Enzymatic Production of Formaldehyde and Hydrogen Peroxide from Methanol

Background

The process uses the enzyme, methanol oxidase, to convert alcohol and oxygen to formaldehyde and hydrogen peroxide. The goal is to produce 50,000 tonne/y of 50 wt% hydrogen peroxide and 60,000 tonne/y of formalin (37 wt% formaldehyde in water) using an enzymatic process. Formaldehyde, methanol, and hydrogen peroxide are considered carcinogenic and/or hazardous materials. In light of this, a process design was made that minimizes the waste and emissions generated.

Currently, many hollow fiber membrane (HFM) technologies are emerging into existing markets, allowing for more cost-effective separations and reactions. HFMs are becoming more useful in the chemical industry. With the recent growth in the areas of biochemical and environmental technologies, many potential future markets are available for the use of HFMs.

The enzyme, methanol oxidase, catalyzes the reaction in the continuous-stirred tank fermentor. HFMs were used in an ultrafiltration unit off of the continuous-stirred tank fermentor to recover the enzyme for recycle.

Process Description

The BFD (Figure 1) and four PFDs (Figures 2-5) show a process to produce formaldehyde and hydrogen peroxide. Methanol (fresh and recycled) at 49.3°C and 11.49 bar mixes with water (fresh and recycled) at 203.4°C and 11.49 bar. Together they enter heat exchanger, E-101, at 139°C and 11.49 bar and leave at 50°C and 11.15 bar. Oxygen (fresh and recycled) is sparged through the liquid mixture of methanol and oxygen. The oxygen must first diffuse into the water before it can be reacted. The enzyme, methanol oxidase, catalyzes the reaction. The reaction is a function of the enzyme concentration. The reactor has a conversion of oxygen of 74.5%.

The reaction must proceed at -22°C! To reach this temperature, a cooling jacket was added to the reactor. Refrigerant-134a (R-134a) flows through the cooling jacket. R-134a is sent through two compressors in series (C-201 A/B, no intercooling) to obtain a pressure of 8 bar. R-134a condenses and subcools to 35°C in E-201. It is then flashed to 0.75 bar, which lowers the temperature of the liquid R-134a to -28°C. The liquid R-134a is sent through the cooling jacket and then is recycled back through the same process. This refrigeration loop is illustrated in Figure 4.

The unreacted oxygen, taken from the top of the reactor, is compressed from 8 bar to 11.15 bar in compressor C-101 and is recycled back to Stream 3. The ultrafiltration unit recovers excess enzyme from the outlet of the reactor. The enzyme is sent back to the reactor for reuse. Stream 6, composed of formaldehyde, methanol, water, hydrogen peroxide, and oxygen, is sent to V-101 at -22°C and 11.15 bar.

Stream 6 is flashed to remove most of the oxygen along with trace amounts of the other products. The top, Stream 7, is sent to the incinerator. The bottom, Stream 8, is sent to T-101. This vacuum distillation column separates almost pure hydrogen peroxide as the bottom product, Stream 10, at 85°C and 0.35 bar. The top, Stream 9, is sent to V-103 at 66.6°C and 0.29 bar. Again, this flash unit separates out the oxygen leaving a negligible amount of oxygen behind in Stream 12.

Stream 12 is pumped to 1.22 bar in P-103 before it enters T-102. This tower removes mostly methanol with some water and small amounts of formaldehyde in Stream

13. P-106 A/B pumps Stream 13 up to 11.15 bar where it is recycled back to the reactor. The bottom, Stream 14, consists mainly of formaldehyde and water at 112.9°C and 1.53 bar. P-105 pumps Stream 14 up to 20 bar before entering T-103.

In T-103, water is separated from formaldehyde to produce a 37% by weight formaldehyde in water solution, Stream 15. This stream is at 207.4°C and 19.97 bar. The bottom of this tower, Stream 16, is mostly water at 239.7°C and 20.36 bar. It is split and some of the water is mixed with Stream 10 to produce the desired 50% by weight hydrogen peroxide in water in Stream 19. This stream is at 179.4°C and 20.36 bar.

Unit 300 provides the steam used in the distillation columns and flash vessels. The steam produced in this unit is at 20 bar. The condensate return from the process was pumped and then sent to H-301. The steam is sent to E-103, E-105, V-101, V-103, and V-103 at 240°C and 20 bar.

Necessary Information and Simulation Hints

Formaldehyde and hydrogen peroxide is produced by the following reaction

$$CH_3OH + O_2 \xrightarrow{\text{Methanol Oxidase}} CH_2O + H_2O_2$$

The enzyme, methanol oxidase, is stable for up to 2 days (1). But, when operating under cryogenic conditions, the enzyme can last for as long as 50 days (2).

The kinetic expression is of the Michaelis-Menten form

$$r_A = \frac{V_{max}\,[C_A]}{K_m + [C_A]}$$

The maximum rate of reaction, V_{max}, for this enzyme is a function of enzyme concentration, $[E_o]$, according to the following equation

$$V_{max} = TO\,[E_o]$$

where TO is the turnover number, 220 mole per minute per mole of active sites (1). The turnover number is the maximum amount of products that can be produced per active site on the enzyme (3). V_{max} was calculated to be 0.3137 mM/min.

The Michaelis-Menten constant, K_m, is dependent on enzyme concentration. However, in this case, the enzyme is at such a high concentration that oxygen becomes rate-limiting (1),

$$K_m = 0.4 \text{ mM}$$

Since, the enzyme is used to catalyze the reaction in the liquid phase, the oxygen must be dissolved into the liquid before it can react. Therefore, the relative rates of reaction and diffusion are important. By using the following equation (4)

$$\Phi = \sqrt{\frac{k_1 D_{AB}}{(k_C)^2}}$$

where k_1 is the reaction rate constant, D_{AB} is the diffusivity of oxygen in water, k_C is the mass transfer coefficient for a bubble in water, and Φ is the ratio of the rate of reaction to the rate of diffusion, it was estimated that

$$\Phi = 0.056$$

This means that the oxygen diffuses approximately 20 times faster than it reacts. Therefore, we can assume that water in the reaction vessel is fully saturated with oxygen.

Thermodynamic models in most simulators do not accurately predict the VLE involving water, methanol, hydrogen peroxide, and formaldehyde. K-values were input based on data for the water-formaldehyde-methanol system (5) and the water-hydrogen peroxide system (6).

References:

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2. Hattfield, G.W., "Enzymatic Process for Manufacturing Formaldehyde and Hydrogen Peroxide," U.S. Patent #5,234,827, 1993.

3. Richardson, J.F., and Peacock, D.G., *Chemical Engineering Volume 3, 3rd Edition*, Pergamon Press, New York, NY, 1994.

4. Cussler, E.L., *Diffusion, Mass Transfer Fluid Systems, 2nd Edition*, Cambridge, New York, 1997, Ch.16.

5. Gmehling, J., U. Onken, and W. Arlt, *Vapor-Liquid Equilibrium Data Collection*, Chemistry Data Series (Aqueous-Organic Systems – Supplement 1), Vol. 1, Part 1a, DECHEMA, 1981, pp. 474-475.

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Equipment Descriptions

R-101 A/B	Continuously Stirred Fermentor
UF-101 A/B	Ultrafiltration Enzyme Recovery
E-101	Reactor Feed Cooler
C-101	Oxygen Recycle Compressor
CJ-101	Reactor Cooling Jacket
V-101	O_2 Flash Unit
T-101	H_2O_2 Vacuum Distillation
E-102	H_2O_2 Condenser
V-102	H_2O_2 Reflux Drum
P-101 A/B	H_2O_2 Reflux Pumps
VU-101	Vacuum Unit
E-103	H_2O_2 Reboiler
P-102 A/B	H_2O_2 Bottoms Pump
V-103	O_2 Flash Unit
P-103 A/B	Product Pumps
T-102	Methanol Distillation Tower
E-104	Methanol Condenser
V-104	Methanol Reflux Drum
P-104 A/B	Methanol Reflux Pumps
E-105	Methanol Reboiler
P-105 A/B	Methanol Bottoms Pump
P-106 A/B	Methanol Recycle Pumps

T-103	Formalin Distillation Tower
E-106	Formalin Condenser
V-105	Formalin Reflux Drum
P-107 A/B	Formalin Reflux Pumps
C-201 A/B	Refrigerant Compressor
E-201	Refrigerant Cooler
V-201	Refrigerant Flash
H-301	Steam Package Boiler
P-301	Steam Loop Pump

Stream No.	1	2	3	4	5	6	7	8	9	10
Temperature (^oC)	49.3	203.4	38.9	50.0	90.2	-22.0	68.0	68.0	66.6	84.9
Pressure (bar)	11.49	11.49	11.15	11.15	11.15	11.15	0.35	0.35	0.29	0.35
Vapor Mole Fraction	0	0	1	0	1	0	1	0	0	0
Total Flow (kg/h)	8,300.4	44,962.0	3,993.6	53,262.4	1,001.6	56,221.0	58.8	56,160.2	53,037.1	3,121.1
Total Flow (kmol/h)	278.9	2,497.0	124.8	2,775.9	31.3	2,868.4	2.5	2,865.9	2,774.1	91.8
Component Flowrates (kmol/h)										
Formaldehyde	--	--	--	--	--	93.0	0.1	92.9	92.9	--
Methanol	234.3	--	--	234.3	0.1	141.2	0.4	140.8	140.8	--
Water	44.6	2,496.0	--	2,540.6	--	2,540.6	1.3	2,539.3	2,539.3	--
Hydrogen Peroxide	--	1.0	--	1.0	--	93.0	0.1	92.9	1.1	91.8
Oxygen	--	--	124.8	--	31.2	0.6	0.6	**	--	--

Stream No.	11	12	13	14	15	16	17	18	19
Temperature (^oC)	68.1	68.1	64.8	112.9	207.4	239.7	239.7	239.7	179.4
Pressure (bar)	0.29	0.29	1.22	1.53	19.97	20.36	20.36	20.36	20.36
Vapor Mole Fraction	1	0	0	0	0	0	0	0	0
Total Flow (kg/h)	1.0	53,036.0	4,942.5	48,092.1	7,502.4	62,198.7	37,465.1	21,609.0	6,249.2
Total Flow (kmol/h)	0.04	2,774.0	173.9	2,600.1	345.9	3,454.0	2,080.6	1,200.0	265.2
Component Flowrates (kmol/h)									
Formaldehyde	**	92.9	0.4	92.5	92.5	--	--	--	--
Methanol	0.01	140.7	128.9	11.8	11.8	--	--	--	--
Water	0.03	2,539.3	44.6	2,494.7	241.6	3,452.4	2,079.6	1,199.4	173.4
Hydrogen Peroxide	--	1.1	--	1.1	--	1.6	1.0	0.6	91.8
Oxygen	**	--	--	--	--	--	--	--	--

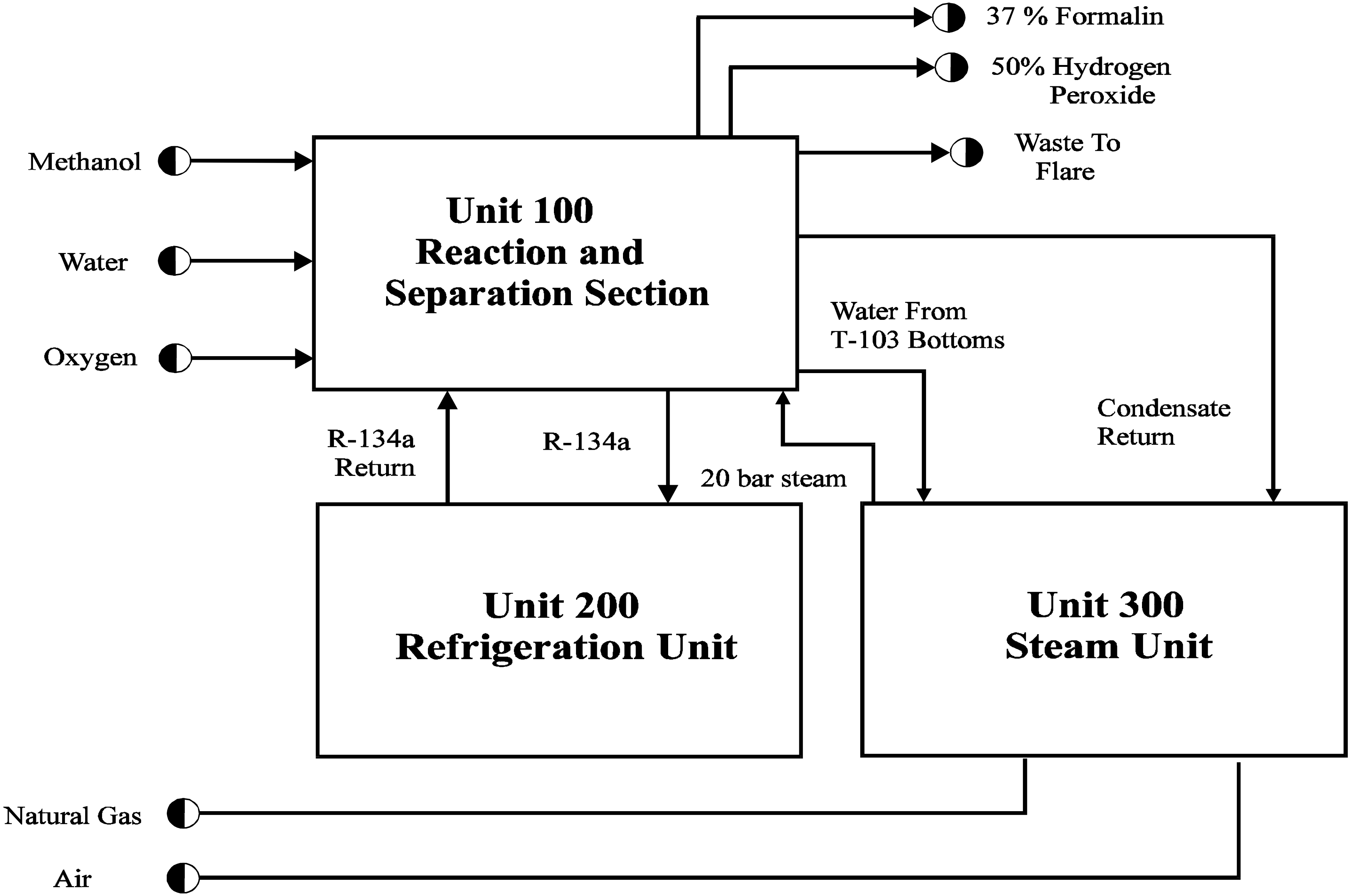

Figure 1 : Formalin and Hydrogen Peroxide Block Flow Diagram

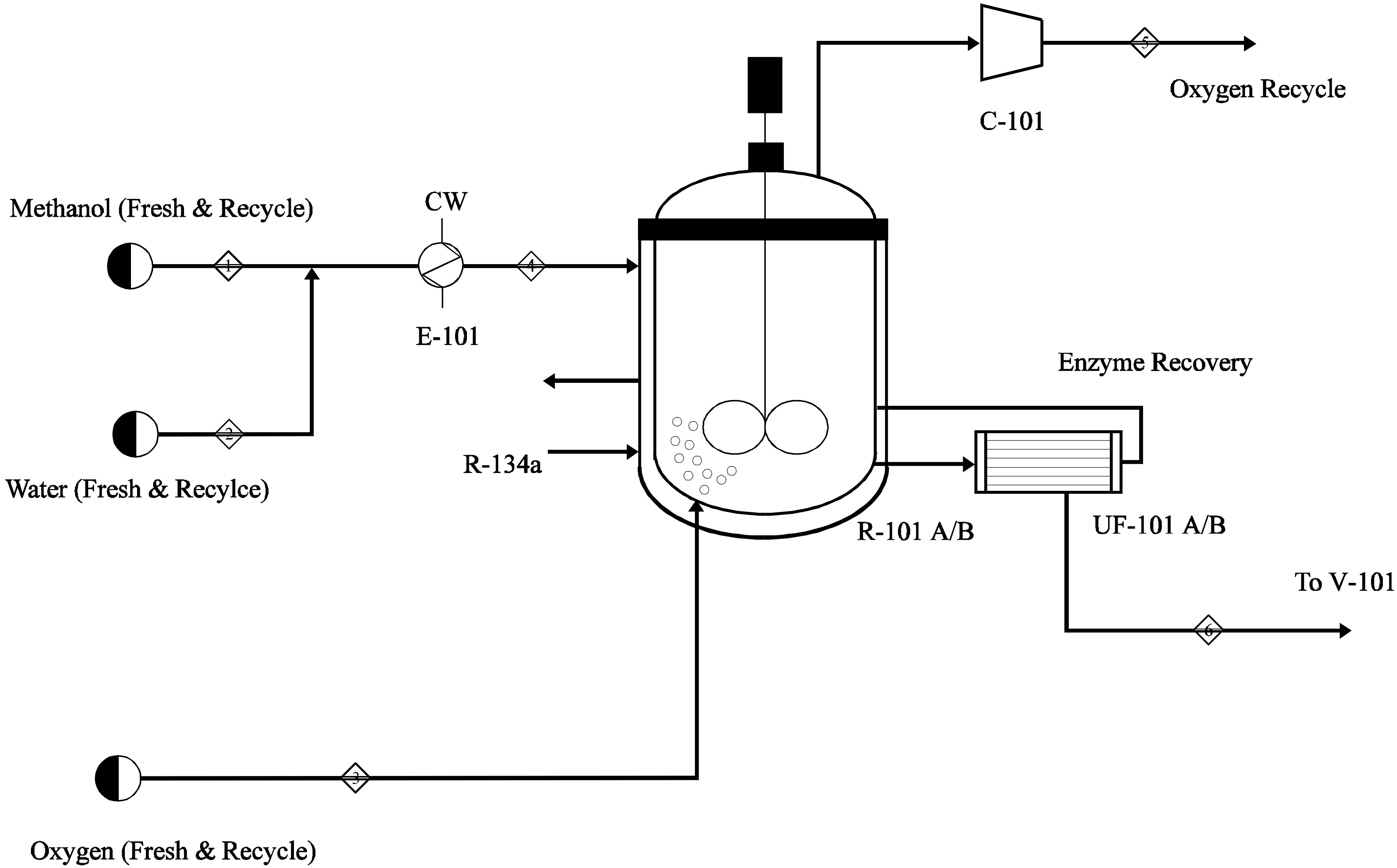

Figure 2 : Formaldehyde and Hydrogen Peroxide Reaction Section

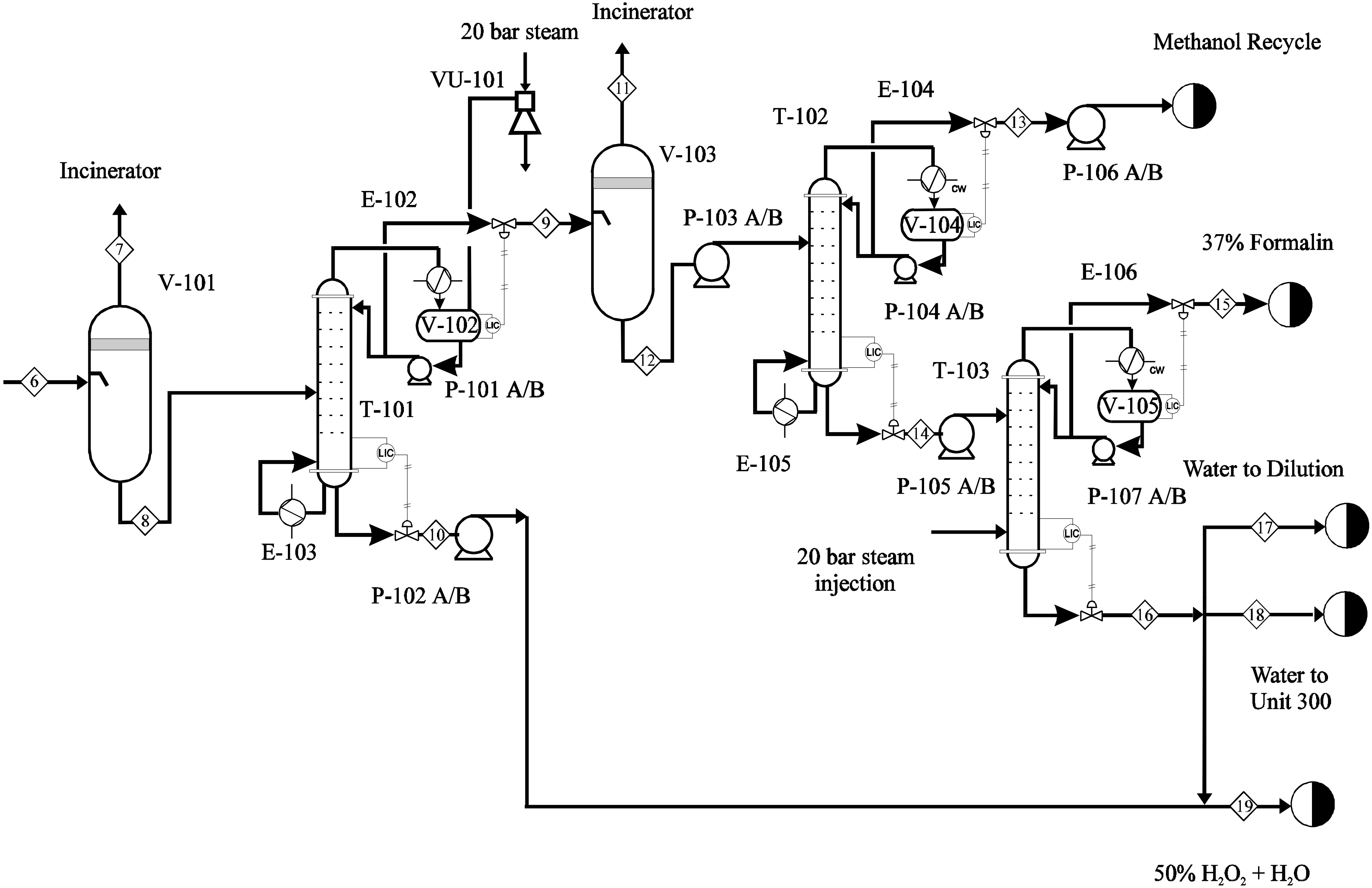

Figure 3 : Formaldehyde and Hydrogen Peroxide Separation Section

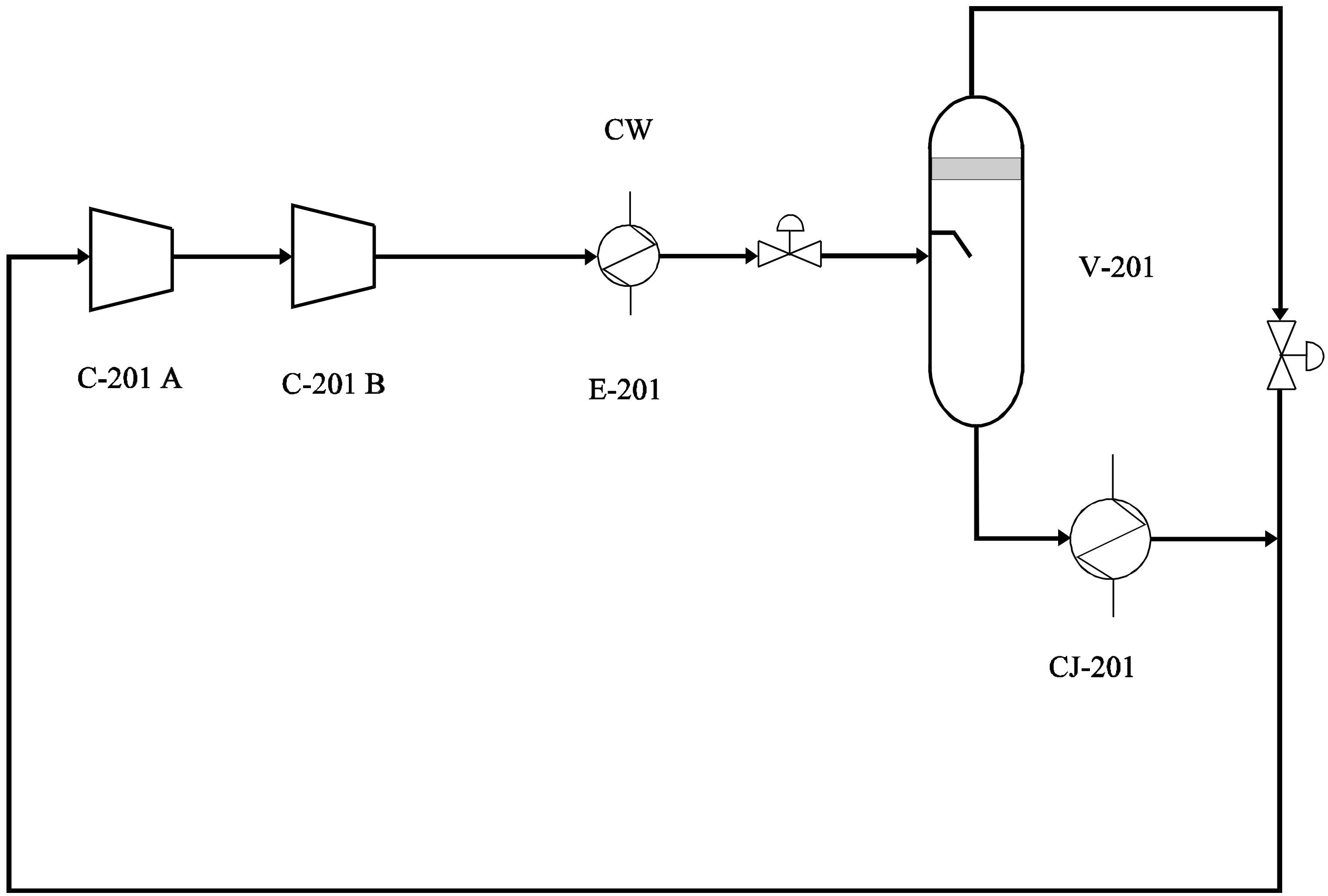

Figure 4 : Unit 200 -- Refrigeration Loop

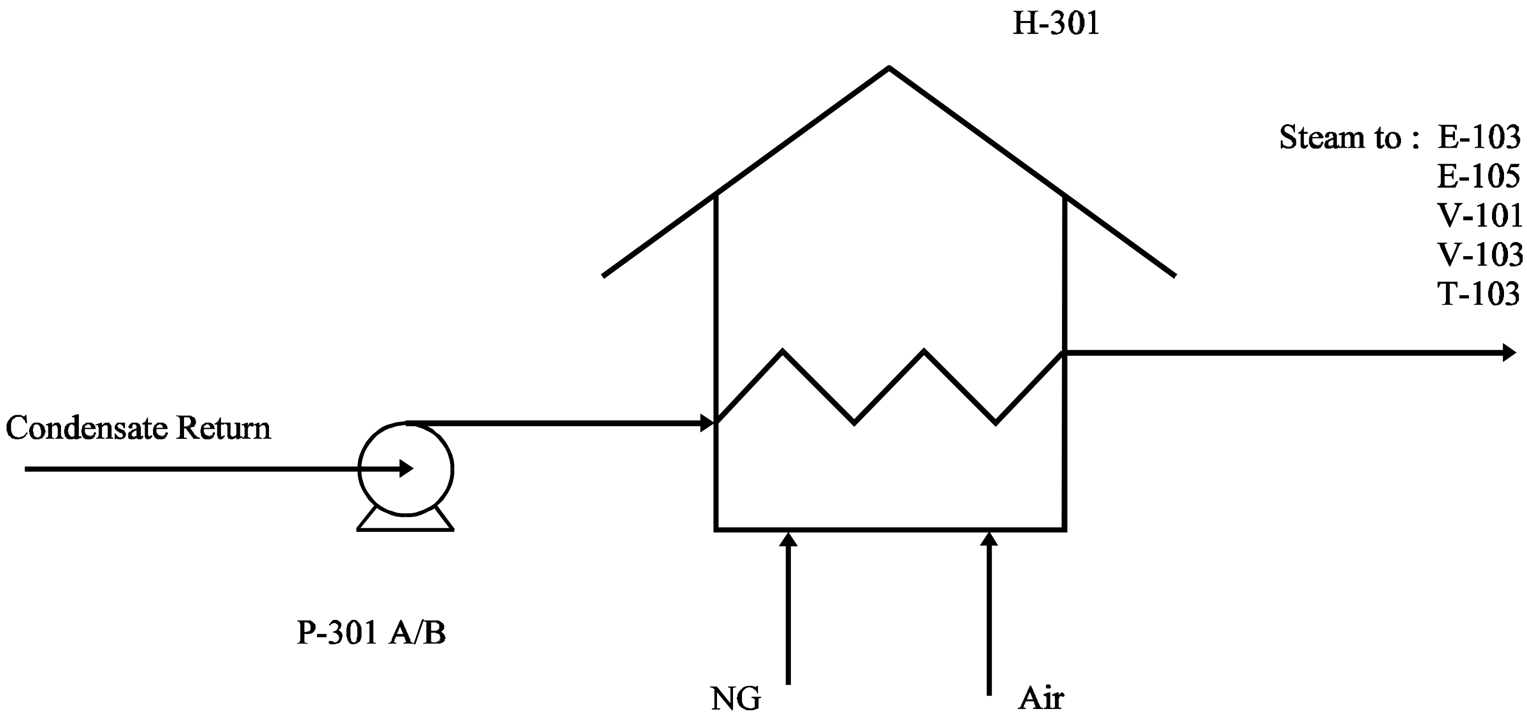

Figure 5 : Unit 300 -- Steam Production