

Validation of a Fast Solvent Evaluation and Selection Model for Extractive Distillation

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Abstract

Extractive distillation is a solvent-based separation used to separate mixtures containing azeotropes or close boiling components. An external component (solvent) is added to the process to overcome the separation barrier. Selecting the optimal solvent for extractive distillation using solvents' physical properties has been studied, but process parameters, such as the number of stages and reflux ratio, must also be considered when selecting a solvent. A fast solvent evaluation and selection (FSSES) model using solvent properties and process parameters has been proposed for designing an optimal extractive distillation process. The FSSES model evaluates and ranks potential solvents to identify the solvent with the minimum total annualized cost (TAC) for the separation. This paper presents a validation study of the FSSES model results for separating two mixtures: acetone-methanol and benzene-cyclohexane. The study employed rigorous process simulation and optimization of extractive distillation for both separations, considering five candidate solvents for each. A derivative-free optimization (DFO) approach was used to identify the optimal process design and operating conditions that minimize the TAC for each solvent. Solvent rankings based on minimum TAC by optimization and predictions by the FSSES model were compared. The FSSES model and TAC-based optimization ranked the potential solvents for the acetone-methanol separation from best to worst as dimethylsulfoxide, water, ethylene glycol, ethanol, and 2-propanol. For the benzene-cyclohexane separation, the solvents were ranked sulfolane, furfural, dimethyl phthalate, N-methyl-2-pyrrolidine, and aniline from best to worst. The TAC-based rankings yielded the same order, except it ranked N-methyl-2-pyrrolidine better than dimethyl phthalate.

Key Words: extractive distillation, derivative-free optimization, process design, solvent selection

Introduction

Extractive distillation (Gerbaud et al., 2019) is a widely applied process for separating azeotrope or close boiling mixtures. In extractive distillation, a third component, solvent or entrainer, is added to overcome the separation barrier. Extractive distillation can perform high-purity separation for azeotrope or close boiling mixtures. An effective solvent facilitates the separation of azeotropic or close boiling mixtures by shifting the composition of the azeotrope. The solvent must also not form any new azeotropes with either mixture component. Since adding the solvent creates a three-component mixture, the process uses two distillation columns to separate the three components.

Fig. 1 gives the vapor-liquid equilibrium curves for the acetone-methanol mixture with and without solvents. In Fig. 1, the x-axis is the acetone liquid mole fraction in the mixture, and the y-axis is the acetone vapor mole fraction. The acetone-methanol mixture contains an azeotrope around liquid and vapor mole fractions of 0.8, as seen by the intersections of the dotted orange curve with the parity line (dashed black line). Adding water or dimethylsulfoxide (DMSO) to the mixture shifts the azeotropic composition (intersection of dashed-dotted blue or solid purple lines with the parity line in Fig. 1). This shift enables the separation of acetone and methanol at high purities.

Water or DMSO can be used as solvents in extractive distillation to separate the acetone-methanol mixture; however, the separation cost or performance would differ for each solvent. For example, adding DMSO so that its mole fraction is 0.2 in the mixture (i.e., $x_{\text{DMSO}}=0.2$)

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shifts the acetone-methanol azeotrope to a higher composition than adding water with the same mole fraction (i.e., $x_{\text{water}}=0.2$), which indicates that DMSO can facilitate a higher purity separation than water.

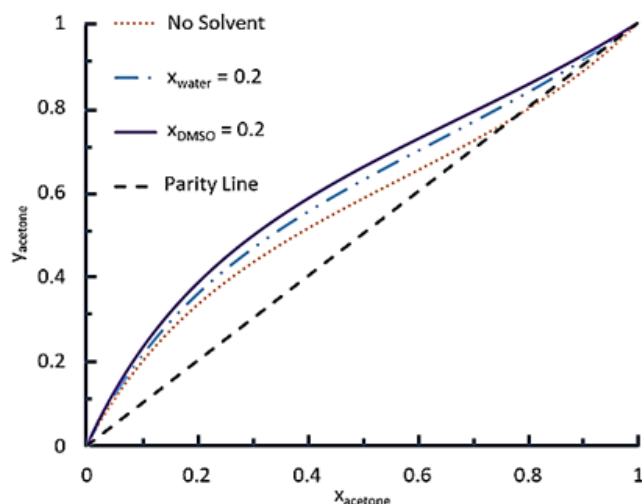


Fig. 1 Vapor-liquid equilibrium plot of acetone-methanol mixture with different solvents. The x and y axes represent acetone liquid and vapor mole fractions. The mole fraction of the solvent, either water or DMSO, in the mixture is 0.2. The acetone mole fractions for the mixture containing a solvent have been adjusted to [0, 1] range for generating the corresponding lines.

Fig. 2 shows the process flow diagram for extractive distillation. A two-component mixture (A, B) and solvent are fed separately to the first distillation column. The distillate of the first column contains pure product A, and the bottoms of the column contains component B and the solvent. This mixture is then separated in the second column to recover the solvent. The regenerated solvent is recycled back to the first column with make-up solvent added to replace the small amount of solvent lost in the distillate streams.

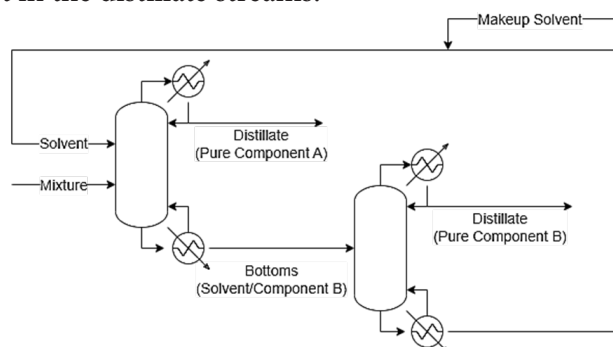


Fig. 2 General extractive distillation process flow diagram.

The extractive distillation process depends on the effectiveness of the solvent used, and different solvents can lead to vastly different designs, operating conditions, and process costs (Shen et al., 2015). Methods for selecting suitable solvents for extractive distillation and other solvent-based separation processes have been proposed. Kossack et al. (2008) proposed a rectification body method that can calculate process properties such as minimum solvent flowrate and minimum energy demand for selecting the optimal solvent. But, the method is computationally expensive. Cignitti et al. (2019) proposed an optimization model to design and identify suitable solvents by maximizing the separation driving force based on the group contribution method. The optimum solvent was validated by rigorous process simulation/optimization. Shen et al. (2015) proposed a solvent screening method based on five solvent physical properties, such as boiling point and selectivity. After adding weighted attributes to these properties, the solvents were ranked based on their 'total score,' and the ranking results were validated by process simulation. However, these methods only use physical properties as their design/screening criteria without considering the effects of process properties. For example, a higher boiling point solvent is often preferred in solvent screening due to its ease of regeneration, but this may result in the use of a higher grade of utility, which has a higher utility cost.

A fast solvent evaluation and selection (FSES) model (Xu et al., 2022) was developed to evaluate solvent performance quickly and efficiently. The FSES model uses both physical properties, such as boiling point, solvent flowrate, and process properties, such as reboiler duty, column stages, and reflux ratio, to predict solvent performance for extractive distillation. This study aims to assess the accuracy of the FSES model solvent recommendations by studying the separation of two mixtures, acetone-methanol, and benzene-cyclohexane, using extractive distillation with multiple solvents. It includes the simulation and derivative-free optimization of the extractive distillation process, which were applied to the acetone-methanol and benzene-cyclohexane separation tasks. The optimization studies minimized the total annualized cost (TAC) of the separation process using each solvent. The solvents were ranked based on their TAC, and the rankings were compared to the FSES model rankings. The results revealed that the

FSES model closely matched the rankings based on minimum TAC.

Methods

Extractive Distillation Process Simulation. Fig. 3 the extractive distillation flowsheet modeled and simulated using Aspen Plus (Aspen Technology, Inc., 2017). As seen in Fig. 3, the process includes two distillation columns and a recycle loop for the solvent. The azeotropic mixture A-B and recycled solvent, SOLVFEED, are fed to the first distillation column, D1. The distillate of D1 contains component A, and the bottoms stream S1 contains the solvent and component B. The bottoms stream S1 is fed to the second distillation column, D2. The distillate of D2 contains component B, and the bottoms stream SOLVOUT contains the recovered solvent. MAKEUP solvent is added to the recovered solvent and recycled back to D1 in stream SOLVFEED.

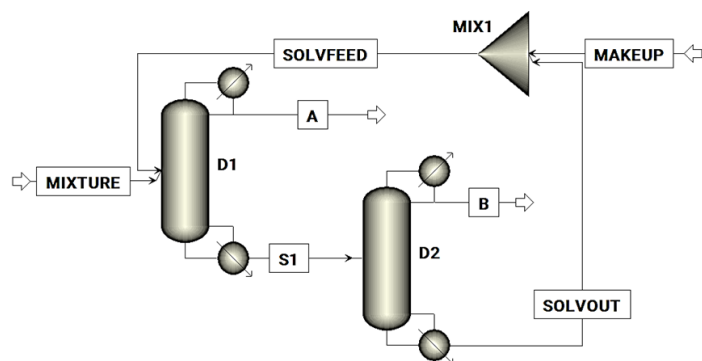


Fig. 3 Aspen Plus simulation flowsheet for extractive distillation for separating a mixture containing components A and B.

The inputs required for the simulation, as described in Fig. 3, were the SOLVFEED, and MIXTURE flowrates and temperatures into column D1, the MIXTURE component concentration, stream and column pressures, the total number of stages for D1 and D2, the feed stages for D1 and D2, the SOLVFEED feed stage for D1, and the MAKEUP flowrate. The values for these inputs were initially set using literature results and a systematic trial-and-error approach.

Distillation columns (D1 and D2 in Fig. 3) were modeled using the RadFrac block in Aspen Plus. An appropriate thermodynamic model was selected to adequately model the behavior of the components in each separation case. Purity and recovery specifications were defined. Only the results of simulation runs that

met these specifications were used to calculate TAC. These specifications were achieved utilizing the Design Spec and Vary features within Aspen Plus. The Design Spec feature allows for process parameters to be set to a certain value, while the Vary feature is utilized to automatically adjust process parameters over a set range to achieve the design specifications. The design specifications in Design Spec must be met with adjusted process parameters from Vary within the set boundaries for a simulation to converge without errors.

Each process simulation was converged without errors using inputs from literature and trial-and-error before it could be used for optimization.

Fast Solvent Evaluation and Selection (FSES) Model.

The FSES model (Xu et al., 2022) uses both physical properties and process parameters to predict solvent performance. The physical properties used include solvent boiling point and flowrate (SOLVFEED in Fig. 3). The process parameters are the minimum number of stages, reboiler duty, and column reflux ratio of D1 and D2 (Fig. 3). The extractive distillation column D1 is divided into stripping, extractive, and rectifying sections for calculating the minimum number of stages because the two-component mixture and solvent are fed separately to D1. The stripping section is below MIXTURE feed of D1, the rectifying section is above SOLVENT feed of D1, and the extractive section occurs between the two feeds (Fig. 3). The Fenske equation is applied separately to calculate each section's minimum number of stages, assuming constant relative volatility within each section. The sum of the resulting minimum number of stages is used as the minimum number of stages required for D1. The minimum reflux ratio is calculated by the intersection of the operating line and vapor-liquid equilibrium curve. Each physical or process property contributes to the overall score for a solvent, and a simple summation method is used to rank the solvents, as shown in Table 1. The best solvent has the lowest overall score and is predicted to yield the lowest TAC for separating A-B mixture using extractive distillation.

In Table 1, Sp is the solvent, $V_{p,r}$ is the value of property r for solvent p , $Score_{p,r}$ is the ranking score of property r for solvent p , and N is the total number of solvents evaluated.

Table 1 Fast Solvent Evaluation and Selection Model Ranking Method for Extractive Distillation.

Solvent, p		S_1	...	S_p	...	S_N
Properties, r	Reflux Ratio	$V_{1,1}$		$V_{p,1,min}$		$V_{N,1}$
		$Score_{1,1}$		1		$Score_{N,1}$
	Stages	$V_{1,2}$		$V_{p,2,max}$		$V_{N,2}$
		$Score_{1,2}$		N		$Score_{N,2}$
	Heat Duty	$V_{1,3}$		$V_{p,3}$		$V_{N,3}$
		$Score_{1,3}$		$Score_{p,3}$		$Score_{N,3}$
Total score of solvent, p		$Score_p = \sum_r Score_{p,r}$				

Derivative-Free Optimization (DFO) of Extractive Distillation Process. The optimization problem was solved using a DFO solver to identify the optimal process design and operating parameters for each separation. The optimum was defined as the parameter values that minimize the TAC of the system, shown in Equations 1-3.

$$\min: TAC = \frac{i(i+1)^n}{(i+1)^n - 1} \times IC + AUC \quad (1)$$

$$st. IC = \sum_j Cost_j(q_{s,j}) \quad (2)$$

$$AUC = 24 \times 300 \times \sum_j Utility_j(q_{o,j}) \quad (3)$$

In Eq. (1), TAC is the total annualized cost, IC is the investment cost, AUC is the annualized utility cost, i is interest, and n is the plant life ($n=5$ was used in this model). In Eq. (2), $Cost_j$ is the investment cost of equipment j , and $q_{s,j}$ is the sizing variable for equipment j . In Eq. (3), $Utility_j$ is the utility cost of equipment j , and $q_{o,j}$ is the operating variable for equipment j . The full cost model was developed following the method in Peters et al. (2003, Appendix A).

Equations 4-7 define the variable bounds on flowrates and column stages used in the DFO.

$$F_{S,L} \leq F_S \leq F_{S,U} \quad (4)$$

$$N_{k,feed,L} \leq N_{k,feed} \leq N_{k,feed,U} \quad (5)$$

$$N_{k,L} \leq N_k \leq N_{k,U} \quad (6)$$

$$N_{1,S,L} \leq N_{1,S} \leq N_{1,S,U} \quad (7)$$

F_s is the solvent flowrate, N_k is the number of stages in column k , $N_{k,feed}$ is the materials feed stage of column k , $N_{1,S}$ is the solvent feed stage of the first column, and L and U represent the lower and upper bounds.

Python was used to link the Aspen Plus simulations with the DFO solver and find the optimum process conditions, i.e., decision variables, that yielded the lowest TAC. The DFO solver RBFOpt (Costa & Nannicini, 2018; Nannicini, 2021) was used to adjust the decision variables, which were the solvent ratio, total stages for both distillation columns, the mixture feed stage for both columns, and the solvent stage in the first column. To aid in simulation convergence and determine the appropriate upper/lower bounds for the decision variables, an optimization structure consisting of an inner and outer loop (Fig. 4) was used to solve this optimization problem.

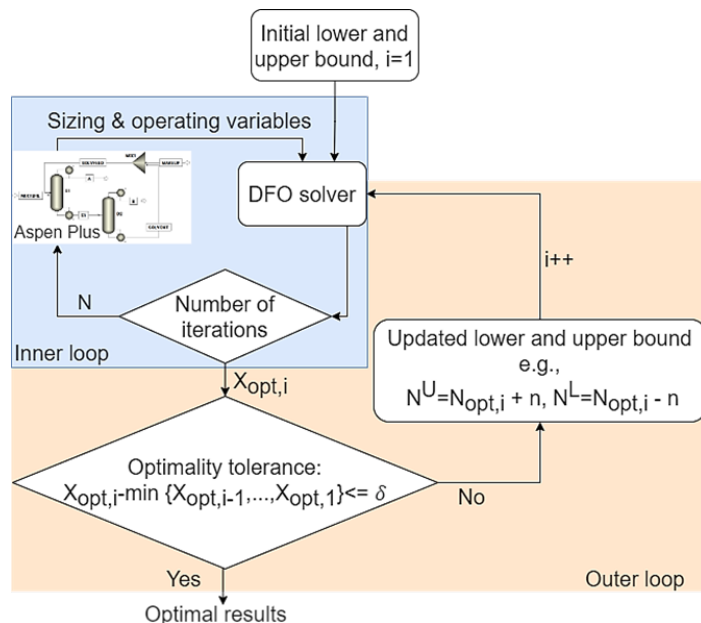


Fig. 4 Derivative free optimization structure.

The inner loop loops between the DFO solver and the process simulation model for 1000 iterations. During these iterations, the solver searches the decision-variable space defined by the bounds for the optimum. The inner loop output, the operating conditions that

yield the lowest TAC, is passed to the outer loop, which compares the current lowest TAC to the TAC of the previous inner loop results and updates the bounds if necessary. The bounds are updated using the decision variable values of the lowest TAC of the completed inner loop iterations. The bounds are set so that the solvent ratio is within ± 0.5 of the previous best value, and all stage values (total number and feed locations) are within ± 10 of the previous best values. If the TAC does not change from one iteration to the next, e.g., Fig. 5, the outer loop terminates and provides the solution with the lowest TAC as the optimum.

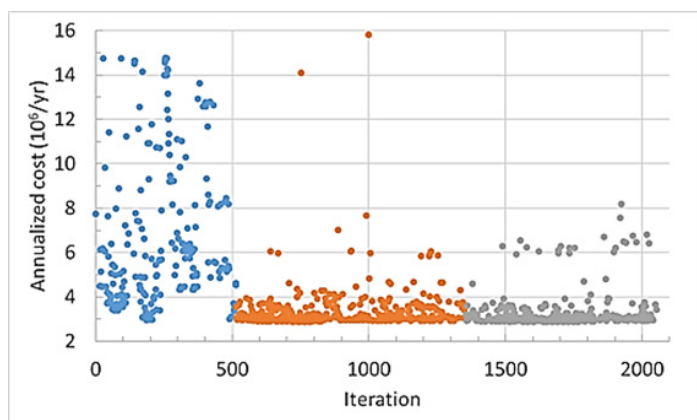


Fig. 5 Total annualized cost for acetone-methanol separation with DMSO as solvent generated using DFO solver using the structure shown in Fig. 4. *Note.* Each color represents a complete inner loop.

Case Studies

Acetone-Methanol Separation. The acetone-methanol mixture contains a minimum-boiling azeotrope. This mixture can be separated using a heavy entrainer with acetone and methanol as the first and second columns' distillate streams. The solvents (Gerbaud et al., 2019) considered were water, DMSO, ethanol, ethylene glycol, and 2-propanol. The thermodynamic package UNIQUAC was selected for each solvent based on the vapor-liquid equilibrium data. A converged process simulation model in Aspen Plus was the first simulation model of the inner loop iterations (Fig. 4) for the DFO structure for each solvent. The solvents were ranked from lowest to highest using their minimum TAC (identified by the DFO). This ranking was compared to the results of the FSES model.

Benzene-Cyclohexane Separation. The benzene-cyclohexane mixture also contains a minimum-boiling

azeotrope and can be separated using a heavy entrainer. Cyclohexane is the product of the first column and benzene the second column. The potential solvents for the acetone-methanol case study were sulfolane, N-methyl-2-pyrrolidone (NMP), furfural, aniline, and dimethyl phthalate. The thermodynamic package NRTL was used for sulfolane and furfural, and UNIFAC was used for NMP, dimethyl phthalate, and aniline.

Results and Discussion

Acetone-Methanol Separation. The rankings based on the minimum TAC were DMSO, water, ethylene glycol, ethanol, and 2-propanol from first to last. The process using the DMSO as the solvent yielded the lowest TAC, and 2-propanol yielded the highest. The details of the optimum process with the DMSO solvent are shown in Fig. 6.

The TAC results of the optimization problem solution and FSES model scores for each solvent are listed in Table 2. The FSES model resulted in the same solvent rankings.

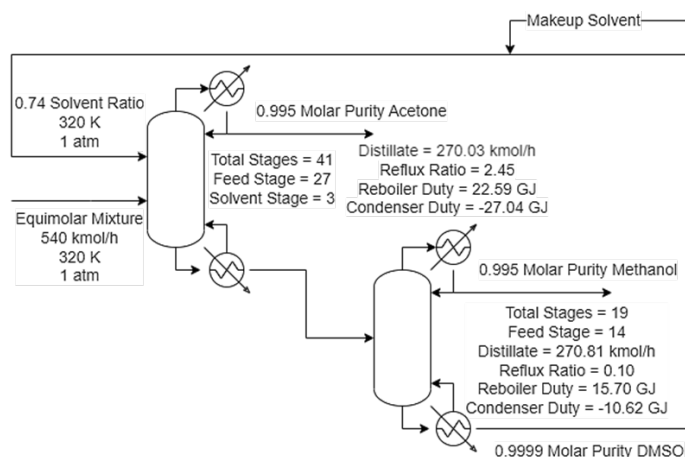


Fig. 6 Optimum acetone-methanol separation process flowsheet with DMSO as solvent.

Table 2 Comparison of optimization and FSES model results for acetone-methanol separation.

Solvent	TAC ($\times 10^6$ \$/yr)	FSES Model Score
DMSO	2.87	15
Water	3.32	19
Ethylene glycol	4.63	24
Ethanol	6.64	27
2-propanol	7.60	35

Benzene-Cyclohexane Separation. The minimum

TACs for the benzene-cyclohexane separation process resulted in a solvent ranking as sulfolane, furfural, NMP, dimethyl phthalate, and aniline from first to last. Sulfolane yielded the process with the lowest TAC and aniline the highest. The optimum separation process with sulfolane solvent is shown in Fig. 7.

The TAC from optimization and FSES model scores for each solvent are given in Table 3. The FSES model yielded a similar solvent ranking but ranked dimethyl phthalate as a better solvent than NMP. The FSES model correctly predicts column stages of dimethyl phthalate and NMP to be similar, but the high boiling point of dimethyl phthalate causes the discrepancy between the optimization and FSES model results. The high boiling point of dimethyl phthalate results in higher column temperatures, requiring a furnace. This causes the capital cost of the dimethyl phthalate system to be higher than the NMP system. While boiling point contributes to the FSES model ranking results, the method in the FSES model does not account for the significant cost effect of the high boiling point of dimethyl phthalate.

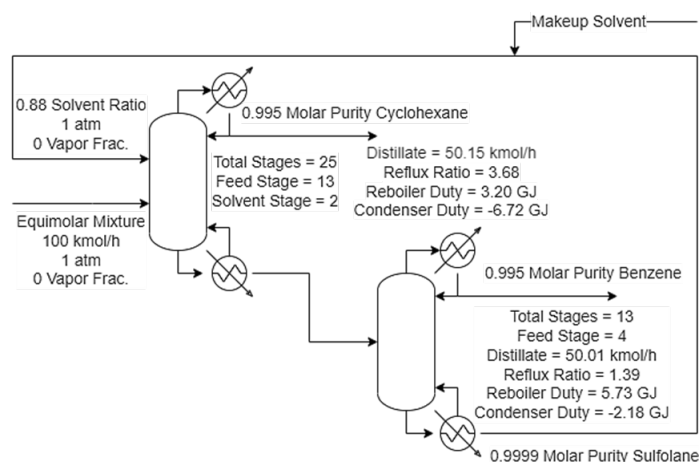


Fig. 7 Optimum benzene-cyclohexane separation process flowsheet with sulfolane as solvent.

Table 3 Comparison of optimization and FSES Model results for benzene-cyclohexane separation.

Solvent	TAC ($\times 10^6$ \$/yr)	FSES Model Score
Sulfolane	0.63	19
Furfural	0.72	21
NMP	0.74	24
Dimethyl phthalate	0.95	22
Aniline	0.96	34

Conclusions and Future Direction

Due to the importance of solvent selection, the FSES model was proposed to quickly and accurately predict solvent performance. This model uses both physical and process properties to rank solvents based on their potential performance. This work validates the proposed FSES model predictions by completing rigorous process simulation and derivative-free optimization of multiple extractive distillation separation processes. After completing process simulation and optimization for the acetone-methanol and benzene-cyclohexane separations with five solvents each, the optimum process design and operating parameters were identified for both separations. The optimum process designs for the acetone-methanol and benzene-cyclohexane separations utilize DMSO and sulfolane as solvents.

The FSES model correctly predicted solvent performance for extractive distillation based on total annualized cost. The optimization and FSES model yielded the same results for the acetone-methanol separation. For the benzene-cyclohexane separation, a similar solvent ranking was obtained between the optimization and FSES models, but the FSES model ranked dimethyl phthalate as a better solvent than NMP. This was due to the high boiling point of dimethyl phthalate. While the solvent ranking for the benzene-cyclohexane separation was imperfect, the FSES model ranked the two best solvents correctly.

Future work will consider integrating the presented FSES model into extractive-distillation process synthesis for either solvent selection or solvent design.

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Nomenclature

FSES – Fast solvent evaluation and selection model
TAC – Total annualized cost
DFO – Derivative-free optimization
DMSO – Dimethyl sulfoxide
S_p – Solvent *p*
V_{p,r} – Value of property *r* for solvent *p*
Score_{p,r} – Ranking score of property *r* for solvent *p*
N – Total number of solvents evaluated
IC – Investment cost
AUC – Annualized utility cost
i – Interest
n – Plant life
Cost_j – Investment cost of equipment *j*
q_{s,j} – Sizing variable for equipment *j*
Utility_j – Utility cost of equipment *j*
q_{o,j} – Operating variable for equipment *j*
F_S – Solvent flowrate
N_k – Number of stages in column *k*
N_{k,feed} – Materials feed stage of column *k*
N_{1,s} – Solvent feed stage of the first column
L – Lower bound
U – Upper bound

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Authors Biography



Toby Crump is a 2023 graduate from Auburn University with a B.S. degree in Chemical Engineering. He has played key research roles in process simulation and optimization. Toby is originally from Nashville, Tennessee and participated in the Auburn University Marching Band playing trumpet. He also served as service chair for the Alabama Alpha chapter of Tau Beta Pi for the 2022-23 academic year.



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Mario R. Eden, Ph.D., is Dean of the Samuel Ginn College of Engineering and Joe T. & Billie Carole McMillan Professor of Chemical Engineering, Auburn University. His research focuses on chemical process design, integration and optimization, as well as molecular synthesis and product design. His group develops systematic methodologies for process/product synthesis, design, and optimization.



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