Process Development for the Production of 100 TPD Dimethylformamide Using Methanol Dehydrogenation Process

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A. Background:

Dimethylformamide (DMF) is a widely used industrial chemical with pale-yellow color, and amine-like odor. It finds application as an extraction solvent for extracting butadiene, ethylene, isoprene and paraffin. It is used as a stabilizing agent for the transport of acetylene gas and as solvent for dissolving Polyurethanes (PU) and Thermoplastic Polyurethanes (TPU) to be utilized as adhesives, coatings and multi-layer films. The Merck in the United States, Anyang Chemicals, Zheijang Jinagshan Chemicals in China are the largest manufacturers of DMF with 225 kilo tonnes per annum respectively. This work was done as a part of the final semester project and involved developing a process to produce 100 TPD DMF using the most suitable process route among the four routes identified, namely, synthesizing using carbon dioxide in aqueous biphasic solvent system, single step synthesis using carbon monoxide, synthesis using carbon dioxide, dimethylamine and hydrogen with various solid catalysts, and synthesis from methanol dehydrogenation. Among the four, methanol dehydrogenation route was chosen the most suitable route.

B. Process Description:

Liquid phase methanol at 25 °C and 1 bar pressure is vaporized to 8 bar and 300 °C at which a conversion reactor is used to execute the dehydrogenation reaction to produce a stream of methyl formate, hydrogen and unreacted methanol. A conversion of 24.84% is fixed for the reactor. Throughout the entire process, Peng-Robinson (PR) property package was used. The hydrogen is separated from the mixture by liquefying methanol and methyl formate and using a compound separator. Methyl formate and dimethylamine reacts to produce dimethylformamide in a conversion reactor at 120 °C and 3 bar with a conversion of 85.94%. The dimethylformamide, unreacted methanol, methyl formate and dimethylamine are separated using a series of three distillation column (DC-1, DC-2, DC-3), the operating conditions of which decided based on sensitivity analysis are using a flash column (the

condition at which maximum enrichment possible is chosen). The purity of the DMF obtained is 99.4% with a yield of 21.9%. Compressors and adiabatic expanders are used to decrease or increase pressure respectively (P1, P2…etc.) while heat exchangers (HE-1, HE-2… etc.) are used to increase or decrease temperature according to process flow.

C. Results

The final product DMF is produced in stream S24 with a purity of 99.4%. The important result streams are tabulated in Table 1 below.

Table 1. Important result streams from process flowsheet for 100 TPD DMF production using methanol dehydrogenation process

Parameter	**S1**	**S4**	**S7**	**S8**	**S10**	**S14**	**S24**	**Units**
Temperature	25	190.06	20	20	15.06	156.2	25	°C
Pressure	1	8	8	8	4.5	3	1.013	bar
ṁ	27716.2	27716.2	429.92	27286.3	32015.9	32016.2	4270.13	kg/h
ṅ	865	969.94	210.07	759.868	864.784	864.784	58.913	kmol/h
n-CH_3OH	1	0.675	0	0.861	0.757	0.861	0.013	
n-$HCOOCH_3$	0	0.108	0	0.138	0.121	0.017	0	
n-H_2	0	0.216	1	0	0	0	0	
n-$(CH_3)_2NH$	0	0	0	0	0.121	0.017	0	
n-$HCON(CH_3)_2$	0	0	0	0	0	0.104	0.986	
ṁ-$HCON(CH_3)_2$	0	0	0	0	0	6590.485	4245.54	kg/h
ṅ-$HCON(CH_3)_2$	0	0	0	0	0	90.164	58.083	kmol/h

ṁ- Mass flowrate, ṅ- Molar flowrate, and n- molar fraction.

CH_3OH-Methanol, $HCOOCH_3$-Methyl Formate, H_2- Hydrogen, $(CH_3)_2NH$- Dimethylamine, $HCON(CH_3)_2$- Dimethylformamide.

D. Further Works

Implementation of alternate route in Reactive Distillation using RadFrac distillation column and compare it with the existing reactor-distillation column route. The distillation column can be optimized for parameters like reflux ratio and number of stages.

E. Reference

Maliszewskyj R. J., Turcotte M. G., Mitchell J. W. (2004). Dimethylformamide Synthesis via Reactive Distillation of methyl formate and dimethylamine (US Patent No. US 6,723,877 B1)