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Robust Flowsheet Synthesis for Ethyl Acetate, Methanol and Water Separation

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ABSTRACT

This work presents a robust flowsheet design for the recovery and purification of waste solvent streams containing ethyl acetate (EtAc), methanol (MeOH), and water. Separation of this mixture is challenging due to the presence of two azeotropes: a homogeneous EtAc-MeOH azeotrope and a heterogeneous EtAc-water azeotrope. These azeotropes create a distillation boundary that divides the ternary composition space into two distinct regions, making separation via conventional distillation difficult. Additionally, the wide variability in waste solvent compositions requires a versatile design, as flowsheets optimized for dilute mixtures may not be feasible for concentrated ones. The key to this design is using a liquid-liquid extractor (LLX) with recycled water as the solvent, ensuring the mixture remains within the liquid-liquid equilibrium (LLE) split region, which facilitates spontaneous separation across the distillation boundary and promotes energy-efficient separation. The raffinate composition lies near the EtAc-water edge in the EtAc-rich region and is stripped to recover pure EtAc, while the extract phase is processed to yield pure MeOH and water. Converged designs are developed for equimolar, EtAc-rich, MeOH-rich, and water-rich compositions, with the proposed robust structure validated for all four compositions. This study represents a significant advancement in sustainable solvent recovery by eliminating the need for separate designs tailored to specific compositions, offering a unified, robust solution for separating various solvent feed mixtures.

Keywords: Liquid Liquid Envelope, Liquid Liquid Extractor, Azeotropes, Robust Flowsheet

INTRODUCTION

Ethyl acetate (EtAc) and methanol (MeOH) are widely used solvents in the pharmaceutical, textile, dyes, and paints industries [1,2]. Significant volumes of organic waste streams containing EtAc and MeOH are generated varying composition based on the specific processes and conditions. Stricter waste discharge regulations and sustainability concerns now mandate the complete recovery, recycling, and reuse of organic solvents. The global shift towards sustainable practices and circular economy principles has intensified the focus on waste minimization, making solvent recovery and recycling from industrial waste streams essential for both environmental and economic reasons.

The separation and recovery of organic solvents from water are challenging due to the presence of two azeotropes—a homogeneous EtAc-MeOH azeotrope and a heterogeneous EtAc-water azeotrope. A line connecting these azeotropes creates a distillation boundary that divides the ternary composition space into two regions, complicating the separation process and making conventional distillation ineffective.

Separation facilities that process waste streams into pure components often face significant variability in EtAc, MeOH, and water concentrations, depending on the source process and operational parameters. This variability poses a design challenge, as flowsheets optimized for dilute compositions may not be suitable for concentrated ones, while those designed for concentrated mixtures may be too costly for dilute streams. Traditional solutions typically involve multiple processing units for different compositions or frequent adjustments to operating conditions, both of which can compromise the economic viability of the recovery process.

Industrial plants typically operate with fixed equipment configurations, such as the number of trays, column diameter, and heat exchangers, which cannot be easily modified once installed. As a result, there is a pressing need for robust flowsheet designs that ensure operational feasibility across the full range of potential feed compositions. Developing such flowsheet structures requires careful consideration of operational constraints and innovative approaches to process synthesis and design. The goal of this work is to design a robust flowsheet capable of handling substantial variability in feed composition for the separation of EtAc-MeOH-water.

The article is organized as follows: the next section discusses the thermodynamics of the process, followed by the synthesis of a flowsheet for MeOH rich feed composition. We then present a near-optimal economic design for that composition. Finally, we explore the robust design that effectively handles variations across all ranges and conclude the article with its main findings.

PROCESS MODELLING

Aspen Plus is used for steady-state simulation, with thermodynamic properties modeled using the NRTL equation for the liquid-phase activity coefficient and the vapor phase treated as an ideal gas. The binary interaction parameters are adapted from the work of Srivastava et al. [3]. Steady-state designs are developed for an inlet feed stream flow rate of 100 kmol/h, considering four distinct feed compositions. These compositions (all in molar percentages) represent different mixture: (1) 33.34% EtAc, 33.33% MeOH, 33.33% Water; (2) 80% EtAc, 10% MeOH, 10% Water; (3) 10% EtAc, 10% MeOH, 80% Water; and (4) 10% EtAc, 80% MeOH, 10% Water. The targeted purities are 99.5% for EtAc and MeOH, and 99.9% for Water.

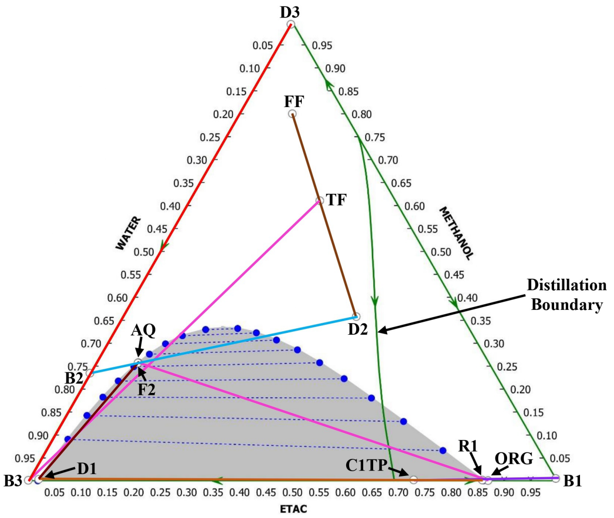

Figure 1: Residue Curve Map at 1 bar

PROCESS FLOWSHEET SYNTHESIS

Figure 1 shows the Residue Curve Map (RCM) for the MeOH rich feed composition, revealing the presence of a Liquid-Liquid Envelope (LLE) and two minimum boiling azeotropes: EtAc/MeOH and EtAc/Water. We leverage the LLE to design the separation process flowsheets. In systems with LLE, the efficient method is to use a decanter to cross the distillation boundary and obtain pure products. However, the RCM indicates that the feed point lies outside the LLE. To address this, we propose using a Liquid-Liquid Extractor (LLX) with recycled water as a solvent to bring the feed point into the LLE. The proposed design is shown in Figure 2.

The fresh feed, mixed with the recycle stream (D2), is fed into the LLX as a total feed (TF) from the bottom, with recycled water introduced from the top in a counter-current manner. This setup brings the feed point within the LLE split region, as shown in Figure 1. The mixture then spontaneously separates into an EtAc-rich organic phase (ORG) and a water-rich aqueous phase (AQ), crossing the distillation boundary without any external energy input. The organic phase is fed into Column 1 (C1), where pure EtAc is recovered at the bottom (B1). The distillate composition (C1TP) remains within the LLE region and is decanted in an adjacent decanter, separating it into an organic phase (R1) and an aqueous phase (D1). The EtAc-rich organic phase (R1) is refluxed back into C1, while the water-rich aqueous phase (D1) is mixed with the aqueous stream (AQ) from LLX.

The resulting F2 stream is fed into Column 2 (C2), which prevents EtAc leakage into the bottom stream

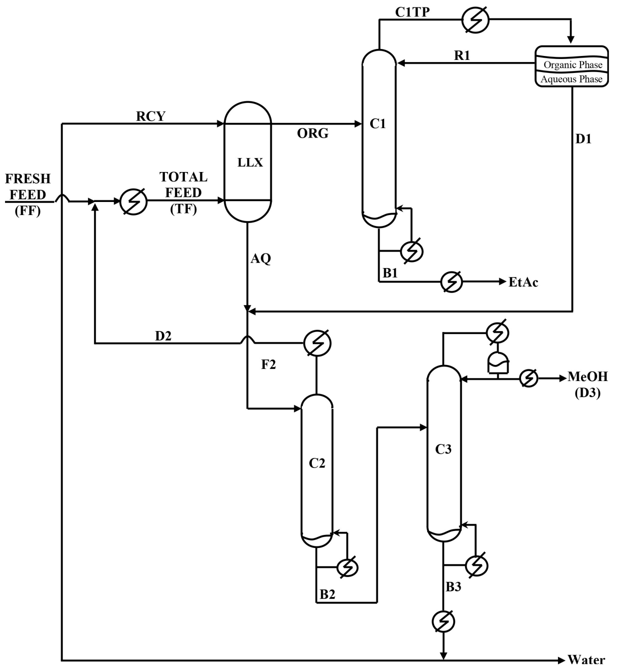

Figure 2: Proposed flowsheet structure

Table 1: Degrees of Freedom and Specifications

S.N.	Degrees of Freedom	Equimolar	EtAc rich	MeOH rich	Water rich
	Steady State DoFs				
1	Fresh feed rate (kmol/hr)	100	100	100	100
2,3	EtAc and MeOH product mole fraction	0.995	0.995	0.995	0.995
4	Water product mole fraction	0.999	0.999	0.999	0.999
5	C2 bottom stream EtAc impurity (ppm)	24	74	20	160
6	Water recycle rate (kmol/hr)	98	104	252	14.71
7	LLX operating temperature (°C)	40	40	40	40
8,9,10	Product temperature (°C)	40	40	40	40
	Design DoFs				
1,2,3,4	LLX and Column pressure (bar)	1	1	1	1
5	Number of stages in LLX	5	6	4	5
6	Number of trays in column C1	18	18	18	18
7	Number of trays in column C2	12	9	12	9
8	Number of trays in column C3	27	30	27	30
9	Feed tray location in column C1	9	11	11	11
10	Feed tray location in column C3	12	14	12	14

(B2). The distillate (D2) lies outside the envelope, so it is recycled back to the LLX for further separation. The methanol-water bottoms (B2) are then distilled in Column 3 (C3) to produce pure methanol distillate (D3) and pure water bottoms (B3). A portion of the bottoms is recirculated to the LLX as the solvent feed. In the next section we will discuss the economic steady state design of the proposed process.

ECONOMIC STEADY STATE DESIGN

The proposed design, depicted in Figure 2, has 20 degrees of freedom (DoFs), comprising 10 steady-state DoFs and 10 design DoFs. These DoFs are adjusted to minimize the Total Annualized Cost (TAC), resulting in an economic steady-state design.

$$TAC = \frac{TCC}{PBP} + \mathrm{YOC}$$

where TCC is the Total Capital Cost, PBP is the Payback Period, and YOC is the Yearly Operating Cost. A payback period of 3 years is used.

We have used engineering heuristics to fix these DoFs, with details provided in Table 1. However, the economically dominant DoFs are optimized for minimizing the TAC using the Aspen Plus *sensitivity analysis* tool. For the MeOH-rich feed composition design, we identified three economically dominant DoFs among the 20: the total number of trays in the LLX (N_{LLX}), the EtAc impurity x_{EtAc} in the C2 bottom stream (B2), and the water flow rate F_{Water} for the recycled water to the LLX.

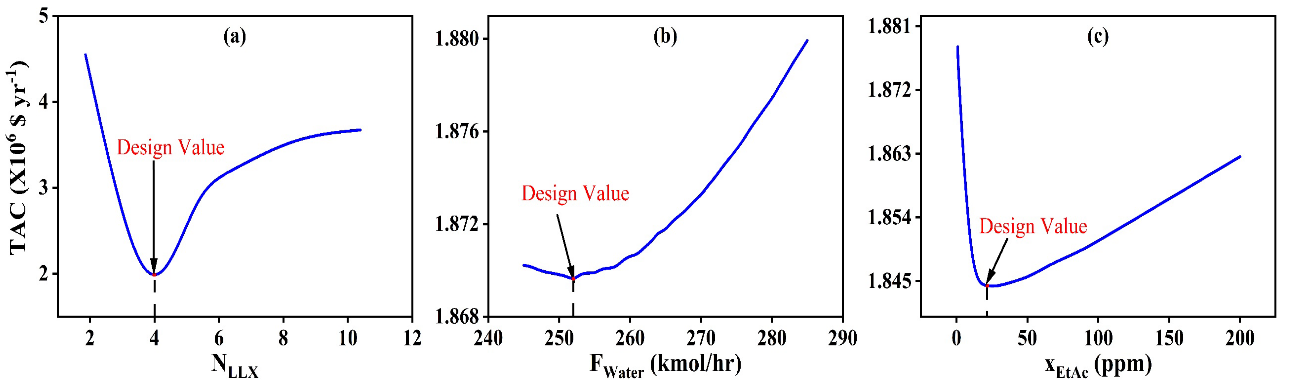

Figure 3: Optimization parameters for MEOH rich composition (a) Number of stages in LLX (b) Water recycle rate to LLX (c) EtAc impurity in B2 stream

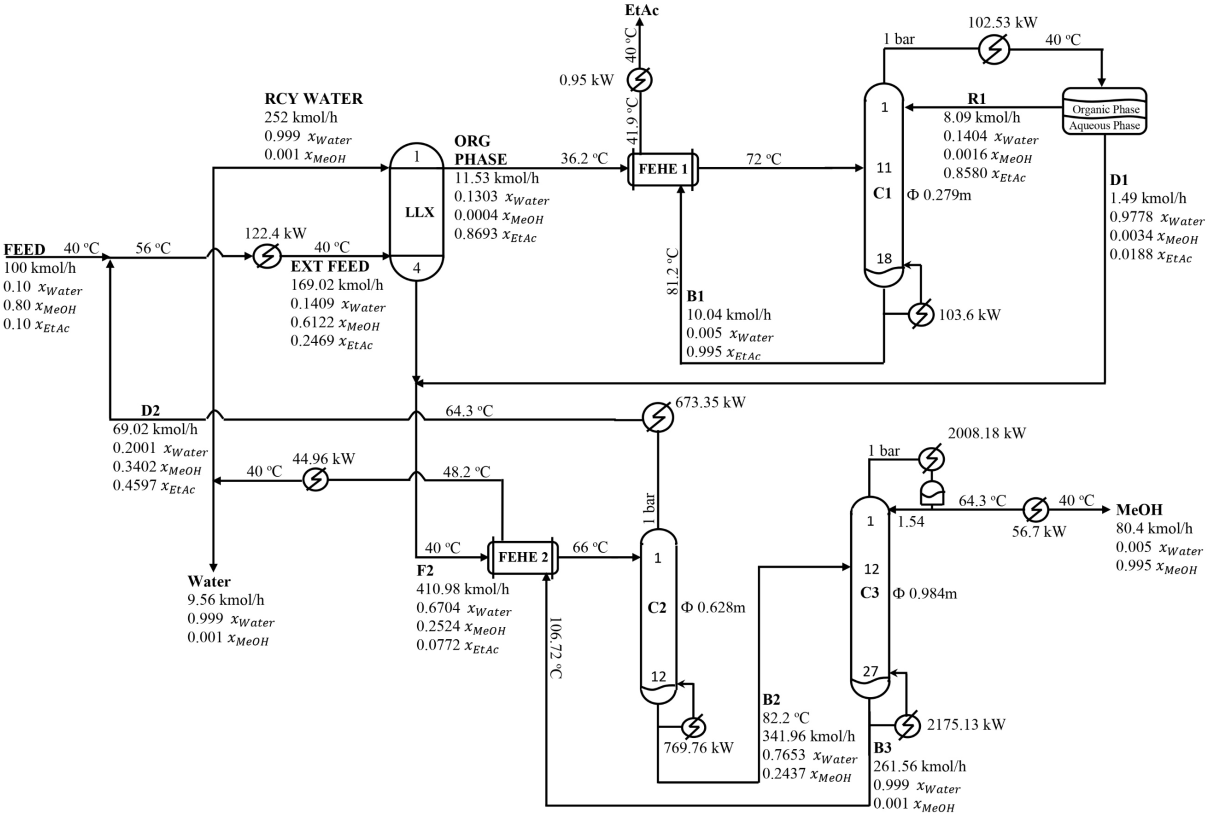

Figure 4: Nominal Design and Operating Condition for MeOH rich Feed

Figure 3 illustrate the variation of TAC with respect to the recommended design values corresponding to the optimum TAC. The optimum N_{LLX} was determined to be 4. Above this value, TAC increases due to the higher capital cost of the LLX, while below it, TAC rises because of the increased water recycle rate needed to maintain the feed point in the LLE region, which increases the total reboiler duty. The optimum x_{EtAc} is set at 20 ppm; exceeding this value leads to higher TAC due to increased reboiler duty in the C3 column, whereas falling below this value raises TAC due to the increase in reboiler duty of the C2 column. The optimum water flow rate F_{Water}; above this value, TAC increases due to a higher solvent water recycle rate, which elevates the reboiler duties of both C2 and C3. Conversely, below this optimum, TAC rises because of the increased reboiler duty in the C1 column, resulting from higher recycling associated with the C1 column.

Similarly, the other three steady-state designs can be developed. For brevity, the details are omitted here, but the DoFs are provided in Table 1. In the next section, we will synthesize the robust flowsheet.

SYNTHESIS OF ROBUST FLOWSHEET

Based on the insights from Table 1, the robust flowsheet is designed by selecting the maximum stage or tray requirement for each unit to ensure effective separation across all compositions. In the LLX unit, the number of stages varies from 4 for MeOH-rich feeds to 6 for EtAc-rich feeds; therefore, 6 stages are incorporated into the robust design to maintain separation efficiency in all scenarios. For column C1, 18 trays are optimal across all compositions, which is retained in the robust configuration. In column C2, 12 trays are selected to facilitate effective separation across all four compositions. Similarly, for column C3, 30 trays are selected in the robust design to ensure reliable performance under all operating conditions. In the LLX, the liquid level corresponds to the dispersed phase, which has a low volume fraction. As seen from Table 1, the water flow rate has a low flow rate, which is why it is considered the dispersed phase here, except for the MeOH-rich composition, where it is the continuous phase. Therefore, the liquid level is in the aqueous phase for all compositions, except for the MeOH-rich case, where the level is in the organic phase. As the composition shifts from MeOH-rich to any other case, the LLX level changes from organic to aqueous, which is not feasible in the design. To address this, the water flow rate is maintained as the continuous phase for all composition cases to ensure effective separation. Thus, the water is in a ratio with the total feed to the LLX (F_{LLX}), which varies from 0.14 to 1.46. We selected the

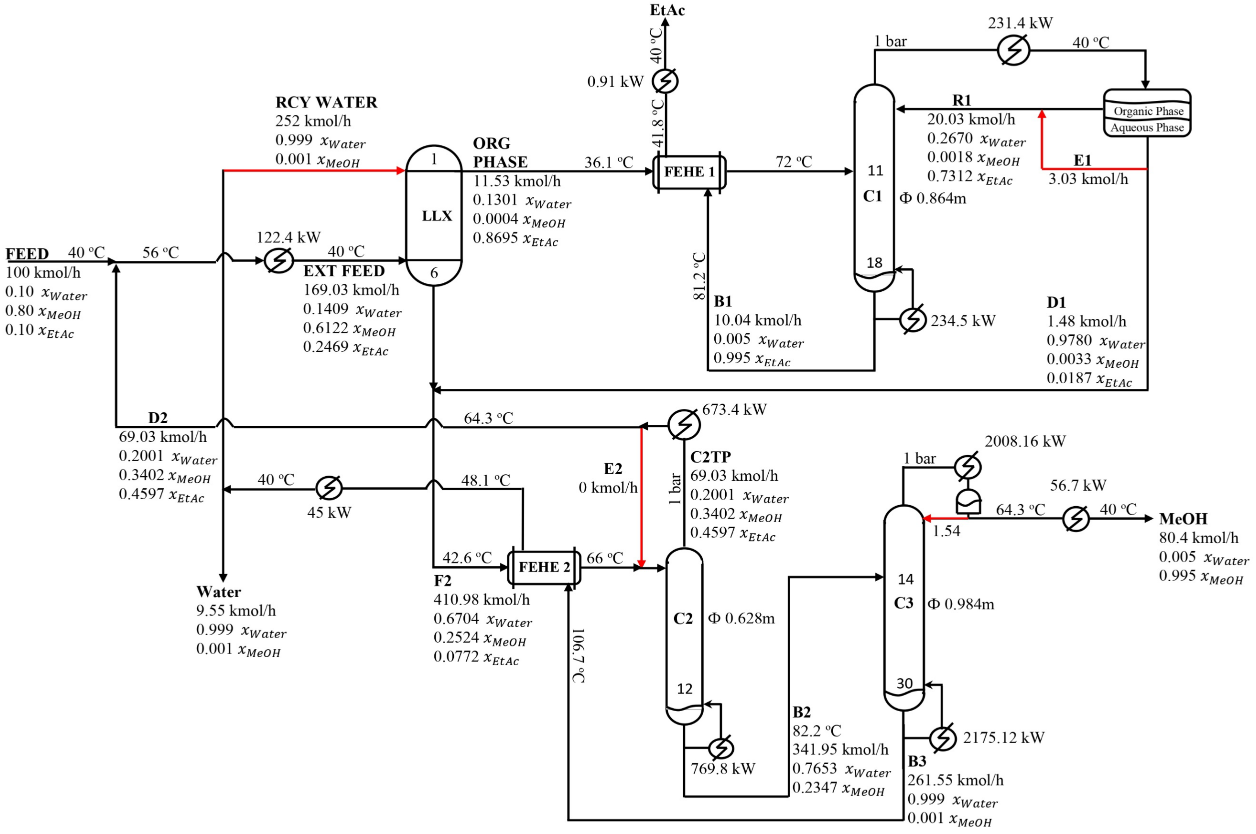

Figure 5: Robust Design and Operating Condition for MeOH rich Feed

highest ratio of 1.46 for the robust design to ensure effective extraction while maintaining operational efficiency across all scenarios.

Having established the basic design parameters, it was crucial to address the operational challenges posed by feed composition variations. As the composition changes from EtAc-rich to MeOH-rich, the feed to column C1 decreases while the feed to columns C2 and C3 increases. These variations significantly impact the reboiler duties required for the desired separation. Increased duties in columns C2 and C3 may lead to flooding, while the decreased duty in column C1 risks low boil-up rates, which can result in weeping and reduced tray efficiency. If the vapor rate falls below a critical point, it may trigger the low vapor boil-up limit, leading to weeping, which adversely affects tray efficiency and separation. The minimum allowable boil-up rate is determined using the turndown ratio, defined as the ratio of normal operating vapor throughput to the minimum allowable vapor throughput. We chose bubble cap trays for their 8:1 turndown ratio [4,5], which offers greater operational flexibility compared to sieve and valve trays. To

Table 2: Economic and sustainability metric for alternative feed composition

Metric	Equimolar		EtAc rich		MeOH rich		Water rich	
	Optimized Design	Robust Design	Optimized Design	Robust Design	Optimized Design	Robust Design	Optimized Design	Robust Design
Energy (kW)	1601.4	1703.2	1437	2112.6	3048.5	3189.8	648.4	1048.8
TCC×10^6 (\$/yr)	1.73	2.56	1.90	2.56	2.12	2.56	0.99	2.56
YOC×10^6 (\$/yr)	0.60	0.64	0.54	0.79	1.14	1.19	0.24	0.39
TAC×10^6 (\$/yr)	1.18	1.50	1.17	1.64	1.85	2.04	0.57	1.24

determine the minimum vapor throughput, we compared the vapor throughput across all four flowsheets and selected the highest value for each column as its design basis. While the 8:1 turndown ratio theoretically permits operation down to 12.5% of normal throughput, operating at this boundary risks weeping conditions. Therefore, we set 25% of normal throughput as the lower operational limit during turndown conditions to maintain a safety margin against weeping. Consequently, the reboiler duties in all columns can safely be reduced to this limit during operation, as required for different feed compositions.

To maintain the minimum vapor throughput of 25%, an additional degree of freedom (DoF) is required for each column to prevent weeping when the feed composition shifts from one composition to the other. In column C1, this involves partial recycling of the D1 stream back into the column, effectively maintaining minimum vapor rates while preserving separation efficiency. Column C2 employs a similar strategy by partially recycling the top product stream. For column C3, separation performance is sustained by carefully adjusting the reflux ratio, which ensures both product purity and operation above the minimum vapor rate limits. The detailed robust flowsheet, incorporating these strategies, is depicted in Figure 5, illustrating the design modifications and their alignment with operational requirements.

Table 2 presents an economic and energy comparison between the optimized flowsheet and the robust flowsheet for all considered feed compositions. As shown in the table, the robust design incurs a higher TCC than the optimized design due to the addition of an extra DoF and changes in design conditions. For a fair comparison, the TAC of the robust design should be compared with the sum of the TAC values for each optimized design. The cumulative TAC of all four optimized designs is **4.77 × 10^6 \$/yr**, whereas the TAC of the robust design—calculated as **(TCC/3 + YOC of individual feed composition)**—is **3.86 × 10^6 \$/yr**, which is **20% lower**. Thus, the robust design demonstrates a lower TAC while offering enhanced operational flexibility and reliability across varying feed compositions. This contributes to the sustainability of the overall process by ensuring long-term efficiency and minimizing the need for frequent process adjustments.

CONCLUSION

This work presents a robust flowsheet design for the recovery and purification of waste solvent streams containing EtAc, MeOH, and water. The design effectively addresses challenges such as azeotropes and the variability in feed compositions. Crux to the design is the use of LLX, with recycled water as the solvent. This ensures that the total feed mixture remains within the LLE split region, regardless of the fresh feed composition. This enables spontaneous separation across the distillation boundary. The design has been validated across a wide range of feed compositions, including equimolar, EtAc-rich, MeOH-rich, and water-rich mixtures.

The robust design shows significant TAC savings of 20% than the cumulative TAC of all four optimized design and also offers greater flexibility in handling diverse feed mixtures. Additionally, it eliminates the need for multiple, composition-specific designs, leading to significant savings in land costs. Ultimately, the proposed design enhances operational flexibility and supports more scalable separation processes, representing a significant advancement in waste solvent recovery technology.

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