Production of Dimethyl Ether

Background

A feasibility study on the production of 99.5 wt% dimethyl ether (DME) is to be performed. The plant is capable of producing 50,000 metric tons of DME per year via the catalytic dehydration of methanol over an acid zeolite catalyst. The goal is to design a grass-roots facility, which safely and efficiently produces DME.

DME is used primarily as a propellant. DME is miscible with most organic solvents and it has a high solubility in water [1]. Recently, the use of DME as a fuel additive for diesel engines has been investigated due to its high volatility (desired for cold starting) and high cetane number.

Process Description

A PFD of the process is shown in shown in Figure 1. The essential operations in the process are the preheating of the raw material (nearly pure methanol), reacting methanol to form DME, product separation, contaminant separation, and methanol separation and recycle.

Crude methanol, containing about 2 mol % impurities, is fed as a liquid in Stream 1, pumped up to 16.8 atm and combined with Stream 19, a methanol recycle stream. Stream 4 is then sent into heat exchanger E-101 where it is heated to a temperature of 250°C before it is sent to a packed bed reactor, R-101, to form DME. The reaction is slightly exothermic and the reaction products are heated to approximately 365°C before leaving the reactor. The reactor effluent is cooled in E-102 and then throttled to 10 atm before entering T-101. Here, the dimethyl ether is separated from the other components as distillate, Stream 9. The bottom product, Stream 10, is throttled to 6.9 atm and sent to T-102 where the methanol and water are separated from the waste components. The waste components exit as distillate, Stream 12, and are sent to a waste treatment facility. The water and methanol exit as the bottoms stream, Stream 13. This stream is then throttled to 1 atm and then sent to T-103 where the water and methanol are separated. The water exits the bottom of the distillation column as Stream 15, and is sent to waste treatment. The methanol exits the column as distillate, Stream 16. Stream 16 is then pumped up to 16.8 atm and recycled back to mix with fresh methanol, Stream 3 in vessel V-104.

Necessary Information and Simulation Hints

The production of DME is via the catalytic dehydration of methanol over an amorphous alumina catalyst treated with 10.2% silica. A methanol conversion of about 80% is achieved in the reactor. DME is produced by the following reaction:

$$2CH_3OH = CH_3OCH_3 + H_2O$$

In the temperature range of normal operation, there are no significant side reactions, and the equilibrium conversion for pure methanol feed exceeds 92%. Therefore, the reactor is kinetically controlled in the temperature range of normal operation.

Above 250°C, the rate equation is given by Bondiera and Naccache [2] as:

$$-r_{methanol} = k_0 \exp\left[-\frac{E_a}{RT}\right] p_{methanol}$$

Where k_0 = 1.21×10^6 kmol/(m^3 reactor h kPa), E_a = 80.48 kJ/mol, and $p_{methanol}$ = partial pressure of methanol (kPa).

Significant catalyst deactivation occurs at temperatures above 400°C, and the reactor should be designed so that this temperature is not exceeded anywhere in the reactor. Since the DME reaction is not highly exothermic, the proper temperatures can be maintained by preheating the feed to no more than 250°C and running the reactor adiabatically.

The process was simulated using the NRTL thermodynamic package for K-values and SRK for enthalpy.

Equipment Descriptions

E-101	Methanol Preheater
E-102	Reactor Effluent Cooler
E-103	Reboiler
E-104	Condenser
E-105	Reboiler
E-106	Condenser
E-107	Reboiler
E-108	Condenser
P-101A/B	Feed Pumps
P-102A/B	Reflux Pumps
P-103A/B	Reflux Pumps
P-104A/B	Reflux Pumps
P-105A/B	Recycle Pumps

R-101	Packed Bed Reactor
T-101	DME Distillation Column
T-102	Impurities Distillation Column
T-103	Methanol Distillation Column
V-101	Reflux Drum
V-102	Reflux Drum
V-103	Reflux Drum
V-104	Feed Drum

References

1. "DuPont Talks About its DME Propellant," *Aerosol Age*, May and June, 1982.

2. Bondiera, J., and C. Naccache, "Kinetics of Methanol Dehydration in Dealuminated H-Mordenite: Model with Acid and Base Active Centres," *Applied Catalysis*, **69**, 139-148 (1991).

Stream Tables for DME Production

Stream	1	2	3	4	5	6
Temp. (°C)	25.00	25.25	25.31	33.64	250.00	365.65
Press. (atm)	1.00	16.78	15.10	15.10	14.99	14.90
Vapor Fraction	0.00	0.00	0.00	0.00	1.00	1.00
Total Flow (kg/h)	8627.85	8627.85	8627.85	10718.96	10718.96	10718.96
Total Flow (kmol/h)	270.14	270.14	270.14	335.99	335.99	335.99
Component Flows (kmol/h)						
Methanol	264.74	264.74	264.74	329.21	329.21	65.84
Dimethyl Ether	0.27	0.27	0.27	0.27	0.27	131.95
Water	4.05	4.05	4.05	5.42	5.42	137.11
Acetaldehyde	0.27	0.27	0.27	0.27	0.27	0.27
Acetic Acid	0.41	0.41	0.41	0.41	0.41	0.41
Acetone	0.41	0.41	0.41	0.41	0.41	0.41

Stream	7	8	9	10	11	12
Temp. (°C)	135.19	125.56	46.00	153.98	138.82	80.13
Press. (atm)	14.90	10.26	10.26	10.26	6.91	6.91
Vapor Fraction	0.50	0.53	0.00	0.00	0.0459	0.00
Total Flow (kg/h)	10718.96	10718.96	6071.47	4645.12	4645.12	64.04
Total Flow (kmol/h)	335.99	335.99	131.81	204.11	204.11	1.49
Component Flows (kmol/h)						
Methanol	65.84	65.84	0.043	65.79	65.78	0.66
Dimethyl Ether	131.95	131.95	131.67	0.26	0.26	0.26
Water	137.11	137.11	--	137.08	137.08	--
Acetaldehyde	0.27	0.27	0.0988	0.1714	0.1714	0.1714
Acetic Acid	0.41	0.41	--	0.4055	0.4055	--
Acetone	0.41	0.41	0.0009	0.4126	0.4126	0.4043

Stream	13	14	15	16	17
Temp. (°C)	138.97	80.93	101.47	66.87	67.21
Press. (atm)	6.91	1.09	1.09	1.09	15.10
Vapor Fraction	0.00	0.14	0.00	0.00	0.00
Total Flow (kg/h)	4581.07	4581.07	2489.96	2091.11	2091.11
Total Flow (kmol/h)	202.62	202.62	136.76	65.85	65.85
Component Flows (kmol/h)					
Methanol	65.13	65.13	0.65	64.48	64.48
Dimethyl Ether	--	--	--	--	--
Water	137.08	137.08	135.71	1.37	1.37
Acetaldehyde	--	--	--	--	--
Acetic Acid	0.4055	0.4055	0.4053	0.0002	0.0002
Acetone	0.0083	0.0083	--	0.0083	0.0083

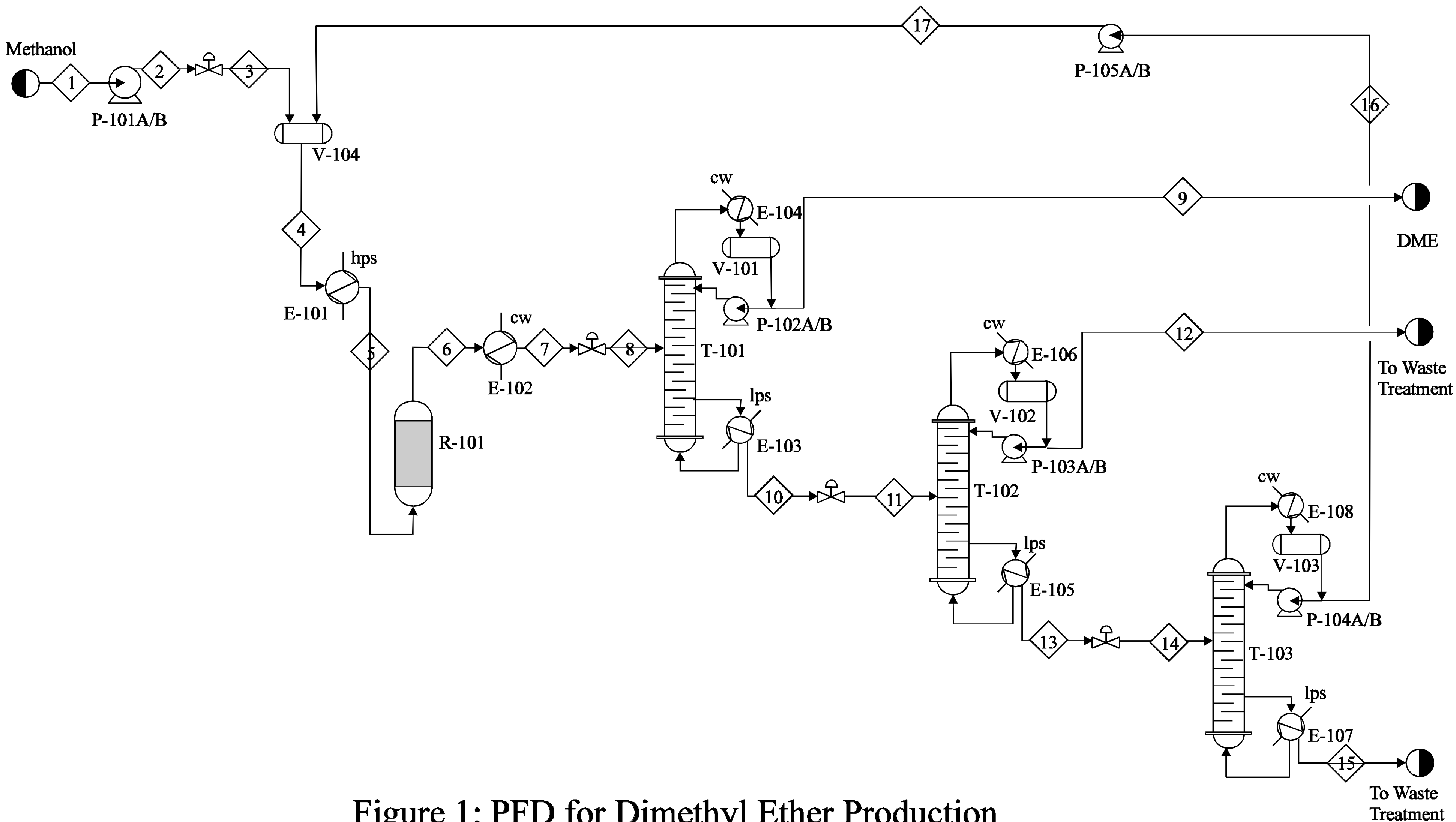

Figure 1: PFD for Dimethyl Ether Production