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Sustainable Optimization of Quaternary Hydrocarbon Distillation: Heat Integration, Exergy Analysis and CO_2 Emission Evaluation

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ABSTRACT

The growing demand for energy-efficient and environmentally sustainable separation technologies highlights the limitations of conventional distillation. This study examines the separation of a quaternary hydrocarbon mixture n-Butane, n-Hexane, n-Heptane, and n-Nonane using three consecutive distillation columns arranged in direct and indirect sequences. Several heat-integration strategies, including preheating, feed splitting, and multi-effect distillation, were applied individually and in hybrid combinations. Rigorous simulations were performed in Aspen HYSYS with the Peng–Robinson equation of state, and exergy and environmental assessments were conducted using custom MATLAB R2021b (The MathWorks, Inc.) codes. The results show that a hybrid configuration combining direct sequencing with feed splitting and multi-effect distillation delivers the best performance, reducing energy consumption by 57.2% (from 3134kW to 1342kW), increasing exergy efficiency to 50.5%, and decreasing CO_2 emissions by 50.7% (from 670 to 330kg/h). These findings highlight strong synergy between internal heat recovery and pressure-differential optimization. In contrast, some configurations, such as direct sequencing with feed splitting alone, produced higher energy use and lower efficiency due to thermal imbalance and excessive vapor loads. Overall, this study offers a robust methodological framework integrating process simulation, exergy-based optimization, and CO_2-emission evaluation, providing guidance for sustainably designing next-generation distillation systems in the chemical and petrochemical industries.

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1. Introduction

Separation processes are fundamental operations in chemical industries, enabling the purification and recovery of valuable products [1]. Among these methods, distillation remains the most widely applied due to its simplicity and versatility [2]. However, not all mixtures can be effectively separated by conventional distillation. A key challenge arises with azeotropic mixtures, in which the vapor and liquid phases exhibit identical compositions at equilibrium, preventing complete separation [3].

To overcome such limitations, advanced distillation techniques, including azeotropic distillation (AD), extractive distillation (ED), and pressure-swing distillation (PSD), have been developed. Alternative separation approaches, such as liquid–liquid extraction (LLE) and membrane technologies, are also considered when appropriate [4–8]. In AD and ED, a third component (entrainer) is introduced to disrupt the azeotrope, requiring additional recovery units [9]. However, these methods are often energy-intensive, necessitating multiple columns and increasing operating costs [10].

A classic example is the separation of the water–ethanol azeotrope, where ethanol must be purified for its use as both an industrial solvent and a renewable biofuel [11–14]. Numerous studies have optimized azeotropic separation processes to address high energy consumption and environmental concerns. For instance, Franke [15] reduced the total annual cost (TAC) of AD by 20% through proper optimization of both continuous and discrete variables. Shang et al. [16] introduced deep eutectic solvents in ED, achieving better performance than conventional ionic liquids with respect to energy use, TAC, and CO_2 emissions.

Driven by global demand for energy-efficient and environmentally responsible processes, recent research has focused on heat integration and process intensification. Pan et al. [17] incorporated thermal coupling into ED, reducing heat duty by 12%. Shi et al. [18] applied heat pump-assisted ED, cutting TAC by 43% and significantly reducing energy costs and CO_2 emissions. Li et al. [19] proposed an extractive–azeotropic dividing wall column combined with heat integration, achieving a 37% TAC reduction. Sun et al. [21] reported that side-stream extractive distillation could cut investment and operating costs by 19.2% while lowering CO_2 emissions by 16.8%. Similarly, Popescu et al. [20] reduced energy use by 50% using a single column for heterogeneous azeotropic distillation.

In addition to economic and energy metrics, recent work increasingly incorporates environmental and safety considerations. Xing et al. [23] evaluated vapor recompression and intermediate reboiler configurations, achieving up to 39% energy savings and a 31% reduction in lost work. Guo et al. [24] developed a double-entrainer ED process with heat pump-assisted preconcentration, reducing energy consumption by 50%.

Among various evaluation tools, exergy analysis has proven particularly valuable for assessing thermodynamic efficiency. Exergy quantifies the maximum useful work obtainable from a system, offering deeper insights into irreversibility and potential process improvements. Liu et al. [25] demonstrated that minimizing exergy losses strongly correlates with reduced CO_2 emissions and improved sustainability.

1.1. Problem statement and purpose

The separation of quaternary hydrocarbon mixtures, such as n-Butane, n-Hexane, n-Heptane, and n-Nonane, is inherently challenging due to their close boiling points and low relative volatilities. Conventional quaternary separation requires three consecutive distillation columns (N–1 for N components), typically arranged in either direct or indirect sequences. These traditional strategies, however, are highly energy-intensive and environmentally burdensome. The purpose of this study is to systematically evaluate both direct and indirect sequencing methods while incorporating advanced heat integration strategies to enhance energy efficiency and reduce environmental impact.

1.2. Innovation of this work

The novelty of this research lies in the development of a hybrid heat integration approach that combines multi-effect distillation (MED) with feed splitting. MED enables thermal coupling between high- and low-pressure columns, while feed splitting reduces reboiler loads by optimizing thermal gradients. This hybrid scheme is systematically compared with conventional and partially integrated alternatives. In addition to energy analysis, the study integrates comprehensive exergy evaluation and CO_2 emission analysis to establish a holistic sustainability framework. Rigorous process simulations were performed in Aspen HYSYSV12 (Peng–Robinson EOS), while custom MATLAB R2021b (The MathWorks, Inc.) codes were employed for exergy calculations and environmental assessments. The overall objective is to identify the optimal configuration that minimizes energy consumption, maximizes exergy efficiency, and reduces CO_2 emissions, thereby providing a replicable framework for sustainable distillation design in the chemical and petrochemical industries.

2. Case study

The feed composition and operating conditions are presented in Table 1. A detailed representation of all streams, columns, condensers, and reboilers was developed to ensure complete mass and energy balance closure across the system [30]. The process parameters were selected based on a combination of literature references, industrial relevance, and practical design considerations. Specifically:

- Feed composition and conditions (temperature, pressure, and mole fractions) were adopted from previous studies on quaternary hydrocarbon mixtures [30] to ensure comparability and industrial relevance.
- Column sequencing and the use of three distillation columns follow the classical distillation design rule of N–1 column for N components, which is standard for quaternary systems.
- Number of trays and operating pressures were chosen to reflect typical industrial practice, ensuring feasible separation while avoiding unrealistic assumptions.
- Heat integration strategies (preheating, feed splitting, and multi-effect distillation) were selected because they are well-documented in the literature as effective methods for energy reduction and sustainability improvement in distillation systems [17, 18, 25, 26].
- Exergy and environmental parameters (emission factors, reference states) were calculated using standard thermodynamic relations and widely accepted emission factor data [31, 39].

Thus, all parameters were carefully selected to reflect realistic operating conditions, industrial feasibility, and alignment with established literature, ensuring that the results are both reliable and broadly applicable.

Table 1. Data for Case Study [30]

Data		Value
Temperature		49°C
Pressure		101.3kPa
Flow rate		100kmole/h
Mole fraction	a. n-Butane (A)	0.05
	b. n-Hexane (B)	0.1
	c. n-Heptane (C)	0.1
	d. n-Nonane (D)	0.75

3. Methods

3.1 Process simulation

This study investigates the separation of a quaternary hydrocarbon mixture composed of n-Butane, n-Hexane, n-Heptane, and n-Nonane using a multi-column distillation system [30]. These linear alkanes exhibit closely spaced boiling points and low relative volatilities, making their separation highly energy-intensive.

Two classical distillation sequencing strategies were investigated for the quaternary hydrocarbon mixture (n-Butane, n-Hexane, n-Heptane, and n-Nonane):

- Direct sequence (Fig. 1): In this arrangement, the lightest component, n-Butane, is removed in the first column as the overhead product. The remaining mixture (n-Hexane, n-Heptane, and n-Nonane) is then sent to the second column, where n-Hexane is recovered. Finally, the third column separates the heavier components, producing n-Heptane and n-Nonane as top and bottom products, respectively. This strategy prioritizes the sequential removal of lighter components, which typically reduces condenser duties but may increase reboiler loads in later columns.
- Indirect sequence (Fig. 2): In this configuration, the heaviest component, n-Nonane, is separated first as the bottom product of the first column. The remaining lighter components are passed to the second column, where n-Heptane is separated, followed by the final separation of n-Butane and n-Hexane in the third column. This strategy prioritizes the removal of heavier components, which can balance thermal loads differently but often results in higher condenser duties compared to the direct sequence.

Fig. 1 and Fig. 2 provide schematic representations of the direct and indirect sequencing strategies, respectively, illustrating the column arrangements, product streams, and process flow.

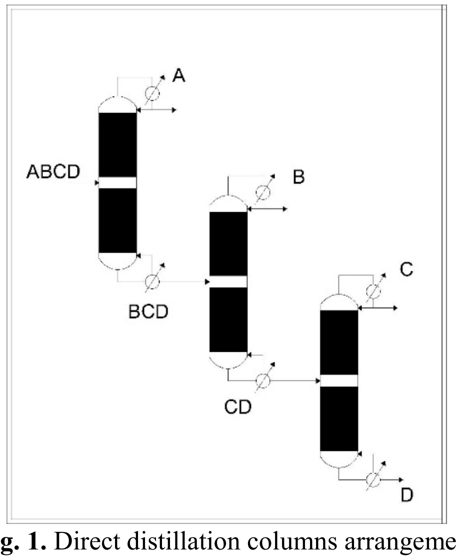

Fig. 1. Direct distillation columns arrangement

The simulations were conducted using Aspen HYSYSV12, a leading process modeling software widely utilized in industrial practice. Peng-Robinson equation of state (EOS) was employed to accurately capture vapor–liquid equilibrium behavior, considering real-gas deviations that are especially significant in hydrocarbon systems under non-ideal conditions.

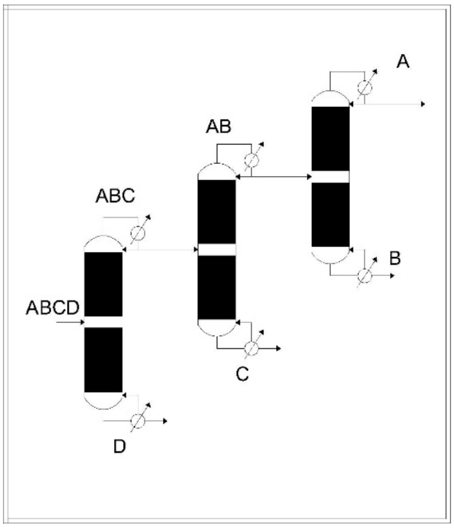

Fig. 2. Indirect distillation columns arrangement

3.2 Heat integration methods

Heat integration is a well-established process intensification strategy that aims to minimize the use of external utilities by recovering and reusing thermal energy within the system. In distillation, where reboilers and condensers typically account for most of the energy demand, heat integration can drastically reduce both operating costs and environmental impacts. In this study, four heat integration approaches were systematically evaluated:

1) Preheating (Preheat): This method involves utilizing hot internal streams (such as column bottoms or side products) to preheat the feed before entering the distillation column. By reducing the temperature difference between the feed and column operating conditions, preheating lowers reboiler duty without significantly altering condenser demand. Although conceptually simple, this technique often provides considerable energy savings, particularly in indirect sequences where thermal mismatches are more pronounced.
2) Feed Splitting (FS): In the feed splitting technique, the incoming stream is divided into two sub streams. One portion is preheated using internal process heat, while the other enters at its original conditions. This reduces the thermal load imposed on a single reboiler stage, leading to more balanced vapor–liquid traffic and enhanced column efficiency. However, improper application of feed splitting may increase condenser duties and total energy use, as demonstrated in the Direct/Feed Splitting configuration of this work.
3) Multi-Effect Distillation (MED): Multi-effect distillation relies on operating two or more columns at different pressure levels. The condenser of a high-pressure column is thermally coupled with the reboiler of a low-pressure column, allowing heat released during condensation to be directly utilized for vaporization. This reduces the need for external heating and cooling utilities, achieving significant energy recovery. MED is particularly effective when column pressure differentials are sufficiently large to enable heat transfer at practical temperature gradients.
4) Hybrid method (Feed Splitting + MED): A novel contribution of this study is the hybridization of feed splitting with multi-effect distillation. This method leverages the strengths of both techniques: feed splitting reduces localized reboiler loads, while MED enables inter-column heat recovery. The hybrid configuration demonstrated superior performance, achieving a 57.2% reduction in energy demand, an exergy efficiency of 50.5%, and a 50.7% reduction in CO_2 emissions compared to the base case. This synergy highlights that

combining complementary strategies can overcome the limitations of individual methods, provided they are applied under thermodynamically favorable condition.

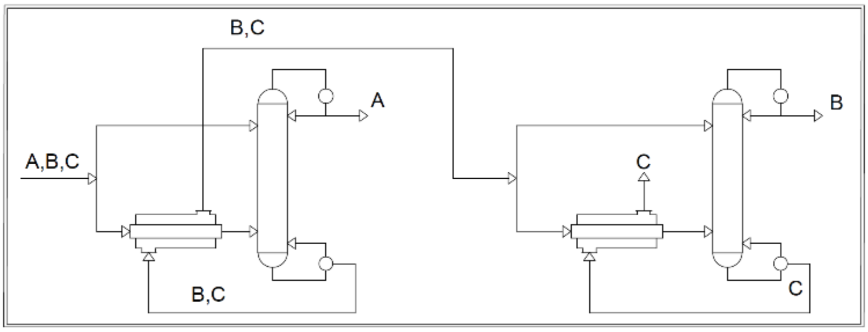

Fig.3. Feed Splitting method

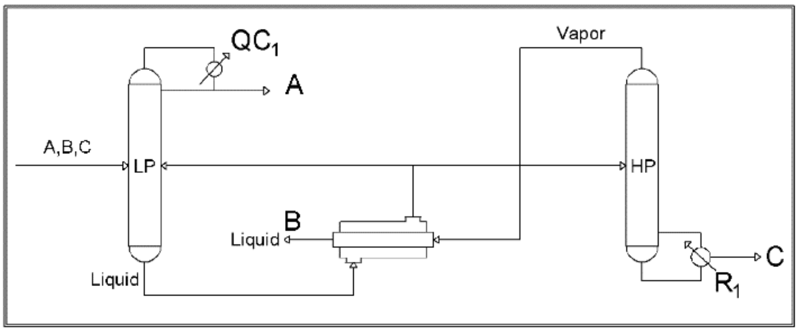

Fig.4. Multi-Effect method

All heat integration techniques were systematically applied to both direct and indirect separation sequences, enabling a consistent comparative evaluation of energy savings and process performance under varying operational strategies. In this study, the separation of a quaternary mixture consisting of n-Butane, n-Hexane, n-Heptane, and n-Nonane is investigated through process simulation. Fig.5. illustrates the direct distillation configuration without heat integration. In this arrangement, the feed stream is introduced to Tray 4 of the first column, which comprises 16 ideal trays and operates under pressure conditions ranging from 95kPa (top) to 110kPa (bottom). The overhead product from this column is pure n-Butane, while the bottom product is directed to Tray 16 of the second column. This second column consists of 29 ideal trays and yields pure n-hexane as the top product. The third column, with 16 ideal trays and operating between 110kPa and 130kPa, receives the feed at Tray 12 and separates pure n-heptane and n-Nonane as its overhead and bottom products, respectively. All columns are modeled under the assumption of ideal stage behavior, and the rigorous Inside-Out algorithm implemented in the modified HYSIM simulator is employed for process calculations.

Fig. 6. presents a simulation of the same direct configuration, but with a different separation sequence. In this modified scheme, n-Nonane is initially separated as the bottom product of the first column, followed by the recovery of n-Heptane from the bottom of the second column. The third column then separates n-Butane and n-Hexane. The number of trays in all columns remains consistent with the original direct configuration. To enhance energy efficiency, several heat integration strategies are evaluated, including Preheating, Multi-Effect, Feed Splitting, and hybrid combinations thereof.

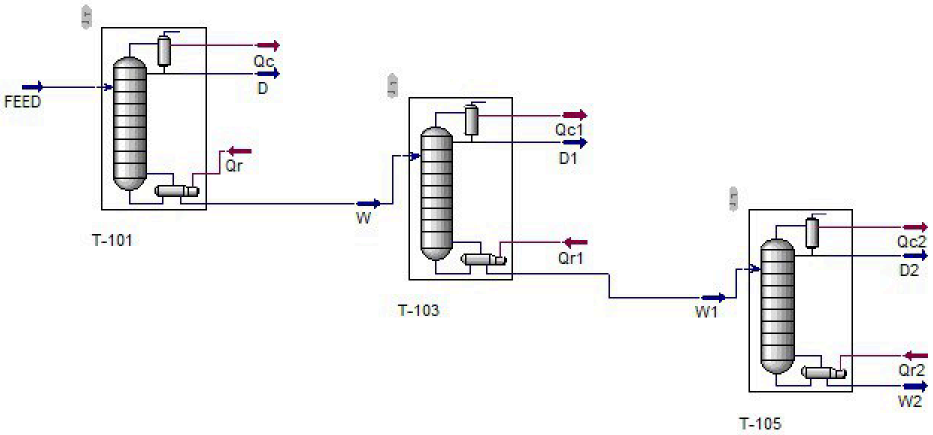

Fig. 5. Direct arrangement simulation without heat integration

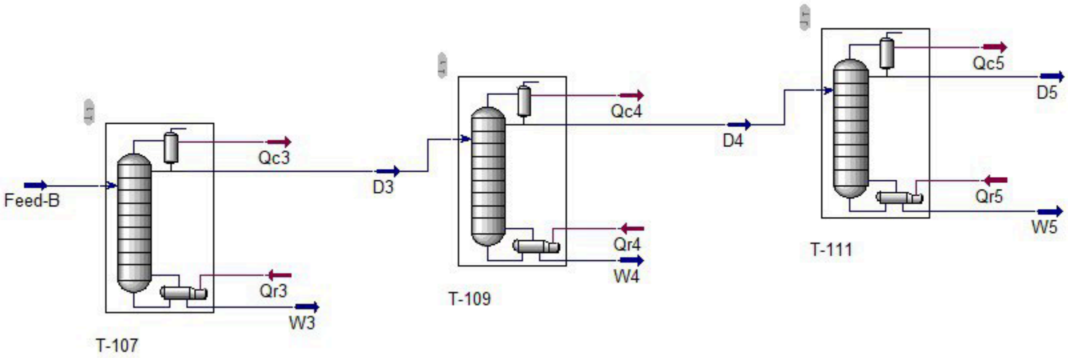

Fig. 6. Indirect arrangement simulation without heat integration

Table 2. present the results of these configurations. Among them, the hybrid approach combining the Multi-Effect and Feed Splitting techniques demonstrates the lowest energy consumption, and is therefore selected as the optimal design. Fig.8. depicts the simulation of this optimized configuration.

Table 2. Eight different arrangements heat duty

Arrangement	1st column		2nd column		3rd column		Q_c total	Q_r total	Total energy
	Condenser	Reboiler	Condenser	Reboiler	Condenser	Reboiler			
Direct	57.3	648.8	569.3	685.5	556.6	616.5	1183.2	1950.8	3134
Direct/Preheating	62.5	497.6	565	606.9	478.7	524.9	1106.2	1629.4	2736
Direct/Feed Splitting	62.49	577	1239	1289	455.8	537.6	1757.3	2403.6	4161
Indirect	1074	1748	466.3	490.3	45.43	62.26	1585.73	2300.6	3886.29
Indirect/ Preheating	597.9	665.2	279	267.8	50.98	50.2	927.88	983.2	1911.08
Indirect/Feed Splitting	571	644.5	284.5	270.4	49.98	45.14	905.48	960.04	1865.52
Direct-Feed Splitting-Multi-Effect	60.32	437	385.8	0	0	458.8	446.12	895.8	1342
Indirect/Multi (2,3)/Feed splitting	624.8	614.2	0	1298	209.6	0	834.4	19122	2746.6
Indirect-Multi (1-2)	508.6	1538	252	0	42.5	55.2	803.1	1593.2	2396.3

According to Fig. 8, the Feed Splitting method is applied to both the first and third columns. In the first column, the feed is divided into two streams: approximately 95% of the stream is preheated using the bottom product from the same column to 72°C and introduced at Tray 12, while the remaining portion enters Tray 8 at the initial temperature of 49°C.

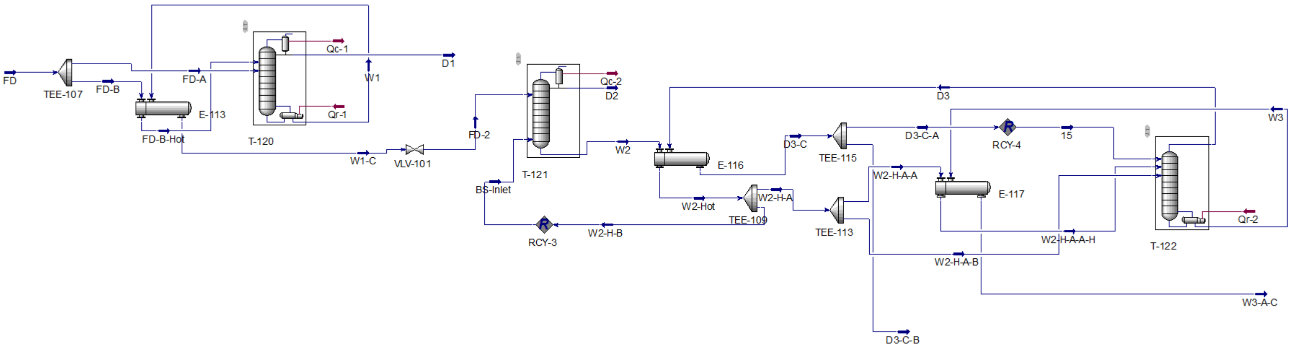

Fig. 8. Simulation of the direct arrangement with a combination of multi-effect and feed splitting methods

Similarly, in the third column, around 94% of the feed is preheated from 101°C to 160°C using the bottom product and introduced to Tray 6, while the rest enters Tray 11 without any temperature change. Furthermore, the Multi-Effect method is implemented between the second and third columns, where the second column operates at 25kPa and the third at 130kPa. To facilitate heat integration, the reboiler of the second column and the condenser of the third are eliminated and replaced with a heat exchanger, effectively coupling the condenser of the third column with the reboiler of the second.

3.3 Exergy analysis

Unlike traditional energy analysis, which only considers the quantity of energy, exergy analysis evaluates both the quantity and the quality of energy, making it a more comprehensive and insightful metric for assessing system performance [31, 32]. Exergy represents the maximum useful work that can be extracted as a system moves toward thermodynamic equilibrium with its surroundings, taking into account the irreversibility inherent in real processes [33]. In this context, exergy is not merely a measure of energy content but also reflects the usefulness or work potential of different forms of energy under specific environmental conditions.

The concept of exergy allows engineers and researchers to identify the locations, magnitudes, and causes of inefficiencies within a process, thus providing crucial guidance for system optimization and sustainable design [31, 34]. Exergy associated with a material stream flowing through a process can be decomposed into two primary components: physical exergy and chemical exergy.

- Physical exergy refers to the maximum work obtainable as a stream is brought from its actual state to the environmental (dead) state purely through physical processes, such as heat transfer and expansion.
- Chemical exergy, on the other hand, accounts for the work potential associated with differences in chemical composition relative to the environment.

For a material stream, the total exergy (EX_{total}) is the sum of its physical exergy (EX_{ph}) and chemical exergy (EX_{ch}). When assuming an ideal gas or ideal mixture behavior, these quantities can be accurately calculated using thermodynamic relations. The mathematical expressions for total, physical, and chemical exergy are typically given by Eqs. (1) to (3) [33, 35].

$$EX_{total} = EX_{ph} + EX_{ch} \tag{1}$$

$$EX_{ph} == \left(H - H_0\right) - T_0\left(S - S_0\right) \tag{2}$$

$$EX_{ch} = \Delta\mu_i \tag{3}$$

where EX_{total} denotes the total exergy of the system, EX_{ph} represents the physical exergy, EX_{ch} refers to the chemical exergy, H and S are the enthalpy and entropy of the system, respectively, H_0 and S_0 correspond to the enthalpy and entropy at the environmental (dead) state, T_0 is the temperature of the reference environment, and $\Delta\mu_i$ indicates the change in chemical potential of the *i*-th component.

Understanding and quantifying exergy in this manner enables a more realistic evaluation of process efficiency compared to energy analysis alone, especially in complex industrial systems such as distillation, heat integration, and chemical manufacturing processes [31]. Besides the exergy associated with material streams entering or leaving the system, the heat exchanged with the surroundings also carries exergy and must be considered in the analysis. The exergy transfer associated with a heat flow Q at boundary temperature T can be calculated using the following Eq. (4):

$$E_Q = Q \times \left(1 - \frac{T_0}{T}\right) \tag{4}$$

where T_0 is the environmental (reference) temperature. Furthermore, the total exergy loss of a system can be determined using an exergy balance, expressed as:

$$EX_{loss} = \sum_{i=1}^{n} \left(EX_{in}\right)_i - \sum_{i=1}^{n} \left(EX_{out}\right)_i - \Delta EX_{system} \tag{5}$$

During steady-state operation, the energy variation within the system is zero. Custom MATLAB codes were developed to automate these calculations. The codes systematically get simulation data from Aspen HYSYS exports, calculate stream properties, determine exergy balances for each unit, and summarize total system exergy destruction and efficiencies for all configurations. A summary of all the results is presented in Table 3.

Table 3. Eight different arrangements exergy loss and exergy efficiency

Arrangement	**Total energy (kW)**	**Exergy loss (∝ Q_r total)**	**Exergy efficiency (η_{ex})**
Direct	3134	1950.8	37.7%
Direct / Preheating	2736	1629.4	40.4%
Direct / Feed Splitting	4161	2403.6	42.2%
Indirect	3886.3	2300.6	40.8%
Indirect / Preheating	1911.1	983.2	48.5%
Indirect / Feed Splitting	1865.5	960.0	48.5%
Direct / Feed Splitting / Multi-Effect	1342	895.8	50.5%
Indirect / Multi (2,3) / Feed Splitting	2746.6	1912.2	30.3%
Indirect / Multi (1-2)	2396.3	1593.2	33.5%

3.4. Environmental assessment

To evaluate the environmental impacts, CO_2 emissions evaluation was performed. The increasing concentration of CO_2 emissions and the associated intensification of global warming, primarily driven by the greenhouse effect, have become critical global environmental concerns. Consequently, the reduction of CO_2 emissions has emerged as a key objective in the development and optimization of chemical processes, serving as a strategic pathway toward sustainable and environmentally responsible industrial practices [35]. Based on the calculated energy consumption for each configuration, the associated carbon dioxide emissions were estimated using standard emission factors [31]. Eq. (6) is employed to quantitatively assess the amount of CO_2 emissions generated during distillation processes. This formulation provides a foundational basis for evaluating the environmental impact of such operations and supports efforts toward improving the sustainability of separation technologies [36]. This integration of energy, exergy, and environmental analyses provides a comprehensive and holistic view of process sustainability, aligning with the growing demands for greener and more efficient chemical process designs.

$$CO_{2|emissions} = \frac{Q_{fuel}}{NHV} \times \frac{C\%}{100} \times \alpha \tag{6}$$

where α is the molar mass ratio of CO_2 and equals 3.67, NHV is the net heating value for heavy fuel oil and equals 39771kJ/kg, C% is the carbon content, which is 86.5%, and Q_{fuel} is the duty of fuel and calculated from Eq. (7) [39].

$$Q_{fuel} = \frac{Q_{proc}}{\lambda_{proc}}\left(h_{proc} - 419\right) \times \frac{T_{FTB} - T_0}{T_{FTB} - T_{Stack}} \tag{7}$$

where Q_{proc} (kJ/h) is the heat duty of the reboiler, λ_{proc} (kJ/kg) the latent heat of low-pressure steam (LPS) or medium-pressure steam (MPS), h_{proc} (kJ/kg) the enthalpy of LPS or MPS, T_0 the reference temperature (T_0=25ºC), T_{FTB} the flame temperature (T_{FTB} =1800ºC), and T_{Stack} is the stack temperature (T_{Stack}=160ºC). The enthalpy of boiler feed water is 419kJ/kg at 100ºC [36].

This section focuses on the development of energy-efficient strategies for the separation of a quaternary hydrocarbon mixture comprising n-Butane, n-Hexane, n-Heptane, and n-Nonane. Various process configurations and heat integration techniques are evaluated to minimize energy consumption. The reference case is the conventional direct distillation sequence without heat integration, which involves three sequential columns, each equipped with a reboiler and condenser, leading to substantial energy demands. To enhance process efficiency, three heat integration approaches—Preheating, Multi-Effect, and Feed Splitting—along with their hybrid configurations, were systematically investigated.

The simulation results indicate that the highest energy savings are achieved when the direct distillation configuration is combined with both the Multi-Effect and Feed Splitting methods. In the optimized design, Feed Splitting is strategically implemented in the first and third columns, allowing for division of the feed streams in a way that reduces temperature gradients, thereby lowering the heating and cooling requirements. Concurrently, the Multi-Effect technique is applied between the second and third columns by operating them at different pressures, enabling heat recovery by replacing conventional reboilers and condensers with an integrated heat exchanger.

Beyond energy savings, heat integration also leads to notable environmental benefits. The hybrid configuration of the direct process with Multi-Effect and Feed Splitting achieved a 62% reduction in CO_2 emissions compared to the direct/feed-splitting scheme, outperforming both the indirect and base-case direct arrangements. These findings underscore the significant potential of heat integration not only for enhancing energy performance but also for reducing the environmental impact of separation processes.

Ultimately, this study highlights the crucial role of heat integration in driving sustainable chemical process design. By optimizing energy-intensive separation operations, industries can achieve improved operational efficiency, reduced environmental footprints, and increased cost-effectiveness—paving the way toward more sustainable and resilient process systems.

4. Results and discussion

4.1. Energy performance across configurations

A comprehensive comparison of energy consumption across all process configurations revealed substantial variability, largely dictated by the application and effectiveness of heat integration techniques. As illustrated in Fig.

9, the reference direct configuration, which employs no heat recovery, incurred the highest baseline energy demand of 3134kW. This configuration served as a benchmark against which all other scenarios were evaluated.

Among all alternatives, the Direct/Feed Splitting/Multi-Effect configuration demonstrated the lowest energy requirement, consuming only 1342kW, representing a remarkable 57.2% reduction relative to the base case. This reduction is primarily attributed to two synergetic mechanisms: (*i*) strategic feed splitting which reduced reboiler loads by distributing thermal gradients more effectively, and (*ii*) multi-effect distillation that thermally linked the condenser of the third column with the reboiler of the second, thus eliminating external utility demands for these units.

On the contrary, the Direct/Feed Splitting configuration, despite incorporating a heat recovery mechanism, paradoxically resulted in the highest energy demand at 4161kW. This counterintuitive result arises from increased vapor and liquid traffic due to non-uniform thermal gradients and absence of inter-column pressure differentials, which led to escalated condenser duty and lower heat utilization efficiency.

Configurations involving indirect sequencing also demonstrated significant energy demand, particularly the conventional indirect case with 3886.3kW, highlighting its suboptimal thermodynamic structure. Nonetheless, the inclusion of Preheating or Feed Splitting strategies within the indirect sequence yielded substantial improvements, lowering energy consumption to 1911.1kW and 1865.5kW, respectively—suggesting that internal thermal adjustments, even in traditionally energy-intensive schemes, can yield significant energy dividends.

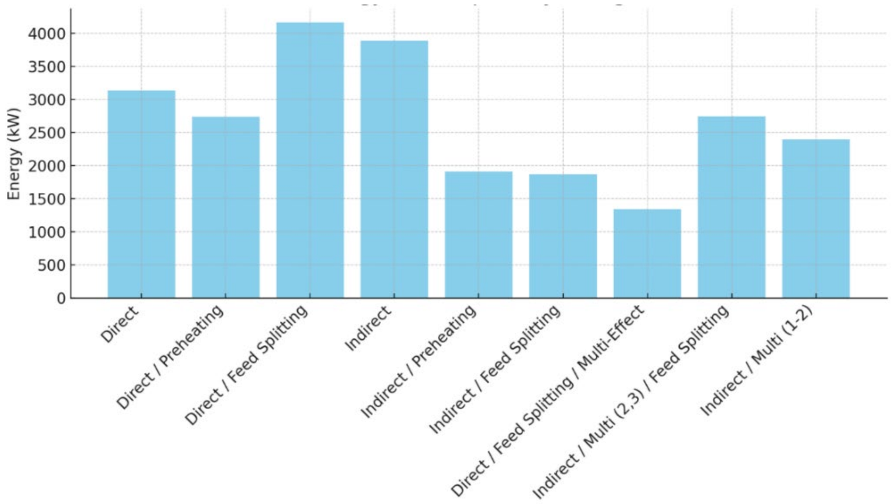

Fig. 9. Total energy consumption by configuration

4.2. Exergy analysis: quality of energy utilization

While energy analysis reflects the quantity of energy consumed, exergy analysis offers a more nuanced assessment by considering energy quality and process irreversibility. The total exergy losses and exergy efficiencies for all configurations are detailed in Table 3 and visualized in Fig. 10.

The Direct / Feed Splitting / Multi-Effect configuration again leads, achieving the highest exergy efficiency at 50.5%, which reflects both a reduction in internal entropy generation and a more effective use of available thermal gradients. Notably, this configuration had the lowest exergy destruction at 895.8kW, underscoring its superior thermodynamic alignment and minimal deviation from equilibrium conditions.

By contrast, the Indirect/Multi (2, 3)/Feed Splitting configuration exhibited the worst exergy performance, with an efficiency of 30.3% and the highest exergy loss of 1912.2kW. The performance gap of 20.2 percentage points between this and the optimized configuration highlights the impact of mismatched heat integration and pressure settings, which led to elevated irreversibility.

It is worth noting that simple integration strategies such as Preheating produced appreciable gains. The Indirect/Preheating and Indirect/Feed Splitting cases achieved 48.5% exergy efficiency, despite being based on the inherently less favorable indirect sequence. This confirms the robustness and effectiveness of low-complexity heat recovery techniques when optimally configured.

Interestingly, the Direct/Feed Splitting configuration, despite high energy use, yielded a respectable exergy efficiency of 42.2%, suggesting that while the process consumed large quantities of energy, it utilized this energy with relatively better quality and lower irreversibility than the traditional indirect cases.

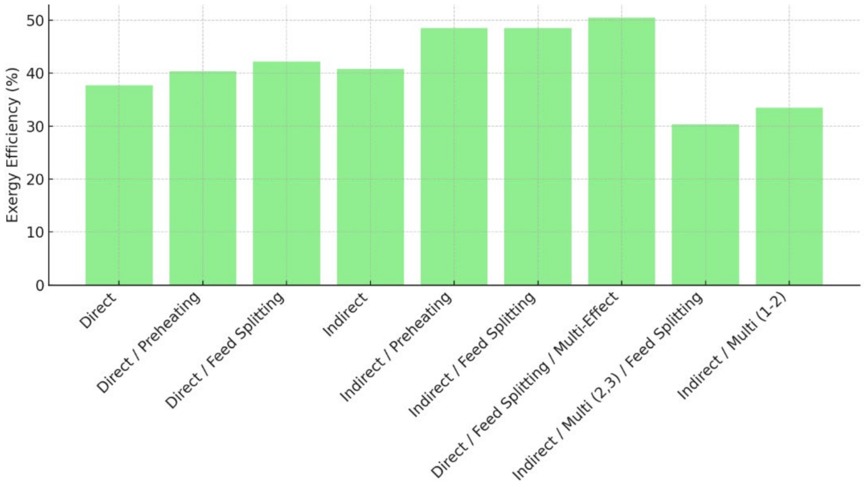

Fig.1 0. Exergy efficiency by configuration

4.3. Environmental impact and CO_2 emissions

The environmental footprint of each configuration was quantified through CO_2 emission calculations based on fuel-derived thermal energy demands, using standardized emission factors. The results, plotted in Fig. 11, strongly correlate with energy consumption patterns.

The Direct/Feed Splitting/Multi-Effect configuration exhibited the lowest CO_2 emissions, producing only 330kg/h, representing a 50.7% reduction relative to the high-emission Direct/Feed Splitting case (850kg/h). This confirms that smart heat integration not only enhances thermodynamic performance but also plays a vital role in carbon mitigation strategies for chemical separation processes (Table 4).

Table 4. CO_2 Emission in arrangements

Configuration	CO_2 emission (kg/h)
Direct	670
Indirect	710
Direct / Preheating	560
Direct / Feed Splitting	850
Indirect / Preheating	360
Indirect / Feed Splitting	350
Direct / Feed Splitting / Multi-effect	330

Configurations using Preheating also achieved substantial emission reductions. Specifically, Indirect/Preheating and Indirect/Feed Splitting both recorded emissions below 360kg/h, achieving near-identical environmental performance despite different internal structures. These results reinforce the concept that thermal input quality and distribution are equally important as total input volume when aiming for emission reductions. The baseline Direct and Indirect processes, devoid of any integration strategy, emitted 670kg/h and 710kg/h, respectively. These figures serve as a stark reminder of the environmental cost associated with non-integrated distillation systems, particularly when operating continuously at industrial scale.

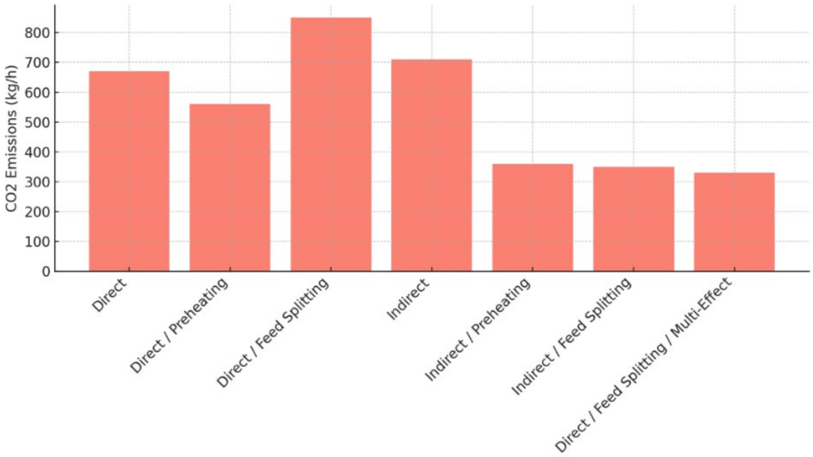

Fig.11. CO_2 emissions by configuration

4.4. Holistic evaluation of process sustainability

By combining energy, exergy, and CO_2 metrics, this study offers a multi-dimensional sustainability assessment for quaternary hydrocarbon separation. The Direct / Feed Splitting /Multi-Effect configuration consistently outperformed other configurations across all performance indicators, highlighting its potential for large-scale deployment in refinery and petrochemical industries where feedstocks contain closely boiling components.

Furthermore, these findings emphasize that process integration must be context-specific. Not all integration leads to improvement—as evidenced by the performance of the Direct/Feed Splitting arrangement. Hence, optimal configurations require careful matching of pressure levels, flow splits, and heat integration locations to avoid creating new bottlenecks or inefficiencies.

This approach of integrating thermodynamic insights (via exergy analysis) with operational performance and environmental evaluation represents a rigorous pathway for the design of green separation processes, contributing to broader industrial decarbonization efforts. Table 5. provides a comprehensive quantitative summary of the results for all configurations.

Table 5. Comprehensive quantitative summary of the results for all configurations

Configuration	Total energy (kW)	Exergy loss (kW)	Exergy efficiency (%)	CO_2 emission (kg/h)
Direct	3134.0	1950.8	37.7	670.0
Direct / Preheating	2736.0	1629.4	40.4	560.0
Direct / Feed Splitting	4161.0	2403.6	42.2	850.0
Indirect	3886.3	2300.6	40.8	710.0
Indirect / Preheating	1911.1	983.2	48.5	360.0
Indirect / Feed Splitting	1865.5	960.0	48.5	350.0
Direct / Feed Splitting / Multi-Effect	1342.0	895.8	50.5	330.0
Indirect / Multi (2,3) / Feed Splitting	2746.6	1912.2	30.3	—
Indirect / Multi (1-2)	2396.3	1593.2	33.5	—

5. Conclusion

Distillation remains the dominant method for separating hydrocarbon mixtures, but it is also one of the most energy- and emission-intensive operations in the chemical industry. Conventional designs often rely on sequential distillation columns without heat recovery, leading to high utility demand, significant exergy destruction, and large CO_2 emissions. This is particularly challenging in the case of quaternary hydrocarbon mixtures with close boiling points (such as n-Butane, n-Hexane, n-Heptane, and n-Nonane), where separations are inherently difficult and energy requirements escalate.

The purpose of this study was to address these challenges by systematically investigating how heat integration and process intensification strategies can be applied to quaternary hydrocarbon distillation. By combining rigorous Aspen HYSYS simulations, exergy-based thermodynamic analysis, and environmental impact assessment (CO_2 emissions), the work sought to provide a holistic framework for the sustainable optimization of distillation processes.

The innovation of this study lies in the development and evaluation of a hybrid configuration that combines feed splitting with multi-effect distillation. While previous studies have applied these techniques separately in binary or azeotropic systems, their synergistic application to quaternary hydrocarbon mixtures has not been reported. This hybrid method demonstrated remarkable performance:

- 57.2% reduction in energy demand compared to the base case (3134 → 1342kW),
- highest exergy efficiency achieved (50.5%), indicating reduced irreversibility, and
- 50.7% reduction in CO_2 emissions (670 → 330kg/h), aligning process design with industrial decarbonization goals.

Key findings include:

- Context-specific integration is essential. Not all heat integration strategies guarantee improvement. For instance, feed splitting alone increased energy consumption due to thermal imbalance, whereas its combination with MED produced the best outcome.
- Even simple strategies can be impactful. Preheating within indirect sequences reduced both energy consumption and emissions by more than 50% relative to the base case.
- Exergy analysis provided critical insights beyond conventional energy balances, enabling the identification of hidden inefficiencies and guiding the development of thermodynamically consistent designs.
- Environmental performance correlated directly with thermodynamic performance, underscoring the necessity of integrating sustainability assessment into process design.

An approximate estimation of annual energy cost was also carried out to evaluate the economic impact of the proposed configuration. Considering a boiler efficiency of 85% and 8,000 operating hours per year, the baseline direct configuration with a total thermal duty of 1950.8kW corresponds to a fuel consumption of 1,661,275.5kg/yr. In contrast, the optimized Direct/Feed-Splitting/Multi-Effect configuration, with a thermal duty of 895.8kW, requires 763,164.4kg/yr of fuel. At a fuel price of \$0.20/kg, the annual fuel cost for the baseline case is approximately \$332,255/yr, whereas the optimized configuration reduces this to \$152,632/yr. This results in annual savings of about \$179,623, corresponding to a utility cost reduction of 54.06%. A similar evaluation for the indirect baseline compared with the optimized Indirect/Feed-Splitting configuration revealed an even greater utility cost reduction of 58.2%. This economic assessment clearly demonstrates that the optimized Direct/Feed-Splitting/Multi-Effect configuration is not only the most energy- and environmentally efficient option but also the most economically attractive, providing strong justification for its industrial implementation.

In summary, this research demonstrates a comprehensive design approach that integrates simulation, thermodynamic analysis, environmental assessment, and economic evaluation to achieve sustainable optimization of quaternary hydrocarbon distillation. By addressing a system that has received limited attention in the literature, the study not only identifies an optimal configuration for linear alkane separation but also establishes a replicable methodology for advancing energy efficiency, emissions reduction, and cost competitiveness in distillation-based separation processes. This contribution strengthens the pathway toward next-generation sustainable distillation systems, where improved operational efficiency is inseparably linked to environmental responsibility and industrial profitability.

Nomenclature

Symbols

EX	Exergy
EX_{ch}	Chemical exergy
EX_{ph}	Physical exergy
EX_{total}	Total exergy
h_{proc}	Enthalpy of LPS or MPS
H	Enthalpy
Q_c	Condenser heat duty
Q_{fuel}	Fuel heat input
Q_{proc}	Process heat duty
Q_r	Reboiler heat duty
S	Entropy
T_0	Reference (Dead-state) temperature
T_{FTB}	Flame temperature of the boiler
T_{Stack}	Stack temperature
η_{ex}	Exergy Efficiency

Greek symbols

α	Molar mass ratio of CO_2
λ_{proc}	Latent heat of LPS or MPS

Abbreviation

AD	Azeotropic Distillation
CPD	Chemical Process Design
ED	Extractive Distillation
EOS	Equation of State
FS	Feed Splitting
LLE	Liquid–Liquid Extraction
LPS	Low-Pressure Steam
MED	Multi-Effect Distillation
MPS	Medium-Pressure Steam
NHV	Net Heating Value
PSD	Pressure-Swing Distillation
PR	Peng–Robinson
TAC	Total Annual Cost
VLE	Vapor–Liquid Equilibrium

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