EXTRACTIVE DISTILLATION OF METHYLAL/METHANOL USING DIMETHYL FORMAMIDE

INTRODUCTION:

Methylal, also called dimethoxymethane, is an important intermediate that is widely used in many fields for its exceptional dissolving ability, extremely low viscosity, amphiphilic characteristics, low surface tension and particularly high evaporation rate. A high purity of methylal is needed when it is used for making perfume,pharmaceuticals or as a molecular weight modifier for polyacetal resin. Unfortunately, methylal and methanol forms a minimum-boiling azeotrope at atmosphere pressure with 94.06 wt % methylal. Thus a methylal-methanol mixture cannot be separated completely through a simple distillation process.

Purification of methylal by a membrane process involves degradations and weak permeating flows which makes it harder to consider an industrial development by using organic membranes. Extractive distillation can be an alternative. It involves adding a third substance(entrainer/solvent) that can alter the molecular properties of the two compounds of interest. Since, it has different affinities to the key components, addition of the entrainer causes an increase in the relative volatility of the light and heavy key components. It is generally preferred when the relative volatility of key component is 1.1 and a small amount of entrainer is added to the products separated which is inevitable. A make-up stream is added to account for the solvent losses.

PROCESS:

The mixture "Methylal/Methanol/Water" is fed to the 42nd stage of 52 staged extractive distillation column with the solvent DMF(Di-Methyl Form amide) fed to the 4th stage. The presence of entrainer alters the relative volatility between the two, causing pure Methylal to move towards the top and mixture toward the bottom of the column.

The mixture is fed into the 9th stage of a 22 stage recovery column to produce almost pure Methanol at the top and almost pure solvent at the bottom. It is recycled back to the extractive distillation column and merged with one additional pure make-up stream to account for the solvent losses.

RESULTS:

	RAW METHYLAL	METHYLAL	METHANOL	MAKE UP DMF	DMF	
Temperature	300	315.286	337.809	300	425.998	K
Pressure	1.1	1.01325	1.01325	1.2	1.01325	bar
Molar Flow	11.9394	10.2625	1.67848	0.00013643	10.9802	mol/s
Methylal	0.858	0.998	0.00120668	0	5.06824E-13	
Methanol	0.139	0.00191995	0.977	0	1.94713E-06	
DMF	0	6.23542E-05	0.000561451	1	0.9999	
Water	0.003	1.76912E-05	0.0212319	0	9.80529E-05	

CONCLUSIONS AND RECOMMENDATIONS:

1. The system is sensitive to thermodynamic models and interaction parameters loaded.
2. Because entrainer is a dominant factor in the feasibility and economy of extractive distillation, several rules for entrainer selection have been proposed. More recently, computer aided molecular design of entrainer for extractive distillation based on a genetic algorithm has been presented. It facilitates the choice of extractive agent through a computer program.
3. For the separation of a methylal/methanol mixture by using extractive distillation, various entrainers

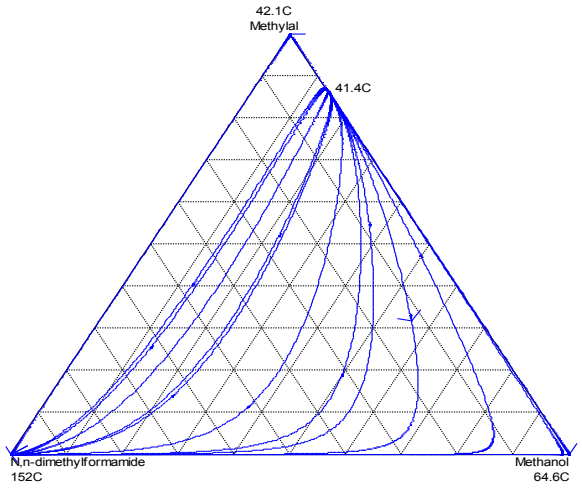
have been recommended such as water, aqueous alkaline solutions, ethylene glycol(EG),paraformaldehyde and dimethylformamide (DMF). DMF introduces no further azeotrope in the system and shows a higher relative volatility (1.833), it is chosen as the most suitable entrainer. This large relative volatility allows an economical separation sequence.

4. Residue curve - composition trajectory of the residue liquid in the still during open equilibrium evaporation.

Residue curve map - diagram that shows residue curves for different initial still compositions for a given mixture in the composition space.

Saddle - singular point with finitely many paths both approaching and departing.

The RCM of the methylal-methanol-DMF ternary system mapped by Chem-Sep using UNIQUAC the model is shown in Figure.It can be seen that the methylal-methanol azeotrope is the unstable node, DMF is the stable node, and both methylal and methanol are the saddles. The resulting residue curves with arrows point to pure DMF. It can be seen that no distillation boundary exists.This is an ideal situation for selection of an extractive distillation process.



5. It is known that for the extractive distillation process, an increase in the entrainer flow rate will reduce the heat duty of the extractive distillation column,but the heat duty of the entrainer recovery column will increase, and a larger column diameter is expected. Thus, a trade-off between the extractive distillation column costs(include both the fixed capital costs and operating costs) and entrainer recovery column costs needs to be made. So there exists an optimal entrainer flow rate that minimizes TAC for fixed theoretical plates. Qiaoyi et al discuss the heat integration with the entrainer recovery costs in detail.

REFERENCES:

1. Design and Control of Distillation System for Methylal/Methanol Separation. Part 1: Extractive Distillation Using DMF as an Entrainer .Qiaoyi Wang, Baoru Yu, and Chunjian Xu

2. Residue Curve Map...RCM tool-ChemSep

3.Flowsheeting reference: http://www.chemsep.com/downloads/index.html