

2. HYDROGEN FUEL FROM COAL PLANTS

Through mid-1999, designs and cost estimates for hydrogen fuel plants utilizing the inorganic membrane were based on information derived from a 1997 conversation with Oak Ridge National Laboratory.⁴ The reporting and presentation of work associated with the membranes stimulated significant levels of interest in membrane applications, both within the DOE and in private industry. The primary documentation from this activity was a letter report prepared in June 1999.⁵ Nearly two years had passed since the initial information exchange, which led to a meeting held at Eastern Tennessee Technology Park (ETTP) in Oak Ridge in November 1999 to review the status of the properties and characteristics of the inorganic membrane for hydrogen transport. As a result of data gained from the meeting, assumptions applied to the membrane that could have an impact on the baseline plant designs and on future membrane applications were updated.

2.1 HYDROGEN SEPARATION DEVICE PROCESS DESIGN

The HSD is a high-temperature membrane device in a shell and tube configuration, with the high-pressure side being on the inside of the inorganic membrane tubes. The inorganic membrane is designed to have pore sizes of controlled diameters, and it can be made of Al_2O_3 or other ceramic materials. According to ORNL,⁴ the confidential manufacturing process is sufficiently flexible to accommodate a variety of gas compositions and design requirements. The resultant membrane material is analogous to a packed bed through which interstitial pores can be controlled to less than 5 angstroms, while acting like a molecular sieve (that is, it excludes larger molecules).

The separation factor (SF) for hydrogen is high, increasing with higher temperatures. The definition of SF is the rate at which hydrogen passes through, relative to the balance of molecules passing through. For example, the purity of hydrogen resulting from an SF of 1,000 would be calculated as follows:

$$\text{Purity} = (1.0 - 1/1000) \times 100 = 99.90\%$$

The balance is made up of the other gases in the initial mixture.

Pressurized syngas, to which steam has been added, enters the tube side of the HSD, which is assumed to have gas contact catalytic properties that promote the water-gas shift reaction. Possibly this will be achieved by lining the inner tube surfaces with catalytic material. However, the hydrogen-deficient surface, resulting from hydrogen migrating through the membrane, will also promote water-gas shift reaction.

It was assumed that, as hydrogen is extracted from the gas stream through the HSD membrane, gas composition at the catalytic surface will become hydrogen deficient and, with excess steam, equilibrium will be shifted to convert available CO to CO_2 and hydrogen. The hydrogen will then migrate to the HSD membrane surface and be transported across. Eventually the CO will reach equilibrium with the steam at the system temperature.

The HSD transports hydrogen across the membrane in proportion to the relative hydrogen partial pressure differentials, where P_1 equals the upstream hydrogen pressure, and P_2 equals the product hydrogen pressure. The initial HSD was designed to operate at an equilibrium temperature of 761°C (1402°F) and at 950 psia. At 950 psia upstream (assuming 42 percent hydrogen), 95 percent of the hydrogen will be separated, with a downstream pressure of 20 psia, according to the following relationship:

$$\begin{aligned} \text{H}_2 \text{ transport} &= (1 - P_2/P_1) \times 100 = \% \text{ transport} \\ &= (1 - 20/(950 \times 0.42)) \times 100 = 95\% \text{ transport} \end{aligned}$$

Fuel value remaining in the separated gas (or retentate) will be about 5 percent of the original feed gas. At that temperature, the hydrogen purity will be better than 99.5 percent. The hydrogen stream leaving the HSD at 20 psia and 1402°F passes through a heat recovery steam generator (HRSG) and a compressor, which reduces hydrogen stream temperature to 117°F and compresses the hydrogen to 346 psia. The steam raised in the HRSG is added to the steam that is injected into the raw gas coming from the gasifier to promote the shift reaction.

2.1.1 UPDATED ASSUMPTIONS FOR HSD DESIGN

The HSD design was modified, based on revised assumptions. This discussion incorporates the latest thinking on inorganic membranes from ETTP at Oak Ridge. The design basis for the revised HSD is the result of conversations with the membrane developers at ETTP. At that meeting, the characteristics of the membrane were identified, and changes were indicated according to Table 2-1. Note that many of the assumptions remain the same. Most significant is the reduced operating temperature.

**Table 2-1
Revised Assumptions for Hydrogen Separation Device**

	Original Assumptions	Revised Assumptions
Separation Factor	>200	~200
Hydrogen Transport Flux	0.1 cc/min/cm ² /cmHgPH ²	0.1 cc/min/cm ² /cmHgPH ²
CO Shift Reaction	On surface of membrane without catalyst	On surface of membrane without catalyst
HSD Tube Size	60 mm OD	0.625 inch OD 0.50 inch ID
Gas Exit Temperature	1402°F (761°C)	1112°F (600°C) 572°F (300°C)
Membrane Cost	\$100/ft ²	\$100/ft ²
Number of Tubes per 8-Foot Vessel Diameter	4,096	11,800
Vessel Pressurization	Shell side	Tube side

The security classification of inorganic membranes is now described in an exclusive “Classification Guide for Inorganic Membranes.” This document was prepared within the last two years. The security level is confidential, essentially requiring a “need to know” for the

manufacturing procedure. The membranes themselves are unclassified. ETTP is now able to talk “freely” about the performance and characteristics of the membranes, but refrains from describing the manufacturing process.

At the meeting, results of the baseline hydrogen fuel plants were discussed, and it was agreed that the HSD can be instrumental in lowering the cost of hydrogen from coal. Parsons’ assumptions were reviewed, which led to discussion of the membrane status and ETTP’s thoughts on membrane performance. ETTP gave Parsons a paper presented at the Pittsburgh Coal Conference by Douglas Fain⁶. In it, the transport mechanism is discussed, along with several comments on the Parsons paper from May 1998.⁷

This led to discussing Parsons’ large membrane vessel. ETTP views the large vessel with many internal tubes as conventional technology. A picture of an ORNL gaseous diffusion vessel was shown, and its dimensions were comparable to the Parsons conceptual vessel. ETTP commented that the pressurization should be from the tube side and the tubes should be smaller diameter, about 10 to 15 mm. Internal pressurization would avoid the cost of a high-pressure shell.

The following salient points were discussed regarding design assumptions for the HSD:

- Separation Factor – The SFs provided by ORNL in 1997 were based on binary gas mixtures. SFs are still based on binary mixtures. At 300°C, the hydrogen SF relative to all gases is ~150.
- Hydrogen Flux through the Membrane – Parsons’ initial assumption was that the gas flux was purely proportional to the hydrogen partial pressure differential. ETTP stated that temperature increase aids hydrogen flow in a non-Knudsen manner. The flux can increase with thinner membranes, but the risk of membrane defect increases.
- Operating Pressure and Temperature – ETTP believes that a 1000 psi pressure differential can be contained by the inorganic membrane. The furnace temperature that is used for testing can reach 650°C, and the operational goal for the membranes is currently 600°C. ETTP uses glass seals to join the membrane tubes to the end support tubes, and these are satisfactory up to 300°C. As a result, a vessel design could be prepared to operate with confidence up to 300°C.
- Sulfur and Steam Tolerance – In reply to being asked if steam or H₂S has any effect on the membrane structure, the ETTP response was negative.
- CO Shift Properties and Requirement for Sweep Gas – Testing is planned, but there are no empirical data available. Parsons will continue to assume shift reaction on the membrane surface without catalyst.
- Membrane Costs – Parsons’ assumptions of \$100/ft² are still “in the ball park.”

Table 2-1 summarizes the revised assumptions for the inorganic membrane and the HSD.

2.1.2 HSD DESIGN

A review of literature for designing vessels for gas separation membranes showed that two approaches can be taken regarding the gas flow to the membrane surface area.⁸ The

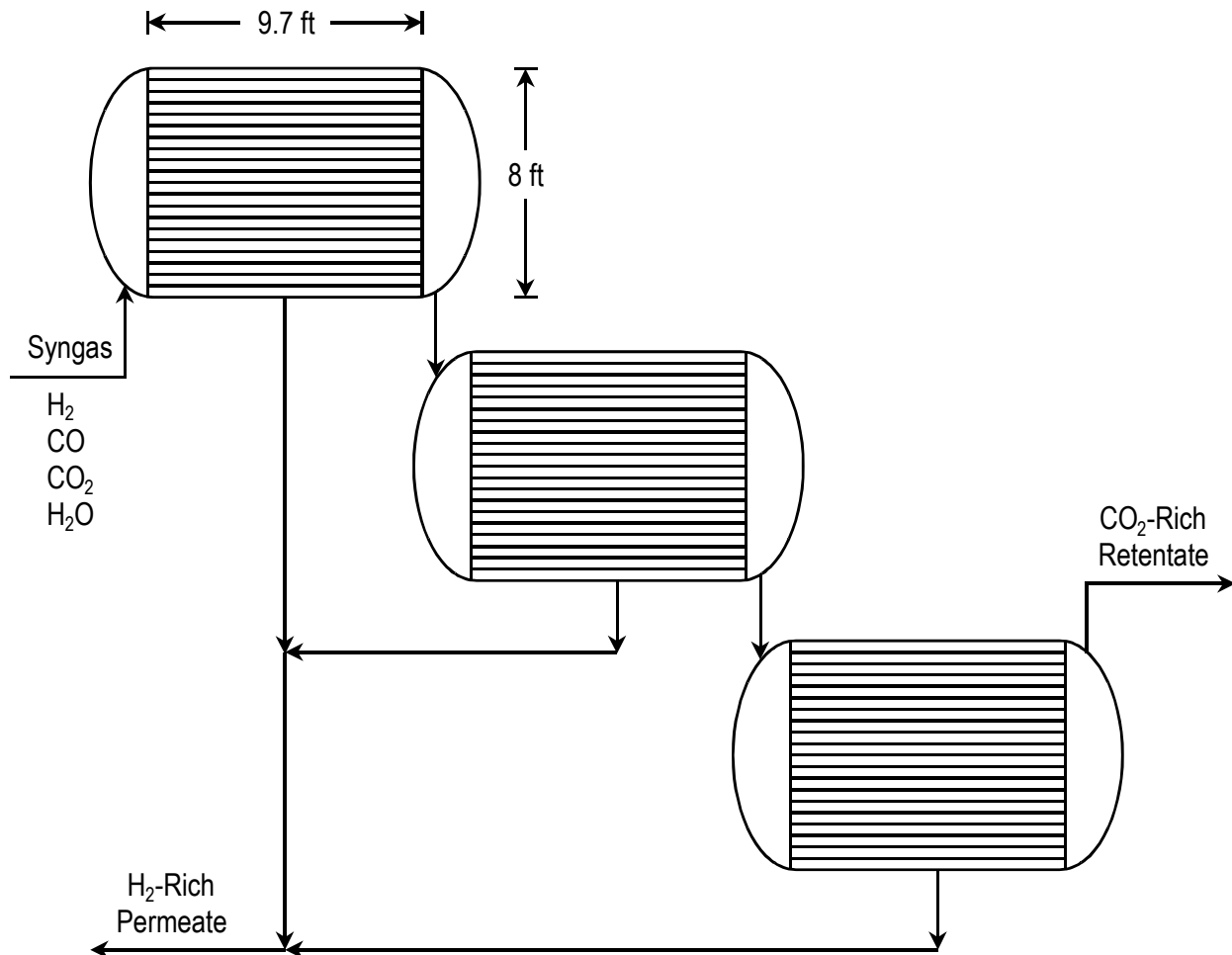
characterization of membrane flux in the laboratory utilizes a long retention time. It appears that an inlet gas flow is used, which results in a retention time of one minute at the membrane. Conversely, concerns were raised as the design of a full-size vessel for integrated gasification combined cycle (IGCC) applications were discussed. The primary concern was the existence of a laminar boundary layer at the membrane surface, which would reduce membrane flux. The final design used a flow velocity of 10 feet per second, and a retention time of 1 second to achieve turbulent flow. The primary difference between the referenced design and the HSD design is their use of catalyst to promote the shift reaction. Their design included shift catalyst in the initial section of membrane tubing, which also created a turbulent region.

The HSD design retains the previous concept to promote the shift reaction by product extraction at the membrane surface. The scenario is based on the gas proceeding along the membrane surface in turbulent flow. Hydrogen product partial pressure is both maintained and extracted at the membrane surface. CO continues to react with steam until the CO-steam equilibrium is reached. The remaining gas then passes from the membrane without further reaction. To ensure the shift reaction going to completion, the membrane path was increased 25 percent above theoretical. Conceptually, the HSD resembles the sketch in Figure 2-1. The basis for the HSD design is shown in Table 2-2.

**Table 2-2
Hydrogen Separation Device Designs**

	Initial Design 761°C HSD	Revised Design 600°C HSD	Revised Design 300°C HSD
Hydrogen Production	35,205 lb/h 1402°F	35,903 lb/h 1112°F	36,564 lb/h 571°F
Syngas Inlet Conditions	684,000 lb/h 1000 psia, 956°F 12,228 acfm	684,000 lb/h 1000 psia, 605°F 10,382 acfm	684,000 lb/h 1000 psia, 404°F 6,771 acfm
Minimum Membrane Area	35,205 ft ²	35,903 ft ²	36,564 ft ²
Minimum Membrane Area Increased by ~25% to Reach Design	45,000 ft ²	45,000 ft ²	45,000 ft ²
Vessel Diameter	8 ft ID	8 ft ID	8 ft ID
Tube Dimensions	0.625 inch OD 0.50 inch ID	0.625 inch OD 0.50 inch ID	0.625 inch OD 0.50 inch ID
Tubes per Vessel	11,800	11,800	11,800
Preliminary Tube Length	29 ft	29 ft	29 ft
Gas Velocity through Tubes	12.7 ft/sec	10.8 ft/sec	7.0 ft/sec
Gas Retention Time	2.3 sec	2.7 sec	4.1 sec
Reynolds Number	~19,000	~22,500	~28,000
Number of Vessels and Configuration of Tube Bundle	3 vessels 8 x 9.7 ft	3 vessels 8 x 9.7 ft	3 vessels 8 x 9.7 ft
Vessel Flow Arrangement	Series	Series	Series

Figure 2-1
Hydrogen Separation Device Concept



2.2 HYDROGEN FUEL PLANT -- 1402°F (761°C) MEMBRANE

This hydrogen fuel production facility conceptual plant design was the initial plant used to evaluate the conversion of coal to synthesis gas, and achieve essentially total separation of hydrogen from the CO₂. This concept utilizes hot gas desulfurization and particulate removal upstream of the HSD along with a modern non-ATS (conventional) gas turbine in the CO₂-rich stream. Table 2-3 provides the design basis established for the plant.

This concept reduces the temperature of the fuel gas stream from the gasifier to 1100°F before the gas is desulfurized and filtered in a transport reactor desulfurizer and a ceramic candle filter. This eliminates the need for a downstream flue gas desulfurization (FGD) unit.

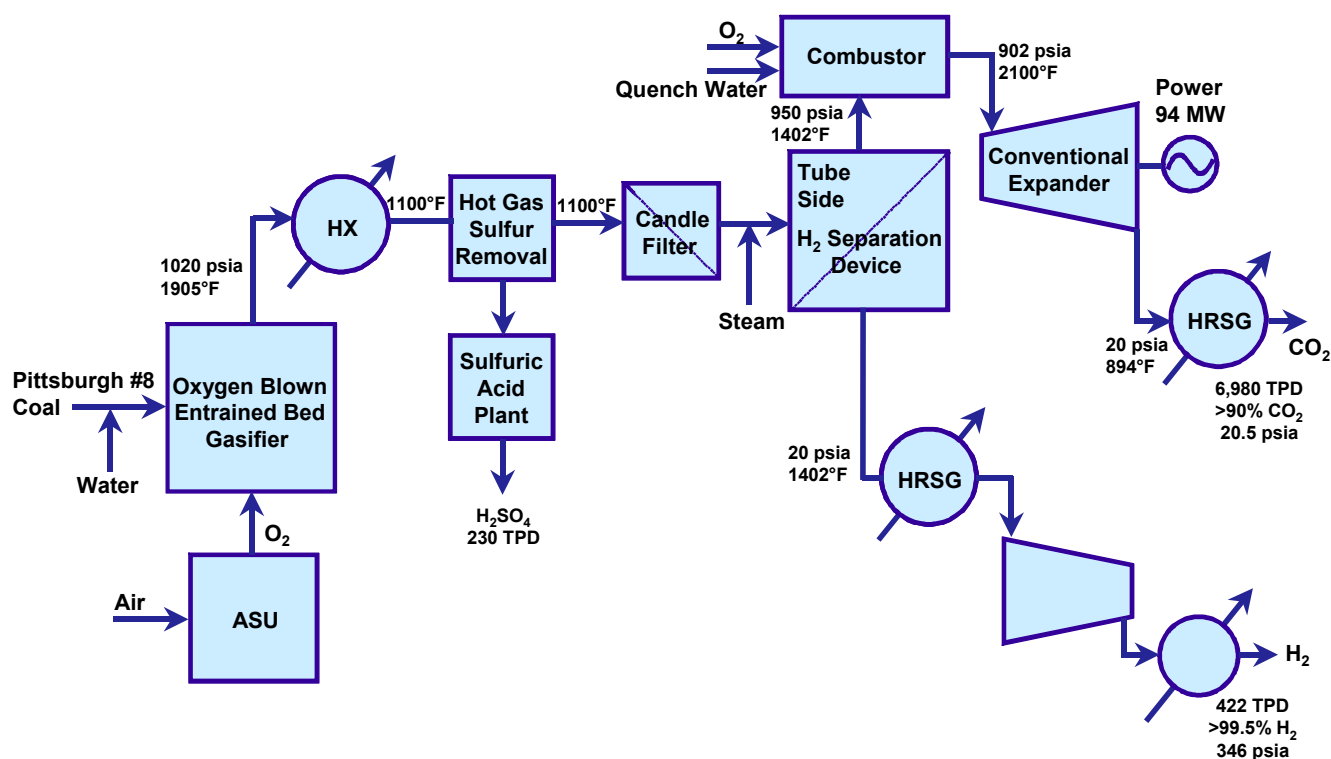
Table 2-3
Design Basis for Hydrogen Fuel Production Facility
with Conventional Expansion Turbine and Hot Gas Cleanup

Hydrogen Fuel Production Facility Parameter	Hydrogen Fuel Production Facility Plant Design Basis
Coal Feed	Pittsburgh No. 8, <10% ash
Limestone Sorbent	None
Gasifier	Oxygen-blown Destec with second stage adjusted for 1905°F output
Hot Gas Temperature	1905°F
Gasifier Outlet Pressure	1000 psia
Ambient Conditions	14.7 psia, 60°F
Hot Gas Desulfurization	Yes, 1100°F
Sulfur Recovery	Sulfuric acid
Ceramic Candle Filter	Before HSD
Hydrogen Separation	H ₂ separation device Shell and tube configuration 95% separation 99.5% pure H ₂ Zero sulfur 20 psia hydrogen compressed to 346 psia
Separated Gas	CO shifted to 1402°F equilibrium 5% of fuel value in gas 950 psia
Separated Gas Utilization	Combustion with oxygen Steam injection conventional turbine expander
CO ₂ Product Pressure	19.4 psia
Hydrogen Utilization	346 psia offsite
Auxiliary Power Block	Conventional turbine expander
Plant Size	Maximum H ₂ production from 2,500 tpd dry gasifier Excess power sold offsite

A block flow diagram of the plant is shown on Figure 2-2. The flows and state points on the attached process flow diagram (Figure 2-3) result from the heat and material balance for the plant. Key process components included in the plant are a Destec high-pressure slurry-feed gasifier, the ORNL HSD, and the transport reactor for desulfurization.

The selected processes exhibit some unique features that result in a simplification of plant design and may contribute to lowering of capital cost. The high-pressure syngas produced in the gasifier is quenched to 1905°F as a result of adjustments in the second stage of the gasifier. The hot raw gas is cleaned of larger particulates in a cyclone and then is cooled in a firetube boiler to 1100°F. A hot gas cleanup system consisting of a transport reactor desulfurizer and a ceramic candle filter removes sulfur and particulates from the fuel gas stream. Sulfur is recovered as sulfuric acid.

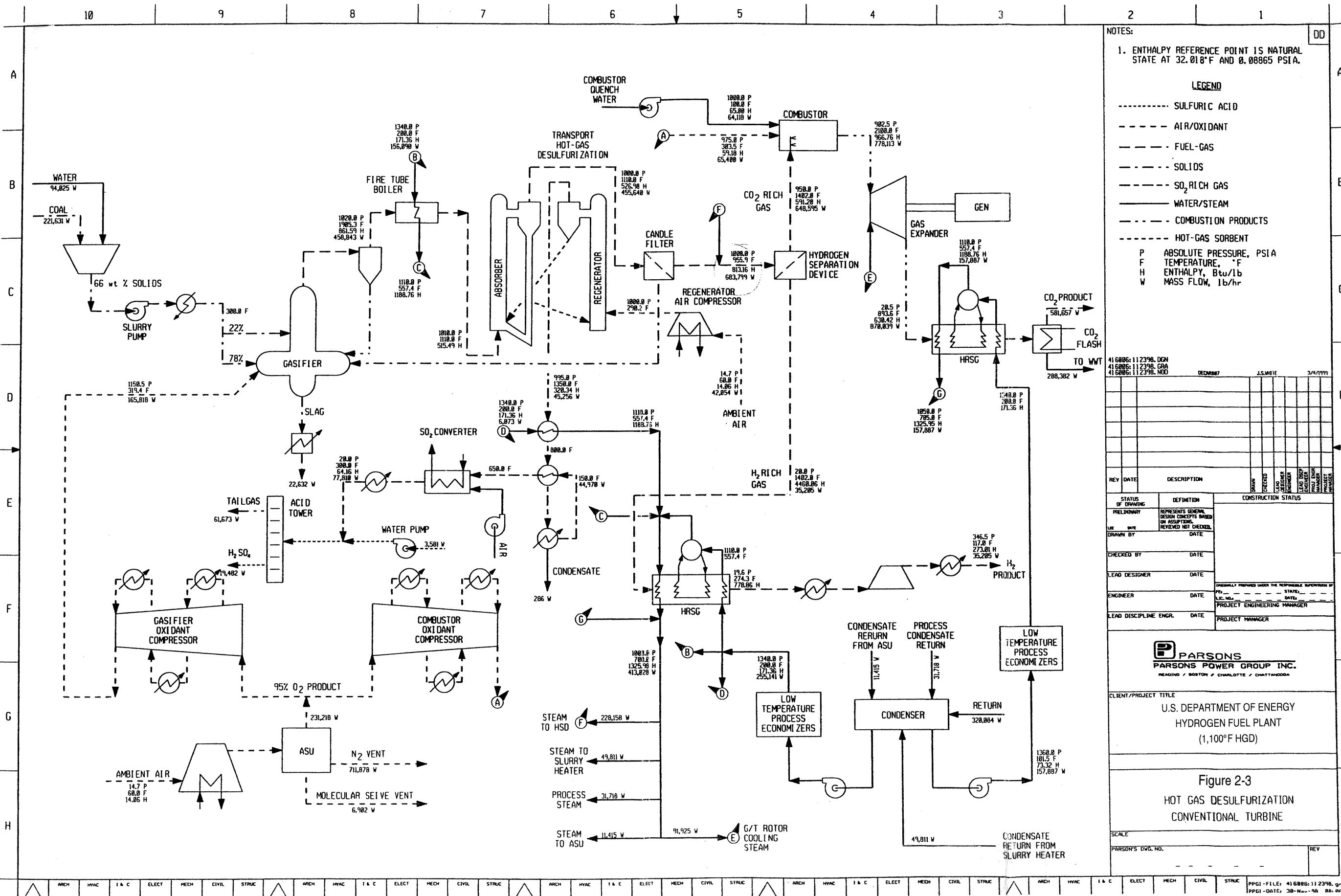
Figure 2-2
Block Flow Diagram
Baseline Hydrogen Fuel Plant
1402°F (761°C) Hydrogen Separation Device



A considerable amount of steam is added, ensuring adequate water content for the high-temperature shift reaction to occur. The gas enters the HSD at 956°F and leaves the HSD at 1402°F as a result of the exothermic shift reaction. The hydrogen produced from the HSD is 99.5 percent pure. It goes through a HRSG and then is compressed to 346 psia.

The CO₂-rich gas leaving the HSD at 950 psia contains about 5 percent of the fuel value of the inlet syngas stream. This gas goes to the gas turbine combustor with which oxygen is injected to convert CO and hydrogen to CO₂ and H₂O, respectively. Water is also injected into the combustor to moderate the temperature to 2100°F. The hot gas is expanded to 20 psia and 894°F through the conventional gas turbine expander to produce 94 MW electric power. The gas is cooled in a HRSG, and steam produced is combined with other steam produced from cooling the hydrogen for process applications. There is no power produced from steam. The CO₂ product is cooled to 100°F, dewatered, and sent offsite.

Figure 2-3



NOTES:
 1. ENTHALPY REFERENCE POINT IS NATURAL STATE AT 32.018°F AND 0.08865 PSIA.

LEGEND
 - - - - - SULFURIC ACID
 - - - - - AIR/OXIDANT
 - - - - - FUEL-GAS
 - - - - - SOLIDS
 - - - - - SO₂ RICH GAS
 - - - - - WATER/STEAM
 - - - - - COMBUSTION PRODUCTS
 - - - - - HOT-GAS SORBENT

P ABSOLUTE PRESSURE, PSIA
 F TEMPERATURE, °F
 H ENTHALPY, Btu/lb
 W MASS FLOW, lb/hr

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 416006:112398.GRA
 416006:112398.NOD

DEC0807 J.S.M/IE 3/4/1999

REV	DATE	DESCRIPTION	DRAWN	CHECKED	LEAD DESIGNER	LEAD ENGINEER	LEAD FACILITATOR	LEAD PROJECT MANAGER

STATUS OF DRAWING	DEFINITION	CONSTRUCTION STATUS
PRELIMINARY	REPRESENTS GENERAL DESIGN CONCEPTS BASED ON ASSUMPTIONS. REVIEWED NOT CHECKED.	

ENGINEER	DATE	STATE	DATE

PROJECT ENGINEERING MANAGER
 PROJECT MANAGER

PARSONS
 PARSONS POWER GROUP INC.
 HEADQUARTERS: BOSTON / CHARLOTTE / CHATTANOOGA

CLIENT/PROJECT TITLE
 U.S. DEPARTMENT OF ENERGY
 HYDROGEN FUEL PLANT
 (1,100°F HGD)

Figure 2-3
 HOT GAS DESULFURIZATION
 CONVENTIONAL TURBINE

SCALE
 PARSON'S DWG. NO. REV

Table 2-4 presents the performance summary for the plant, and Table 2-5 identifies the plant power requirements.

**Table 2-4
Performance Summary**

Coal Feed	221,631 lb/h
Oxygen Feed (95%)	231,218 lb/h
Hydrogen Product Stream	35,205 lb/h
CO ₂ Product Stream	581,657 lb/h
Sulfuric Acid Product	19,482 lb/h
Gross Power Production	94 MW
Auxiliary Power Requirement	76 MW
Net Power Production	18 MW
Effective Thermal Efficiency (ETE), HHV	80.2%

**Table 2-5
Auxiliary Power Load, kW**

Gasifier Auxiliary Oxygen Compressor	10,300
Combustor Oxygen Compressor	4,000
ASU Air Compressor	30,900
Gasifier Slurry Pumps	190
Water Spray Pump	350
Boiler Feedwater Pumps	640
Coal Handling	210
Slag Handling	530
Regenerator Air Blower	2,960
Gas Turbine Auxiliary	400
Hydrogen Compressor	25,180
Miscellaneous Balance of Plant	750
Total Auxiliary Load	76,410 kW

Following are more detailed descriptions of the key process elements.

2.2.1 PROCESS DESCRIPTION

2.2.1.1 GASIFIER

The high-pressure system for producing hydrogen has resulted in utilizing two Destec gasifier trains, each having a capacity of 1,250 tpd coal (dry basis).⁵ The Destec high-pressure entrained flow gasifier consists of two stages to gasify a coal-water slurry feed with oxygen. The slurry is prepared by fine grinding coal to about 200 mesh and mixing with water to achieve a ratio of 65 percent solids and 35 percent water, including the moisture content of the coal. The gasifier can operate at any pressure up to the capability of the oxygen compressor. By operating in two

stages, it is possible to adjust the flow split between stages to achieve a desired outlet temperature of the product gas. A typical operating temperature for the Destec gasifier is 1900°F. This temperature is reached by using a 78/22 flow split between the first and second stages of the gasifier. Slag produced in the high-temperature gasifier reaction flows to the bottom of the first stage, where it falls into a water bath and is cooled and shattered to become an inert frit.

Gas leaving the gasifiers at 1905°F goes through an internal cyclone that separates entrained particles from the gas for recycle to the gasifiers, a firetube boiler to cool the gas to 1100°F, and a hot gas cleanup system. Steam is then injected into the gas stream, promoting the shift reaction, which will occur downstream in the HSD.

2.2.1.2 AIR SEPARATION UNIT

Oxygen supply for this plant is provided through a conventional cryogenic air separation unit (ASU). The air separation plant is designed to produce a nominal output of 3,000 tons/day of 95 percent pure O₂. The high-pressure plant is designed with two 50 percent capacity production trains, with liquefaction and liquid oxygen storage providing an 8-hour backup supply of oxygen.

2.2.1.3 HOT GAS CLEANUP SYSTEM

The transport reactor desulfurizer consists of a riser tube, a disengager, and a standpipe for both the absorber section and regeneration section. Sorbent from the absorber passes through the regenerator riser, disengages, and transfers back to the absorber through the standpipe. Regeneration is conducted with neat air to minimize heat release and limit temperature. The regeneration heat has negligible effect on the sorbent temperature in the absorber. The regeneration off-gas containing predominantly SO₂ is sent to the sulfuric acid plant. Elutriated particles are disengaged from the gas by high-efficiency cyclones at the top of the absorber. A final ceramic candle filter is located downstream.

2.2.1.4 SULFURIC ACID PLANT

Key to the double-absorption contact sulfuric acid plant process is use of an intermediate absorber in the four-pass converter developed by Monsanto. The reaction from SO₂ to SO₃ is an exothermic reversible reaction. Using a vanadium catalyst, a contact plant takes advantage of both rate and equilibrium considerations by first allowing the gases to enter over a part of the catalyst at about 800°F, and then allowing the temperature to increase adiabatically as the reaction proceeds. The reaction essentially stops when about 60 to 70 percent of the SO₂ has been converted, at a temperature in the vicinity of 1100°F. The gas is cooled in a waste heat boiler and passed through subsequent stages until the temperature of the gases passing over the last portion of catalyst does not exceed 800°F. The gases leaving the converter, having passed through two or three layers of catalyst, are cooled and passed through an intermediate absorber tower where some of the SO₃ is removed with 98 percent H₂SO₄. The gases leaving this tower are then reheated, and flow through the remaining layers of catalyst in the converter. The gases are then cooled and pass through the final absorber tower before discharge to the atmosphere. In

this manner, more than 99.7 percent of the SO₂ is converted into SO₃ and subsequently into product sulfuric acid.

CO₂-Rich Separated Gas Stream/Conventional Turbine Expander

The gas, which is separated from the hydrogen, leaves the HSD at 950 psia and 1407°F, and has a fuel value of about 15 Btu/scf. A conventional expansion turbine is utilized to extract the energy from the gas stream by producing power and steam. The gas stream is fired with oxygen in the combustor, resulting in conversion of CO and hydrogen to CO₂ and water vapor, respectively. Water is injected into the combustor to moderate the stream temperature to 2100°F, making it suitable for expansion through the turbine expander. The turbine expander reduces the gas pressure to 20 psia and its temperature to 894°F, while generating 94 MW power. In-plant power requirements and transformer losses amount to 76 MW, resulting in export power sales of 18 MW. The gas then passes through a HRSG where it is cooled to 250°F, while raising steam for in-plant process use. The CO₂ product is cooled to 100°F, dried, and sent offsite. Table 2-6 identifies the overall water balance for the plant.

**Table 2-6
Plant Water Balance**

Water Source	
Makeup Water	193,426 lb/h
Recycled from Stack Condenser	288,382 lb/h
Water Consumption Point	
Boiler Feed	320,084 lb/h
Gasifier Coal Slurry Preparation	94,025 lb/h
Combustor Quench	64,118 lb/h
Sulfuric Acid Water	3,581 lb/h

2.2.2 EFFECTIVE THERMAL EFFICIENCY (ETE)

For comparative purposes and to arrive at a figure of merit for the plant design, an ETE was derived for the plant performance based on HHV thermal value of hydrogen produced and offsite power sales, divided by the fuel input to the plant. The formula is:

$$ETE = \frac{(\text{Hydrogen Heating Value} + \text{Electrical Btu Equivalent})}{\text{Fuel Heating Value (HHV)}}$$

$$ETE = \frac{35,205 \text{ lb H}_2/\text{h} \times 61,095 \text{ Btu/lb} + 18,000 \text{ kW} \times 3,414 \text{ Btu/kWh}}{221,631 \text{ lb coal/h} \times 12,450 \text{ Btu/lb}}$$

$$ETE = 80.2\%$$