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A Computational Study on the Separation of Methanol/ Chloroform Azeotropic Mixture Using Pressure Swing Distillation (PSD) Process

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Abstract
The pressure-swing distillation process is found more significantly economical than the homogeneous extractive distillation process. In pressure-swing distillation process no extra solvent is required for separation of methanol/chloroform mixture. So, now day pressure-swing distillation process is used mostly for separation of methanol/chloroform mixture than the other conventional methods. In this study, a computational study has been performed to separate over 99.5 mol% of chloroform from binary azeotropic mixture of methanol and chloroform using a Pressure Swing Distillation process (PSD). Methanol-chloroform binary mixture exhibits an azeotrope at 34 mol % methanol at 34 0C under atmospheric pressure. The PSD process is used to separate azeotropic mixtures using the difference between the relative volatilities and azeotropic compositions by changing the system pressure. Chloroform cannot be completely separated from methanol, ethanol or isopropanol by conventional distillation or rectification because of the minimum boiling azeotrope between chloroform and the alcohols. Chloroform can be readily separated from methanol, ethanol or isopropanol by extractive distillation but it requires extra solvent to achieve the separation.
Keywords: *Pressure-Swing Distillation, Separation, Methanol/Chloroform, azeotrope.*

I. INTRODUCTION

Pressure-swing distillation is a specialized form of distillation that is used to separate two or more components in a mixture based on their boiling points. It works by altering the pressure within the distillation column, rather than changing the temperature as in traditional distillation. In a pressure-swing distillation process, the distillation column is divided into several zones, each operating at a different pressure. The pressure in each zone is cycled between high and low values, causing the components with higher boiling points to condense and collect in the lower pressure zones while the components with lower boiling points are collected in the higher pressure zones. This process is particularly useful for separating mixtures with azeotropic behaviour, which are mixtures that boil at a constant temperature and are difficult to separate by traditional distillation methods. By altering the pressure in the distillation column, pressure-swing distillation can break the azeotrope and separate the components in the mixture. Pressure-swing distillation is commonly used in the petrochemical industry for the separation of different components in crude oil and natural gas streams. It is also used in the production of high-purity chemicals, such as solvents and pharmaceuticals, where precise separation of components is necessary.

Whether pressure-swing distillation is more economically advantageous than homogeneous extractive distillation depends on the specific application and the properties of the mixture being separated. In some cases, pressure-swing distillation may be more cost-effective, while in others, homogeneous extractive distillation may be more advantageous. In general, pressure-swing distillation has lower energy requirements compared to homogeneous extractive distillation since it does not require the addition of a separate solvent. However, pressure-swing distillation may require more sophisticated equipment and control systems to maintain the cycling pressure changes, which can increase the capital costs of the process.

Homogeneous extractive distillation, on the other hand, may require less sophisticated equipment and control systems but may be more expensive due to the cost of the solvent used in the process. The choice between these two methods will depend on the specific properties of the mixture being separated, such as the boiling points and the solubility of the components in the solvent. Ultimately, the most cost-effective separation process will depend on a range of factors, including the properties of the mixture, the required purity of the products, the energy and capital costs, and the availability of appropriate equipment and expertise.

Pressure-swing distillation is a common way to separate azeopropes. It is based on the changes in relative volatilities and the shifts of the azeotropic composition by changing the operating pressure. Two operating columns including a high pressure column (HPC) and a low pressure column (LPC) are determined by the composition variation of azeotrope under different pressures. Two high-purity products could be pulled out from the bottom streams or distillate streams according to the boiling behaviour 1. Many scholars indicate that pressure- swing distillation technology exhibits superiority over other methods in some azeotrope separations. Methanol is the simplest alcohol, being only a methyl group linked to a hydroxyl group. It is a light, volatile, colorless, flammable liquid with a distinctive odor very similar to that of ethanol (drinking alcohol). However, unlike ethanol, methanol is highly toxic and unfit for consumption. At room temperature, it is a polar liquid. It is used as an antifreeze, solvent, fuel, and as a denaturant for ethanol 1-3. It is also used for producing biodiesel by trans-esterification reaction. Methanol is used primarily as a feedstock for the manufacture of chemicals, and as a fuel for specialized vehicles. Chloroform, or tri chloromethane, is an organic compound with formula CHCl3. It is a colorless, sweet-smelling, dense liquid that is produced on a large scale as a precursor to PTFE. It is also a precursor to various refrigerants. In terms of scale, the most important reaction of chloroform is with hydrogen fluoride to give monochlorodifluoromethane (CFC-22), a precursor in the production of polytetrafluoroethylene. It is also used as an anaesthetic, solvent and a reagent in several other chemical processes. PSD is used as an alternative process of azeotropic and extractive distillation. Recently, interest has grown in PSD as an alternative process to azeotropic and extractive distillation processes, and considerable efforts have been made for many azeotropic mixtures 4-7.

PRESSURE-SWING DISTILLATION PROCESS

Pressure-swing azeotropic distillation uses two columns operating at two different pressures to separate azeotropic mixtures by taking high-purity product streams from one end of the columns and recycling the streams from the other end with compositions near the two azeotropes. Figure 1 shows the schematic representation of Pressure-swing distillation process. It is widely used to separate minimum-boiling azeotropes when the azeotropic composition has significant pressure dependence. The two columns operate at different pressures with distillate streams having compositions close to their respective azeotropes. Pressure-swing distillation can be applied to both minimum-boiling and maximum- boiling homogeneous azeotropic mixtures. With minimum-boiling systems, the distillate streams are recycled. With maximum-boiling systems, the bottoms streams are recycled. Heat integration is typically used since column temperatures are sufficiently different to permit heat transfer.

A novel modification to achieve process intensification has recently been proposed that uses vapor recompression on both columns. Pressure swing distillation (PSD) is a process alternative to the broadly applied azeotropic and extractive distillations. The principle of pressure swing distillation (PSD) is based on the fact that a change in pressure can alter the relative volatility of a liquid mixture, even for liquid mixtures with a close boiling point or those that form an azeotrope. If the operating pressure is increased, the azeotropic point shifts to lower composition values of the light component. The significant positive change in the azeotrope point and enlargement of the relative volatility of azeotropic mixtures allow the separation to take place without any need for a separating agent.

Table 1: List of Azeotropic Mixtures Separated by Pressure-Swing Distillation Process 1-13

No.	Azeotropic Mixture	No.	Azeotropic Mixture
1.	Acetone / methanol	19.	Methanol / THF
2.	Acetone / chloroform	20.	Methanol / trimethoxysilane
3.	Acetone / chloroform /toluene	21.	Methanol / benzene / acetonitrile
4.	Acetonitrile /water	22.	Methylal / methanol
5.	Acetic acid / toluene	23.	Methyl acetate / methanol
6.	Acetic acid / DMAC	24.	methyl ethyl ketone / benzene
7.	Aniline / octane	25.	Methanol / methyl ethyl ketone
8.	Benzene / isopropanol	26.	MIBK / butanol
9.	Carbon tetrachloride/ethyl acetate	27.	*N*-Heptane / isobutanol
10.	Chloroform / methanol	28.	*N*-Pentane / acetone / cyclohexane
11.	Cyclohexanone / phenol	29.	*N*-Pentane / acetone
12.	Ethanol / water	30.	Phenol / butyl acetate
13.	Ethanol / ethyl acetate	31.	Propanol / toluene
14.	Ethanol / 1-4 dioxane	32.	Propanol / cyclohexane
15.	Isobutyl alcohol/isobutyl acetate	33.	Tettahydofuran (THF) / water
16.	Isopentane / methanol	34.	Tettahydofuran (THF) / ethanol
17.	Methanol / dimethyl carbonate	35.	Toluene / 1-butanol
18.	Methanol / ethyl acetate	36.	Water / ethylenediamine

Advantages and disadvantages of Pressure-Swing Distillation (PSD) 9

Pressure-Swing Distillation (PSD) process itself has same main advantages compared to other unit operations for the separation of homogenous azeotropic mixtures. Some advantages and disadvantages are mentioned below.

Advantages:

- Low investment cost because of a smaller number of distillation columns (compared to concepts with entrainer).
- Energy savings is high in the case of the continuous PSD operation.
- No additional substances (entrainer) are needed for the separation in PSD.
- Energy efficiency: Pressure-swing distillation requires less energy compared to traditional distillation processes, as it operates at lower temperatures and pressures.
- High purity separation: Pressure-swing distillation can achieve high-purity separation of components in a mixture, even for difficult-to-separate mixtures such as azeotropes.
- Cost-effectiveness: In some cases, pressure-swing distillation can be more cost-effective than other separation methods, such as homogeneous extractive distillation or membrane separation.
- No solvent required: Pressure-swing distillation does not require the use of a separate solvent, which can reduce the cost and complexity of the separation process.

Disadvantages:

- Available and reliable azeotropic data.
- More complex control structure and automation concept.
- Pressure sensitiveazeotropic mixture.
- Equipment complexity: Pressure-swing distillation requires sophisticated equipment and control systems to maintain the cycling pressure changes, which can increase the capital costs of the process.
- Limited applicability: Pressure-swing distillation may not be suitable for all separation applications, as the cycling pressure changes may not be effective in separating certain mixtures.
- Maintenance: The cycling pressure changes can place additional strain on the equipment, which may require more frequent maintenance and repair.
- Process optimization: Pressure-swing distillation requires careful process optimization to achieve the desired separation efficiency, which can be challenging and time-consuming.
- In the case of a low temperature azeotrope, the products are in the column bottom, which could be mean that there are also all contaminations (high boiling by- products).

SIMULATION

DWSIM Introduction

"DWSIM" is a free and open-source chemical process simulator that can simulate chemical processes under steady state conditions. It follows the sequential modular approach. It is typically used for simulation problems, where for a given input to a process unit the output is computed. It does not support direct simulation of chemical processes under dynamic or transient state. DWSIM consists of various built-in unit operations such as mixer, heater, distillation column, etc. represented in the form of blocks. These blocks are connected with each other to construct a flow sheet in such a way that the flow sheet mimics the process exactly. Fig. 1 shows a simple flow sheet constructed using DWSIM for separation of mixture containing benzene and chloroform into its components. It also contains various thermodynamic packages that can be applied to simulate a chemical process. It also has a user-friendly Graphical User Interface (GUI) through which users can enter input parameters and view the necessary outputs, Steady-state and dynamic simulation, thermodynamic models for various types of fluids and mixtures, unit operations, and data regression. It is built using the .NET Framework and can be used on Windows, macOS, and Linux operating systems. Some of the key features of DWSIM include:

- Support for multiple thermodynamic models, including the Peng-Robinson, Soave-Redlich-Kwong, and Cubic-Plus-Association (CPA) equations of state.
- A wide range of unit operations, including distillation columns, reactors, heat exchangers, and separators.
- Built-in property databanks for pure components and mixtures.
- Advanced tools for data regression, including regression of binary interaction parameters and model parameters.
- Comprehensive reporting and visualization capabilities, including 2D and 3D graphical representations of process flow sheets and unit operations.

DWSIM has become increasingly popular in the chemical and process engineering communities due to its robust features, user-friendly interface, and open-source nature, which allows users to modify and extend the software to meet their specific needs.

Steps Used for Simulation

To simulate the Pressure-Swing Distillation (PSD) process using DWSIM, you can follow these steps:

- Define the components and their properties: Enter the physical and thermodynamic properties of the components in the mixture, such as boiling points, densities, and molar masses, using the built-in property databanks or by creating your own custom properties.
- Define the thermodynamic model: Choose a thermodynamic model for the mixture, such as the Peng-Robinson or Soave-Redlich-Kwong equation of state, and set the model parameters.
- Set up the distillation column: Set up the PSD distillation column by adding the appropriate unit operations, such as reboilers and condensers, and configuring the column specifications, such as the number of trays and feed locations.
- Define the pressure-swing cycles: Define the pressure-swing cycles by specifying the high and low pressure levels, cycle times, and hold-up times for each zone in the column.
- Run the simulation: Run the simulation and monitor the output variables, such as the composition of the overhead and bottom products, the temperature and pressure profiles along the column, and the reflux and boil-up ratios.
- Optimize the process: Optimize the process by adjusting the operating parameters, such as the cycling times and pressures, to achieve the desired separation efficiency and product purity.

DWSIM provides a user-friendly interface for setting up and running PSD simulations, and also includes a range of tools for analysing and visualizing the simulation results. In simulating the Pressure swing distillation process we need to follow the following steps and simulate the PSD process

1. Create new simulation
2. Select component
3. Property package
4. Unit System Configuration Interface
5. Draw Low Pressure Column
6. Input to LPC and assign Tray geometry
7. Simulation of LPC
8. Draw and connect HPC to LPC
9. Connect recycle stream to the input of LPC
10. Simulate the flow sheet

- The “Create a new steady-state simulation” button in the welcome window can be used to create a new simulation. After the simulation is created, the configuration window is shown. The simulation configuration interface consists in a tabbed window:
- Add or remove compounds to/from the simulation and petroleum fractions (pseudo components) utilities.
- Property Package configuration, phase equilibrium flash algorithm selection and other advanced thermodynamic model settings.
- Management of Systems of Units.
- Simulation info (title, author and description), number formatting and password settings.
- Definition of objects properties to be shown on flow sheet floating tables.

II. RESULT AND DISCUSSION

Steady State Simulation

In this simulation, both the columns consist of 24 stages (including a partial condenser with a partial reboiler). Different thermodynamic models were analysed using DWSIM to predict the VLE data of Methanol/Chloroform system. The model that predicts the VLE data most accurately has been selected for the simulation.

Description of the Problem

This work aims at obtaining high purity Methanol and chloroform by simulating the pressure swing distillation column. In Pressure Swing Distillation (PSD) process first the feed stream containing 0.5 mole fractions Methanol and 0.5 mole fractions Chloroform is sent to a distillation column which has 24 stages. The feed is send to stage number 9 whereas the recycled feed is sent to stage number 18. The flow rate of the feed is around 100 kmol/hr. , 300 K and the recycle ratio of the tower is 0.55 The first distillation column produces bottom with 0.995 mole fraction methanol. The distillates of the first column are sent to a second distillation column. The second distillation column has a reflux ratio of 0.95 and it produces distillates which are recycled back to the first distillation column and the bottom product has a composition of 0.995 mole fraction Chloroform. The first distillation column is a low pressure distillation column maintained at a pressure of 1 atm whereas the second distillation column is a high pressure distillation column maintained at a pressure of 10 atm.

Simulation Result

In order to use the simulation software, it is necessary to predict the VLE data accurately using the appropriate thermodynamic property model. Various thermodynamic property models like WILSON, WILSON-RK and UNIFAC have been tested to predict the VLE data of Methanol/Chloroform system at 1 atm. The predicted VLE data has been compared with the reported experimental VLE data (Perry and Green, 2001). The Low Pressure Column (LPC) and High Pressure Column (HPC) were simulated separately using DWSIM software. The DWSIM is very effective and powerful simulation software and it is freely available. By using Pressure Swing Distillation we got maximum separation of Methanol-Chloroform mixture. In low pressure column we got 99.5% Methanol and in high pressure column we got 99.5% Chloroform. The detail simulation report is given below.

Table 5.1 Simulation Result

Object	B1	B2	D1	D2	Feed	Recycle feed
Temperature (K)	337.51523	425.233	326.12399	404.85893	300	404.85893
Pressure (atm)	1	10	1	10	1	10
Molar flow (Kmol/hr)	49.939817	49.95334	134.4035	84.450164	100	84.450164
Molar fractionmethanol	0.995	0.005	0.35538956	0.56264941	0.5	0.56264941
Molar fraction chloroform	0.005	0.995	0.64461044	0.43735059	0.5	0.43735059

III. CONCLUSION

The present work addresses the simulation of Pressure Swing Distillation process for separation of methanol Chloroform azeotropic mixture. The key objective of the proposed work is to simulate a Pressure Swing Distillation process to obtain high purity product. The methanol- Chloroform system has to been chosen for the study because of its industrial importance; however other systems may also be investigated in a similar manner. The low pressure column and high pressure column used in Pressure Swing Distillation process and operates at 1 atm and 10 atm respectively. The simulation results indicate that the separation of methanol-chloroform azeotrope is physible using Pressure Swing Distillation process achieving the high purity methanol-chloroform 99.5 mole % is obtain in the low pressure column and 99.5 mole % of chloroform is separated in high pressure column. In the face of the requirement for sustainable development and environmental protection research in Pressure Swing Distillation should be given sufficient attention by researchers and scholars. The work can be extended for reactive Pressure Swing Distillation, Pressure Swing batch distillation etc.

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