Course Project

Residual Curve Mapping & Process Analysis for MeOAc Production: Conventional vs. Reactive Distillation

ChE352: Chemical Process Synthesis & Design

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Residual Curve Mapping & Process Analysis for MeOAc Production: Conventional vs. Reactive Distillation

by

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Introduction

Methyl Acetate (MeOAc) is an important solvent and chemical intermediate widely used in coating, adhesives, and pharmaceutical applications. Its production via esterification of methanol (MeOH) and acetic acid (AcOH) requires both reaction and separation steps, making process optimization crucial for efficiency and economic feasibility.

$$\mathrm{CH_3COOH} + \mathrm{CH_3OH} \rightleftharpoons \mathrm{CH_3COOCH_3} + \mathrm{H_2O} \tag{1.1}$$

Catalyst Used: H_2SO_4
Reaction Temperature: $60\,^{\circ}\mathrm{C} - 80\,^{\circ}\mathrm{C}$

A major challenge in MeOAc production lies in the simultaneous occurrence of reaction and separation processes. Conventional esterification involves multiple stages, including a reaction step followed by complex distillation processes to separate the desired product from unreacted reactants and by-products. These additional separation steps increase energy consumption and capital costs, making process intensification techniques such as reactive distillation an attractive alternative.

We will analyse the conventional manufacturing setup involving 8 distillation columns and 1 liquid extraction column apart from the CSTR reactor, step by step to understand the big picture behind the manufacturing process.

To address these challenges, this project compares the conventional process with an alternative approach using reactive distillation, where reaction and separation occur within a single column. This method not only reduces equipment requirements but also enhances conversion efficiency by continuously removing reaction products, thereby shifting equilibrium towards ester formation.

This project explores Residual Curve Maps (RCMs) as a powerful tool for analyzing the feasibility of separation steps in distillation columns.By studying these maps, we can determine the feasible separation pathways, identify azeotropes, and understand how different components behave during distillation.

RCMs help predict the location of key product and residue streams, allowing engineers to assess whether a given separation is feasible under industrial conditions. This information is crucial in optimizing the Process Flow Diagram (PFD) of the system, as it helps in selecting the most efficient distillation sequence, reducing energy consumption, and minimizing product losses.

Furthermore, RCMs provide insights into whether conventional distillation is sufficient for separating MeOAc from reactants and by-products or if an alternative approach—such as reactive distillation—is required to enhance efficiency. By leveraging these maps, we can better design and optimize the overall process for improved yield and cost-effectiveness.

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Residue Curve Maps

ASPEN Plus V14 was used to generate the RCMs for the system involving Methanol, Acetic Acid, Methyl Acetate & Water.

Physical Property Model: NRTL **Valid Phase:** VAP-LIQ-LIQ

Mixture Investigated For Azeotropes At A Pressure Of 1 Bar

Comp ID	Component Name	Pressure (BAR)	Boiling Point (°C)
AcOH	ACETIC ACID	1	117.58
MeOAc	METHYL ACETATE	1	56.68
WATER	WATER	1	99.65
MeOH	METHANOL	1	64.20

The following binary azeotropes were present in the system, which are also indicated on the Ternary Star RCM on the upcoming page.

AcOH: Stable Node, MeOAc: Saddle, Water: Saddle

Number Of Components: 2		**Temperature: 56.61 C**
Homogeneous		**Classification: Unstable node**
01	**MOLE BASIS**	**MASS BASIS**
MeOAc	0.9597	0.9899
WATER	0.0403	0.0101

MeOH: Saddle, MeOAc: Saddle, AcOH: Stable Node

Number Of Components: 2		**Temperature: 53.27 C**
Homogeneous		**Classification: Unstable node**
01	**MOLE BASIS**	**MASS BASIS**
MeOH	0.3308	0.1762
MeOAc	0.6692	0.8238

NOTE: Repeated binary azeotropes obtained from ASPEN Plus are not mentioned above to avoid repetitions.

The Ternary Star RCM obtained is as follows:

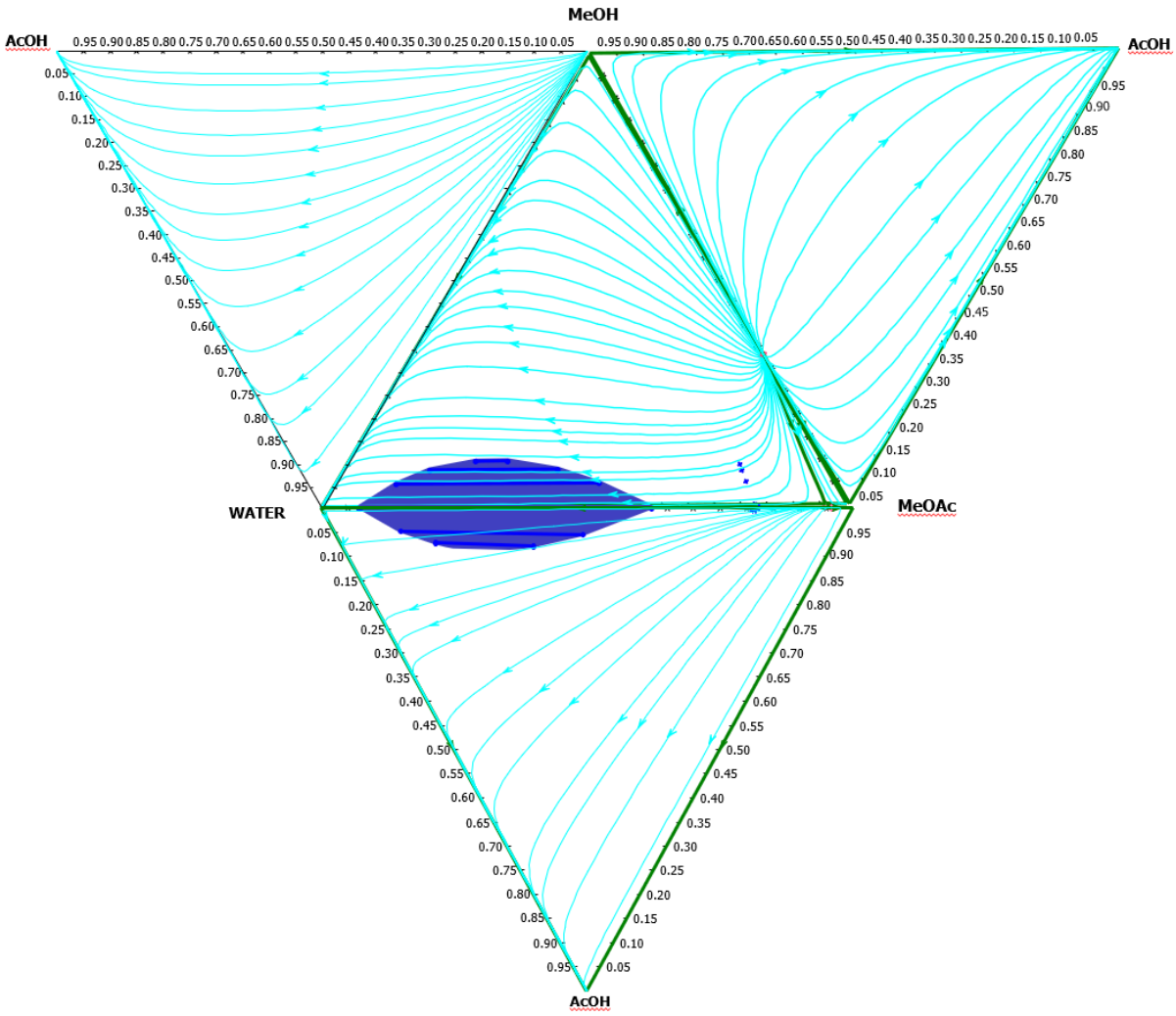

Figure 2.1: Residue Curve Map Of The Ternary Systems

The MeOAc - MeOH azeotrope can be seen in the RCM in the upper-right RCM and the MeOAc - Water azeotrope can be seen in the RCM in the middle most RCM and the bottom most RCM near the MeOAc edge.

Due to these azeotropes, we can't separate the components beyond a certain limit due to thermodynamic constraints and hence the conventional process needs Homogenous Extractive Distillation with an entrainer (here, Ethylene Glycol) to execute the process.

We can also notice the liquid-liquid envelope in the middle-most RCM and the bottom-most RCM on the MeOAc-Water edge, this liquid-liquid envelope will the be reason which will require the liquid extraction column in the conventional process for MeOAc production.

In the next page, we will use the insights obtained from the RCM above to understand the conventional process to manufacture MeOAc

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Conventional & Reactive Distillation Process For MeOAc Production

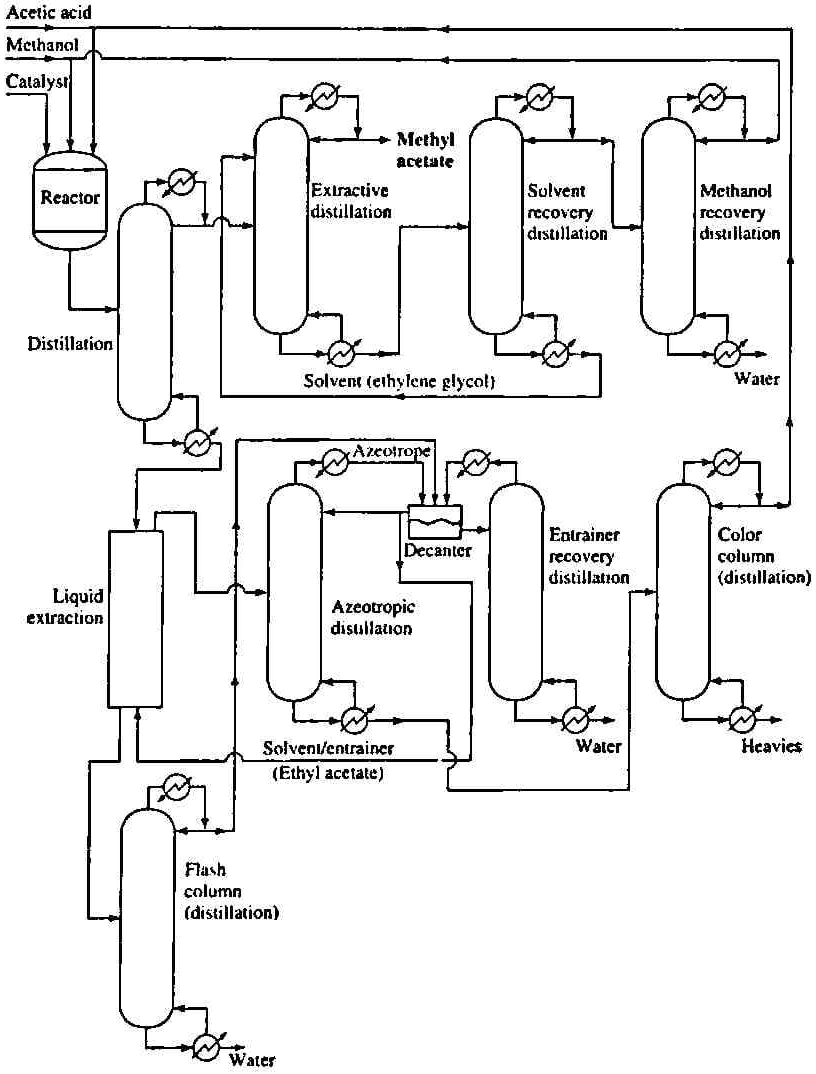

Figure 3.1: Process Flow Diagram Of Conventional Manufacturing Process Of MeOAc [1]

Initially, our raw materials (reactants) AcOH and MeOH along with catalyst (Sulfuric Acid) is fed to the reactor at a temperature of around 60-80 C and a nominal pressure of 1 bar.

Further, we can describe the role of each unit operation involved in the process as following:

1. **Reactor:** AcOH and MeOH react to yield MeOAc and Water. The following reaction takes places inside the reactor chamber.

$$\mathrm{CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O} \tag{3.1}$$

2. **Distillation Column 1:**
    - **Feed:** Reactor Output containing (AcOH, MeOH, MeOAc, Water)
    - **Distillate:** The lighter components MeOH, MeOAc, and Water
    - **Bottoms:** AcOH and Water
    - **Rectifying Section:** Prevents the leaking of AcOH from the top.
    - **Stripping Section:** Prevents the leaking of MeOH from the bottom.
3. **Distillation Column 2 (Extractive Distillation Column):**
    - **Feed:** Output from Column 1 and Ethylene Glycol from Column 3
    - **Distillate:** MeOAc
    - **Bottoms:** MeOH, Water, and Entrainer
    - **Rectifying Section:** Prevents the leaking of MeOH from the top.
    - **Extractive Section:** Prevents the leaking of MeOH and Entrainer from the top.
    - **Stripping Section:** Prevents the leaking of MeoAc from the bottom.
4. **Distillation Column 3 (Solvent Recovery Column):**
    - **Feed:** Bottoms of Column 2
    - **Distillate:** MeOH and Water
    - **Bottoms:** Entrainer
    - **Rectifying Section:** Prevents the leaking of Entrainer from the top.
    - **Stripping Section:** Prevents the leaking of Water from the bottom.
5. **Distillation Column 4 (Methanol Recovery):**
    - **Feed:** Top stream of Column 3
    - **Distillate:** MeOH which is recycled back to the reactor.
    - **Bottoms:** Water
    - **Rectifying Section:** Prevents the leaking of Water from the top.
    - **Stripping Section:** Prevents the leaking of MeOH from the bottom.
6. **Liquid Extraction Column:**
    - **Feed:** AcOH and Water from Column 1 + Entrainer (Ethyl Acetate is used here as an entrainer)
    - **Distillate:** AcOH, Water, EtOAc
    - **Bottoms:** Water and EtOAc
7. **Distillation Column 5 (Azeotropic Distillation Column):**
    - **Feed:** Top product from the liquid extraction unit (AcOH, EtOAc, Water)
    - **Distillate:** EtOAc, Water which are sent downstream to the decanter.
    - **Bottoms:** Acetic acid which is sent downstream to Distillation Column 7
    - **Rectifying Section:** Prevents the leaking of AcOH from the top.

- **Stripping Section:** Prevents the leaking of EtOAc azeotrope from the bottom.

8. **Distillation Column 8 (Entrainer Recovery):**
   - **Feed:** EtOAc, Water coming from the decanter
   - **Distillate:** EtOAc (entrainer) which recycled back to the decanter.
   - **Bottoms:** Water
   - **Rectifying Section:** Prevents the leaking of Water from the top.
   - **Stripping Section:** Prevents the leaking of EtOAc from the bottom.
9. **Flash Column:**
   - **Feed:** Water with a small amount of Ethylene Glycol
   - **Distillate:** EtOAc which recycled back to the decanter.
   - **Bottoms:** Water (removed)
   - **Rectifying Section:** Prevents the leaking of Water from the top.
   - **Stripping Section:** Prevents the leaking of EtOAc from the bottom.
10. **Color Column:**
    - **Feed:** AcOH along with the heavies.
    - **Distillate:** AcOH which is recycled back to the feed.
    - **Bottoms:** Water (removed)
    - **Rectifying Section:** Prevents the leaking of heavies from the top.
    - **Stripping Section:** Prevents the leaking of AcOH from the bottom.

Reactive Distillation Column For MeOAc Production [1] [2]

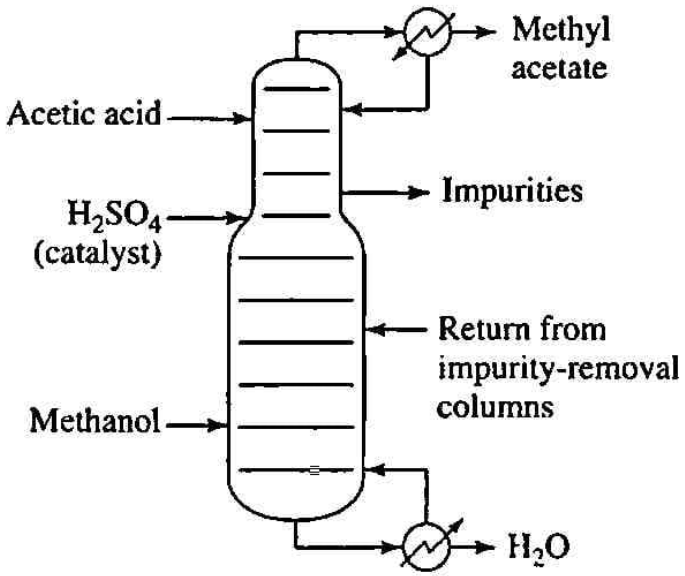

Figure 3.2: Process Flow Diagram Of Reactive Distillation Process Of MeOAc

One of the major successes in the project was the development of efficient techniques for complex separations. The most significant advancement was the complete replacement of the conventional separation system in the methyl acetate plant with an innovative reactive distillation column.

This single column enables the production of high-purity methyl acetate without the need for any additional purification steps or recovery of unconverted reactants. It also effectively drives the equilibrium-limited reaction toward high conversion without requiring a large excess of either reactant. This is accomplished by allowing the liquid-phase reacting mixture to vaporize methyl acetate during the reaction, thereby shifting the equilibrium forward.

The reactive distillation column is designed with stoichiometrically balanced feeds:

- **Methanol** (lighter reactant) is introduced at the bottom section of the column.
- **Acetic acid** (heavier reactant) is fed at the top section.

This configuration ensures countercurrent contact between the reactants, promoting effective reaction kinetics. The main reaction zone is located in the middle of the column, just below the point where sulfuric acid catalyst is introduced.

As methyl acetate forms, it creates a minimum-boiling azeotrope with methanol. This azeotrope is the lightest component in the mixture and is withdrawn as the distillate from the top of the reactive zone.

The column can be divided into functional sections:

- **Lower Section (below methanol feed):** Performs methanol-water separation, producing high-purity water as the bottom product.
- **Middle Section (reaction zone):** Facilitates the esterification reaction between methanol and acetic acid in the presence of sulfuric acid catalyst.
- **Upper Section (above catalyst feed):** Operates as an extractive distillation zone using acetic acid as an entrainer to break the methyl acetate–methanol azeotrope. This enables the recovery of high-purity methyl acetate as the distillate.

This reactive distillation column effectively integrates reaction and separation processes, functioning as a complete chemical plant within a single unit.

References

[1] M. F. Doherty and M. F. Malone. *Conceptual Design Of Distillation Systems*. McGrawHill, 2001.

[2] M. F. Doherty Robert S. Huss Fengrong Chen and M. F. Malone. “Reactive Distillation For Methyl Acetate Production”. In: *Computers and Chemical Engineering* 27.12 (2003), pp. 1855–1866.