Dimethylformamide from Supercritical Carbon Dioxide

Background

Dimethylformamide (DMF) is a solvent that dissolves a wide variety of organics. It has been called the universal solvent because of its wide organic and inorganic solvency. DMF owes this versatility to its high dielectric constant, wide liquid range, and low volatility. DMF is completely miscible in water and is both chemically and thermodynamically stable. DMF is used primarily in the pharmaceutical processing and acrylic fiber production industries. These uses account for about 50% of the total demand. DMF is also used in various extraction and absorption processes as well as being extensively used as a solvent, reagant and catalyst in synthetic organic chemistry.

Most of the current methods for the production of DMF use carbon monoxide, which is flammable and highly toxic, as well as liquid organic solvents which are problematic due to their flammability, toxicity, and disposal costs. The method discussed here uses supercritical carbon dioxide as both a reactant and the reaction medium.[1] The process proceeds in two steps, both occurring in one reactor. In the first step, carbon dioxide is hydrogenated to formic acid catalyzed by a ruthenium (II) phospine homogeneous catalyst. The second step is the reaction of formic acid with dimethylamine to form DMF.

Environmental Significance

environmentally-friendly process

Process Description

The PFD is attached. The hydrogen is fed as a gas in Stream 1, and compressed by compressor C-801 to the reaction pressure. The carbon dioxide feed stream, Stream 3, is compressed by compressor C-802 to the necessary pressure. These two streams will mix with Stream 7, the dimethylamine feed, which has been pumped up to reaction pressure by pump P-

801 A/B and heated to reaction temperature by E-801. Stream 8, which contains the three feed streams after mixing, enters the reactor, R-801, at 116°C and 210 atm. The reactor is a packed bed with a ruthenium (II) phosphine catalyst.

After the reaction takes place, a temperature and pressure reduction is used to drive the reaction products from the supercritical phase to the aqueous phase, prior to the separation section. The reactor effluent in Stream 9 is flashed in V-801 at 50°C and 130 atm. The supercritical phase, composed of hydrogen, carbon dioxide, and trace amounts of other components, is removed from the aqueous phase, which contains DMF and other reaction products. The supercritical phase in Stream 10 can be recycled back to be used in the reactor again. The aqueous stream, Stream 11, is flashed again prior to the distillation towers in vessel V-802. The off gas, Stream 12, containing mostly hydrogen and carbon dioxide can be flared. The aqueous stream, Stream 13, is then sent to the separation section.

The first distillation tower, T-801, separates the remaining carbon dioxide, hydrogen, dimethylamine, and water from formic acid and DMF. The distillate stream, Stream 14, containing mostly water and dimethylamine, then enters the DMA stripping tower, T-802. Here, the remaining carbon dioxide, hydrogen, and dimethylamine are separated from the wastewater, as the distillate stream, Stream 15. This stream can be recycled back to the reactor. The wastewater exits as the bottoms product in Stream 16 and must be treated. The DMF tower, T-803, is fed from the bottoms of the first tower. Here, the DMF product is separated from formic acid. The DMF product exits in the distillate stream, Stream 18. The bottoms stream, Stream 19, which contains a DMF/formic acid azeotrope, can be recycled back to the reactor.

Necessary Information and Simulation Hints

The reaction proceeds in two steps:

$$CO_2 + H_2 \xrightarrow{\text{Ru catalyst}} HCO_2H$$

$$HCO_2H + HN(CH_3)_2 \rightarrow HCON(CH_3)_2 + H_2O$$

Rate laws for the two reactions were derived from graphical data at 100°C.[2] The rate law for the first reaction is:

$$\text{rate} = k_1[CO_2][H_2]$$

$$k_1 = 0.01 \text{ L/(mol h)}$$

The rate law for the second reaction is:

$$\text{rate} = k_2[DMA]^{\alpha}[FA]^{\beta}$$

$$k_2 = 2.6 \text{ L/(mol h)}$$

$$\alpha = 1$$

$$\beta = 0.4$$

The reactor is operated so that the exit temperature is at 100^{o}C. Since the reaction is exothermic, heat must be removed from the reactor.

Two azeotropes are encountered in the separation section. One is between water and formic acid, and the other is between formic acid and DMF. Vapor-liquid equilibrium data at atmospheric pressure are available for these binary systems.[3,4] The separation section was modeled using the available VLE data using UNIQUAC as the K-model. SRK was used for the K-model as well as enthalpies for all processes prior to the separation section. These models accurately predict the observed data, the azeotropes, and the component split in T-801.

References

1. Jessop, P.G., Y. Hsiao, T. Ikariya, R. Noyori, “Catalytic Production of Dimethylformamide from Supercritical Carbon Dioxide,” *Journal of the American Chemical Society,* Vol. 116, pp. 8851-8852 (1994).

2. Bann, E., D. Camposano, S. Shabazz, “Dimethylformamide from Supercritical Carbon Dioxide,” University of Pennsylvania School of Engineering and Applied Science, Senior Group Project Report, Spring 1996.

3. Gironi, F., A. Marocchino, L. Marrelli, “Vapor-Liquid Equilibria of the Formic Acid-Dimethylformamide System,” *Journal of Chemical and Engineering Data*, Vol. 26, No. 4, pp. 370-374 (1981).

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Equipment Descriptions

C-801	Hydrogen Feed Compressor
C-802	Carbon Dioxide Feed Compressor
P-801 A/B	Dimethylamine Feed Pump
E-801	Dimethylamine Feed Heater
R-801	DMF Reactor
V-801	Flash Vessel, Phase Separator
V-802	Flash Vessel, CO_2/H_2 Waste Gas Separator
T-801	Preliminary Distillation Column
E-802	Preliminary Distillation Column Reboiler
E-803	Preliminary Distillation Column Condenser
P-802 A/B	Preliminary Distillation Column Reflux Pump
V-803	Preliminary Distillation Column Reflux Drum
T-802	DMA Stripper
E-804	DMA Stripper Reboiler
T-803	DMF Column
E-805	DMF Column Reboiler
E-806	DMF Column Condenser

P-803 A/B	DMF Column Reflux Pump
V-804	DMF Column Reflux Drum

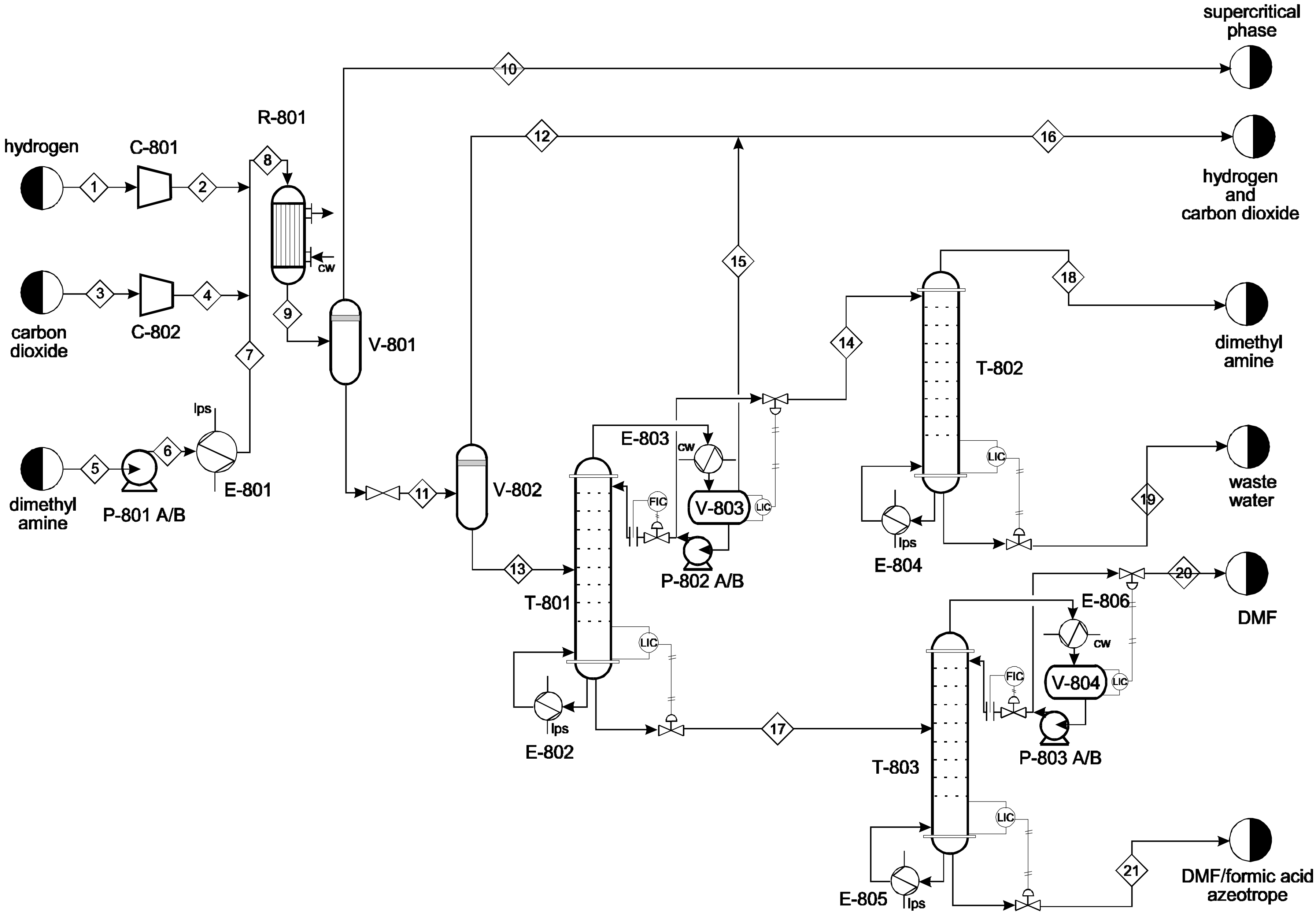
DMF Production Stream Table

Stream No.	1	2	3	4	5	6	7
Temperature (°C)	25.00	147.00	27.00	141.00	24.00	32.89	100.00
Pressure (atm)	27.20	210.00	1.00	210.00	2.00	210.34	210.00
Phase	Vapor	SCF*	Vapor	SCF*	Liquid	Liquid	Liquid
Total Flow (kg/h)	14.45	14.45	1452.33	1452.33	211.89	211.89	211.89
Total Flow (kmol/h)	7.17	7.17	33.00	33.00	4.70	4.70	4.70
Component Flowrates (kmol/h)							
Hydrogen	7.17	7.17	--	--	--	--	--
Carbon Dioxide	--	--	33.00	33.00	--	--	--
Dimethylamine	--	--	--	--	4.70	4.70	4.70
Formic Acid	--	--	--	--	--	--	--
Dimethylformamide	--	--	--	--	--	--	--
Water	--	--	--	--	--	--	--

Stream No.	8	9	10	11	12	13	14
Temperature (°C)	116.04	100.00	50.00	50.00	50.00	50.00	37.60
Pressure (atm)	210.00	209.66	130.00	1.00	1.00	1.00	1.00
Phase	SCF*	SCF*	SCF*	Liquid	Vapor	Liquid	Liquid
Total Flow (kg/h)	1678.67	1678.67	1234.65	444.03	11.83	432.20	86.23
Total Flow (kmol/h)	44.87	40.05	30.30	9.75	0.28	9.47	4.66
Component Flowrates (kmol/h)							
Hydrogen	7.17	2.35	2.34	0.002	0.002	--	--
Carbon Dioxide	33.00	28.18	27.93	0.25	0.25	0.002	--
Dimethylamine	4.70	0.094	0.008	0.086	0.009	0.08	0.08
Formic Acid	--	0.22	--	0.22	--	0.22	0.005
Dimethylformamide	--	4.61	0.003	4.60	0.003	4.60	--
Water	--	4.61	0.014	4.59	0.017	4.57	4.57

Stream No.	15	16	17	18	19	20	21
Temperature (°C)	37.60	49.92	50.00	85.13	96.57	152.99	155.42
Pressure (atm)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Phase	Vapor	Vapor	Liquid	Vapor	Liquid	Liquid	Liquid
Total Flow (kg/h)	0.09	0.37	432.20	1.37	84.79	286.90	59.07
Total Flow (kmol/h)	0.002	0.28	9.47	0.04	4.61	3.93	0.88
Component Flowrates (kmol/h)							
Hydrogen	--	0.002	--	--	--	--	--
Carbon Dioxide	0.002	0.252	0.002	--	--	--	--
Dimethylamine	--	0.009	0.08	0.02	0.06	--	--
Formic Acid	--	--	0.22	--	0.005	0.006	0.21
Dimethylformamide	--	0.003	4.60	--	--	3.92	0.68
Water	--	0.017	4.57	0.02	4.55	--	--

*Supercritical Fluid



PFD for DMF Production using Supercritical CO_2