Extractive Distillation of Methylal/Methanol Mixture Using Ethylene Glycol as Solvent

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Background & Description:

This project investigates the simulation and optimization of the Methylal/Methanol separation process via extractive distillation, using Aspen HYSYS. The methanol-methylal mixture forms a minimum boiling azeotrope, making their separation by simple distillation inefficient. Extractive distillation using Ethylene Glycol (EG) as entrainer significantly modifies the relative volatility, enabling an effective separation. Methylal is an important chemical intermediate in cosmetics, pharmaceuticals, and fuel additives.

The distillation process is based on adding a high-boiling entrainer (EG) to the system. The separation involves two main steps:

1. **Extractive Distillation Column:**

- **Feed**: Methanol-Methylal mixture (95 mol% Methylal, 5 mol% Methanol) introduced at stage 7 of an 11-stage column.
- **Solvent**: Ethylene Glycol fed at stage 3.
- **Products**:
    - **Top product**: Pure Methylal (0.999 mole fraction).
    - **Bottom product**: Mixture of Methanol with residual Methylal (0.0052 mole fraction).

2. **Separation**:

- **Feed**: Bottoms from the first column, mainly methanol with traces of methylal.
- **Products**:
    - **Top product**: Methanol with a purity of 90.14 mole % (contaminated with methylal).
    - **Bottoms**: Minor residual heavy components, negligible Ethylene Glycol presence.

Despite challenges such as residual methylal in the bottoms and contamination in the methanol stream, the process achieves a high recovery of methylal and an acceptable methanol purity for further treatment or use.

Thermodynamic properties were calculated using the NRTL model, which was chosen due to its robustness for highly non-ideal systems and azeotropes.

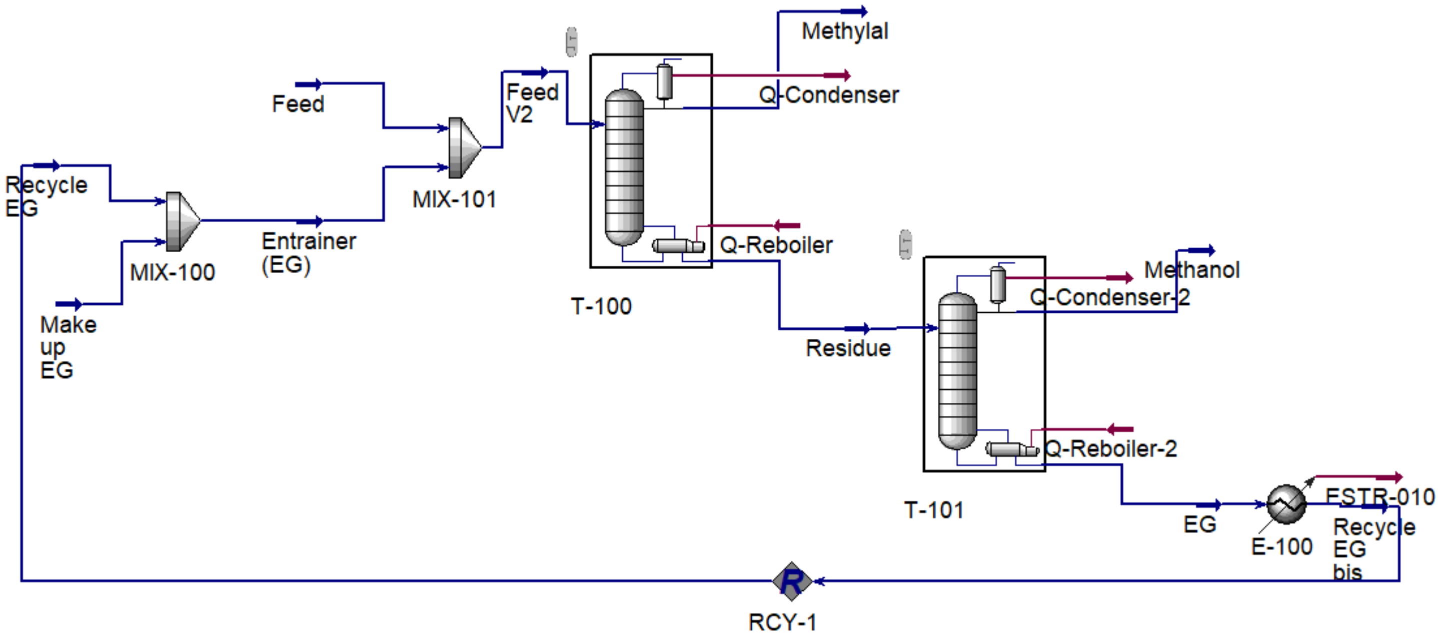
Simulations showed that while excellent methylal separation could be achieved (>99.9 % purity at the condenser), traces of methylal migrating with methanol were challenging to fully eliminate without further purification steps.

This project demonstrates the potential of extractive distillation for challenging azeotropic separations, and highlights the importance of minimizing entrainer loss and optimizing stage distributions.

Thermodynamic package: The NRTL (Non-Random Two-Liquid) model was selected because:

- It accurately handles strongly non-ideal mixtures (like alcohols and ethers).
- It is better suited for systems where azeotropes or complex phase behavior occur.
- It predicts liquid activity coefficients with high precision across a wide composition range.

Flowsheet



Results:

Master Property Tableau								
Object	**Feed**	**Entrainer (EG)**	**Make Up EG**	**Recycle EG**	**Methylal**	**Residue**	**Methanol**	**EG**
T (°C)	**25.00**	**25.00**	**25.00**	**25.00**	**42.31**	**152.3**	**64.22**	**193.7**
P (atm)	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Mass Flow (kg/h)	**100.0**	**90.03**	**3.925e-03**	**90.03**	**97.28**	**92.75**	**2.273**	**90.03**
Mole Fract (Methylal)	**0.95**	**0.0004**	**0**	**0.0004**	***0.9999***	**0.0052**	**0.0986**	**0.0004**
Mole Fract (Methanol)	**0.05**	**0.0026**	**0**	**0.0026**	**0.0001**	**0.0467**	***0.9014***	**0.0026**
Mole Fract (EGlycol)	**0**	**0.9970**	**1**	**0.9970**	**0**	**0.9481**	**0**	**0.9970**

Nb : Insignificant quantities (<0) of components in the product streams can be considered negligible, effectively approximating them to zero without impacting the overall process results or conclusions (see flowsheet).

References: Dong, Y., Dai, C., & Lei, Z. (2018). Extractive distillation of methylal/methanol mixture using ethylene glycol as entrainer. Fluid Phase Equilibria, 462, 172-180. https://doi.org/10.1016/j.fluid.2018.01.038