processes is limited to 50-85%.

EHS systems may offer a substantial potential for recovering hydrogen from the dilute FCCU offgas. The different separation schematics for this application are compared in Figure 19. EHS feed pretreatment only consists of adding a dedicated scrubbing column to remove sulfur compounds which would share the solvent regeneration of the existing system, since FCCU offgas must be scrubbed to meet fuel gas system specifications. The EHS approach eliminates the need for offgas compression, reduces the product hydrogen compression requirement, produces a higher purity hydrogen stream, and is less complex.

The cost of hydrogen recovery using the EHS approach was estimated for a 382,000 scfh FCCU offgas stream. The FCCU offgas was assumed to contain 14 percent hydrogen and less than 20 ppmv hydrogen sulfide. The EHS was presumed to operate at an FCCU offgas pressure of 200 psig. A hydrogen recovery of 90% and a purity of 99.0% were also assumed. The EHS operates at 107 mV at 280 amps/square foot, leading to a power consumption of 6.77 kWh per 1000 scf hydrogen and a total cell area of 10,850 ft^2. The cost of the EHS is estimated at \$45.12/ft^2. The cost of

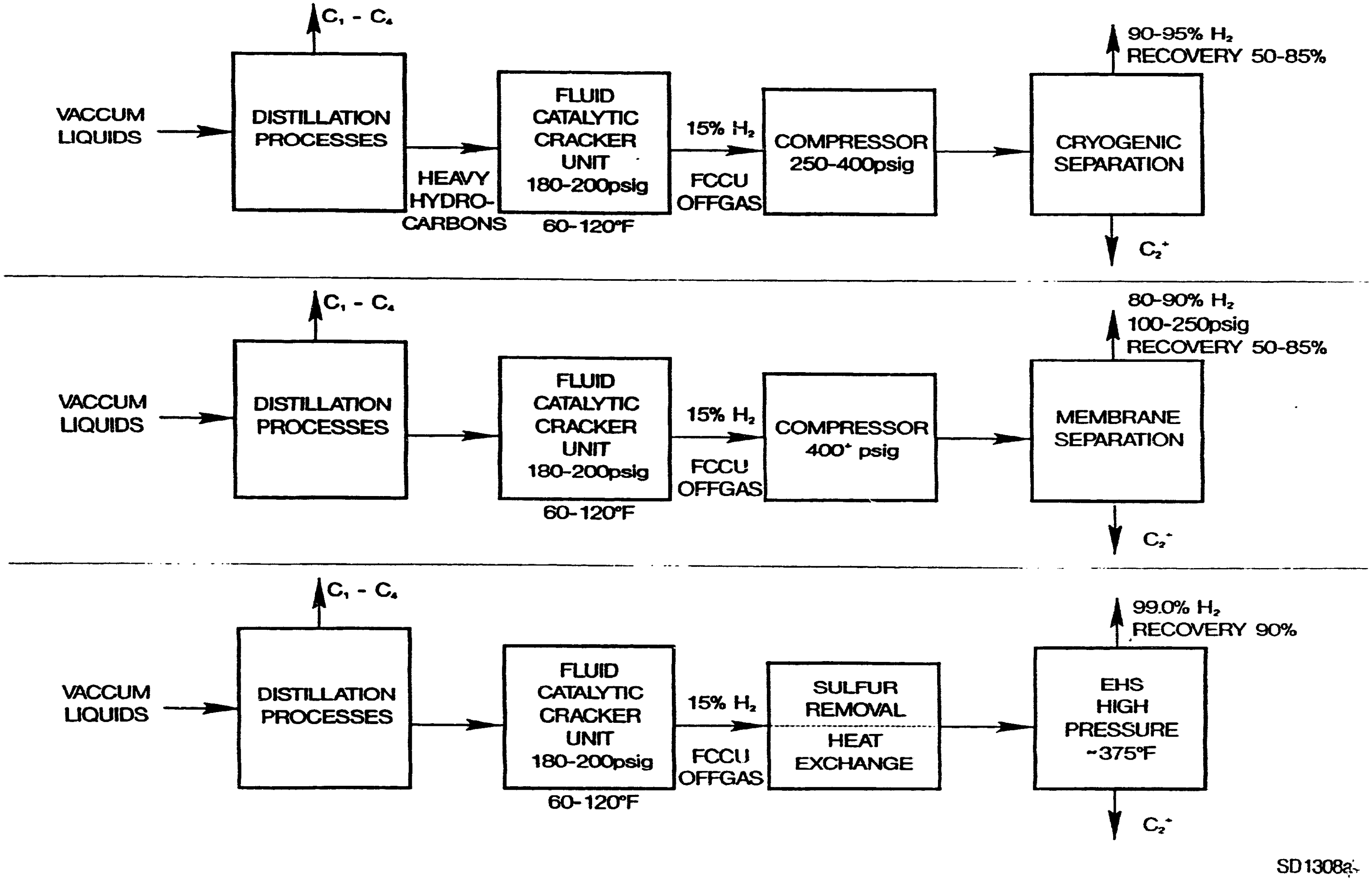


FIGURE 19. FLUID CATALYTIC CRACKER UNIT SCHEMATICS
The EHS Eliminates the Need for Offgas Compression and
Reduces FCCU H_2 Feed Requirement by Providing Higher Hydrogen Recovery

humidification (probably by steam injection) was ignored. An annual capitalization factor of 30% was used, which is typical for an industrial enterprise. With a power cost of $0.05 per kW, the cost of recovered hydrogen in mid-1993 dollars was estimated at $1.40 per 1000 scf.

Hydrogen Purification of Hydrotreater Recycle Gas

Hydrogen is commonly recovered from hydrotreater purge gases and recycled to minimize makeup hydrogen requiremets. In general, hydrotreaters have high pressure (800-2500 psig) purge and low pressure (100-250 psig) flash gas streams. Depending upon the severity of the hydrotreater application, the amount of hydrogen contained in the low pressure flash stream can be significant to consider the use of a hydrogen recovery system. The low pressure flash streams typically have hydrogen contents of 40% to 60%, and also include paraffinic hydrocarbons up to C_4, carbon dioxide, and hydrogen sulfide.

PSA units, though better suited for hydrogen recovery from the high pressure purge streams, can also be used for the low pressure flash streams because of the small flow rates, highly variable stream composition, low pressure, and moderate hydrogen content. Compression of feed gases which are at 200 psig or lower is normally necessary.

Hydrogen recovery via EHS systems may be attractive for low pressure hydrotreater flash gases which would require compression for a PSA system and which have lower hydrogen concentrations. The hydrogen product purity would be comparable to that of a PSA unit in this application, and a higher hydrogen recovery might be achievable than with a PSA unit. Humidification of the purge gases would be required prior to feeding them to the EHS, however, and H_2S may have to be removed to the required levels.

A screening level analysis was conducted to compare the costs of a PSA system and an EHS system which recovers hydrogen from low pressure hydrotreater recycle gas. The hydrotreater conditions were assumed to be the same for both cases, and the H_2S content was assumed to be below 20 ppmv. The purge gas was assumed to have a hydrogen concentration of about 64 percent and a total flow of 4.1 MMSCFD. Comparisons were made at purge gas pressures of 500 psig and 200 psig. An evaluation with atmospheric pressure purge gas, although not realistic, was also performed to provide a comparison of these two separation systems at ambient pressures.

The PSA unit was assumed to operate with an inlet pressure of 500 psig, a hydrogen recovery of about 65%, and a hydrogen product purity of 99.9%. A feed gas reciprocating compressor was included for the 200 psig and atmospheric pressure purge gas cases.

The EHS system was assumed to operate at the purge gas pressure for all three cases, with the EHS contained in pressure vessels for the 200 psig and 500 psig purge gas cases. A hydrogen recovery of 89.2% and a hydrogen product purity of 99.0% were also assumed. The EHS was assumed to operate at a cell voltage of 75 mV and a current density of 300 amps per square foot, leading to an EHS power consumption of 4.8 kWh per 1000 scf hydrogen (about the same as the 4.7 kWh/1000 scf H_2 obtained with the 10 ft^2 module in Task II) and a total cell surface requirement of 21,050 ft^2. The performance and cost of the EHS was assumed not to be affected by pressure. The EHS system also included a circulating gas cooling system to remove the excess heat generated by the DC power input and an AC to DC rectifier to provide the electric power. The cost of the EHS was estimated at \$45.12/ft^2 in mid-1993 dollars. The cost for humidification of the feed gas (probably by steam injection) was ignored.

The results for this economic comparison are shown in Table 4. The savings associated with the reduced hydrogen makeup requirement in the EHS systems are not included in the analysis. Mainteance and operating costs are assumed equal for both systems. An annual capitalization factor of 30% was used, which is typical for an industrial enterprise. These results inducate that an EHS system may offer considerable savings with lower pressure purge gas feeds if the competing PSA system requires feed compression, but that the EHS system is probably not competitive when the purge gas feed is at higher pressures. The competitiveness of the EHS system is further improved with lower purge gas hydrogen content and lower cost power.

Secondary Hydrogen Recovery

EHS systems may also be used to recover additional hydrogen from the tail gas strems of existing PSA or membrane hydrogen separation systems, or be used in tandem with either of these technologies in new applications as a lower overall cost alternative. The use of EHS systems to recover additional hydrogen from the dilute tail gas streams may provide a synergistic combination of processes that offers increased hydrogen recovery at comparable capital cost. For example, adding an EHS system to the back end of a hydrogen plant with a PSA unit would reduce the required size of the upstream reformer and CO shift reaction train.

Potential EHS Applications in Other Markets

Hydrogen Recovery in Chemicals Manufacturing

Hydrogen can be recovered from offgas streams in many chemical production processes, although the costs of treating the gas to make it suitable for feeding to an EHS system can be significant. Some hydrogen cyanide plants, for example, produce large quantities of an atmospheric pressure offgas stream containing hydrogen at dilute (eg. 10-15%) concentrations. Feed stream pretreatment is required, however, to reduce the CO content from about 5% to less than 1% and the ammonia content from about 1.5% to less than 0.2%. In these types of applications, the recovered hydrogen can be recycled to the process or fed to an adjacent H_2 consumer.

Table IV. ECONOMIC COMPARISON OF HYDROGEN RECOVERY FROM LOW PRESSURE HYDROTREATER PURGE GAS (MID-1993 DOLLARS)

PURGE GAS PRESSURE	500 PSIG		200 PSIG		0 PSIG	
H_2 RECOVERY SYSTEM	**EHS**	**PSA**	**EHS**	**PSA**	**EHS**	**PSA**
CAPITAL COST, $						
Cell Stacks @ $45.12/ft^2	950,000	-	950,000	-	950,000	-
Other Equipment	249,000	964,000	249,000	964,000	69,000	964,000
Total Equipment Cost (Skid Mounted)	1,199,000	964,000	1,199,000	964,000	1,019,000	964,000
Installation Cost	360,000	289,000	360,000	289,000	306,000	289,000
Direct Field Cost	1,559,000	1,253,000	1,559,000	1,253,000	1,325,000	1,253,000
Indirects/HOC/Sales Tax/Contingency	1,053,000	847,000	1,053,000	847,000	897,000	847,000
H_2 Recovery System, Installed Cost	2,612,000	2,100,000	2,612,000	2,100,000	2,222,000	2,100,000
Feed Gas Compressor, Installed Cost	-	-	-	1,128,000	-	1,825,000
Total Installed Cost	2,612,000	2,100,000	2,612,000	3,228,000	2,222,000	3,925,000
OPERATING COST, $/Yr						
With Power @ 3c/kWh	120,000	-	120,000	65,000	120,000	187,000
With Power @ 5c/kWh	201,000	-	201,000	109,000	201,000	311,000
With Power @ 10c/kWh	402,000	-	402,000	218,000	402,000	622,000
Other Utilities	-	200	-	200	-	200
H_2 PRODUCTION, MMSCFD 100% Basis	2.37	1.72	2.37	1.72	2.37	1.72
H_2 PRODUCTION COST, $/1000 SCF						
With Power @ 3c/kWh	1.16	1.11	1.16	1.82	1.01	2.40
With Power @ 5c/kWh	1.26	1.11	1.26	1.90	1.11	2.62
With Power @ 10c/kWh	1.52	1.11	1.52	2.09	1.37	3.17

Small hydrogen plants employing steam reforming of natural gas can also be used with an EHS system to provide a purified hydrogen gas for use in chemicals manufacturing or foods preparation as an alternative to purchasing merchant hydrogen. The process scheme is similar to that described for petrochemical plants and refinery applications. A modular system similar to that developed for natural gas-fueled PAFC power generation applications could be used, with the primary difference being that the PAFC is run as an EHS.

CONCLUSIONS

The design and operating parameters of the EHS were evaluated and it was established that the capital cost of the EHS could be reduced by lowering the platinum content in the electrodes without affecting performance. Resistive power losses were minimized by reducing the EHS matrix thickness. Power requirement of the EHS is independent of the feed gas composition (with the exception of CO which increases the power demand) and pressure. A mathematical model was developed that predicts EHS power requirement as a function of hydrogen flux, hydrogen feed concentration and recovery and fits well with experimental data. High product hydrogen purity was obtained (>99% dry basis). Trace quantities of NH_3 and H_2S do not affect EHS power requirement. Scale-up ability and stability were established in the 3800 hour test run of a 10-cell module.

The EHS can be utilized for cost-effective hydrogen recovery. Although operable at high pressure, the EHS is most economically attractive with dilute low pressure streams when compared to conventional separation technologies. EHS systems will prove most attractive under conditions which are unfavorable to currently commercial processes including:

- Recovery/purification of hydrogen from low pressure (200 psig or less) gases where commercial processes require feed gas compression, particularly where the hydrogen product and tail gas are both required at or above the feed gas pressure.

- Recovery of hydrogen from hydrogen sreams which are too dilute for commercial processes to recover the hydrogen economically.

In particular, the most attractive near-term EHS applications are (i) hydrogen recovery from dilute, low pressure FCCU offgas, (ii) small hydrogen generation plants, especially those where the hydrogen is required at low pressure (similar to the fuel gas preparation systems in commercial PAFCs) and (iii) niche markets where the EHS can recover hydrogen from low pressure or dilute gases with a minimum of feed preparation (e.g. hydrogen recovery from the spent fuel exiting carbonate fuel cell anodes). More detailed studies are required to investigate the suitability and economics of EHS systems under these and other applications.

REFERENCES

Abens, S.G., et al., "Apparatus for Purifying Hydrogen", U.S. Patent 4,620,914.

Baker, B.S., et al., "Fuel Cell System", U.S. Patent 4,532,192.

Baker, R. 1988. Low Cost Hydrogen/Novel Membrane Technology for Hydrogen Separation from Synthesis Gas. In *Proceedings of the Eighth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting, Volume II*. Ed. V.P.Kothari and J.R.Longanbach, p. 425.

Baris, J.M., personal contact, May 18, 1993.

Brooks, K.W. Jan. 16, 1985. Membrane's Push into Separation. *Chemical Week*.

Chin, D.T., et al. December 1986. Hydrogen Sulfide Poisoning of Platinum Anode in Phosphoric Acid Fuel Cell Electrolyte. *Journal of the Electrochemical Society, Volume 13*, p. 2447.

Dhar, H.P., et al. December 1987. Nature of CO Desorption During H_2 Oxidation in Relation to Modeling for CO Poisoning of a Fuel Cell Anode. *Journal of the Electrochemical Society, Volume 134*, p. 3021.

Farooque, M., et al. 1990. Novel Electrochemical Hydrogen Separation Device Using Phosphoric Acid Membrane Cell. *Separation Science and Technology*, 25(13-15), pp. 1361-1373.

Giner, J.D., Method and Apparatus for Converting Hydrogen-Containing Feedstocks, U.S. Patent 3,446,674.

Kinoshita, K., DOE Fuel Cells A Handbook, U.S. Department of Energy, May 1988.

Langer, S.H., et al, Electrochemical Hydrogen Purification and Recovery of Same, U.S. Patent 3,475,302.

Maclean D.L., et al. PRISM™ Separator Hydrogen Applications Present and Future. *Hydrogen Energy Progress-IV, Volume 2*. Ed. T.N. Veziroglu, et al.

McEvory, J.E., Electrolytic Method of Gas Separation, U.S. Patent 3,401,099.

Monsanto Literature. Simple Separation Systems for Hydrogen Recovery. Not dated.

Ross, P.N., The Effect of H_2S and COS in the Fuel Gas on the Performance of Ambient Pressure Phosphoric Acid Fuel Cells. Interim Report for EPRI Contract RP-1676-2, April 1985.

Ibid, Addenum to EPRI Study on the Effect of H_2S and COS on Phosphoric Acid Fuel Cells Anode Tolerance to H_2S and COS at Electric Utility Operating Conditions (Pressurized).

Sandler, H.S., and S.J. Meyers, "Integrating Coal Gasification in Carbonate Fuel Cell Power Plants", presented at the Eleventh Conference on Gasification Power Plants sponsored by Electric Power Research Institute, Palo Alto, CA, October 1992.

Schell, William J. 1976. *Membrane Application to Coal Conversion Pressures*. Final Report. Contract No. E(49-18)-2000.

Szymanski. July 1980. The Effect of Ammonia on Hydrogen-Air Phosphoric Acid Fuel Cell Performance. *Journal of Electrochemical Society, Volume 127, No. 7*.

Tomter, S.S., Electrochemical Cell for Separation of Gaseous Mixtures, U.S. Patent 3,410,783.

Watson, A.M. March 1983. Use of Pressure Swing Adsorption for Low Cost Hydrogen. *Hydrocarbon Processing*, p. 91.

Yamashiro, H., et al. February 1985. Plant Uses Membrane Separation, *Hydrocarbon Processing*, p. 87.