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Redefining Stage Efficiency in Liquid-Liquid Extraction: Development and Application of a Modified Murphree Efficiency

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ABSTRACT

Liquid-liquid extraction stages often deviate from equilibrium due to factors like insufficient mixing, making accurate efficiency modeling essential for process simulation. This study addresses the limitations of Aspen Plus (AP), which distorts equilibrium calculations by directly multiplying efficiency with the distribution coefficient. A modified Murphree efficiency definition, more suitable for liquid-liquid systems but absent in AP's Extraction Column module, was implemented using Aspen Custom Modeler (ACM). The custom multi-stage extraction column model replaces mole fractions with mole flows to better represent mass transfer and phase interactions, enhancing simulation accuracy when imported into AP. Two test cases validated the custom model's effectiveness. Test Case I, utilizing the UNIQ-RK thermodynamic model, compared the ACM model to AP's built-in module, revealing that the ACM model provides a more realistic representation of extraction processes under varying stage efficiencies. It captured gradual efficiency changes and aligned with expected mass transfer behavior, while the built-in module showed reduced sensitivity and accuracy. Test Case II, using the UNIF-LL thermodynamic model, demonstrated the model's robustness across different thermodynamic frameworks. It highlighted how varying Murphree efficiency from 0 to 1 directly affects separation performance, with higher efficiencies leading to better separation and increased extract phase composition. These findings confirm that the modified Murphree efficiency is a reliable and effective approach, enabling engineers to optimize liquid-liquid extraction processes with greater accuracy and efficiency.

Keywords: Liquid-liquid extraction, Murphree efficiency, Aspen Custom Modeler, Extraction column, Process simulation

INTRODUCTION

Liquid-liquid extraction (LLX) is a widely used separation process in chemical engineering, particularly for systems where the components to be separated are not suitable for conventional distillation due to factors such as thermal sensitivity or low relative volatility [1]. In LLX, components are distributed between two immiscible liquid phases—typically an aqueous phase and an organic solvent phase—based on their relative solubility or affinity for each phase. This process is employed in diverse industries, including petrochemicals, pharmaceuticals, hydrometallurgy, and wastewater treatment [2].

Despite its broad applicability, LLX processes are often plagued by inefficiencies that result in deviations from ideal equilibrium. These inefficiencies arise from factors such as insufficient mixing, poor phase dispersion, non-ideal phase interactions, and mass transfer limitations [3, 4]. Insufficient mixing reduces the interfacial area available for mass transfer, leading to incomplete component transfer between phases. Similarly, operational factors such as stage design, solvent-to-feed ratios, and flow patterns can further exacerbate these inefficiencies, resulting in lower extraction performance. Experimental studies have shown that deviations from ideal mixing and equilibrium are significant, particularly in multi-stage extraction columns where the cumulative effect of inefficiencies can drastically reduce overall

separation performance [5].

Traditional approaches for modeling stage efficiency in liquid-liquid extraction (LLX) often oversimplify these complex behaviors. For example, simulation tools like Aspen Plus (AP) apply a concept sometimes referred to as "vaporization efficiency," which originates from its use in systems such as steam distillation. This method defines stage efficiency by scaling the component distribution coefficient (Ki) with an efficiency term (Ei), as represented in Equation 1:

$$E_i = \frac{x_i^{L2}}{K_i x_i^{L1}} \quad (1)$$

Here, x_i represents the mole fractions of a component in stage i in the liquid phases L_1 and L_2, respectively. While this formulation simplifies equilibrium calculations, it introduces significant limitations when applied to LLX systems. The concept of vaporization efficiency, as detailed in references such as Wankat's Equilibrium Staged Separations, is more relevant to steam distillation, where it is directly defined using vapor pressures [6]. This basis is not applicable to LL systems, where equilibrium is governed by distribution coefficients rather than vapor pressures. In LLX systems, directly scaling the equilibrium coefficient inherently distorts the mass transfer behavior, especially in non-ideal conditions where deviations from equilibrium are pronounced [7]. This limitation is particularly critical in systems with low efficiencies, where stage performance depends strongly on factors such as mixing quality, interfacial mass transfer rates, and phase equilibrium dynamics. Such discrepancies underscore the need for approaches better tailored to the specific complexities of LLX processes.

To address these challenges, this work introduces a modified Murphree efficiency definition tailored for LLX processes. The Murphree efficiency, traditionally applied in vapor-liquid systems, compares the actual performance of a stage to its ideal counterpart, effectively capturing deviations from equilibrium. For LLX systems, however, the use of mole fractions in the traditional Murphree definition fails to account for the continuous nature of mass transfer and phase interactions. Instead, this study proposes a modification wherein mole flows replace mole fractions, ensuring a more consistent and physically accurate representation of stage performance. The modified efficiency better reflects real-world process behavior by incorporating both the composition and the flow dynamics of the system.

The importance of accurately modeling stage efficiency cannot be overstated. Experimental studies have shown that small inefficiencies at individual stages can propagate through multi-stage columns, significantly reducing overall extraction efficiency and leading to suboptimal solvent utilization [8]. Furthermore, non-idealities such as solvent entrainment, phase back-mixing, and viscosity effects can further complicate the extraction process [9]. Addressing these inefficiencies requires models that not only account for equilibrium deviations but also reflect the dynamic interactions between feed and solvent phases. The modified Murphree efficiency presented here provides a step toward bridging the gap between idealized models and real-world LLX systems.

The proposed efficiency model was implemented in a multi-stage extraction column using Aspen Custom Modeler (ACM) and imported into AP for verification. It is important to emphasize that the tools used in this study, namely ACM and AP, serve merely as implementation platforms. The modified Murphree efficiency can be applied in any appropriate modeling environment capable of supporting custom efficiency definitions. This flexibility broadens the applicability of the approach, making it suitable for a wide range of LLX systems and scenarios.

In summary, this work presents a modified efficiency definition that addresses the limitations of existing models for LLX processes. By accounting for mass transfer dynamics and phase interactions more rigorously, the proposed approach provides a robust framework for simulating and optimizing LLX systems in a realistic way. The findings have implications for the design and operation of extraction columns, particularly in processes where deviations from equilibrium play an important role in determining overall performance.

METHODOLOGY

The accurate modeling of stage efficiency in LLX processes requires an approach that accounts for both mass transfer and deviations from equilibrium. The proposed methodology addresses these challenges by redefining the Murphree efficiency for liquid-liquid systems, making it more applicable and realistic in representing stage performance.

The Murphree efficiency is traditionally defined for vapor-liquid equilibrium systems, evaluating the performance of a stage based on the deviation of the actual composition change from the ideal change. The original definition for vapor-liquid is expressed as:

$$E_i^M = \frac{x_i^V - x_{i-1}^V}{K_i x_i^L - x_{i-1}^V} \quad (2)$$

Here, E^M represents the Murphree efficiency of stage i. V and L are stand for vapor and liquid phases, respectively. This definition is well-suited for vapor-liquid processes.

In liquid-liquid systems, the traditional Murphree efficiency is less effective because equilibrium is rarely achieved at each stage due to slower mass transfer rates and insufficient mixing. Additionally, it is worth noting that in liquid-liquid systems, the distinction between the two phases, analogous to vapor and liquid in vapor-liquid systems, is less clear. LL systems exhibit a more symmetric behavior in this regard, making it ambiguous which

phase should correspond to "V" or "L." Trials with both interpretations showed similar results, further supporting this symmetry. Furthermore, traditional mole fraction-based efficiencies for LL systems were also tested but presented challenges, particularly in cases where total molar flows varied. In such scenarios, linking mole fractions at the inlet and outlet becomes less logical, leading to somewhat inconsistent results. This issue is effectively addressed in the present formulation by using mole flows, which inherently account for variations in total molar flow and ensure consistency in the efficiency calculation. mixing. Moreover, mole fractions alone are insufficient to capture the phase interactions and mass transfer dynamics that are essential to understanding the performance of LLX stages. Instead, the mass transfer behavior in such systems is better represented by mole flows, which consider both the amount of material transferred and the phase equilibrium composition. To address these challenges, the Murphree efficiency was modified by substituting mole flows for mole fractions in the traditional definition. The modified efficiency for components is expressed as:

$$E^M = \frac{x_i^{L2}\,\dot{n}_i^{L2} - x_{i-1}^{L2}\,\dot{n}_{i-1}^{L2}}{K_i x_i^{L1} \varphi^{*,L1}\left(\dot{n}_i^{L1}+\dot{n}_i^{L2}\right) - x_{i-1}^{L2}\,\dot{n}_{i-1}^{L2}} \tag{3}$$

Here, $\dot{n}$ represent the molar flow rate, $\varphi*$ denotes the equilibrium phase fraction. This modification ensures that the efficiency definition aligns with the physical principles of mass transfer and captures the continuous nature of phase interactions in liquid-liquid systems. To incorporate this modified efficiency into the modeling framework, component and overall mole balances were established for the system. The component mole balance for the second liquid phase can be calculated from the overall mole balance of each component:

$$x_i^{L1}\,\dot{n}_i^{L1} + x_i^{L2}\,\dot{n}_i^{L2} = x_{i-1}^{L1}\,\dot{n}_{i-1}^{L1} + x_{i-1}^{L2}\,\dot{n}_{i-1}^{L2} \tag{4}$$

The overall mole balance for the system becomes:

$$\dot{n}_i^{L1} + \dot{n}_i^{L2} = \dot{n}_{i-1}^{L1} + \dot{n}_{i-1}^{L2} \tag{5}$$

These equations relate the modified Murphree efficiency to the principles of mass transfer and phase equilibrium, offering a framework for accurately representing stage performance. By incorporating the interplay between stage efficiency, composition and flow rates, the approach captures the dynamics of LLX systems.

To apply the modified efficiency, a multi-stage LLX column model was implemented. The model accounts for gradual changes in efficiency and composition across stages, reflecting the interactions between feed and solvent phases in a counter-current setup as represented in Figure 1.

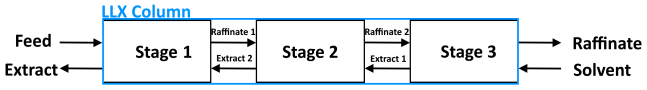


Figure 1. Counter-current LLX scheme with 3 stages.

The model was implemented using ACM, where the modified Murphree efficiency and mass balance equations were defined. It was then imported into AP for comparison with the built-in extraction modules. While ACM and AP were used for this study, the methodology itself is flexible and can be applied in other simulation environments capable of supporting custom efficiency definitions.

RESULTS AND DISCUSSION

The performance of the modified Murphree efficiency in LLX was evaluated through two test cases that assessed its implementation in a custom ACM model imported into AP. These cases demonstrate the model's capacity to simulate stage efficiencies and its superiority over the built-in AP extraction module for realistic system behavior and accuracy. The system configuration for the LLX process is shown in Figure 2, where the feed and solvent streams enter the extraction column (LLX Column), and the resulting extract and raffinate streams exit the column. This setup highlights the counter-current interaction of the phases, which drives the separation process.

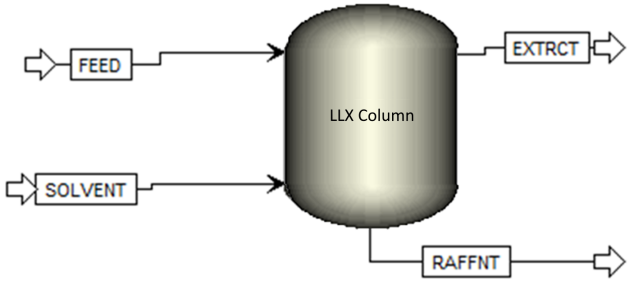


Figure 2. Schematic representation of a LLX column showing the flow of feed, solvent, extract, and raffinate streams.

Test Case I: Comparison Between ACM and AP Built-In Models

The performance of the modified Murphree efficiency implemented in the ACM model was evaluated in comparison to AP's built-in extraction module. Test Case II focused on a LLX system involving three components: acetic acid (HAC), water, and n-hexane, operating over 3 to 7 stages with varying stage efficiencies. To model the phase behavior and distribution of components between the aqueous and organic phases, the UNIQ-RK thermodynamic model was employed.

Table 1 provides an overview of the feed and solvent

components along with their respective flow rates. The analysis emphasized column efficiency, component distributions, and overall extraction performance.

Table 1: Test case I feed and solvent components with flow rates.

Stream	Description	Flow
Feed	Water	8 kmol/hr
	HAC	2 kmol/hr
Solvent	N-hexane	30 kmol/hr

The results from the ACM model, illustrated in Figure 3, showed a clear and consistent increase in column efficiency as the number of stages increased. The behavior aligns with expected mass transfer dynamics, where increasing the number of stages and improving efficiency enhances the separation performance. As illustrated in the Figure 3, constant Murphree efficiencies of 0.25, 0.5, and 1 demonstrated progressively higher column efficiencies. At an efficiency of 1, the column approaches equilibrium, achieving the maximum possible separation. Conversely, when the efficiency was set to 0, no separation occurred, and the extract and raffinate compositions mirrored the feed and solvent, confirming the physical expectation of no phase interaction.

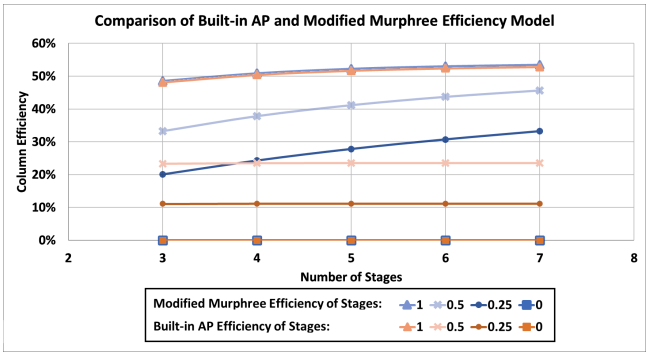


Figure 3. Comparison of column efficiency for built-in AP and modified Murphree models at varying efficiencies.

In contrast, the built-in AP model fails to capture the gradual and realistic changes in column performance, particularly at lower efficiencies. The results exhibit a discontinuous and overly simplistic response to variations in efficiency, where changes in stage performance are not reflected accurately. This lack of sensitivity is problematic for systems that require precise predictions of mass transfer behavior and separation performance across multiple stages. The inaccuracies become especially apparent when the efficiency is set to zero. Under this condition, the AP model produces physically unrealistic results, redistributing all of the solvent into the raffinate phase, as shown in Figure 4. This outcome violates fundamental mass balance principles and misrepresents the behavior of the system, where, in reality, no separation should occur, leaving the extract and raffinate phases identical to the feed and solvent compositions.

The results confirm that incorporating the modified Murphree efficiency into a custom ACM model provides a more realistic representation of liquid-liquid extraction. While the ACM model occasionally encountered convergence issues during integration with AP, its flexibility and ability to realistically simulate stage efficiencies offer significant benefits for process optimization. By addressing real-world inefficiencies, such as non-ideal mixing and deviations from equilibrium, the modified Murphree efficiency model provides a framework to evaluate extraction performance in multi-stage systems.

Test Case II: Effect of Stage Efficiency on Column Performance

In the second test case, a system consisting of acetone and water as the feed and 3-methylhexane as the solvent was simulated in a multi-stage LLX column. The thermodynamic model used in this case was UNIF-LL, a liquid-liquid activity coefficient model tailored for systems with significant non-ideal behavior. This test case was specifically designed to demonstrate the robustness and versatility of the implemented modified Murphree efficiency model in handling different thermodynamic frameworks.

The feed and solvent components and their flow rates are summarized in Table 2. The model simulated constant Murphree efficiencies of 0, 0.25, 0.5, and 1 across 3 to 7 stages. Column efficiency, defined as:

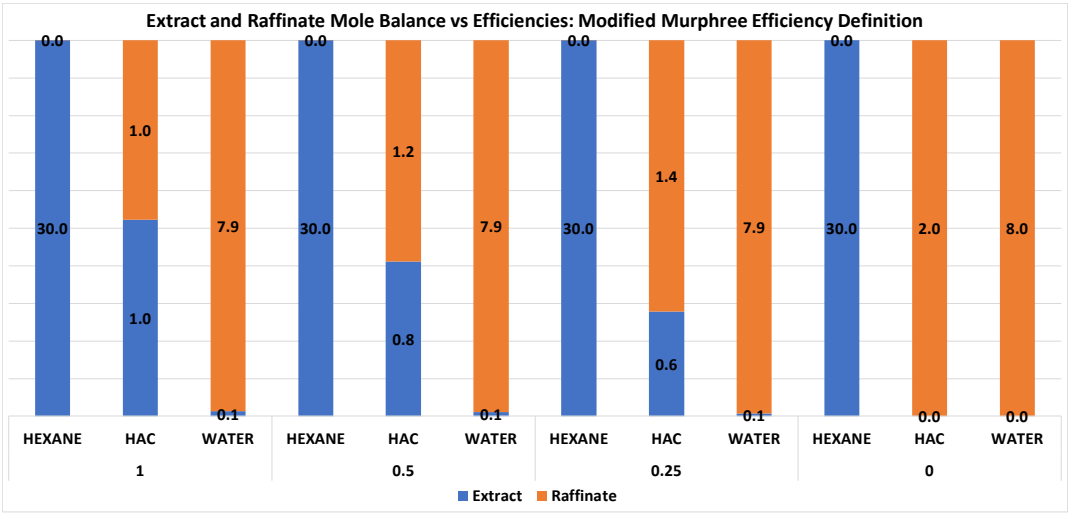
$$Column\ Efficiency\ = \frac{n_E^{Feed} - n_E^{Raffinate}}{n_E^{Feed}} \qquad (6)$$

where $\dot{n}_E$ represents the molar flow rate of the extracted component E (in this case, acetone) in the feed and raffinate phases.

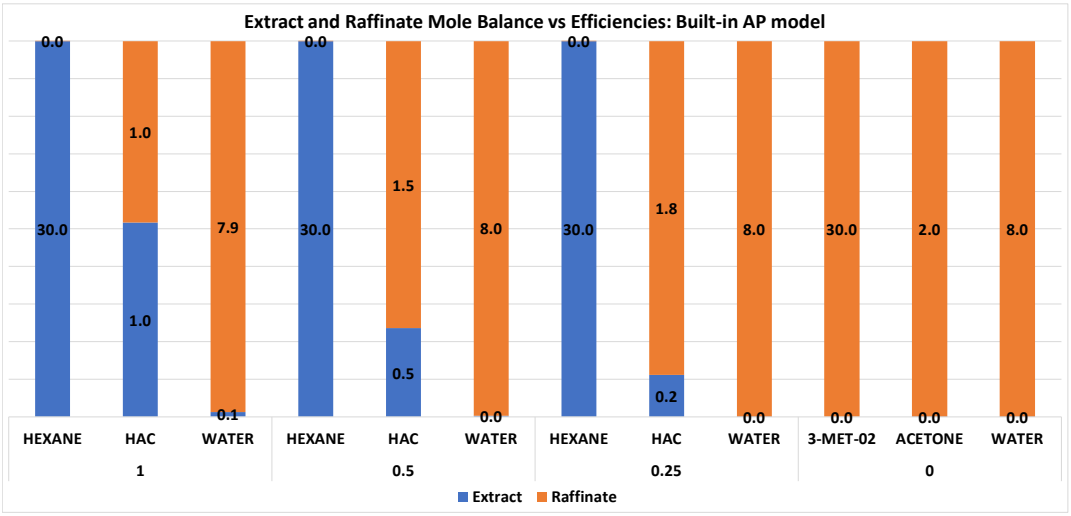
Table 2: Test case II feed and solvent components with flow rates.

Stream	Description	Flow
Feed	Water	8 kmol/hr
	Acetone	2 kmol/hr
Solvent	3-methylhexane	10 kmol/hr

The results, illustrated in Figure 5, show a clear relationship between Murphree efficiency and column performance. When Murphree efficiency was set to zero, no separation occurred, and column efficiency remained at 0%, as indicated by the flat blue line. This scenario reflects a system with no mass transfer, where the composition of the extract and raffinate phases is identical to the feed and solvent. As Murphree efficiency increased to 0.25 and 0.5, column efficiency improved steadily with the number of stages. This trend highlights the effect of additional stages in enhancing separation performance



(a)



(b)

Figure 4. Extract and raffinate mole balances at varying stage efficiencies for (a) the modified Murphree efficiency model developed using ACM and (b) the built-in AP model. The modified Murphree efficiency model shows a gradual and realistic distribution of components, while the built-in AP model demonstrates less sensitivity and unrealistic behavior at lower efficiencies.

under moderate efficiencies. At a Murphree efficiency of 1, the system achieved equilibrium conditions, resulting in the maximum column efficiency, as shown by the yellow line approaching 100%. Under these conditions, the separation was optimal, and the extract phase contained the highest amount of acetone.

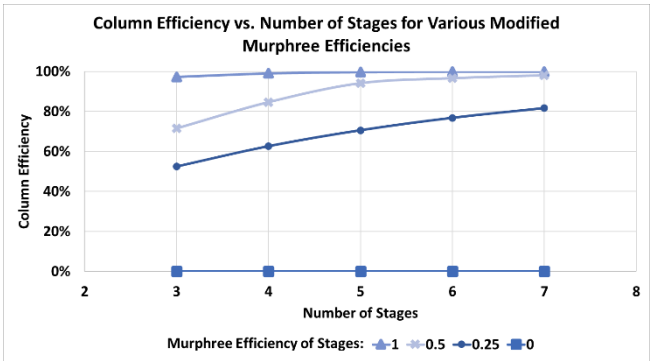


Figure 5. Effect of Murphree efficiency on column efficiency as a function of the number of stages. Lower efficiencies show limited separation performance.

The results highlight the significant influence of Murphree efficiency on extraction performance. Higher efficiencies lead to improved separation, whereas deviations from ideal conditions result in a notable decline in column performance. This emphasizes the importance of accurately modeling stage efficiency to better represent the behavior of LLX systems in practice.

CONCLUSION

This work introduced a modified Murphree efficiency definition to address challenges in modeling stage efficiencies in LLX processes. By using mole flows instead of mole fractions, the approach provides a framework that better reflects the mass transfer and phase interactions in systems where deviations from equilibrium occur.

The implementation of this approach in a custom ACM model and its integration into AP were used to evaluate its applicability. Through test cases, the model demonstrated its capacity to capture the relationship between stage efficiency and separation performance under varying conditions. The observations showed how stage efficiencies influence the distribution of components between extract and raffinate phases and highlighted the limitations of existing built-in simulation modules.

The methodology is not restricted to the tools used in this study. It can be implemented in other simulation platforms capable of supporting custom efficiency definitions. This general applicability allows the approach to be used for further studies and practical applications in different extraction systems. By addressing the relationship between stage performance, efficiency, and mass transfer, the modified Murphree efficiency provides a foundation for understanding and improving LLX processes.

DIGITAL SUPPLEMENTARY MATERIAL

Digital supplementary material, including data sheets, simulation files, models, and source code, is available upon request.

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