

# Efficiency Ranking through Exergy Analysis in Azeotropic Distillation Systems

Jonathan Wavomba Mtogo<sup>a,b,\*</sup>, Péter Mizsey<sup>c</sup>

<sup>a</sup>Department of Chemical and Environmental Process Engineering, Budapest University of Technology and Economics, 1111 Budapest, Hungary

<sup>b</sup>Chemical Engineering Division, Kenya Industrial Research and Development Institute, P.O. Box 30650 – 00100 Nairobi, Kenya

<sup>c</sup>Advanced Materials and Intelligent Technologies Higher Education and Industrial Cooperation Centre, University of Miskolc, 3515 Miskolc, Hungary  
[jmtogo@edu.bme.hu](mailto:jmtogo@edu.bme.hu)

This study employs and validates a methodology for the efficient selection of optimal energy-integrated distillation configurations for azeotropic separations of binary mixtures. The study focuses on minimum-boiling tetrahydrofuran/water and maximum-boiling acetone/chloroform azeotropes, utilizing exergy, economic, and controllability analyses to identify the most suitable rectification structures. The evaluated distillation structures include those based on extractive and pressure swing distillations for non-heat-integrated and fully heat-integrated configurations. The selection of the most appropriate configuration is contingent upon the process energy requirements, exergy efficiency, and controllability. The findings reveal that, while there are expected energy savings from heat integration, the economic viability is determined by the pressure sensitivity of the azeotrope. The non-heat-integrated sequences consistently outperform other configurations in controllability while heat-integrated systems perform better in terms of exergy efficiency and total annual costs. This underscores the pivotal role of heat integration in azeotropic distillation systems, showcasing significant benefits from energetic, exergetic, and economic standpoints and highlighting its potential for substantial savings. Conversely, the use of heat integration in the extractive distillation of acetone/chloroform exhibits less favorable properties and alternative separation technologies may be considered.

## 1. Introduction

The separation of binary azeotropic mixtures poses a significant challenge due to their constant boiling behavior (Yang et al., 2022). The selection of the appropriate distillation technique plays a vital role in achieving successful separation. Pressure swing distillation (Mtogo et al., 2022) and extractive distillation (Mtogo et al., 2023) are effective techniques for overcoming these challenges. These methods leverage the differences in volatility and solubility of the components to achieve successful separation, making them indispensable in various industries, including petrochemical, pharmaceutical, and food processing. Research and development in distillation technologies continue to drive innovations in the field, leading to more efficient and sustainable separation processes (Kiss, 2019). The ongoing advancements in equipment design, process optimization, and sustainable solvents contribute to the continuous improvement of azeotropic distillation techniques. As industries evolve and demand for high-quality products increases, the increasing costs of energy underscore the growing significance of energetic efficiency (Laitner, 2015).

Tetrahydrofuran/water and acetone/chloroform azeotropes, characterized by their challenging separations, require innovative approaches for energy-efficient configurations. The integration of distillation processes with energy considerations has emerged as a key strategy for improving overall efficiency. Previous research has focused on optimizing extractive and pressure swing distillations from the economic perspective (Qin et al., 2022), but a comprehensive study integrating exergy, economic, and controllability analyses for the selection of distillation configurations remains limited. This study addresses this gap, aiming to enhance our understanding

of the complex interdependencies influencing the performance of azeotropic distillation systems. This involves evaluating the synergies between different objectives to identify the most optimal configuration.

## 2. Methodology

### 2.1 Controllability Analysis

The controllability analysis, which is crucial for assessing the control performance of dynamic systems, is based on a method introduced by Gabor and Mizsey (2008), allowing for faster computation of controllability indices in the frequency domain. This methodology relies on the Aspen Plus Dynamics Control Design Interface (CDI) module to derive a state space representation, achieved by matching input and output variables in the CDI script and computing state space matrices at steady state. Controllability indices, including the Morari Resiliency Index (MRI), Condition Number (CN), and Relative Gain Array number (RGAno), are then determined as functions of frequency using these matrices. The resulting controllability indices are graphically depicted using a Matlab program, aiding in the visualization of their behavior with respect to frequency. Specifically, the MRI, representing the least singular value of the open-loop frequency function matrix, offers insights into controllability improvement, while the CN, a ratio of singular values, identifies ill-conditioned processes. The acceptable CN range is defined between 1 and 10 (Skogestad and Postlethwaite, 2005). The RGAno serves as a metric indicating the interactions among the control loops.

In this complex evaluation of controllability, the various indicators are transformed into individual desirability values (denoted as "d") within the desirability function model and are shown in Eq(1), Eq(2) and Eq(3).

$$d_{MRI} = 1 - e^{-(10 \times MRI)} \quad (1)$$

$$d_{CN} = e^{-(a+b \times CN)} \quad (2)$$

$$d_{RGAno} = e^{(-0.1 \times RGAno)} \quad (3)$$

These individual desirability functions are continuous functions chosen from a family of either linear or exponential functions. The aggregation of these individual functions gives the overall desirability function ( $D_{fct}$ ), as per Eq(4).

$$D_{fct} = \sqrt[3]{d_{MRI} \times d_{CN} \times d_{RGAno}} \quad (4)$$

$D_{fct}$  is defined as the geometric average of the three individual desirability functions, where they are tailored to reflect the significance of each parameter, eliminating the need for weighing factors. A higher value of  $D_{fct}$  signifies that all  $d_k$  values align with the target value, indicating the most suitable process alternative (Gabor and Mizsey, 2008).

### 2.2 Evaluation of Total Annual Costs

The intricate interplay between capital and operating costs and how they impact the total annual cost is essential for making informed decisions about the economic feasibility of a distillation process. By conducting a comprehensive analysis of these costs, it is possible to optimize the operation of the distillation unit and maximize its economic efficiency. A comprehensive cost estimation is conducted for all the prospective systems. Utilizing equations proposed by Douglas (1998), the capital cost is estimated. The subsequent determination of the Total Annual Cost (TAC), outlined in Eq(5), incorporates both annual capital cost and annual operating cost.

$$TAC = \frac{\text{total capital costs}}{\text{payback period}} + \text{Total operating cost} \quad (5)$$

The annual capital cost is distributed uniformly over the plant's designated lifetime ensuring an accurate reflection of the economic viability of the distillation system throughout its operational span. In this work, a 3-y payback period is selected as it aligns with industry standards and is driven by the benefits of risk mitigation, faster capital turnover, and enhanced liquidity. This approach minimizes the risk associated with the potential obsolescence of technologies or projects in the long term.

### 2.3 Energy and Exergy Analysis

Energy and exergy analysis is an important method for evaluating energy levels and efficiency in distillation processes. It allows for a comprehensive evaluation of the efficiency of thermal processes using the first and second laws of thermodynamics and provides insights into the sources of irreversibility and energy loss (Ostadi et al., 2019).

Over the years, efforts have been dedicated to optimizing distillation processes for energy efficiency; however, the intrinsic value of energy is frequently disregarded. This discrepancy in value emerges from the conversion of energy types, particularly in the context of heat energy. It is noteworthy that the significance of a given amount of heat energy varies based on its temperature. Despite its heat energy content, lower temperature heat encounters limitations in its applicability to specific processes. This emphasizes the crucial link between the availability temperature of heat energy and its utility value, showcasing the relationship between energy temperature and practical utilization.

In contrast, exergy distinguishes between highly and less valuable energies, even in heat integrated processes (Modarresi et al., 2009). Exergy, defined as the maximum useful work during a process bringing the system to thermodynamic equilibrium with the environment, provides a comprehensive measure. Physical exergy is expressed by Eq(6). T, H, and S denote the temperature, enthalpy, and entropy of material streams. The subscript O denotes properties at the heat reservoir temperature.

$$Ex_{ph} = [(H - H_o) - T_o(S - S_o)] \quad (6)$$

An alternative physical exergy expression is shown in Eq(7) where Q is the heat energy.

$$Ex_{ph} = Q \left( 1 - \frac{T_o}{T} \right) \quad (7)$$

Energy analysis alone does not differentiate heat and work, it is simply an enthalpy balance. Exergy analysis, however, shows that heat energy and work are not equivalent. Additionally, it indicates the degradation of heat as it transitions from higher to lower temperatures. In distillation, heat undergoes a sequential transfer: initially through the reboiler, followed by the column where it performs useful work, and ultimately recovered in the condenser at a lower temperature. This degradation of heat enables a reduction in entropy, facilitating the separation of liquid mixtures. The approach used for calculating exergy loss and thermodynamic efficiency is based on the work of Seader et al. (2006). Firstly, the irreversible entropy loss is determined through Eq(8), which involves the summation of the entropic changes in both the reboiler and condenser.

$$\Delta S_{irr} = \sum_{out} \left( n \times S + \frac{Q_c}{T_c} \right) - \sum_{in} \left( n \times S + \frac{Q_r}{T_r} \right) \quad (8)$$

Once the entropy loss is determined, along with knowledge of the heat reservoir temperature, the exergy loss is calculated using Eq(9).

$$Ex_{loss} = T_o \Delta S_{irr} \quad (9)$$

The work of separation, representing the disparity in exergy inflow and outflow, is essential and computed by Eq(10).

$$W_{sep} = \sum_{out} (n \times Ex_{ph}) - \sum_{in} (n \times Ex_{ph}) \quad (10)$$

Lastly, the thermodynamic efficiency is computed by dividing the useful work by the consumed exergy, encapsulated by the sum of useful work and exergy loss in Eq(11).

$$\eta = \frac{W_{sep}}{Ex_{cons}} = \frac{W_{sep}}{Ex_{loss} + W_{sep}} \quad (11)$$

The basic data for exergy analysis in this work are obtained from Aspen Plus process simulations.

## 2.4 Evaluation of CO<sub>2</sub> emissions

Given the paramount significance of greenhouse gas (GHG) emissions, it is strongly advised to incorporate this aspect into every design process. The emission of carbon dioxide (CO<sub>2</sub>) is intricately tied to the energy input during the process. Typically, the steam supplying essential heat to the reboiler is generated by burning fossil fuels. For simplification, this study assumes the use of heavy fuel oil as a heating medium to generate steam. Consequently, CO<sub>2</sub> emissions serve as a pivotal metric for evaluating the environmental sustainability of distillation operations. The evaluation of the CO<sub>2</sub> emissions is determined through the methodology proposed by Gadalla et al. (2005). This method integrates factors such as the net heating value, carbon content, and fuel duty to calculate emissions, as demonstrated by Wu and Chien (2022).

### 3. Simulation of Case Studies

Two case studies are simulated, minimum-boiling THF/water and maximum-boiling acetone/chloroform. The flowsheets for the extractive and pressure-swing distillations are shown below. The feeds are equimolar with a flow rate of 100 kmol/h at 278.15 K. The flowsheets for extractive distillation are shown in Figure 1 and the design parameters are shown in Table 1. Both THF/water and acetone/chloroform have a similar flowsheet. In THF/water, A corresponds to THF, and B corresponds to water. Conversely, in acetone/chloroform, A represents acetone, and B represents chloroform, with E denoting the entrainer in both cases.

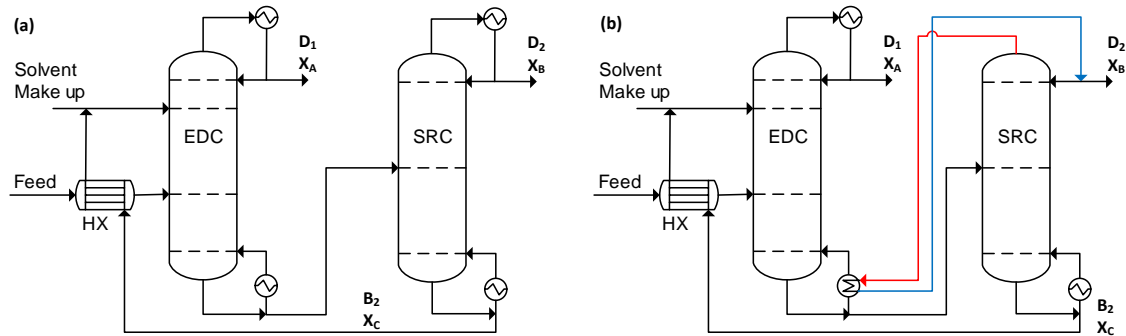


Figure 1: Flowsheet for extractive distillation (a) base case (b) backward full heat integration.

Table 1: Results from Simulations and Optimization of Extractive Distillation Columns

	THF/water		Acetone/chloroform		
	EDC	SRC	EDC	SRC	
Molar reflux ratio	0.4	0.1	1.7	0.7	
Theoretical plates	21	14	32	15	
Column diameter (m)	0.7	1.0			
Feed rate (kmol/h)	100	50.002	100	214.4	
Feed stage	17	6	13	5	
Entrainer feed rate (kmol/h)	25	24.998	164.4		
Entrainer feed stage	5	-	4		
Reboiler duty (kW)	625.5	668.9			
Column pressure (bar)	1.0	0.15	1.1	1.1	
$X_D$	A (mol%)	99.9	99.9	0.1	
	E (mol%)	0.02	0.00	ppm	ppm
	B (mol%)	0.06	99.9	0.1	99.9

Figure 2 and Table 2 depict PSD backward heat integration flowsheets and design parameters, respectively.

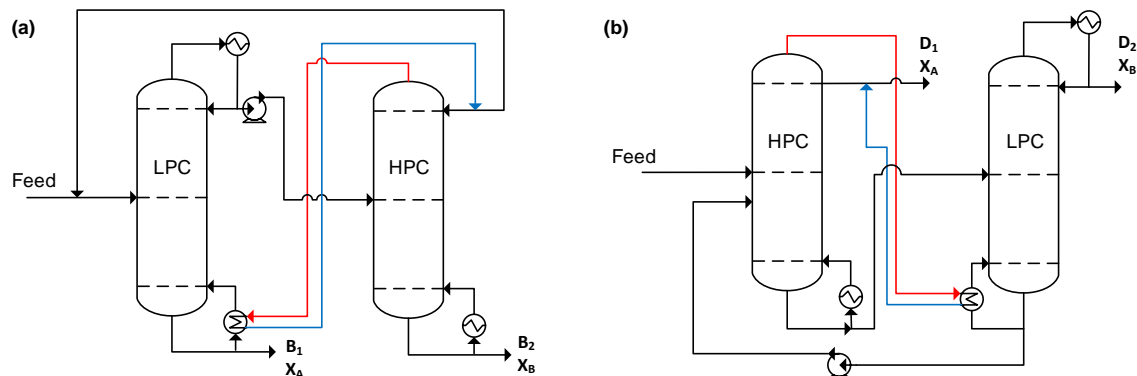


Figure 2: Flowsheet for full heat integration for (a) THF/water PSD (b) acetone/chloroform PSD.

Table 2: Results from Simulations and Optimization of PSD Columns

	THF/water		Acetone/chloroform	
	LPC	HPC	HPC	LPC
Molar reflux ratio	0.2	0.3	27.6	19.8
Theoretical plates	13	16	82	43
Column diameter (m)	0.8	0.6	2.5	2.2
Feed rate (kmol/h)	100.0	103.4	100.0	620.3
Feed stage	10	8	21	21
Reboiler duty (kW)	1,169.2	1,011.1	12,186.1	8,761.1
Column pressure (bar)	1.0	10.0	10.7	0.8
$X_D$ A (mol%)	99.9	0.1	99.9	0.1
$X_D$ B (mol%)	0.1	99.9	0.1	99.9

#### 4. Results

The results for all the extractive distillation alternatives are calculated and are shown in Table 3. The annual operational duration used in these calculations is 8,000 h.

Table 3: Controllability, Energy, Exergy, and Economic results for Extractive Distillation.

System	NHI	FHI	NHI	FHI
	THF/water	THF/water	Acetone/chloroform	Acetone/chloroform
Energy consumption (kW)	1,263.8	844.4	2,944.4	3,463.9
TAC (\$/y)	469,500	343,693	952,700	1,112,016
Exergy efficiency (%)	8.7	11.3	3.5	1.2
CO <sub>2</sub> emissions (t/y)	2,788.0	1,771.9	7,728.6	9,092.2
Aggregated desirability ( $D_{fct}$ )	8.7E-8	4.2E-12	3.4E-11	6.3E-15

The analysis of the minimum boiling THF/water system yields straightforward observations. The TAC results for non-heat integrated extractive distillation are consistent with previous studies (Liu et al., 2017). Implementing full heat integration results in reduced energy consumption, total annual cost (TAC), and CO<sub>2</sub> emissions. A noteworthy finding emerges in the case of the maximum-boiling acetone/chloroform azeotrope, where full heat integration surprisingly increases energy consumption. This trend is consistent in the comparison of CO<sub>2</sub> emissions, given their direct correlation with energy usage. As anticipated, thermodynamic efficiency for acetone/chloroform separation also diminishes. Furthermore, examination of aggregate desirability values indicates that fully heat-integrated systems exhibit poorer controllability compared to non-heat-integrated schemes. This is attributed to a decrease in control degrees of freedom.

The results for the PSD alternatives are calculated and are shown in Table 4.

Table 4: Controllability, Energy, Exergy, and Economic Results for Pressure-Swing Distillation.

PSD system	NHI	FHI	NHI	FHI
	THF/water	THF/water	Acetone/chloroform	Acetone/chloroform
Energy consumption (kW)	2,180.3	1,475.0	20,947.2	13,080.0
TAC (\$/yr)	575,800	456,100	5,767,100	3,745,300
Exergy efficiency (%)	11.2	17.9	7.5	12.4
CO <sub>2</sub> emissions (t/y)	5,076.8	3,592.0	55,209.6	31,756.8
Aggregated desirability ( $D_{fct}$ )	0.192	0.008	0.382	0.009

Full heat integration in THF/water and acetone/chloroform PSDs reduces energy consumption, TAC, and CO<sub>2</sub> emissions while enhancing thermodynamic efficiency. However, fully heat-integrated systems show poorer controllability, as indicated by aggregate desirability values, compared to non-heat-integrated schemes in both cases.

## 5. Conclusion

Comparative analysis highlights that TAC of extractive distillation is marginally lower than pressure-swing distillation at the same product rate and purity. Extractive distillation stands out as the desirable choice for THF/water separation due to its minimal energy consumption and TAC. However, it has drawbacks, including lower thermodynamic efficiency and controllability issues resulting from the entrainer introduction. In the case of acetone/chloroform, partially heat-integrated extractive distillation proves the most economical, outperforming even fully heat-integrated PSD in energy efficiency. The application of exergy analysis provides valuable insights into configurations, while the aggregate desirability function streamlines decision-making by offering a concise indicator. These findings underscore the importance of considering trade-offs and specific system characteristics when selecting optimal configurations for industrial applications.

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