Synthesis of Dimethyl Carbonate by Reactive Distillation

Mohik Modi and Darshil Tailor
Sardar Vallabhbhai National Institute of Technology, Surat
(modim34@gmail.com, tailordarshil@gmail.com)

Introduction

Dimethyl Carbonate is an environmentally benign and biodegradable chemical and it is being widely used in the chemical industries as a substitute to replace dimethyl sulfate and methyl halide (which are major pollutants or toxic for environment) in methylation reactions, or as a carbonylation agent. Dimethyl Carbonate is also used as an additive to fuel because of its high oxygen content and octane number. There are various method of synthesis of Dimethyl Carbonate. One method is Urea methanolysis which is limited by the selectivity of product and needs high molar ratio of Methanol to Urea. Second method may be the direct reaction between Propylene Carbonate and Methanol which is also limited by equilibrium conversion. The second method may be enhanced by using reactive distillation. This approach may also be helpful to reduce the energy requirement, and ultimately total capital cost and total annual cost [1].

Development of Flowsheet in DWSIM

All the specifications of the unit operations and thermodynamics are elaborated in the literature. So we have used all the specifications as they are. Here, we have used NRTL as the thermodynamic property package instead of UNIQUAC (used in literature).

For more details about the unit operation specifications and the stream properties, please refer to the flowsheet and literature.

Purpose of Study

The reason for using RD here is to reach the desired equilibrium concentration of the product. What happens here is we continuously remove the product in the column and due to Le Chatelier's Principle the reaction would now proceed in forward direction only. The main advantage of the RD is - there is no need of separation of azeotropic mixture of DMC and MeOH (minimum boiling at 86.5% MeOH and 63.8 ^{o}C).

Description of Flowsheet

A stream containing a mixture of MeOH and PC enters the RD column (operated at 1 bar) at the top of the reaction section while fresh MeOH and recycled stream rich in MeOH enters the bottom and middle of the reaction section respectively. The top product of the RD column contains the product DMC and unreacted MeOH which enters the second high pressure column (operated at 11 bar). The bottom product of the RD column mainly contains 1,2-Propylene Glycol (PG). Here, the limiting reactant, Propylene Carbonate (PC) is totally consumed because of the higher molar ratio of MeOH to PC is maintained by the recycled stream. The second column produces almost pure DMC as the bottom product and nearly azeotropic mixture of MeOH and DMC as the distillate. This distillate is recycled back to the RD column and it helps to shift the equilibrium and we get higher conversion of PC (almost 99.9%).

Result

Object	MeOH 1	PC	MeOH 2	D1	B1	D2 (Recycle)	B2	Unit
Flow Rate	630	2508	1425	14381.7	2267.98	12192.3	2189.45	**kg/h**
Methanol	1	0	1	0.731	0.161	0.86	0.004	**kg/kg**
Propylene Carbonate	0	1	0	0	0.052	0	0	**kg/kg**
1,2-Propylene Glycol	0	0	0	0	0.785	0	0	**kg/kg**
Dimethyl Carbonate	0	0	0	0.269	0.0015	0.14	0.996	**kg/kg**

References

[1] Zhixian Huang, Yixiong Lin, Xiaoda Wang, Changshen Ye, Ling Li, Optimization and Control of a Reactive Distillation Process for the Synthesis of Dimethyl Carbonate, (2017).

doi: 10.1016\j.cjche.2017.03.039