Use of Byproduct Hydrogen for Electricity Cogeneration Using a Fuel Cell

This project involves the design of a natural-gas-fed production unit to produce 10,000 metric tons per year of raw-material-grade carbon monoxide. The major reaction that is used to produce the carbon monoxide is the equilibrium steam-reforming of natural gas

$$CH_4 + H_2O \rightleftarrows 3H_2 + CO \tag{1}$$

A valuable by-product of this reaction is hydrogen.

In highly industrial areas, where a market for hydrogen gas is present, this hydrogen stream can be sold for a profit. For example, refineries and petrochemical plants are often hydrogen deficient and need to supplement the process with hydrogen. However, when no hydrogen market exists in the region other uses for the hydrogen stream must be investigated. A common use for this hydrogen is to burn it to produce steam. An interesting alternative is to feed the hydrogen to a fuel cell to produce electricity to supplement the power requirements of the chemical plant. For some fuel cells, steam also may be produced, along with electricity, through the use of co-generation from the heat generated in the fuel cell.

The design of the carbon monoxide production unit can be broken down into four sections. The first section of this process is to remove the hydrogen sulfide from the pipeline natural gas feed to the unit. The removal of the H_2S from this stream is essential because the nickel-based catalyst used in the reformer will be poisoned by a concentration of greater than one part per million of H_2S in the feed. Standard pipeline natural gas has approximately four parts per million sulfur. This unit is designed to remove three parts per million of H_2S from the design feed of natural gas by using two parallel beds of molecular sieve. Alternative methods would be needed to remove sulfur in the form of mercaptans, which are typically added to residential natural gas to produce an odor for safety reasons.

The second section of the facility is the natural gas reformer. This reformer is in the form of a fired heater with tubes filled with the nickel-based catalyst. This reformer is fed with the natural gas feed stream and steam at the designed steam ratio. Additionally, natural gas is used to provide heat to the reformer through combustion. The major optimizations performed on the reformer included the reformer reaction temperature, the reformer reaction pressure, and the steam ratio of the reformer feed.

The next section of the process is the gas separations section. The requirements of this section were to produce a stream of carbon monoxide that is less than one percent hydrogen and methane with the remainder being inert. Additionally, the hydrogen must be separated into a stream that meets the feed requirements for the alternative fuel cell technologies, such as solid oxide fuel cells, phosphoric acid fuel cells, and proton exchange membrane fuel cells.

The final section of the unit is the use of the purified hydrogen. Four different possible uses for the hydrogen stream are: electricity production in a solid oxide fuel cell (SOFC), electricity production in a phosphoric acid fuel cell (PAFC), electricity production in a proton exchange membrane fuel cell (PEMFC), and the standard practice of burning the side product hydrogen to produce steam.

A block flow diagram for the system configuration is given in Figure 1. A stream table for the overall process is given in Table 1. The stream numbers referenced by this table are given in the individual unit process flow diagrams.

The first unit in this system is a combined sulfur removal and natural gas reformer unit, Unit 100. A process flow diagram for Unit 100 is given in Figure 2. The desulfurized natural gas stream is sent to a reformer. This stream is combined with steam at a ratio of one to one and fed to the natural gas reformer, R-101. This reformer is a reactive fired heater in which the natural gas feed is passed through tubes filled with the nickel-based catalyst required to form the desired carbon monoxide product. The outlet from the reformer is then sent to Unit 200 to be separated into the desired product streams.

Unit 200 is the gas separations unit. The gas separation method illustrated is pressure-swing adsorption. This technology uses alternating packed beds of an adsorption agent to first adsorb and then to desorb the carbon monoxide. A process flow diagram of Unit 200 is given in Figure 3. In pressure-swing adsorption, there are three cycles each bed passes through in 30 minutes: adsorption, flushing, and desorption. There are three adsorption beds, two running in an alternating pattern and the third acting as a back up. The valves leading to each bed are labeled as A and B to designate the different beds. For the description given here, Bed A will be in the desorption mode.

At the beginning of a cycle, the bed adsorbs the carbon monoxide, a little carbon dioxide, and nitrogen. This occurs for 15 minutes, and a solid line shows its path through the bed. During adsorption, valves 1 and 4 will be opened to allow Stream 15 to enter the bed and the carbon monoxide to adsorb onto the copper exchanged sodium Y zeolite. Once the bed has run 15 minutes, valves 1 and 4 are closed and then the beds are flushed with carbon monoxide stored in V-202 at 15 bar. This carbon monoxide flushes out the trapped hydrogen and methane by opening valves 3 and 6, allowing them to be recycled back to Stream 15. The path of the flushing cycle is shown as a dashed line on Figure 3. The flushing occurs for 30 seconds. Once the hydrogen and methane are flushed from the bed, the carbon monoxide can be desorbed without contaminants. Pure carbon monoxide is fed into Bed A at 30°C and 0.58 bar by opening valves 2 and 5. The desorption takes place for 14.5 minutes. During the desorption cycle, V-202 is refilled for the next flushing cycle. A summary of the valve configurations for each part of the cycle is shown on the table in Figure 3.

The outlet flow rate of carbon monoxide from this unit is sufficient to provide the required annual flow rate of carbon monoxide. Additionally, this system provides a hydrogen and methane stream to feed the fuel cell unit.

The illustrated fuel cell technology is the solid oxide fuel cell. The fuel cell unit, Unit 300, produces an annual output of electricity and steam that range from $1.9 million in the first year of production to $800,000 in the tenth year of operation. Figure 4 is a process flow diagram for Unit 300. This loss in revenue is due to the decreased electrical efficiency of the fuel cell over this time period. The capital cost estimate used to determine the fixed capital investment required for the fuel cell was $3000/kW. This is the best estimate available for the current cost of a solid oxide fuel cell; although, there are predictions that suggest that improvements in fuel cell technology and mass production of fuel cells could reduce this value to the order of $500/kW.

General References

American Institute of Chemical Engineers, *2000 National Design Problem*, New York, 1999.

Fuel Cell Handbook. 5th Ed. U.S. Department of Energy, National Energy Technology Laboratory, 2000, Pittsburgh, PA.

Kirk-Othmer Encyclopedia of Chemical Technology, John Wiley and Sons. New York: NY, 1976, Vol. 1 pp. 497-506 & 522-568.

Rase, F. Howard, *Chemical Reactor Design For Process Plants: Volume Two: Case Studies and Design Data,* Wiley-Interscience, New York, 1977, pp. 133-137.

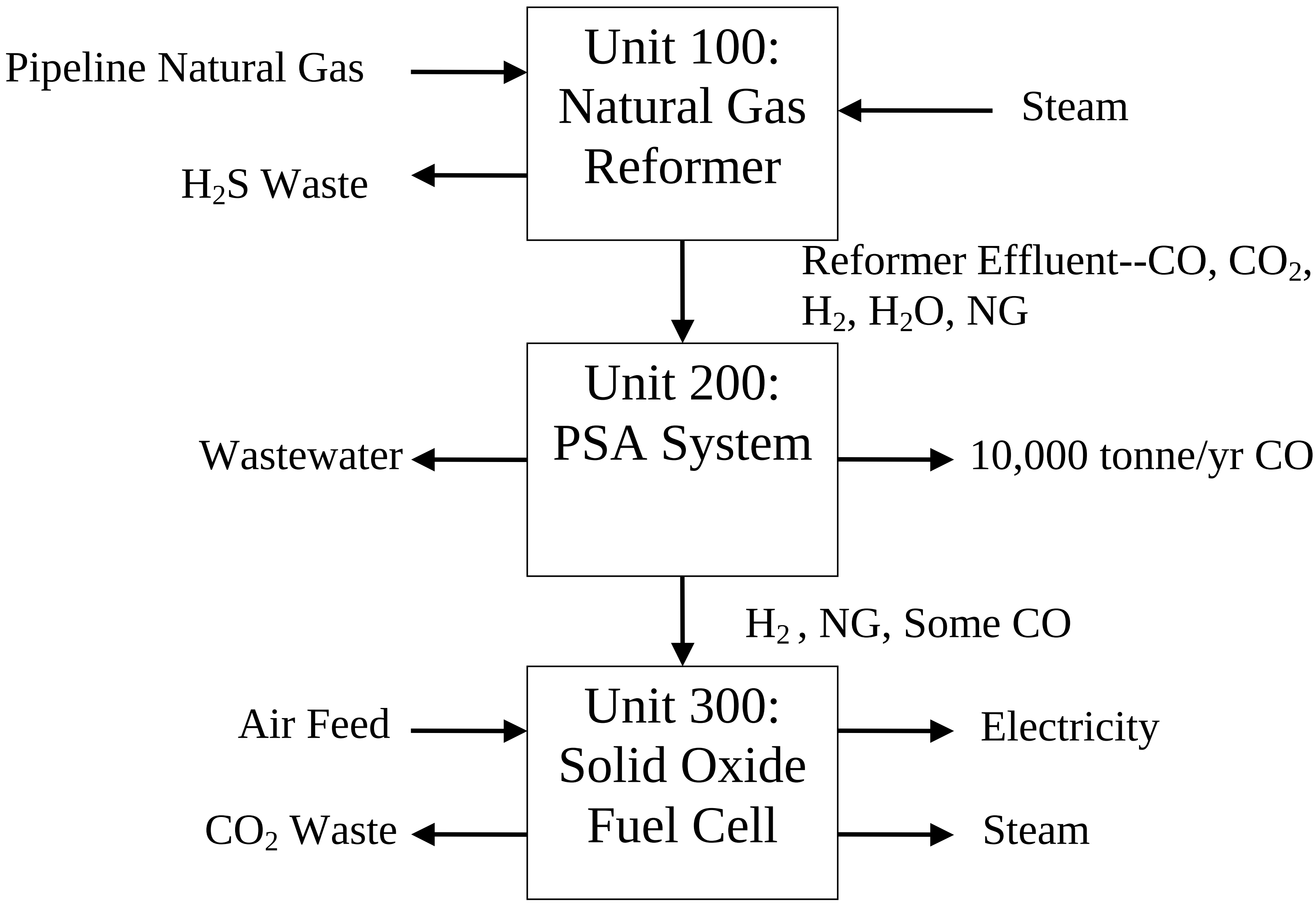


Figure 1: Block Flow Diagram of Process

Table 1. Stream Tables

Unit 100--Natural Gas Reformer Unit

Stream Number	1	2	3	4	5	6	7
Temperature (°C)	20.0	20.0	177.0	159.0	152.0	160.0	1000.0
Pressure (bar)	1.1	6.0	5.0	5.0	5.0	5.0	4.8
Vapor Fraction (molar)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mass Flow (tonne/hr)	0.83	0.83	0.83	0.83	0.83	1.66	1.66
Mole Flow (kmol/hr)	47.50	47.50	47.50	47.50	47.50	95.00	184.73
Component Mole Flow (kmol/hr)							
Methane	45.041	45.041	45.041	0.000	0.000	45.041	2.907
Ethane	1.222	1.222	1.222	0.000	0.000	1.222	0.002
Hydrogen	0.000	0.000	0.000	0.000	0.000	0.000	133.275
Water	0.000	0.000	0.000	47.500	47.500	47.500	2.539
Carbon Monoxide	0.384	0.384	0.384	0.000	0.000	0.384	44.765
Carbon Dioxide	0.000	0.000	0.000	0.000	0.000	0.000	0.482
Propane	0.095	0.095	0.095	0.000	0.000	0.095	0.000
Nitrogen	0.758	0.758	0.758	0.000	0.000	0.758	0.758
Oxygen	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2S	4 ppm	4 ppm	1 ppm	0.000	0.000	<1 ppm	<1 ppm

Unit 200--Pressure-Swing Adsorption Unit

Stream Number	8	9	10	11	12	13	14	15.0
Temperature (°C)	1000.0	536.7	35.0	20.0	20.0	20.0	66.4	30.0
Pressure (bar)	5.0	4.9	4.8	4.7	4.7	4.7	6.9	6.8
Vapor Fraction (molar)	1.00	1.00	1.00	1.00	0.00	1.00	1.00	1.00
Mass Flow (tonne/hr)	1.66	1.66	1.66	1.66	0.03	1.63	1.63	1.63
Mole Flow (kmol/hr)	184.73	184.73	184.73	184.73	1.62	183.21	183.11	183.10
Component Mole Flow (kmol/hr)								
Methane	2.907	2.907	2.907	2.907	0.000	2.907	2.907	2.907
Ethane	0.002	0.002	0.002	0.000	0.000	0.000	0.000	0.000
Hydrogen	133.275	133.275	133.275	133.275	0.000	133.275	133.275	133.275
Water	2.539	2.539	2.539	2.539	1.618	0.922	0.922	0.292
Carbon Monoxide	44.765	44.765	44.765	44.765	0.000	44.765	44.765	44.765
Carbon Dioxide	0.482	0.482	0.482	0.482	0.000	0.482	0.482	0.482
Propane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Nitrogen	0.758	0.758	0.758	0.758	0.000	0.758	0.758	0.758
Oxygen	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2S	<1 ppm	<1 ppm	<1 ppm	<1 ppm	0.000	<1 ppm	<1 ppm	<1 ppm

Stream Number	17	18	19	20	21	22
Temperature (°C)	700.0	29.1	175.7	175.7	35.0	30.0
Pressure (bar)	4.4	0.5	1.5	1.5	1.5	1.4
Vapor Fraction (molar)	1.0	1.0	1.0	1.0	1.0	1.0
Mass Flow (tonne/hr)	0.33	1.30	1.30	0.19	0.19	0.19
Mole Flow (kmol/hr)	137.10	52.72	46.01	6.71	6.71	6.71
Component Mole Flow (kmol/hr)						
Methane	2.907	0.000	0.000	0.000	0.000	0.000
Ethane	0.000	0.000	0.000	0.000	0.000	0.000
Hydrogen	133.275	0.000	0.000	0.000	0.000	0.000
Water	0.922	0.000	0.000	0.000	0.000	0.000
Carbon Monoxide	0.000	51.480	44.928	6.552	6.552	6.552
Carbon Dioxide	0.000	0.482	0.420	0.061	0.061	0.061
Propane	0.000	0.000	0.000	0.000	0.000	0.000
Nitrogen	0.000	0.758	0.662	0.097	0.097	0.097
Oxygen	0.000	0.000	0.000	0.000	0.000	0.000
H_2S	<1 ppm	0.0000	0.0000	0.0000	0.0000	0.0000

Unit 300--Solid Oxide Fuel Cell Unit

Stream Number	23	24	25
Temperature (°C)	700.0	25.0	175.0
Pressure (bar)	1.0	1.0	1.0
Vapor Fraction (molar)	1.0	1.0	1.0
Mass Flow (tonne/hr)	0.33	20.45	20.78
Mole Flow (kmol/hr)	137.10	802.58	733.03
Component Mole Flow (kmol/hr)			
Methane	2.907	0.000	0.000
Ethane	0.000	0.000	0.000
Hydrogen	133.275	0.000	0.000
Water	0.922	0.000	0.000
Carbon Monoxide	0.000	0.000	0.000
Carbon Dioxide	0.000	0.000	2.907
Propane	0.000	0.000	0.000
Nitrogen	0.000	634.037	634.037
Oxygen	0.000	168.542	96.090
H_2S	<1 ppm	<1 ppm	<1 ppm

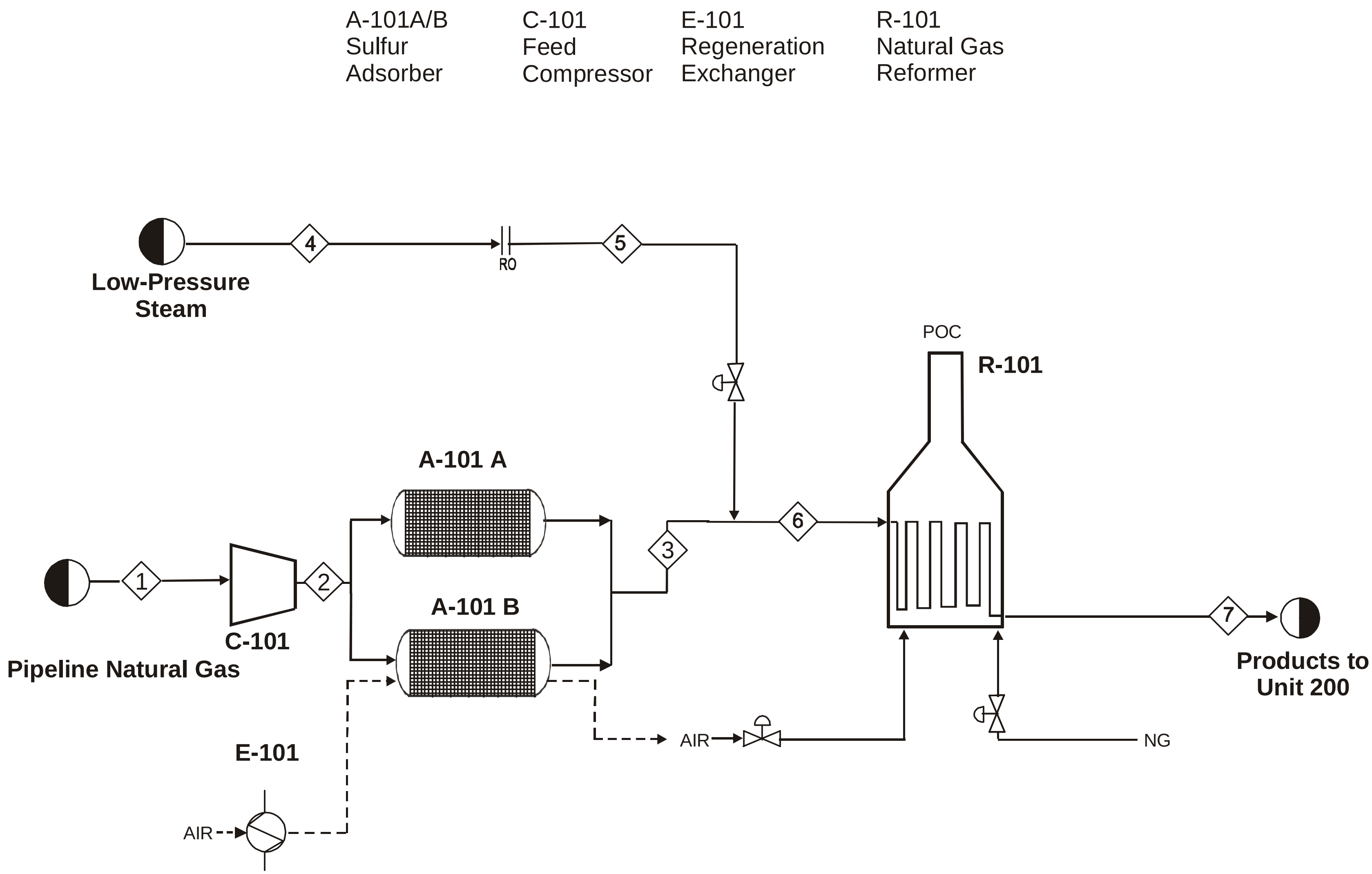
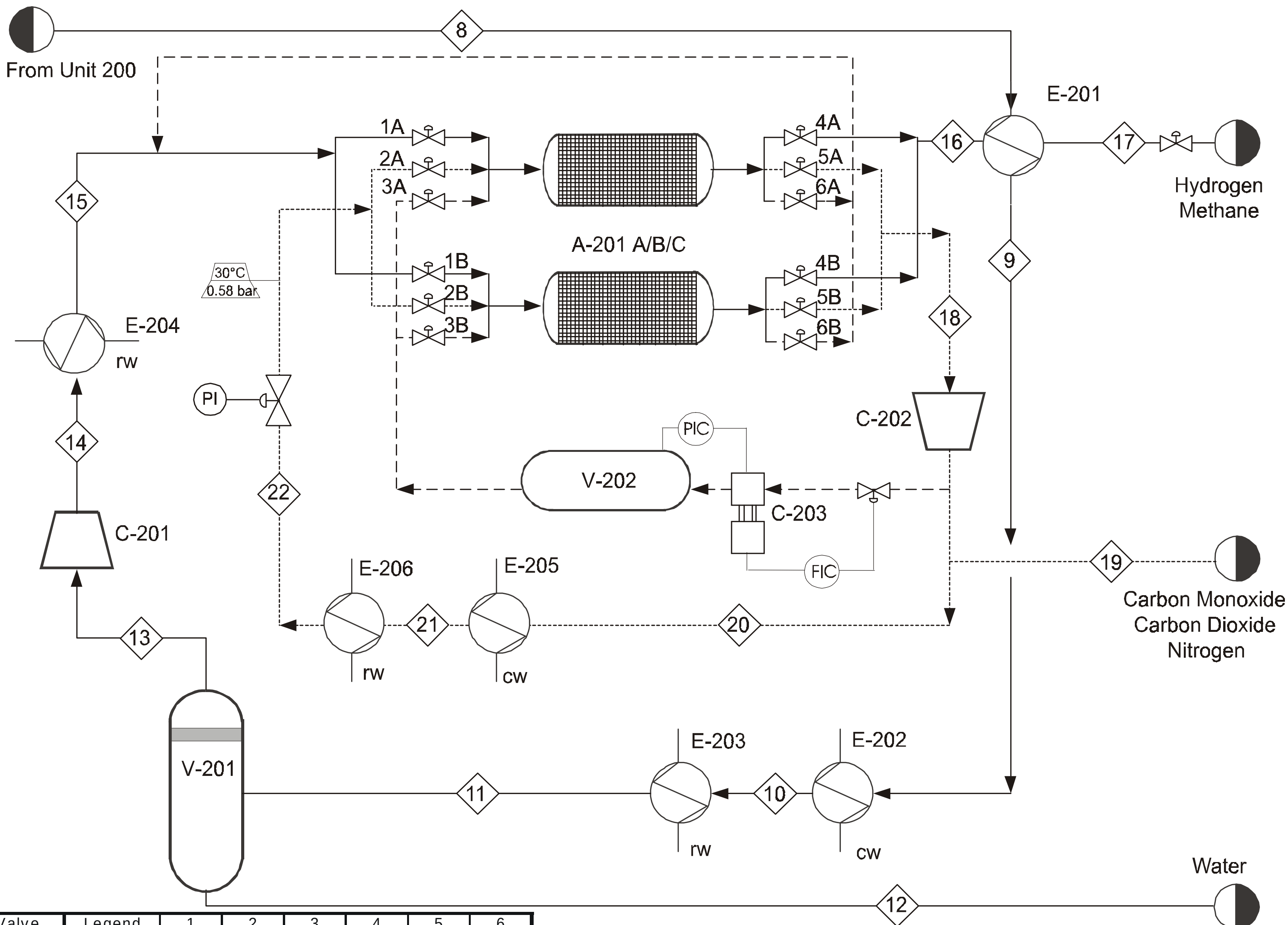


Figure 2. Process Flow Diagram for Unit 100



Valve	Legend	1	2	3	4	5	6
Adsorption		**O**	C	C	**O**	C	C
Flush	– – – – –	C	C	**O**	C	C	**O**
Desorption	···········	C	**O**	C	C	**O**	C

Figure 3. Unit 200 Process Flow Diagram

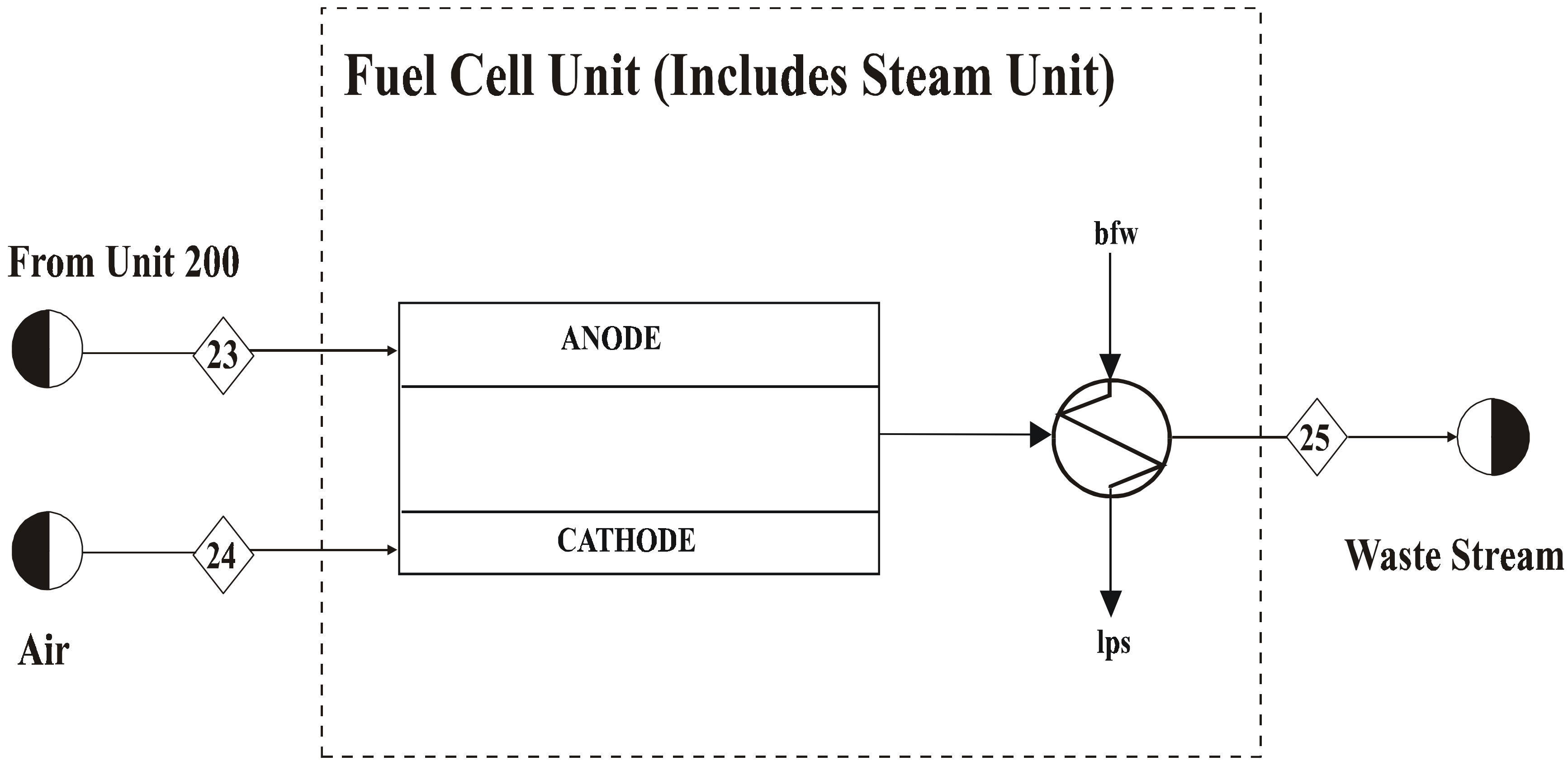


Figure 4. Unit 300: The Solid Oxide Fuel Cell Unit