Simulation studies of Extractive Distillation for separating the Isoamyl acetate/Isoamyl alcohol Binary Azeotrope Mixture using N-octyl acetate green solvent

Chintan Modi, M H Joshipura*

Abstract—**Isoamyl acetate, also known as banana oil, is a versatile compound with wide-ranging applications in diverse industries, including food, paint, pharmaceuticals, textiles, and essence production. However, its synthesis poses a challenge due to the formation of an azeotrope with Isoamyl alcohol under atmospheric pressure. To separate azeotropes effectively, reduce waste, reuse resources, and maintain environmental cleanliness and sustainability, the industry uses extractive distillation. The primary focus of this study was on applying extractive distillation for the separation of the binary azeotropic system involving Isoamyl acetate and Isoamyl alcohol, with the use of N-Octyl acetate as the designated solvent. The process characteristics were simulated using CHEMCAD simulator with the UNIFAC thermodynamic model, followed by sensitivity analysis to optimize the flow sheets. To achieve the optimized design of the extractive distillation column, the impact of solvent flow rate, reflux ratio, feed stage, and solvent feed stage were investigated.**

Index Terms— **Extractive distillation, green solvent, Azeotrops, sensitivity analysis**

I. INTRODUCTION

ISOAMYL acetate (IAA) also known as banana oil, is a versatile solvent with a variety of applications, including paints, food, textiles, pharmaceuticals and essence production Its unique properties make it an ideal solvent for various industrial products, such as paints, nitrocellulose, varnishes and printing inks. In addition, IAA is an effective remover for tobacco, chemicals, cobalt, iron, and nickel. The main process for IAA synthesis involves the esterification of acetic acid and isoamyl alcohol, with sulfuric acid or p-toluene acting as a catalyst [1]. Since the formation of azeotropes between IAA and isoamyl alcohol at atmospheric pressure under therefore, conventional distillation methods face limitations in their separation are also objectionable to alcohol recovery [2,].

The separation of volatile compounds with volatile or similar azeotropic properties presents challenges to conventional distillation methods. Advanced methods such as pressure distillation, reactive distillation, and extraction distillation provide effective alternatives to this separation. The efficiency of extraction distillation depends on the selection of a suitable intruder, which is a third variable of relatively weak. The interaction between the solvent and the azeotropic mixture determines the separation process will be successful. This requires the addition of a heavy infiltrator with a slight volatility close to 1 or containing azeotropes to separate the mixture. In extraction distillation, the selection of an intruder that effectively promotes separation is important for efficient development.N-Octyl acetate, a green solvent with suitable high boiling point, emerges as a potential solvent for the separation of IAA and Isoamyl acetate[5]. This research delves into the behavior of N-Octyl acetate as an entrainer in this context.

Despite the considerable amount of research in the field, separation of Isoamyl alcohol and Isoamyl acetate has received limited attention and has not yet been simulated. Conducting laboratory experiments to investigate the various parameters involved is time-consuming and costly. Hence, employing simulation tools to anticipate experimental outcomes emerges as a cost-effective strategy. For process design computer simulations have evolved into a widely accepted standard in the chemical industrial sectors, serving process development and process optimization purposes.[6] This research introduces the simulation of extractive distillation process aimed at segregating the azeotropic mixture of IAA and Isoamyl acetate using CHEMCAD. The azeotrope was identified at a 0.7411 mole fraction of Isoamyl alcohol (refer to Figure 1). The primary objective is to identify the operating conditions for extractive distillation of Isoamyl alcohol and Isoamyl acetate, employing N-Octyl acetate as the solvent. To accomplish the desired separation, the entrainer must possess specific characteristics, including high boiling point, low toxicity, thermal stability, easy recovery and selectivity. Separation process, particularly the distillation process, necessitates the utilization of TPXY chart in CHEMCAD, which is the vital tool for identifying the effective entrainer for obtaining the desired separation which is shown in figure 1 & 2. Physical properties of the system's components Isoamyl alcohol/Isoamyl acetate/N-Octyl acetate is represented in Table 1.

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Table 1. Physical properties of Isoamyl alcohol/Isoamyl acetate/N-Octyl acetate

Component	**Moleculer weight (gm/mol)**	**Boiling Point (^{0}C)**	**Liquid density (Kg/m^3)**
Isoamyl alcohol	88.15	131	0.809
Isoamyl acetate	130.18	142	0.876
N-Octyl acetate	172.26	210	0.870

Because the experimental vapor–liquid equilibrium (VLE) data of Isoamyl alcohol/Isoamyl acetate/N-Octyl acetate system are not available, we choose UNIFAC as the thermodynamic model which is widely used in the chemical industry for the design and optimization of separation processes, such as distillation, extraction and absorption[7]. It has been shown to provide accurate predictions of phase equilibria for a wide range of systems, including hydrocarbons, alcohols, acids, and esters. In CHEMCAD the BIP data was generated with UNIFAC BIP matrix using COSMO-SAC.

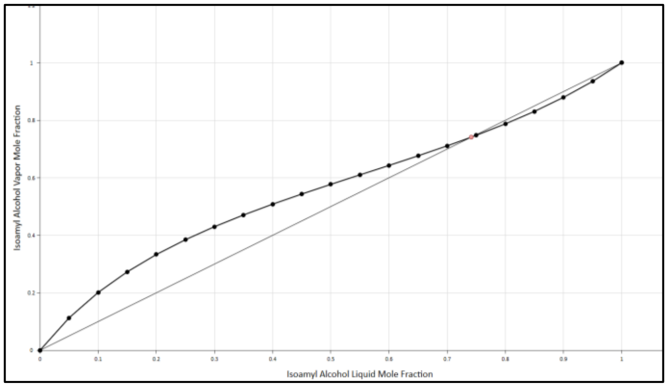

Figure 1. Binary XY diagram for the Isoamyl alcohol/Isoamyl acetate system without Solvent

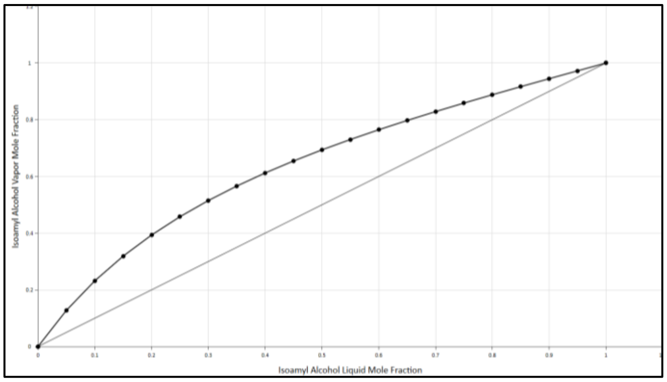

Figure 2. Binary XY diagram for the Isoamyl alcohol/Isoamyl acetate system with Solvent n-octyl acetate

2. SIMULATION PROCEDURE AND METHODS

CHEMCAD is commonly used software tool for process simulation in the chemical and engineering industry, including the simulation of extractive distillation. In CHEMCAD, the simulation procedure entails modeling the extractive distillation column, describing the component's physical characteristics, and establishing the process's operational parameters. Additionally, CHEMCAD enables the selection of thermodynamic methods and the customisation of simulation models according to the particular needs of the process. A range of analytical techniques, including sensitivity analysis and process design optimization, are also offered for the purpose of optimizing the extractive distillation process.

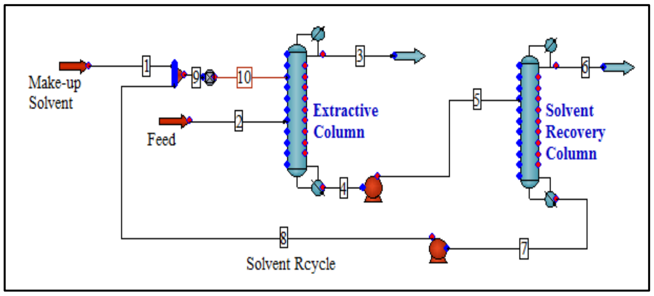

Figure 3. Extractive distillation process using CHEMCAD

In order to simulate the Extractive Distillation (ED) process for the study, the UNIFAC thermodynamic model was applied as the suitable fluid package and the pseudo-binary VLE data of azeotropic mixture was predicted using the UNIFAC model. Figure 1 shows the azeotrope point based on the mixes' vapor-liquid equilibrium (VLE) data on a solvent-free basis. Furthermore, the solvent foundation mixes' VLE is depicted in Figure 2.

A two-column extractive distillation process (depicted in Figure 3) was utilized to separate the azeotropic mixture of Isoamyl alcohol and Isoamyl acetate. The initial column, designated as C1, received a predefined saturated liquid feed mixture and pure solvent as the second feed, both introduced at atmospheric pressure. The primary objective for C1 was to achieve a minimum distillate purity of 99% Isoamyl alcohol. Subsequently, the simulated bottom stream from C1 was directed to the second column, C2, with a targeted minimum distillate purity of 99% Isoamyl acetate. Both columns were equipped with a total condenser at the top and operated at 101325 Pa. The residual solvent in the bottom product of C2 was maintained at a minimum of 0.99 mole fraction. A thorough solvent analysis was conducted based on product purity.[8].

Table 2. Details of sensitivity analysis for SCDC column (C1)

Sr. No	Manipulated variable	Observed variable
1	Reflux ratio (R.R.)	Purity of Isoamyl alcohol in distillate
2	Reflux ratio (R.R.)	Condenser duty (Qc) and reboiler duty (Qr)
3	Number of stages & R.R.	Purity of Isoamyl alcohol in distillate
4	Inlet stage of feed and solvent	Purity of Isoamyl alcohol in distillate
5	Number of stages & R.R.	Condenser duty (Qc) and reboiler duty (Qr)
6	Inlet stage of feed & R.R.	Purity of Isoamyl alcohol in distillate
7	Inlet stage of solvent & R.R.	Purity of Isoamyl alcohol in distillate
8	Solvent flowrate & R.R.	Purity of Isoamyl alcohol in distillate & Qr, Qc

3. RESULT AND DISCUSSION

3.1. Sensitivity Analysis

A sensitivity analysis was conducted to determine the optimal parameters for the Extractive Distillation (ED) column. The variables investigated included the number of stages, reflux ratio, feed and solvent stages, and solvent flow rate.

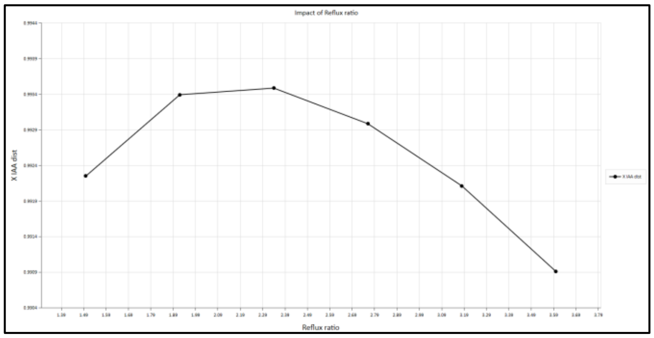

Figure 4. Effect of R.R on mole recovery of Isoamyl alcohol

Figure 4 presents the maximum X_{IAA} was attained at a reflux ratio of 2. As the reflux ratio exceeds 2, the mole fraction of Isoamyl alcohol in the distillate diminishes. The high reflux rate causes the concentration of solvent in the liquid phase to decrease, since more solvent is being evaporated and returned to the system than is being added. When the reflux is increased, the concentration of the solvent in the liquid phase of the column gets diluted, which means that more stages are needed to extract the lighter components.

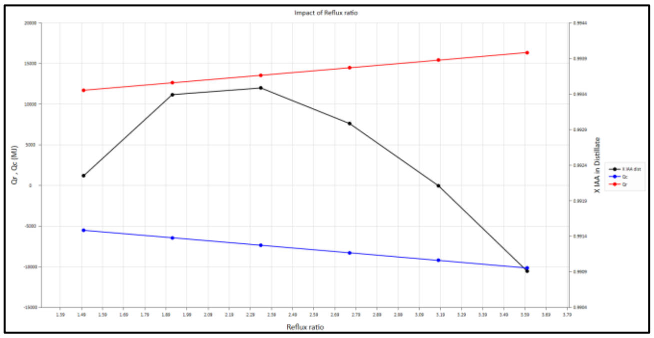

Figure 5. Impact of reflux ratio on distillate composition and heat duty (condenser and reboiler)

Figure 5 presents the relationship between the reflux ratio, distillate composition, and the energy consumption of the condenser and reboiler. Notably, increasing the reflux ratio leads to a significant rise in the duties of both the condenser and reboiler. This necessitates careful selection of the optimal reflux ratio, aiming to achieve the highest purity of Isoamyl acetate while minimizing energy consumption.

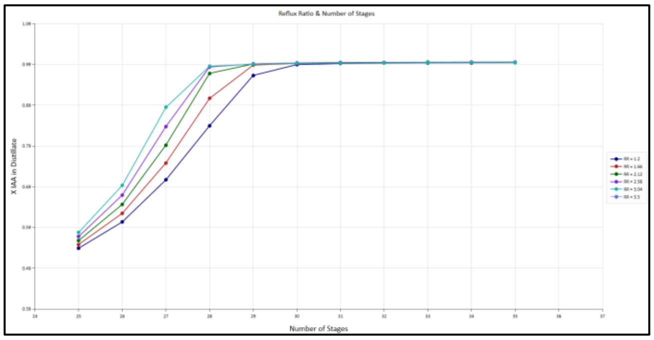

Figure 6. Effect of the number of stages & Reflux ratio of C1 on mole recovery of Isoamyl alcohol

Figure 6 illustrates The relationship between the number of stages and reflux ratios on the mole fraction of Isoamyl alcohol (X_{IAA}) was investigated. It was observed that there was no significant change in the distillate composition when the number of stages exceeded 30. The results indicated that the column can attain its highest purity of Isoamyl alcohol by operating at 30 stages and a reflux rate of 2.

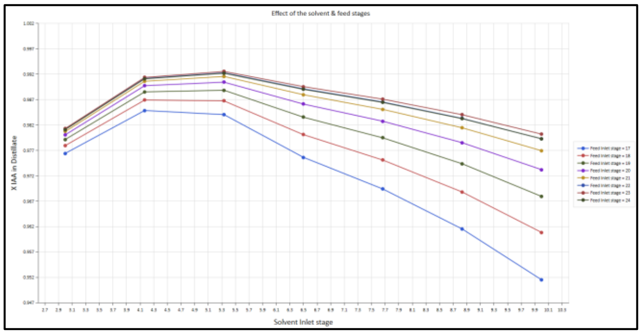

Figure 7. Effect of the solvent & feed stages of C1 on mole recovery of Isoamyl alcohol

Figure 7 illustrate the relationship between the solvent feed stage and binary feed stage and its effect on the mole fraction of Isoamyl alcohol (X_{IAA}) can be demonstrated. The results show that there was a reduction in the composition of Isoamyl alcohol at the 5th stage of solvent feed and 22nd stage of binary mixture feed. It can be concluded that the column can achieve its highest purity of Isoamyl alcohol by feeding the solvent and binary mixture at the 5th and 22nd stages, respectively.

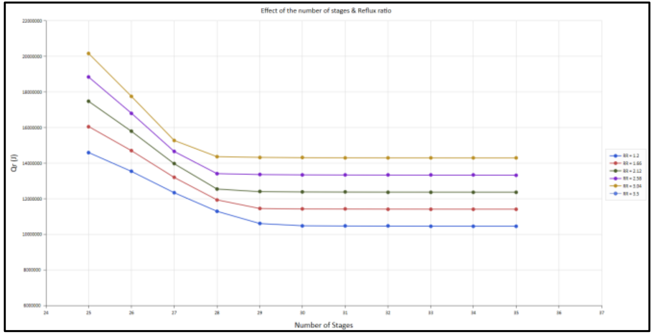

Figure 8. Effect of the number of stages & Reflux ratio of C1 on Reboiler duty

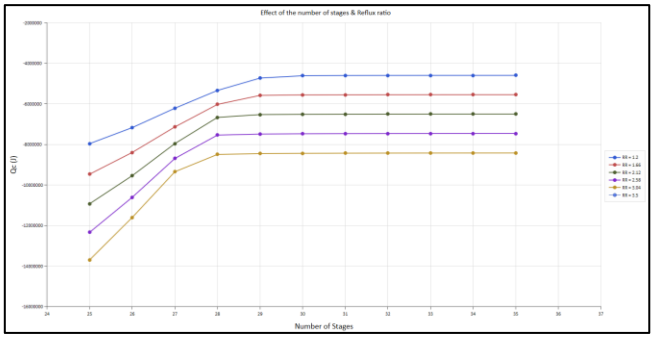

Figure 9. Effect of the number of stages & Reflux ratio of C1 on Condenser duty

Figures 8 and 9 illustrate the variations in reboiler (QR) and condenser (QC) heat duties with respect to the number of stages and reflux ratio. The energy consumption of the column was significantly affected by the reflux rate. However, the influence of the number of stages on the duties was insignificant, particularly beyond the 30th stage, regardless of the applied conditions. The heating and cooling requirements were directly proportional to the reflux ratio. Based on the sensitivity analysis, a reflux ratio of 2 satisfies the criteria for distillate composition and energy consumption.

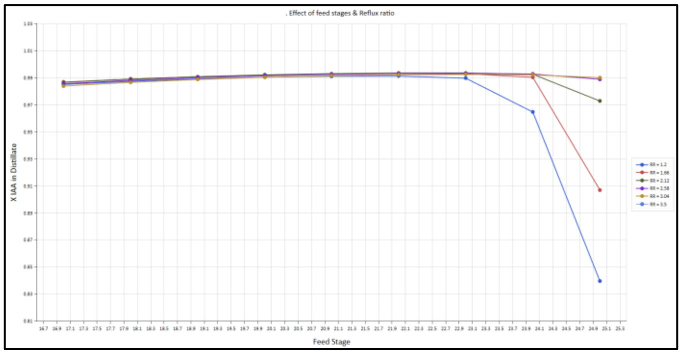

Figure 10. Effect of feed stages & Reflux ratio of C1 on mole recovery of Isoamyl alcohol

Figure 10 illustrate the impact of feed stage on the mole composition of Isoamyl alcohol (X_{IAA}) in distillate at various reflux ratios is illustrated in the figure. The results indicate that for attaining high purity of Isoamyl alcohol in the distillate, the feed mixture should be introduced within the 21st to 23rd stages and at reflux rates ranging from 2.0 to 3.0. Consequently, the azeotropic feed mixture was introduced on the 22nd stage due to its extended contact duration with the solvent, leading to a higher purity of Isoamyl alcohol in the distillate.

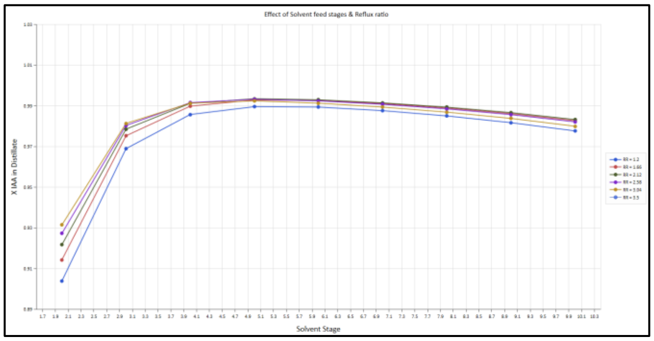

Figure 11. Effect of Solvent feed stages & Reflux ratio of C1 on mole recovery of Isoamyl alcohol

Figure 11 depicts the impact of solvent stage on mole composition of Isoamyl alcohol in distillate at different reflux ratios. The outcomes indicated that reflux ratios of 2.0 and 3.0 resulted in the highest concentration of Isoamyl alcohol in the distilled product. Moreover, a decrease in Isoamyl alcohol purity was observed at higher solvent stages. To maintain a uniform distribution of solvent throughout the lower sections of the distillation column, the solvent was injected at the upper stages. This study indicates that the 5th stage is the most suitable location to introduce solvent to maximize Isoamyl alcohol concentration.

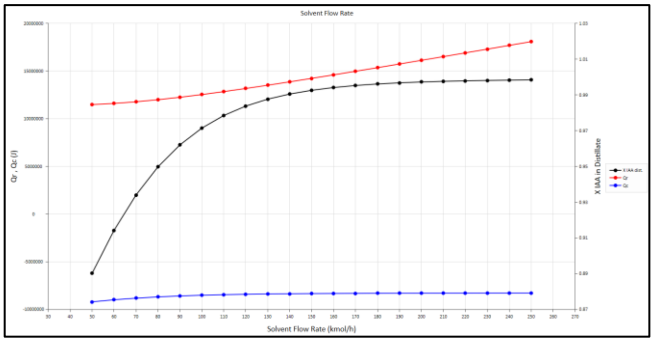

Figure 12. Effect of solvent flowrate & Reflux ratio on mole recovery of Isoamyl alcohol in C1

Figure 12 demonstrates the impact of solvent flow rate on the mole composition of Isoamyl alcohol at a fixed reflux ratio of 2. It was observed that the mole composition of Isoamyl alcohol increased with increasing solvent flow rate. Higher solvent flow rates reduced solvent dilution caused by reflux, thereby enhancing distillate purity. The optimal solvent flow rate depends on the desired concentration of Isoamyl alcohol, as well as cost considerations. Additionally, figure reveals that the reboiler duty varied significantly with increasing solvent flow rate, while the condenser duty remained nearly constant across the solvent flow rate ranges investigated. High solvent flow rates require a large amount of liquid to be evaporated, resulting in increased energy consumption by the reboiler. A solvent flow rate of 150 kmol/h may be the optimal value as it allows for high purity of Isoamyl alcohol while minimizing energy consumption.

The configuration and operational parameters of the main column, derived from the outcomes of sensitivity analysis, are outlined in Table 3.

Table 3. Design Parameter

Column	Parameter	Value
Extractive	Az. mix flow rate (kmol/h)	100
	Entrainer (Solvent) flow rate (kmol/h)	150
	Feed temperature (K)	380
	Solvent temperature (K)	380
	Number of stages	30
	Feed stage	22
	Solvent stage	05
	Reflux ratio	2
	Pressure (pa)	101325
Recovery	Number of stages	26
	Feed stage	15
	Reflux ratio	1.2
	Pressure (pa)	101325

CONCLUSIONS

This study delved into the separation of an Isoamyl acetate/Isoamyl alcohol azeotrope mixture through the simulation and design of an ED process. N-Octyle acetate emerged as a suitable solvent. A sensitivity analysis was executed to evaluate the influence of key parameters. The simulation outcomes revealed that the reflux ratio had the most profound impact on consumption of energy and necessitated low settings. Furthermore, the solvent flow rate proved to be a critical factor in achieving high-purity Isoamyl alcohol in top stream. The results indicated that a solvent flow rate of 150 kmol/h, a reflux ratio of 2, 30 stages, a feed stage of 22, and a solvent stage of 5 were essential for obtaining high-purity Isoamyl alcohol.

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