Production of Formalin from Methanol

Background

JWR, a chemical corporation, is a diversified company. Current economic conditions have made JWR embark on a restructuring program in which it will focus on commodity chemicals while it divests itself of specialty and consumer products. Among the chemicals that JWR produces is methanol, mostly for internal consumption. A major use of internal methanol is to produce formalin, which is 37 wt% solution of formaldehyde in water. Formaldehyde and urea are used to make urea-formaldehyde resins, which are used as adhesives and binders for particleboard and plywood.

The preliminary design for this plant is to produce 50,000 tons/yr of formalin from methanol. A new catalyst has been identified which will simplify the reactor design and operation. This is an oxide catalyst that has approximately uniform activity over a one-year period, and catalyzes the oxidation reaction

$$CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O$$

This process produces 50,000 tons/yr of formalin (37 wt% formaldehyde in water) from methanol using the silver catalyst process (Figure 1).

Process Description

The PFD (Figure 1) shows a process to produce formaldehyde and water. Fresh methanol, Stream 2, at 30°C and 14.7 psia mixes with recycled methanol, Stream 15, at 68.3°C and 16 psia. Stream 3 (recycled and fresh methanol) is at 35.4°C and 14.7 psia. Pump, P-101, raises the pressure up to 35 psia. Stream 4 enters a heat exchanger where the methanol is vaporized. Stream 5 is then at 150°C and 29 psia. Fresh air is available at 25°C and 14.7 psia in Stream 1. Compressor, C-101, raises the pressure to 35 psia in Stream 5. This stream is then heated by medium-pressure steam. The temperature is raised to 150°C in Stream 7. Stream 6 and Stream 7 mix at a pressure of 29 psia. The combined mixture is at 149.6°C and 28 psia in Stream 8.

The reactor converts 87.4% of the methanol. The exit reactor temperature is 343°C. Heat is removed by making high-pressure steam from boiler feed water. The outlet, Stream 9, is at 343°C and 25 psia. A valve drops the pressure of this stream to 5 psia before it enters the absorber, T-101. Fresh water is sent through the T-101 at 30°C and 20 psia. T-101 is set to absorb 99% of the formaldehyde that enters. Stream 13 is then heated to 102°C before entering T-102, the formalin distillation column.

T-101 recovers a 37 wt% solution of formaldehyde in water. Most of the methanol is recovered in the distillate. Stream 15, the distillate, is recycled back to the inlet of fresh methanol at 68.3°C and 16 psia. The bottoms, Stream 16 is pumped, by P-103, up to 38.5 psia for storage. Deionized water at 30°C in Stream 18 is added to achieve the 37 wt% solution of formaldehyde in water. Storage of formalin is tricky. At high temperatures, undesirable polymerization of formaldehyde is inhibited, but formic acid formation is favored. At low temperatures, acid formation is inhibited, but polymerization is favored. With $\leq$ 2 wt% methanol, the storage tank contents must be maintained between 35°C and 45°C.

Necessary Information

Formaldehyde and water are formed in the following reaction:

$$CH_3OH + \frac{1}{2}O_2 \rightarrow HCHO + H_2O$$

The rate expression may be simplified to

$$-r_m \text{ [mole/g catalyst h]} \frac{k_1 p_m}{1 + k_2 p_m}$$

where p is a partial pressure in atm, and m refers to methanol (1). The catalyst bulk density is 100 lb/ft^3. The above constants are defined as (1)

$$\log_{10} k_1 = 11.43 - \frac{3810}{T}$$

$$\log_{10} k_2 = 10.79 - \frac{7040}{T}$$

where T is in Kelvin.

The existing absorber, T-101, has 10 trays each of which is 30% efficient. If a problem occurs in simulating the absorber, one solution is to use a component separator for the absorber. Use a mixer before the separator to add the distilled water. All of the non-condensables are sent to the top with small amounts of methanol, formaldehyde, and water. Then add a “fake” heat exchanger to cool the absorber effluent stream to 1°C subcooled.

Table 1 shows the *K*-values used for the simulation (2). Most process simulators allow these data to be input, and then the simulator interpolates temperatures and extrapolates pressures. These are used for all units containing liquid water and formaldehyde. Large *K*-values are used for the light gases so that they all exit in Stream 12.

Table 1: *K*-values for Formaldehyde/Water/Methanol System			
***P* (psia)** =14.696			
***T* (°C)**	**Formaldehyde**	**Water**	**Methanol**
0.1	0.123	1.000	0.273
67.1	0.266	0.491	1.094
72.1	0.336	0.394	1.435
74.8	0.374	0.453	1.598
84.6	0.546	0.607	2.559
97.6	0.693	1.105	2.589
99.9	0.730	1.198	2.595
150.1	1.220	2.460	3.004

Equipment Description

P-101 Methanol pump

E-101 Methanol vaporizer

C-101 Air Compressor

E-102 Air heater

R-101 Fluid bed reactor

T-101 Formalin absorber

E-103	Heater
T-102	Formalin distillation column
E-104	Methanol condenser
E-105	Formalin reboiler
P-102	Reflux pump
V-101	Reflux drum
P-103	Formalin pump
E-106	Formalin cooler

Reference

1. Mann, R.S. and K.W. Hahn, "Kinetics of the Vapor-Phase Oxidation of Methyl Alcohol on Manganese Dioxide-Molybdenum Trioxide Catalyst," *Journal of Catalysis*, vol. 15, pp. 329-341 (1969).

2. 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.

Stream Table for the Production of Formalin

Stream	1	2	3	4	5	6
Temp. (°C)	25.0	30.0	35.4	35.5	126.3	150.0
Press. (psia)	14.7	14.7	14.7	35.0	32.0	29.0
Vapor Fraction	1.0	0.0	0.0	0.0	1.0	1.0
Total Flow (kg/h)	13607.77	5668.26	6524.10	6524.10	13607.77	6524.02
Total Flow (kmol/h)	471.71	176.90	205.01	205.01	471.71	205.01
Component Flows (kmol/h)						
Methanol	--	176.90	201.80	201.80	--	201.80
Oxygen	98.73	--	--	--	98.73	--
Formaldehyde	--	--	0.01	0.01	--	0.01
Water	--	--	3.19	3.19	--	3.19
Nitrogen	372.98	--	--	--	372.98	--

Stream	7	8	9	10	11	12
Temp. (°C)	150.0	149.6	343.0	342.2	30.0	80.0
Press. (psia)	29.0	28.0	25.0	20.0	20.0	20.0
Vapor Fraction	1.0	1.0	1.0	1.0	0.0	1.0
Total Flow (kg/h)	13607.77	20131.70	20131.70	20131.70	2574.01	10904.77
Total Flow (kmol/h)	471.71	676.71	764.91	764.91	142.88	388.75
Component Flows (kmol/h)						
Methanol	--	201.80	25.41	25.41	--	0.25
Oxygen	98.73	98.73	10.53	10.53	--	10.53
Formaldehyde	--	0.01	176.41	176.41	--	1.76
Water	--	3.19	179.59	179.59	142.88	3.22
Nitrogen	372.98	372.98	372.98	372.98	--	372.98

Stream	13	14	15	16	17	18
Temp. (°C)	80.0	102.0	68.3	103.5	103.6	35.0
Press. (psia)	20.0	17.0	16.0	16.0	38.5	38.5
Vapor Fraction	0.0	0.0	1.0	0.0	0.0	0.0
Total Flow (kg/h)	11800.94	11800.94	855.84	10945.11	10945.11	3186.87
Total Flow (kmol/h)	519.04	519.04	28.11	490.93	490.93	176.90
Component Flows (kmol/h)						
Methanol	25.15	25.15	24.90	0.25	0.25	--
Oxygen	--	--	--	--	--	--
Formaldehyde	174.64	174.64	0.01	174.63	174.63	176.90
Water	319.24	319.24	3.19	316.05	316.05	--
Nitrogen	--	--	--	--	--	--

Stream	19	20
Temp. (°C)	62.2	35.0
Press. (psia)	38.5	35.5
Vapor Fraction	0.2	0.0
Total Flow (kg/h)	14131.98	14131.98
Total Flow (kmol/h)	667.83	667.83
Component Flows (kmol/h)		
Methanol	0.25	0.25
Oxygen	--	--
Formaldehyde	174.63	174.63
Water	492.95	492.95
Nitrogen	--	--

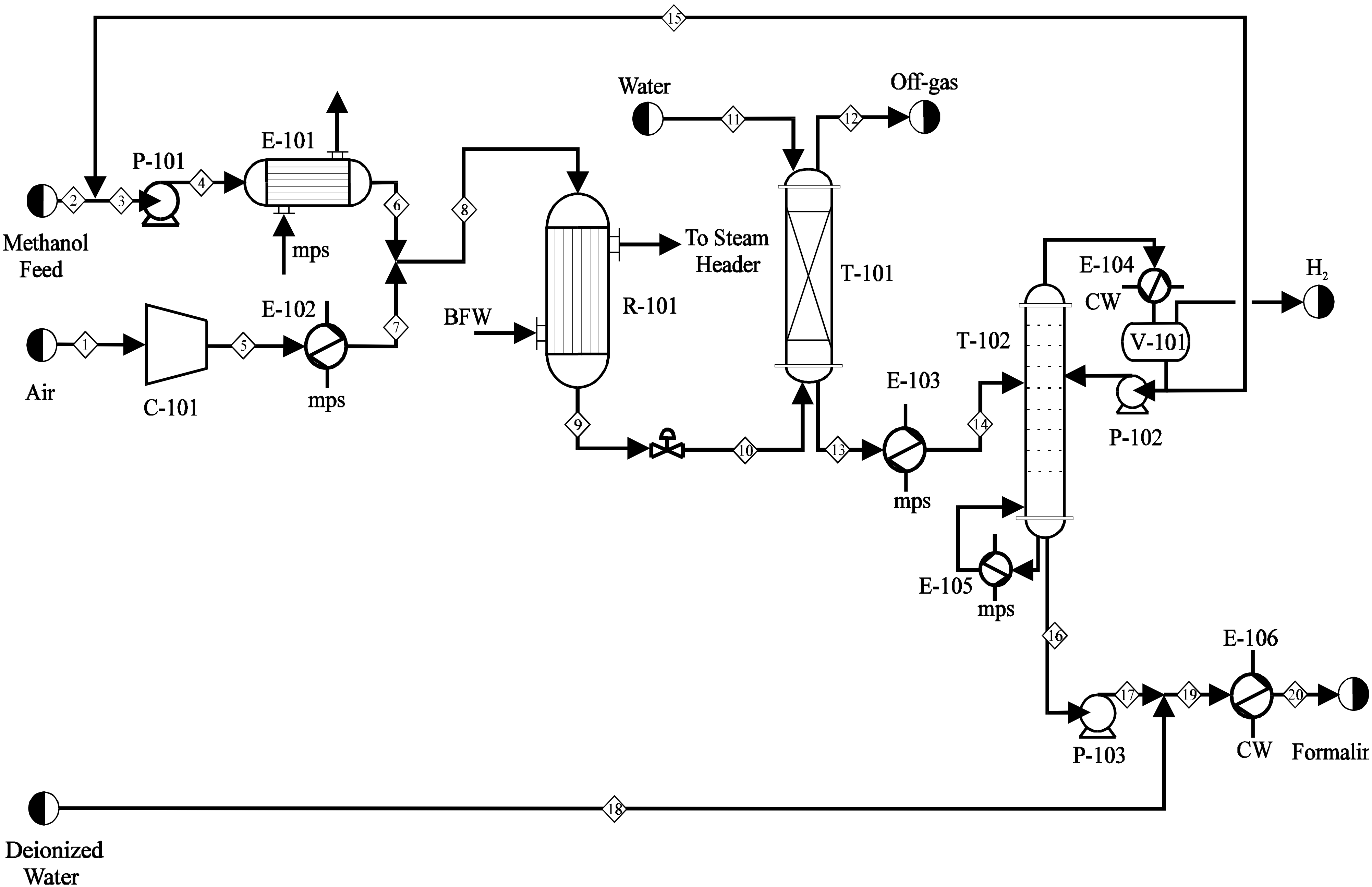

Figure 1: Production of Formalin from Methanol