Production of Dimethyl Carbonate

Background

Currently, dimethyl carbonate (DMC) is produced from phosgene and methanol, with HCl produced as a side product:

$$2CH_3OH + COCl_2 \rightarrow CH_3 - OCOO - CH_3 + 2HCl$$
methanol phosgene DMC

Phosgene is an extremely toxic and dangerous chemical. An environmentally-friendly alternative reaction path would eliminate the use of phosgene and minimize side-product formation.

In the presence of a copper chloride catalyst with a 5% KCl additive, DMC can be produced from methanol, carbon monoxide, and oxygen by:

$$2CH_3OH + CO + O_2 \rightarrow CH_3 - OCOO - CH_3 + H_2O$$
dimethyl carbonate

Formal, a by-product for which there is a market, is produced by the following side reaction:

$$2CH_3OH + CO \rightarrow CH_3 - O - CH_2 - O - CH_3 + \tfrac{1}{2}O_2$$
formal

DMC can be used as a reactant in place of phosgene in the manufacture of polyurethanes. Additionally, its high oxygen content makes it a candidate to replace MTBE as an oxygenated fuel additive.

Environmental Significance

Alternative reaction path

Production of an environmentally-friendly product

Process Description

There is a BFD and two PFDs attached. Here, oxygen, carbon monoxide, and methanol are mixed along with the recycle (Stream 27) and sent to the preheater (E-101) along with the flash recycle stream (Stream 13). E-101 vaporizes all components and sends them to the reactor (R-101) at 130°C and 2000 kPa. In R-101, the feed streams react to form DMC and formal. The stream leaving the reactor is immediately cooled to 50°C and then sent to the flash (V-101) where all light gases are flashed to the overhead stream. Ninety-nine percent of light gases are compressed and recycled back to E-101. One percent of the gases are purged and sent to the off-gas to avoid build up of CO_2 and N_2. The bottom of the flash is sent to tower, T-101, where methanol is separated to the top (Stream 16) and water is separated to the bottom (Stream 17). The DMC forms azeotropes with both components and is, therefore, split between both the top and the bottom streams. Stream 16 is sent to tower T-102 where pure methanol is separated from the bottom and recycled, and the top stream is sent to tower, T-104. In this tower, formal is purified and taken off as the bottom product, and all unreacted feeds and impure products are recycled back to E-101. Stream 17 is mixed with a recycled stream of water and DMC (Stream 34) and sent to tower, T-103, where wastewater is separated from the process. The remaining water and DMC are sent to tower T-105 where 70 kmol/hr of DMC is produced. The bottom of this tower is recycled and mixed with the feed to T-103.

Necessary Information and Simulation Hints

This reactor utilizes catalyzed vapor phase reactions. These reactions take place on a solid activated carbon substrate that is impregnated with the copper chloride catalyst. A heat transfer medium (Dowtherm A) flows through the shell side of the reactor in order to remove the exothermic heat of the reactions. The methanol, carbon monoxide, and oxygen feeds are mixed with the gas recycles from the flash and the separations section and are fed into the fired heater. This stream is vaporized and superheated to 130°C before entering the reactor. To remain within the constraints of the patent literature, the feed ratios entering the reactor for methanol/carbon monoxide/oxygen must be 0.9/1.6/1.0, respectively[1]. The reactor pressure must be 2000 kPa[1], as dictated by available sources.

In order to perform the detailed design of the reactor, the rate law for the formation of DMC was assumed to be first order in carbon monoxide. This seems reasonable, since the rate limiting step in the formation of DMC is the insertion of carbon monoxide into the cupric methoxychloride intermediate[1]. A rough value for the specific rate constant, *k*, was calculated from patent literature under the assumption of the first order kinetics[1]. Next, a high-end estimate for the activation energy of 200 kJ/mol was used to calculate the frequency factor of 2.58×10^{22} sec^{-1}. This is a conservative estimate to control temperature spikes. Because of the deactivation of the catalyst, it is necessary to operate two packed bed reactors in parallel to achieve a continuous process. As the catalyst in the first reactor begins to deactivate, it would be isolated for regeneration while the second reactor would be brought on-line.

Due to the explosive nature of the reactor feed stream (high percentage of hydrocarbons in the presence of oxygen), and the inherent possibility of temperature excursions within the packed bed reactor, it is necessary to inert the reactor feed stream with nitrogen. In order to keep the concentration of oxygen below the minimum oxygen concentration of 22% (for the reactor feed stream), approximately 3 kmol/hr of nitrogen are fed to the process.

For the production of DMC and formal, DMC is separated from water and methanol, and formal is separated from methanol. To perform the separations required for the production of DMC and formal, vapor/liquid equilibrium data were found. DMC and water, DMC and methanol, and formal and methanol form azeotropes. The equilibrium data for DMC and methanol were found at 38 kPa[2]. These experimental data were entered into Chemcad™, and Chemcad regressed the parameters to produce a best-fit equilibrium curve against the experimental information. Experimental equilibrium data for formal (also known as methylal or dimethoxymethane) and methanol were also found[3]. These data were entered into Chemcad and the parameters were regressed to produce a best-fit curve against the experimental information. Since Chemcad contained the equilibrium data for methanol and water, and the equilibrium data for DMC and methanol were found, Chemcad was able to predict the azeotrope formed between DMC and water.

The azeotropic point can be adjusted by manipulating the pressure. By changing the pressure, the azeotropic point will move allowing the feed concentration to the column to be shifted to the desired side of the azeotrope allowing for the appropriate separation.

Equipment Descriptions

P-101 A/B	Methanol pump
E-101	Reactor preheater
R101 A/B	Reactor
E-102	Waste heat boiler
P-102 A/B	Dowtherm A pump
C-101	Recycle compressor
E-103	Reactor effluent cooler
V-101	Flash vessel
T-101	Water-methanol separator
E-104	Condenser for T-101

E-105	Reboiler for T-101
V-101	Reflux drum for T-101
P-104 A/B	Reflux pump for T-101
P-105 A/B	Water/DMC pumps
T-102	Methanol-formal separator
E-106	Condenser for T-102
E-107	Reboiler for T-102
V-103	Reflux drum for T-102
P-106 A/B	Reflux pump for T-102
T-103	Water-DMC separator
E-108	Condenser for T-103
E-109	Reboiler for T-103
V-104	Reflux drum for T-103
P-107 A/B	Reflux pump for T-103
P-108 A/B	Formal pump
T-104	Formal purification tower
E-110	Condenser for T-104
E-111	Reboiler for T-104
V-105	Reflux drum for T-104
P-109 A/B	Reflux pump for T-104
T-105	Methanol-formal separator
E-112	Condenser for T-105
E-113	Reboiler for T-105

V-106	Reflux drum for T-105
P-110 A/B	Reflux pump for T-105
P-111 A/B	Methanol recycle pump

References

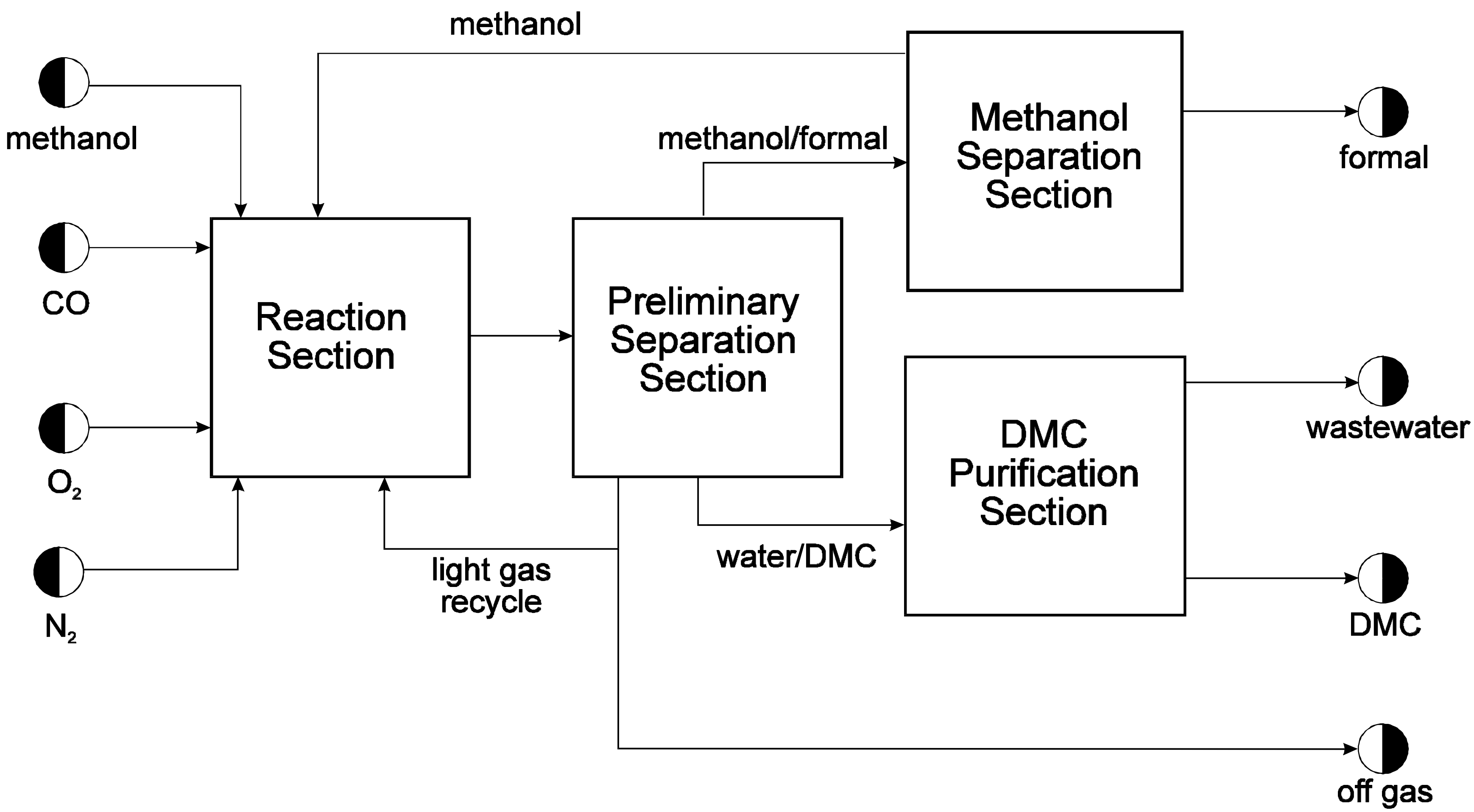
1. U.S. Patent #5523452, June 4, 1996, Z. Kricsfalussy, et al.
2. Fancesconi, R., *Journal of Chemical Engineering Data*, **41** 736 (1996).
3. Data available from Harry Kooijman and Ross Taylor at http://www.clarkson.edu/~chengweb/faculty/taylor/maple/data/nrtl.ipd

Stream Table for DMC Production

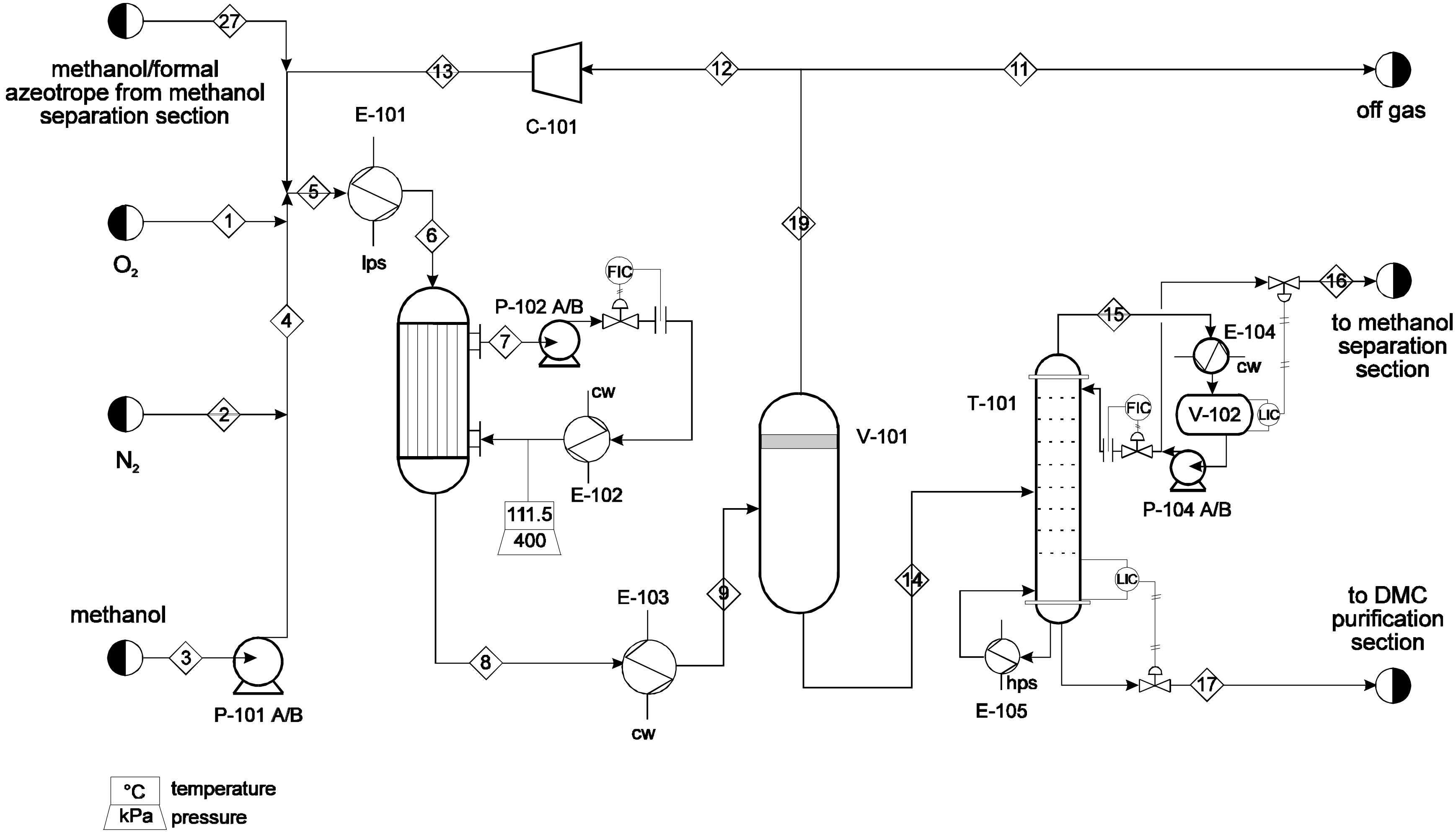
Stream No.	1	2	3	4	5	6	7	8	9	10	11	12
Temperature (°C)	25.0	25.0	25.0	25.0	46.3	130.0	118.2	137.0	45.0	45.0	45.0	45.0
Pressure (kPa)	2000	2000	100	2000	2000	2000	500	2000	2000	1900	1900	1900
Vapor mole fraction	1.0	1.0	0.0	1.0	1.0	1.0	0.0	1.0	1.0	1.0	1.0	1.0
Total Flow (kg/h)	1601.8	2681.7	5604.5	8286.2	106517.84	106517.84	1400000	106517.8	106517.8	94811.9	948.1	93863.8
Total Flow (kmol/h)	52.8	95.7	174.9	270.6	3346.5	3346.5	8428	3209.4	3209.4	2999.8	30	2969.8
Component Flowrates (kmol/h)												
Nitrogen	22.0	-	-	-	2170.6	2170.6	dowtherm	2170.6	2170.6	2170.6	21.7	2148.9
Oxygen	30.8	-	-	-	190.8	190.8		161.6	161.6	161.6	1.6	160
Carbon Dioxide	-	-	-	-	427.1	427.1		431.6	431.6	431.6	4.3	427.1
Carbon Monoxide	-	95.7	-	95.7	240.6	240.6		146.1	146.1	146.1	1.5	144.7
Formal	-	-	-	-	80.7	80.7		98.1	98.1	56.6	0.6	56
Methanol	-	-	174.9	174.9	224.8	224.8		45.0	45.0	20.9	0.2	20.7
DMC	-	-	-	-	7.6	7.6		79.5	79.5	7.7	0.1	7.6
Water	-	-	-	-	5.0	5.0		76.9	76.9	5.0	0.1	4.9

Stream No.	13	14	15	16	17	18	19	20	21	22	23	24	25
Temperature (°C)	51.0	45.0					59.9						
Pressure (kPa)	2000	1900					200.0						
Vapor mole fraction	1.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow (kg/h)	93863.8	11705.9	9066.6	4346.0	7600.7	57143.0	3571.4	3571.4	774.6	18095.1	17573.4	17573.4	2261.9
Total Flow (kmol/h)	2969.8	209.6	162.7	78.0	140.7	862.5	53.9	53.9	24.1	293.6	402.7	402.7	36.7
Component Flowrates (kmol/h)													
Nitrogen	2148.9	-	-	-	-	-	-	-	-	-	-	-	-
Oxygen	160.0	-	-	-	-	-	-	-	-	-	-	-	-
Carbon Dioxide	427.1	-	-	-	-	-	-	-	-	-	-	-	-
Carbon Monoxide	144.7	-	-	-	-	-	-	-	-	-	-	-	-
Formal	56.0	41.5	87.36	41.86	-	672.8	41.86	41.86	-0.00	196.71	-	-	24.65
Methanol	20.7	24.1	75.00	35.97	0.04	189.8	12.05	12.05	23.93	96.89	0.04	0.04	12.04
DMC	7.6	71.8	0.16	0.07	70.30	-	-	-	0.07	-	143.18	143.18	-
Water	4.9	71.9	0.16	0.07	70.32	-	-	-	0.07	-	259.48	259.48	-

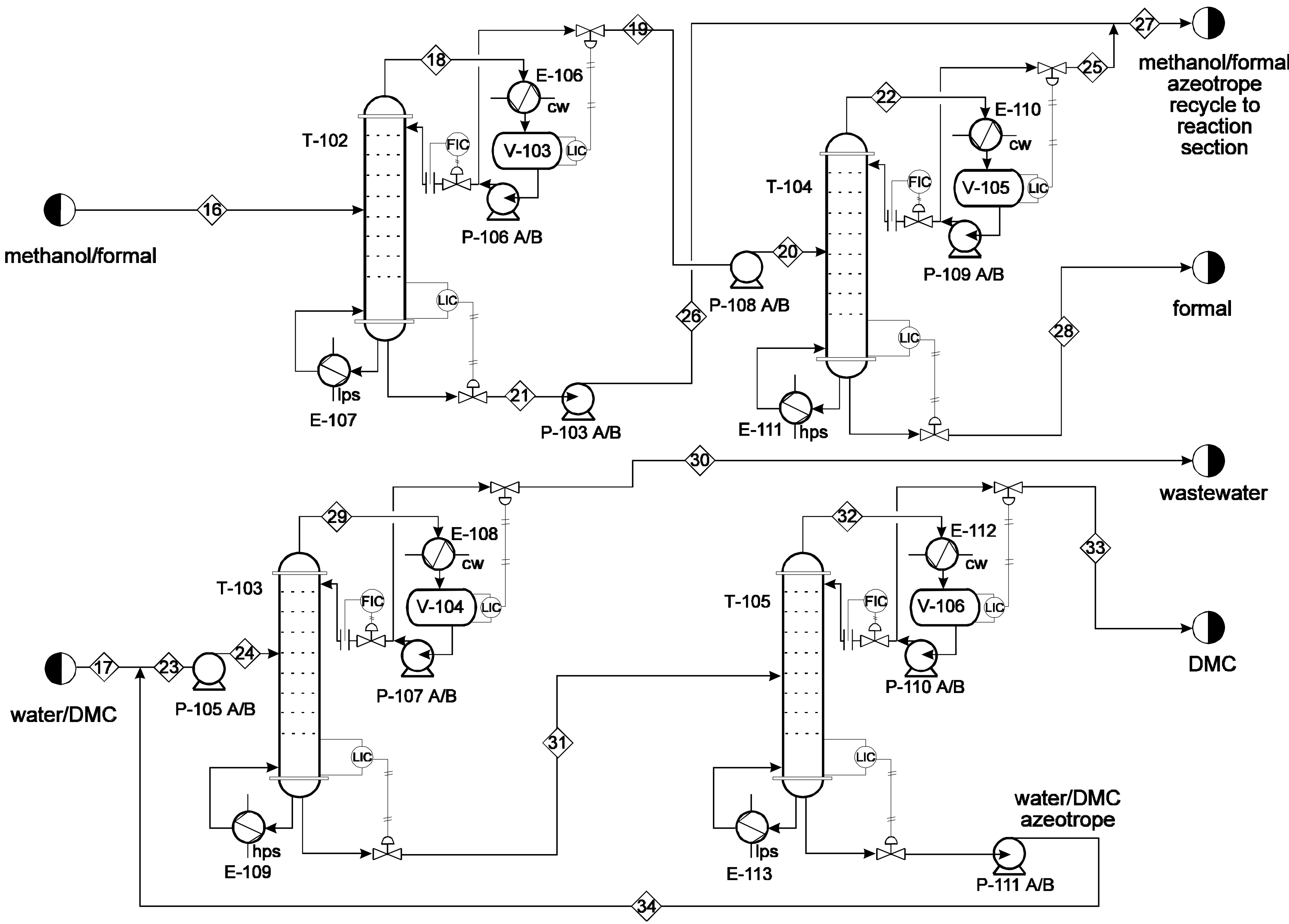
Stream No.	26	27	28	29	30	31	32	33	34
Temperature (°C)									
Pressure (kPa)									
Vapor mole fraction	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Flow (kg/h)	774.6	3036.4	1309.4	32855.4	1263.7	16305.0	67605.1	6335.7	9969.2
Total Flow (kmol/h)	24.1	60.8	17.2	1823.0	70.1	332.4	751.1	70.4	262.0
Component Flowrates (kmol/h)									
Nitrogen	-	-	-	-	-	-	-	-	-
Oxygen	-	-	-	-	-	-	-	-	-
Carbon Dioxide	-	-	-	-	-	-	-	-	-
Carbon Monoxide	-	-	-	-	-	-	-	-	-
Formal	-	24.65	17.21	-	-	-	-	-	-
Methanol	23.93	35.97	-	-	0.04	-	-	-	-
DMC	0.07	0.07	-	-	-	143.16	751.10	70.32	72.84
Water	0.07	0.07	-	1823.00	70.08	189.23	-	0.07	189.16



DMC Production Block Flow Diagram



DMC Reaction and Preliminary Separation Sections



DMC Purification and Methanol Separation Sections