

A More Comprehensive Formulation to Rapidly and Reliably Screen for Energy-Efficient Distillation Configurations

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Abstract. There are too many distillation configurations to systematically analyze using just a process simulator. Shortcut models are essential in efficiently screening the vast search space and selecting only the most promising candidates for further expensive detailed simulations. However, the source of their expediency has also been a reason for limited applicability. In this work, we make shortcut models more reliable by developing methods to relax the often-criticized assumptions of constant relative volatilities and constant molar overflow, as well as check feasibility of heat integration in a computationally cheaper manner. After implementing these advances, our optimization formulation can identify energy-efficient distillation configurations for a multicomponent separation while accounting for modest variations in relative volatilities and differing latent heats and taking advantage of the benefits of heat integration. We demonstrate the formulation on a five-component separation of alcohols.

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Introduction

One of the first steps in designing a flowsheet is deciding the high-level skeletal structure, and for multicomponent distillation, there is a vast search space of flowsheets. While restricting the use of only basic sharp splits makes the search space tractable, both sloppy splits and thermal couplings are known to bring about substantial energy savings (1,2). However, introducing these two features causes the size of the search space to explode into the thousands for just five components. At this magnitude, standard process simulators are intractable in systematically analyzing and comparing each configuration.

Shortcut models offer an attractive solution to this dilemma. When they are carefully built to properly capture the essential physics, shortcut models can be run to quickly evaluate all options and correctly predict the top-performing configurations, which can subsequently be analyzed in a process simulator for fine-tuning and comparison on a more detailed basis. This screening approach can be orders of magnitude more efficient than the straightforward approach of evaluating all configurations in a detailed process simulator. To give a feel of the savings, for a simple four-component separation, evaluations in a commercial process simulator required months of tedious sensitivity analysis to determine the globally minimum heat duties for just 18 relevant configurations (3). But using our shortcut model, we were able to correctly predict in minutes the ordering of configurations on the basis of minimum heat duty, as well as provide a good estimate of the relative values of heat duty between the configurations (4).

The grounds for this tractability are the simplifications made to reduce computational complexity. However, these simplifications must be adroitly made to adequately capture the inherent performance of the flowsheet. For example, it is well known that increasing the number of stages in a distillation column is likely to decrease the overall heat duty. Hence, when determining the minimum heat duty of a column, we can analyze distillation from the simplification of infinite stages, also referred to as minimum reflux operation. Two other simplifications which are commonly used are constant relative volatilities (CRV) and constant molar overflow (CMO). A celebrated application of these simplifications is the Underwood method for predicting minimum reflux, whose equations are comparatively much simpler than stage-by-stage calculations (5). However, while these simplifications have been demonstrated to bear fruit on numerous occasions, there are limitations to their applicability.

CRV may be observed in practice for near-ideal mixtures at a single pressure. But as one moves away from ideality, and considers a range of operating pressures, the relative volatilities of components can vary widely (4). CMO, constant

molar vapor and liquid traffic within a column section, requires components to have the same latent heats of vaporization, so that equal numbers of molecules are adiabatically exchanged between vapor and liquid phases on all the stages. But the latent heats of real species can differ greatly, leading to varying molar traffic across stages.

From the perspective of energy minimization, heat integration is an important tool to account for during analysis. Any proposed heat integration is feasible only if the driving forces are in the correct direction, i.e., the heat source is hotter than the heat sink. Moreover, practitioners desire these driving forces to be big enough to keep the required heat exchanger area manageable and capital costs down. Both of these requirements are usually checked by calculating temperatures from standard thermodynamic models. But the incorporation of such models in optimization formulations can hamper their convergence characteristics.

In this paper, we present our solutions to the aforementioned challenges of CRV and CMO, as well as tractable implementation of heat integration constraints. We incorporate these techniques in a shortcut model formulation to determine the minimum heat duty of multicomponent distillation configurations, and demonstrate the power of the shortcut model approach on a five-component example.

Optimization Formulation

Our formulation, written in a non-linear programming (NLP) framework, determines the minimum heat duty of a given multicomponent distillation configuration for a particular separation (6,7). It is formulated in such a manner that the individual NLPs can be automatically generated and run for each configuration in the search space. Configurations are modelled as networks of columns with streams among them, and each column being a consolidation (vertically) of individual splits. Mass and energy balances are applied for both the feed and products of every split. The Underwood method is employed to ensure each part of the column is operating at or above minimum reflux conditions, as well as to impose feasibility constraints on component distributions in sloppy splits (5). Relevant constraints are imposed on streams depending on where they are produced from the column and whether they are thermally coupled. Next, we discuss the advances we made in the model to improve its performance and capabilities.

Addressing the Constant Relative Volatilities Assumption

Relative volatility, α_{ij} for a pair of components i and j , is commonly measured as the ratio of equilibrium constants, K_i/K_j , for those components. α_{ij} is often also calculated as the ratio of vapor pressures, $P_i^{\text{vap}}/P_j^{\text{vap}}$, however this expression is equivalent to the previous two expressions only when the ideal form of Raoult's and Dalton's laws of partial pressures is obeyed, i.e., for ideal mixtures. In this work, we use the definition of α_{ij} as the ratio of component mole fractions in vapor and liquid phases to characterize the vapor-liquid equilibrium (VLE) of a mixture,

$$\alpha_{ij} = \frac{y_i/x_i}{y_j/x_j} \quad (1)$$

Since mole fractions sum to 1, the above expression is rearranged to form an explicit equation for the vapor composition, y_i , in terms of relative volatility, α_i , and liquid composition, x_i . α_i is the relative volatility of component i w.r.t the heaviest component n , which is chosen as the reference component.

$$y_i = \frac{\alpha_i x_i}{\sum_{j=1}^n \alpha_j x_j} \quad (2)$$

In the above simplified VLE equation, CRV implies that α_i take constant values, though in reality relative volatility varies with the composition, temperature, and pressure of a mixture. We address this discrepancy by relaxing the requirement that α_i be a measurable physical value. Instead, we treat it as a mathematical parameter and Eq. 2 to be a surrogate model for the true VLE (4,8). α_i should then be determined by parameter estimation, so that this surrogate model best fits the true VLE. In our optimization formulation, these fitted values for α_i are plugged into the Underwood method (5), which was derived using Eq. 2 for the VLE, for improved estimation of minimum reflux conditions and sloppy split distributions.

Addressing the Constant Molar Overflow Framework

CMO is built from the following set of assumptions, collectively known as the McCabe-Thiele assumptions: ideal mixing, negligible sensible heat, constant component latent heats, and equal component latent heats. The primary benefit of CMO is that energy balances, which can be complex constraints involving enthalpies, simplifies into linear balances on molar vapor and liquid flowrates separately. For example, the molar flowrate of vapor leaving a stage within a column section equals that entering, implying constant molar traffic within the section. At the feed stage, the molar flowrate of vapor leaving above (rectifying section vapor) is the sum of that entering from below (stripping section vapor) and that fed in (feed vapor). Similarly for liquid flowrates.

As mentioned earlier, one of the critical issues why CMO may not hold up in practice is due to the differing latent heats of vaporization among components. For an adiabatic stage, the total heat released by the condensing molecules must equal that absorbed by the vaporizing molecules. Then when components have the same latent heats, the number of condensing molecules equals the numbering of vaporizing molecules and there is no net change in molar flowrates. Hence, CMO is applicable. However, when components have different latent heats, the number of molecules being exchanged between the two phases does not need to match, causing net changes in molar flowrates and making CMO invalid.

To address this, researchers in the past have devised a simple variable transformation using latent heats (λ_i), shown below, that creates a new framework which is referred as Constant Heat Transport (CHT) (9). While numerous works have discussed this transformation, we highlight the contributions of Mole (10) and Ravi (11), where the form of the transformation organically arose during their derivations.

$$f_i^{LH} = f_i \lambda_i, \quad F^{LH} = F \sum_{j=1}^n z_j \lambda_j, \quad z_i^{LH} = \frac{z_i \lambda_i}{\sum_{j=1}^n z_j \lambda_j}, \quad q^{LH} = q \frac{\sum_{j=1}^n x_j \lambda_j}{\sum_{j=1}^n z_j \lambda_j} \quad (3)$$

The transformation creates new variables, which we refer to as latent-heat variables, that correspond to existing molar variables. For example, f_i^{LH} (resp. F^{LH}) is the heat required to completely vaporize f_i moles of component i (resp. F moles of the mixture). z_i^{LH} is the fraction of total latent heat in a mixture that is for component i , and q^{LH} is the thermal quality of the mixture (in contrast to molar quality, q). The advantage of this specific transformation is that, when the CMO equations are re-written by simply replacing molar variables by their latent-heat counterparts, the resulting equations are valid even when component have different latent heats. This constitutes the CHT framework.

For example, on a stage, the latent-heat flowrates of vapor entering and leaving are balanced, which is in agreement with its adiabatic nature. The total heat released by the condensing molecules must equal that absorbed by the vaporizing molecules, and so there is no net change in the latent-heat content of each of the phases and thus latent-heat flowrates are same from stage to stage. Thus, with the CHT framework, we can use simple linear balances on latent-heat flowrates, which are mathematically similar to the CMO balances but now account for the different latent heats of vaporization.

Accounting for Benefits of Heat Integration

Heat integration, the re-use of heat in a process, is a standard tool for improving energy efficiency. While the general problem considers integration of distillation with other parts of the chemical plant (12), here we focus on heat integration among the reboilers and condensers of the columns, i.e., within a given distillation configuration. One part of heat integration is the design of the heat exchanger network, which continues to receive great attention in the literature. Another part is the feasibility conditions for heat transfer. By the second law of thermodynamics, the heat released by a condenser can be re-used to vaporize liquid in a reboiler only if the condenser is hotter than the reboiler. In addition, a minimum approach temperature during heat exchange is desired for implementation. As mentioned earlier, when temperatures are calculated using complex equations, this can hinder the optimization.

One approach of reducing the computational complexity is to use a surrogate model for temperature. However, a challenge for this approach is coming up with a general form that is both simple and can be expected to be satisfactory for a wide range of mixtures. To solve this challenge, we take inspiration from the characteristic parameter of the simplified VLE: relative volatility. While relative volatility, α_i , is often perceived to be a measure of the “lightness” of a component, it also serves as an inverse proxy for temperature: the component with higher α_i has lower T_i . Although relative volatility is strictly defined only for components, we can use an average relative volatility, $\beta \equiv \sum_{j=1}^n \alpha_j x_j$, to

compare mixtures: the mixture with higher β has lower T . Next, we know that temperature increases with pressure. So, we use a scaled average relative volatility, $\rho = \beta/p$, to account for the effects of pressure: the mixture with higher ρ has lower T . Thus, ρ serves as an inverse proxy for temperature of mixtures (7). Combining Antoine's equation, Raoult's law, Dalton's law, and the simplified VLE, we analytically relate ρ to T , and subsequently obtain the following equation for the temperature of a mixture,

$$T = \frac{B}{A + \ln(\sum_{j=1}^n \alpha_j x_j) - \ln P} - C \quad (4)$$

The parameters A, B, C arise due to the use of Antoine's equation relating temperature to vapor pressure for pure components, where they were known as the Antoine constants for specific components. However, in the above equation we fit new values for A, B, C , pseudo-Antoine constants, so that it can predict mixture temperature. Thus, Eq. (4) is the new surrogate model that we propose for temperature, which requires only the composition and pressure of the mixture. α_i can either be fitted along with the pseudo-Antoine constants or chosen from the fitting of the simplified VLE. We caution the reader that Eq. (4) should be used only to predict mixture temperatures during phase change.

The parameters in both the VLE (Eq. 2) and temperature (Eq. 4) surrogate models are estimated by minimizing the non-linear least squares between predictions and values from a thermodynamic package over a spread of compositions and pressures. This parameter estimation can be performed with standard local solvers, such as those in Excel. For the optimization of distillation configurations, we expect the surrogate models to be satisfactory for zeotropic systems without substantial non-idealities, such as paraffins, alcohols, and aromatics.

Case Study

Here, we demonstrate our optimization formulation in which the advances of the previous section were incorporated. We consider the separation of a five-component mixture of alcohols (Table 1) at 1 atm. We want to identify an energy-efficient distillation configuration for this separation. Heat integration is considered among ends of columns and final product sidedraw locations, and columns are allowed to have an operating pressure of 1–2 atm. The pseudo-Antoine constants used are 10.41, 4010.40, and 244.17.

Table 1.

Feed data for case study

Label	A	B	C	D	E
Species	Methanol	Ethanol	2-Propanol	1-Propanol	Butanol
f (kmol/h)	27	26	5	16	26
α^{VLE}	7.33	4.26	3.70	2.12	1
α^T	6.35	3.71	3.32	1.89	1
λ (kJ/mol)	34.6	38.4	39.5	40.6	41.8

Among the 6,128 configurations possible (1), we determined, through global optimization using BARON (13,14), that the configuration shown in Figure 1a has the least heat duty of 2.36 MW. Three of its columns are operated at a higher pressure of 2 atm, and there is a single heat integration with a minimum approach temperature of 15°C. However, the configuration with the least heat duty need not be the best option. In Figure 1b, we show a similar configuration that the process engineer could consider with a slightly higher heat duty of 2.38 MW (1% higher). Since the heat duties are very close, detailed simulations in a process simulator, as well as other considerations such as operability, manufacturability, etc. should be performed to decide which of the two are attractive for the separation. The conventional sharp split configurations, such as the basic direct split (4.13 MW, 75% higher) and the basic indirect split (3.74 MW, 58% higher), have much higher heat duties, with the lowest sharp split configuration (3.14 MW, 33% higher) shown in Figure 2a. Meanwhile the fully thermally coupled configuration shown in Figure 2b (15), which has

the lowest heat duty when only the traditional thermal coupling without heat integration is permitted (16), has a higher duty (2.98 MW, 26% higher) on top of its increased complexity.

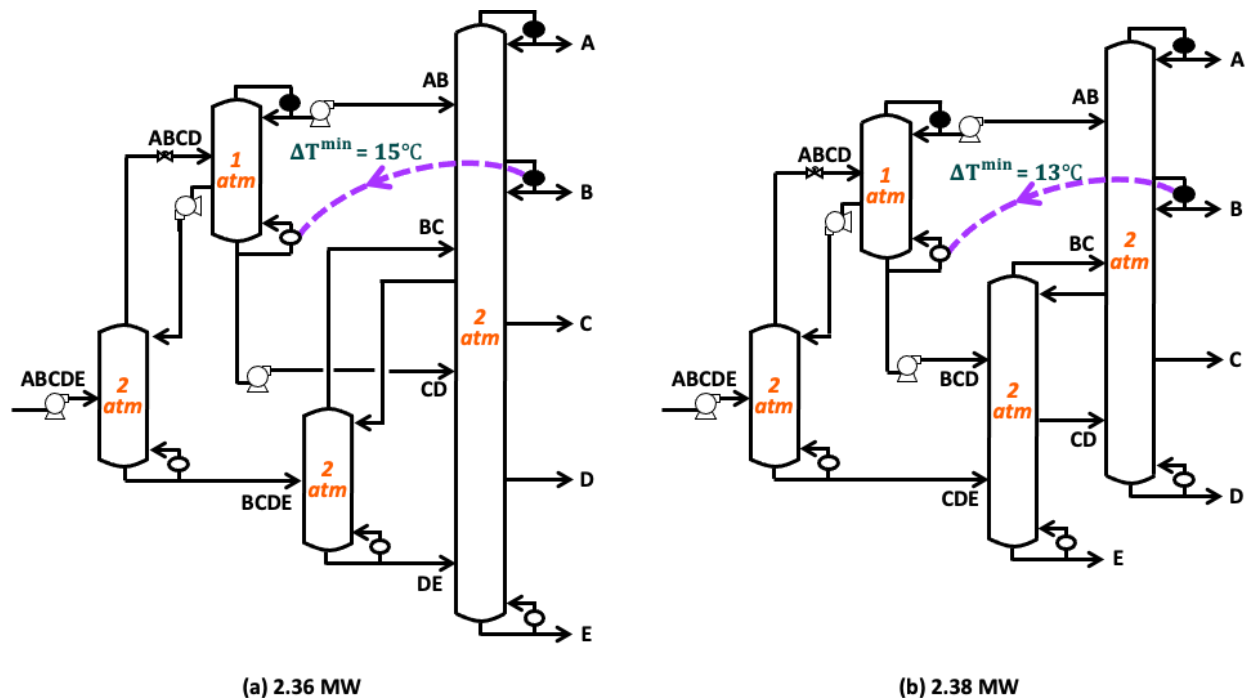


Fig. 1 Two configurations identified for the case study.

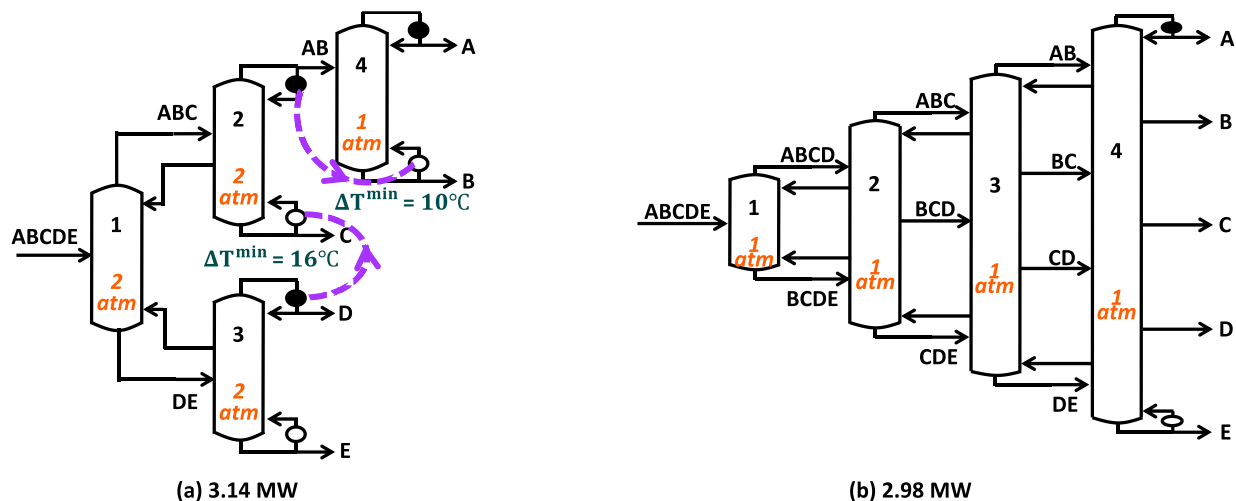


Fig. 2 Least heat duty configurations when using a) only sharp splits and b) only traditional thermal coupling.

The important result is that, among the 6,128 different configurations for this five-component separation, we were able to identify two promising candidates. The required computations took less than a day on a desktop computer. Thus, this case study shows off the power of our method in quickly identifying energy-efficient and heat-integrated configurations for a given separation.

Conclusions

Shortcut models are valuable in identifying energy-efficient configurations in a faster and less tedious manner than with process simulators. However, their application has been limited on various facets. Constant relative volatilities and constant molar overflow are beneficial for computational expediency, but do not strictly hold in reality. Heat integration is advantageous for energy-efficiency, but complex temperature equations for checking feasibility hinder optimization. We have developed methods to overcome the hurdles associated with these factors while keeping our model computationally tractable for searching the vast space of configurations, and demonstrated the resulting formulation on a five-component separation of alcohols. The power of our shortcut model is that even though it is a simplified model for distillation, it captures the essential physics that govern the ranking of configurations.

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