Production of Acrolein

Background

Acrolein is a highly toxic, flammable material with extreme lacrimatory properties. At room temperature acrolein is a liquid with volatility and flammability somewhat similar to acetone, but unlike acetone, its solubility in water is limited. Acrolein has been produced commercially since 1938. In 1995, worldwide-refined acrolein nameplate capacity was about 113,000 ton/yr. Because of its antimicrobial activity, acrolein has found use as an agent to control the growth of microbes in process feed lines, thereby controlling the rates of plugging and corrosion. Acrolein at a concentration of <500 ppm is also used to protect liquid fuels against microorganisms [1]. The goal of this project is to design a grass roots facility that will safely and efficiently produce 50,000 metric tons per year of acrolein from propylene, air, and steam.

Process Description

A base case PFD is shown in Figure 1. Propylene (Stream 2), steam (Stream 4), and compressed air (Stream 6) are mixed and heated to 250°C. The resultant stream (Stream 8) is sent to a catalytic packed bed reactor where propylene and oxygen react to form acrolein. The reactor effluent is quickly quenched to 50°C with deionized water (Stream 13) to avoid further homogeneous oxidation reactions. Stream 14 is then sent to an absorber, T-101, where it is scrubbed with water and acrolein is recovered in the bottoms (Stream 17). The off gas, Stream 16, is sent to an incinerator for combustion. Stream 17 is then distilled in T-102 to separate acrolein and propylene from water and acrylic acid. The bottoms (Stream18) consisting of wastewater and acrylic acid are sent to waste treatment. The distillate (Stream 19) is sent to T-103 where propylene is separated from acrolein and the remaining water in the system. The distillate from T-103, contains 98.4% propylene. The possibility of recycling this stream can be investigated. The bottoms (Stream 21) is then sent to T-104 where acrolein is separated from water. Stream 23 is sent to waste treatment, and the distillate (Stream 22) consists of 98% pure acrolein.

Necessary Information and Simulation Hints

For safety reasons, the following criteria for the inlet composition to the reactor, R-101, must be strictly observed [2]:

mol% inert must be > 40%

mol% oxygen must be < 12%

mol% propylene must be< 12%

The temperature throughout the reactor must be kept below 330°C. At temperatures above 330°C, coke deposits form on the catalyst.

The following reactions and side reactions lead to the production of acrolein [2]:

$$C_3H_6 + O_2 \rightarrow C_3H_4O + H_2O \qquad (1)$$

$$C_3H_4O + \frac{7}{2}O_2 \rightarrow 3CO_2 + 2H_2O \qquad (2)$$

$$C_3H_4O + \frac{1}{2}O_2 \rightarrow C_3H_4O_2 \qquad (3)$$

$$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O \qquad (4)$$

These reactions are accompanied by the following kinetics [2]:

$$r_i = \frac{k_i(1+K_1+K_2+K_3)e^{-\frac{E_i}{R}\left(\frac{1}{T}-\frac{1}{\overline{T}}\right)\left[\frac{P_{O_2}}{\overline{P}_{O_2}}\right]\left[\frac{P_x}{\overline{P}_x}\right]}}{\left\{1+K_1\frac{P_{C_3H_6}}{\overline{P}_{C_3H_6}}+K_2\frac{P_{O_2}}{\overline{P}_{O_2}}+K_3\frac{P_{C_3H_4O_2}}{\overline{P}_{C_3H_4O_2}}\right\}}$$

K_1 =2, K_2 =4, K_3 =2, $\overline{T}$ =623K, R =1.987cal/mole/K, $\overline{P}_{C_3H_6}$ =28.1kPa, $\overline{P}_{O_2}$ =13.1kPa,

$\overline{P}_{c_3H_4O_2}$ =6.6kPa.

Reaction	Activation Energy	Pre-exponential Factor	x
i	(kcal/kmol)	(kmol/ft^3 reactor/hr)	
1	15,000	0.1080	C_3H_6
2	25,000	0.0162	C_3H_4O
3	20,000	0.0108	C_3H_4O
4	25,000	0.0054	C_3H_6

The process was simulated using the UNIFAC thermodynamic package for K-values and SRK for enthalpy. Other thermodynamic packages considered for the k-value (SRK, Peng Robinson, UNIQUAC) suggested an azeotrope between acrolein and water which would not allow purification of the acolein to the purity obtained here. The formation of an azeotrope must be considered in the final design since this may have a substantial impact on the design of the separation system.

Equipment Description

C-101	Feed Air Compressor
E-101	Reactor Preheater
E-102	Condenser
E-103	Reboiler

E-104	Condenser
E-105	Reboiler
E-106	Condenser
E-107	Reboiler
P-101A/B	Water Pump
P-102A/B	Reflux Pump
P-103A/B	Reflux Pump
P-104A/B	Reflux Pump
R-101	Packed Bed Reactor
T-101	Acrolein Absorber
T-102	Water Distillation Tower
T-103	Propylene Distillation Tower
T-104	Acrolein Distillation Tower
V-101	Reflux Vessel
V-102	Reflux Vessel
V-103	Reflux Vessel

References

1. "Acrolein and Derivatives," *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., vol. 1, 1997, pp. 232-247.

2. Personal Communication. Jean Cropley. Union Carbide Corporation.

Stream Tables

Stream	1	2	3	4	5	6	7	8
Temp. (°C)	204	197	159	144	25	111	140	250
Press. (kPa)	1157	203	600	203	101	203	203	203
Vapor Fraction	1	1	1	1	1	1	1	1
Total Flow (kmol/h)	240	240	1100	1100	1473	1473	2813	2813
Component Flows (kmol/h)								
Propylene	240.0	240.0	--	--	--	--	240.0	240.0
Water	--	--	1100.0	1100.0	--	--	1100.0	1100.0
Nitrogen	--	--	--	--	1158.0	1158.0	1158.0	1158.0
Oxygen	--	--	--	--	315.0	315.0	315.0	315.0
Acrolein	--	--	--	--	--	--	--	--
Acrylic Acid	--	--	--	--	--	--	--	--
Carbon Dioxide	--	--	--	--	--	--	--	--

Stream	9	10	11	12	13	14	15
Temp. (°C)	327	25	25	50	25	26	47
Press. (kPa)	197	101	197	197	101	101	101
Vapor Fraction	1	0	0	0	0	0	0
Total Flow (kmol/h)	2813	45000	45000	47814	10000	1386	56427
Component Flows (kmol/h)							
Propylene	78.8	--	--	78.8	--	44.4	34.4
Water	1310.9	45000.0	45000.0	46311.0	10000.0	46.2	56264.7
Nitrogen	1158.0	--	--	1158.0	--	1157.8	0.2
Oxygen	55.2	--	--	55.2	--	55.1	--
Acrolein	113.2	--	--	113.2	--	8.3	104.8
Acrylic Acid	23.1	--	--	23.1	--	--	23.2
Carbon Dioxide	74.6	--	--	74.6	--	74.5	0.2

Stream	16	17	18	19	20	21
Temp. (°C)	100	-71	-91	52	48	82
Press. (kPa)	101	101	101	101	101	101
Vapor Fraction	0	0	0	0	0	0
Total Flow (kmol/h)	56233	195	34.6	160	105.3	55.1
Component Flows (kmol/h)						
Propylene	--	34.4	34.00	0.3	0.3	--
Water	56208.0	56.3	--	56.3	1.8	54.52
Nitrogen	--	0.2	0.24	--	--	--
Oxygen	--	--	0.03	--	--	--
Acrolein	1.0	103.8	0.1	103.7	103.2	0.53
Acrylic Acid	23.1	--	0.18	--	--	0.02
Carbon Dioxide	--	0.2	--	--	--	--

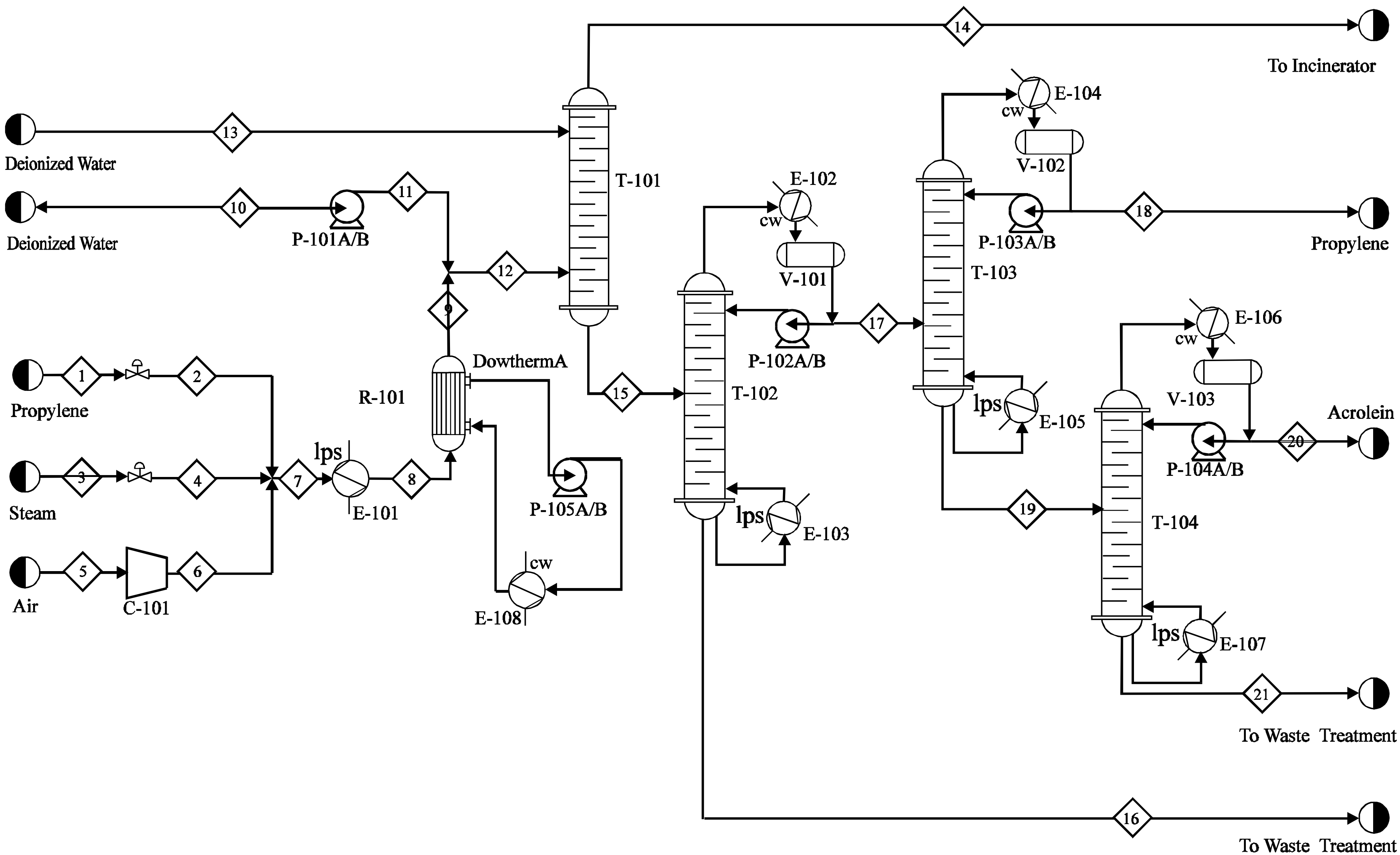

Figure 1: PFD for Production of Acrolein