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Sustainable separation of Xe from the noble gas mixture of Ar, Kr, and Xe using cryogenic distillation and gas hydrates hybrid methods

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ABSTRACT

To date, cryogenic distillation remains the traditional method used for the separation of air components mainly oxygen and nitrogen, the trace components xenon, krypton, and argon are obtained as by-products. This method is known to be very energy-intensive as it involves the liquefaction of gas components at very low temperatures. In this work, thermally coupled distillation sequences and hydrate-hybrid processes were proposed as alternative separation processes to achieve the same effective separation of xenon with less energy consumption. The simulated alternative processes were compared based on energy savings and reduction of operating costs in the distillation section, and the overall xenon recovery relative to the conventional process. From all the simulated processes, a hydrate-hybrid process was found to be the best-performing configuration, achieving the desired separation of xenon with significant energy savings. Using this hybrid method, approximately, a 33% reduction of annual operating costs and 36% energy savings were achieved whilst maintaining a xenon system recovery of 99%, ensuring efficient use of the extracted air components. The use of gas hydrate promoters was recommended for the moderation of the pressure conditions for gas hydrate formation, to reduce overall operating costs. A simulation of the gas hydrate separation method, more comprehensive than the simplified approach taken in this study based on experimental data, was also recommended. This hybrid separation method contributes to sustainability by significantly reducing energy consumption and operating costs, which in turn mitigates greenhouse gas emissions and decreases dependence on nonrenewable energy sources.

KEYWORDS

Energy consumption; Xe recovery; thermally coupled distillation; gas hydrates hybrid separation; noble gasses; sustainability

Introduction

Xenon (Xe) is a rare noble gas that is colorless, odorless, and nontoxic, found in the atmosphere at trace concentrations of about 0.087 ppm. Industrial applications for xenon include medical imaging, spacecraft propellants, insulation, commercial lighting, and lasers (Zhang et al. 2022). Xenon, krypton (Kr), and argon (Ar) are found in trace amounts in the air and are typically recovered as by-products of the air separation process. The diverse applications of these gases across various industries have led to a significant increase in their demand and sparked considerable interest among researchers. The demand for xenon (Xe), in particular, has been rising steadily since 2017 and is projected to continue growing until at least 2028. This upward trend in Xe market demand is largely driven by the expansion of industries and sectors that utilize it, with notable applications in satellites, lighting, and imaging being the primary contributors to this growth (FortuneBusinessInsights 2020). The separation of Xe is important to industry and human life as evidenced by this high demand and its many different applications, thus deeming the separation of Xe an area worthy of research efforts.

In current technologies used to separate and obtain noble gases, cryogenic distillation remains the predominant and conventional method in industrial practices. However, the economic viability of this separation technology is significantly challenged by the high energy investments it

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demands, primarily due to the need for gas liquefaction at extremely low temperatures (Yan et al. 2021).

The significant energy demands and associated economic constraints of cryogenic distillation have spurred research into alternative, cost-effective separation technologies for noble gases, such as gas hydrate technology (Eslamimanesh et al. 2012; Babaee et al. 2015; Vorotyntsev et al. 2016; Matizakurima 2020; Babaee et al. 2021), membrane technology (Baker 2002; Abedini and Nezhadmoghadam 2010; Bernardo and Clarizia 2013), and adsorption with metal-organic frameworks (MOFs) (Czaja et al. 2009; Kang et al. 2017), zeolites (Jensen et al. 2012; Kosinov et al. 2016), and activated carbon (Sircar et al. 1996; Kostoglou et al. 2017). However, for high-purity products, cryogenic distillation remains the better separation technology (Yan et al. 2021). Hybrid methods involving these alternative separation methods together with cryogenic distillation have also been considered in the literature as potential energy-saving separation configurations (Benali and Aydin 2010).

One of the most considered cost-effective alternatives to cryogenic distillation for the separation of noble gas mixtures is physical adsorption by the aid of zeolites and metal-organic frameworks (MOFs) and absorption by dissolution in a solvent (Matizakurima 2020). The main challenge in the applicability of separation technologies of this nature lies in the selection of a suitable material for a particular gas mixture and determining the resulting separation efficiencies (Banerjee et al. 2018). MOFs, also known as porous coordination polymers (PCPs), constitute a novel class of permeable materials comprising metal nodes and organic ligands (Zhou and Kitagawa 2014). Due to their customizable structures and tunable chemical functionalities, this promising class of porous crystalline materials has been extensively researched for the separation of Xe and Kr. Banerjee et al. (2018) demonstrated the ability of nickel-based MOFs to recover and recycle xenon from anesthetic gas mixtures (Banerjee et al. 2018).

From the comparisons made (Forster et al. 2014), it was concluded that zeolites proved to be a better option for the materials used for the adsorption of gas components due to their being less expensive and more robust (Forster et al. 2014). The experimental investigations by Kukulka et al. (2019) revealed that at the conditions of atmospheric pressure and room temperature activated carbon shows a Xe uptake of approximately 54% by weight, which is double that of an investigated MOF-505 at the same environmental conditions (Kukulka et al. 2019).

Another separation technology that has piqued the interest of researchers as a potential alternative to cryogenic distillation is the use of gas hydrates. Gas hydrates are compounds of a crystalline structure made up of water molecules forming cages inside which guest molecules of a gas can be trapped (Sloan 2010; Babaee 2015g). The water molecules are connected through hydrogen bonds which stabilize the cages formed thus making nano-porous ice-like structures within which some components of a gas mixture can be trapped whilst others cannot, depending on their atomic diameters and hydrate dissociation pressure (Matizakurima 2020). The concept revolves around exploiting the selective encapsulation of gas molecules within gas hydrate crystals under precise temperature and pressure conditions. Figure 1 illustrates the separation achieved through selective encapsulation of a component of the gas mixture within gas hydrates.

The study of Vorotyntsev and Malyshev (2011) revealed that the Xe gas component can be concentrated from 33 mol % in a feed of xenon, krypton, and argon, to a product of 97 mol% over two gas hydrate formation steps (Vorotyntsev and Malyshev 2011).

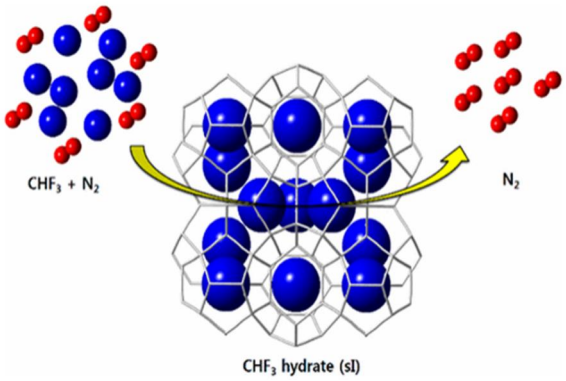


Figure 1. Separation of a $CHF_3 + N_2$ mixture into individual components by the selective encapsulation of gas-hydrate technology (extracted from Kim et al. 2017)).

Membrane technology serves as a versatile separation method capable of addressing a broad spectrum of challenges, from particles to molecules, with a variety of membrane options available for selection (Miandoab et al. 2021). For a membrane-based technique to be practical in separating Xe and Kr, the membranes must possess adequate intrinsic selectivity. Harnessing this selectivity necessitates adjusting operational conditions accordingly (Miandoab et al. 2021). Benali and Aydin (2010) investigated the use of membranes in the highly energy-intensive separation of a propylene-propane mixture by cryogenic distillation. The membrane technology was used together with a distillation column, making a hybrid-membrane distillation configuration. The study demonstrated the potential of the use of membranes to reduce distillation energy costs (Benali and Aydin 2010).

Though these separation technologies show the potential of being used as alternatives to cryogenic distillation, the main challenge lies in low efficiencies compared to the separation by cryogenic distillation. The comparison of these existing separation technologies done by Omer et al. (2017) showed that challenges lie in lower product purity and low or undetermined economical production ranges compared to the conventional cryogenic distillation process. Moreover, these alternative processes are typically in the developing or semi-mature progress status, thus the process of cryogenic distillation remains robustly employed in industrial applications amid the challenges with its energy-intensiveness (Omer et al. 2017).

The process of cryogenic distillation is primarily used for the separation of air into the main components of oxygen and nitrogen. The trace components of Xe, Kr, and Ar are recovered as by-products using auxiliary columns. Figure 2 represents the typical operation of an air separation cryogenic distillation unit (Omer et al. 2017). The components are separated based on the differences in boiling points and volatilities. This method involves the liquefaction of gas components at very low temperatures to induce a phase change for an effective separation, which is the primary reason for the process being excessively energy-intensive (Babaee 2015). Therefore, there exists a need to investigate potential alternate or hybrid separation methods.

In efforts to improve energy efficiency and cut down on energy consumption, thereby reducing costs in cryogenic distillation technology, researchers have investigated several column configurations in the literature (Rizk et al. 2012). The study by Rizk et al. (2012) demonstrated fewer exergy losses and improved energy efficiency through the use of thermally coupled distillation configurations (Rizk et al. 2012). The study by Saxena et al. (2017) demonstrated energy savings of 31–35% relative to conventional distillation using thermally coupled distillation, which is a reconfiguration of the Petyluk distillation sequence (Saxena et al. 2017).

In the work of Matizakurima (2020), a hybrid–hydrate process which is a combination of conventional distillation with the hydrate separation technology was proposed as a process of achieving energy savings and high product quality in the separation of Xe from a ternary mixture of Xe + Kr + Ar. The study was based on the experimental measurements of gas hydrates for the separation of Xe from the mixture of Ar, Kr, and Xe. However, the study did not thoroughly explore the economic evaluation and process simulation.

The hybrid method proposed in this paper offers a sustainable approach to gas separation and distillation processes by integrating gas hydrate separation and thermally coupled distillation. By utilizing gas hydrates to enhance the concentration of Xe in the feed stream, followed by cryogenic distillation to decrease energy consumption in distillation columns, the method aims to improve energy efficiency, conserve resources, and reduce environmental impact. Through simulation and optimization using Aspen Plus, the process can be fine-tuned for maximum efficiency, highlighting the importance of technological innovation in achieving sustainability goals within the chemical engineering domain.

This approach aligns with the principles of sustainability by minimizing energy usage, maximizing resource utilization, and mitigating environmental pollution associated with traditional separation processes. This also contributes to

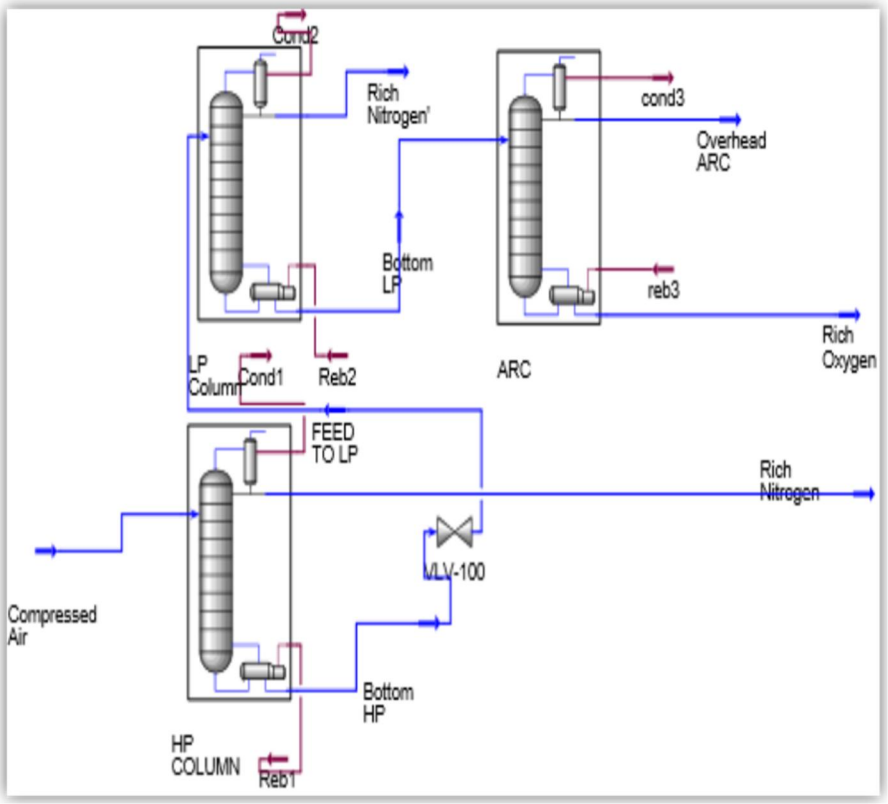


Figure 2. Conventional cryogenic distillation process for an air separation unit (extracted from (Omer et al. 2017).

several Sustainable Development Goals (SDGs). By focusing on energy efficiency and resource conservation, the method directly supports SDG 7 (Affordable and Clean Energy) and SDG 12 (Responsible Consumption and Production). Additionally, by reducing environmental impact through decreased energy consumption and optimized resource utilization, the approach aligns with SDG 13 (Climate Action) and SDG 9 (Industry, Innovation, and Infrastructure). Furthermore, the use of technological innovation, such as simulation and optimization with Aspen Plus, underscores progress toward SDG 9.

Method

The feed used in the simulation process in this work was a 100 kmol/hr gas mixture with the composition of 0.257 mol Xe, 0.336 mol Kr, and 0.407 mol Ar, similar to the study by Matizakurima (Matizakurima 2020). The noble gas mixture of Xe, Kr, and Ar is typically recovered as by-products of the air separation process by the use of auxiliary columns. The temperature and pressure conditions of the feed in this study were at −185 °C and 1.2 bar, respectively, similar to the by-product of air separation in the study by Aneke and Wang (2015). Table 1 summarizes the stream conditions of the feed gas mixture used in this study.

Table 1. Gas mixture feed conditions.

Total molar flow (kmol/hr)	100
Xe composition (mol/mol)	0.257
Kr composition (mol/mol)	0.336
Ar composition (mol/mol)	0.407
Temperature (°C)	−185
Pressure (bar)	1.2

The conventional process of air separation utilizes two columns in series, a high-pressure (5.6 bar) and a low-pressure (1.5 bar) column in a direct distillation sequence (Linde 2020). These were specified as the operation pressures for the high-pressure (C1) and low-pressure columns (C2) in the conventional distillation process simulated in this study. The heaviest component in the system, Xe, with a boiling point of approximately −108 °C (Linde 2020), is recovered as the bottom stream of the second column. The stream 'Bott2' in Figure 3 was the Xe-rich stream recovered, with Ar as the lightest component

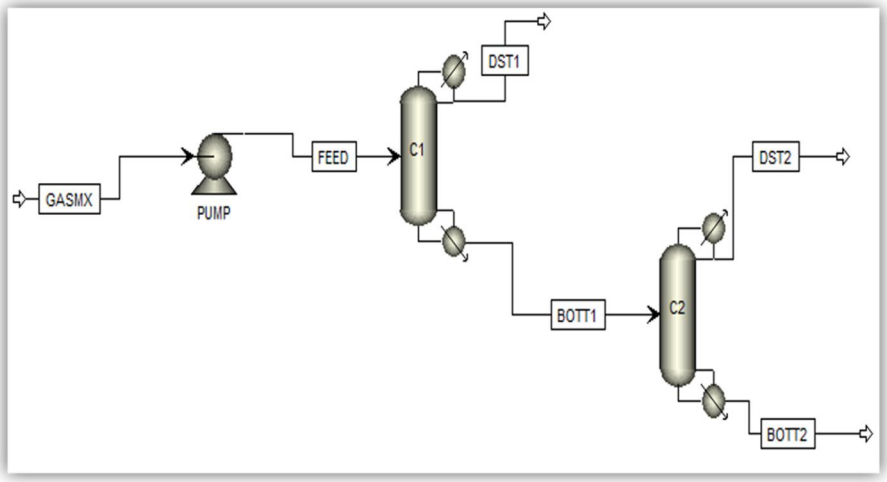


Figure 3. Simulation of the conventional cryogenic distillation separation.

mainly recovered in the distillate stream of column C1 viz. stream DST1, and Kr in that of column C2, stream DST2.

The conventional distillation process was initially simulated with the shortcut design performed by the DSTWU (Distillation Shortcut with Winn-Underwood-Gilliland) model on the Aspen Plus software. This initial simulation determined the minimum reflux ratio (RR) and the minimum number of stages. The actual number of stages was determined from the obtained concentration profiles, focusing on the required number of stages to achieve the target product purity of 0.9999 mol Xe. The number of stages was found to be 25 and 10 for the high-pressure and low-pressure columns, respectively. The number of stages was kept consistent across all alternative processes simulated for a fair comparison between configurations, as the system performance can be influenced by the number of stages (Larijani et al. 2019).

The process was then simulated with the RADFRAC model for more rigorous computations. In this distillation model, the Peng-Robinson equation of state (PR-EOS) was selected for the thermodynamic description of the process during simulations. The suitability of the PR-EOS thermodynamic model for cryogenic distillation has been demonstrated by several authors. Matizakurima (2020) reported that the strongest adherence of simulation results to the VLE experimental data was found for the simulations conducted with the PR-EOS compared to the modified Peng-Robinson (PRWS) and the Predictive Soave-Redlich-Kwong PRSK) for Xe + Kr system at low temperatures. Leiva et al. (2020) found simulation results to be within 1.5% error relative to operational Air Liquide plant data from using the PR-EOS in the simulation of a cryogenic distillation process.

The performance of each column and the energy consumption for the separation during the distillation processes are primarily influenced by the feed stages and the reflux/boil-up ratios (Larijani et al. 2019). The effects of these critical parameters have to be evaluated and adapted for the specific system for optimal (high recovery of key components, low energy consumption) performance. The relationships between these critical parameters and the process performance were observed through sensitivity analyses, from which the optimal setpoints of the critical parameters were identified.

A Conventional distillation process was simulated to be used as the basis for comparison of alternative process configurations. Thermally coupled and Hydrate–hybrid distillation configurations were simulated as alternative configurations. Each simulated configuration aimed to separate the same gas mixture feed using two columns, with the number of stages (as determined from the shortcut design DSTWU) in each column kept constant and the column pressures informed by common operating pressures as reported by Linde (2020). The feed stages and the reflux/boil-up ratios were optimized for each

column in each configuration for an efficient separation, characterized by maximum component separation for minimum energy consumption. This approach was similar to the simulation and optimization of a distillation process through sensitivity analyses conducted in the study by Saxena et al. (2017) and Larijani et al. (2019).

Conventional process

The feed stage and molar reflux ratio (RR) were the critical parameters influencing the performance of the cryogenic distillation separation as indicated by the Xe recovery and total duty. Therefore, an optimization of the columns in the conventional distillation configuration was performed based on the sensitivity analyses representing the relationship between these key process parameters. The primary objectives of the optimization were to identify the feed stage and reflux/boil-up ratio that reduce the total energy duty of each column, whilst maintaining a high Xe concentration of 99.99 mol%. In addition to the specifications of the number of stages and operating pressures, the identified optimal feed stage and molar reflux ratio are shown in Table 2. The optimal feed stage and reflux ratio were selected for a high Xe recovery at minimum total energy duty for this configuration, as informed by the conducted sensitivity analyses.

During sensitivity analyses, the Aspen software performs numerous simulations and computations, initialized by guesstimates, at incremental levels of the independent variable (feed stage or molar reflux ratio) whilst recording the changes in the system response(s) of interest (Xe concentration in Xe-recovery stream or total duty). During simulation, computations are conducted within system constraints as set by the specified feed stream conditions and models (RADFRAC + PR-EOS). The optimal feed stage and reflux ratio can then be identified based on the observed relationships with the Xe-recovery and total duty for the desired system performance.

Table 2. Column main operating specifications for the simulations of the conventional process.

	Column C1	Column C2
Pressure	5.6 bar	1.5 bar
Number of stages	25	10
Feed stage	23	3
Molar reflux ratio	0.031	0.5

After the optimal feed stage and reflux ratio were identified, the simulation was carried out again at the optimal column specifications for minimum duty requirement and high Xe recovery, as desired. The alternative process configurations were optimized similarly. The optimized simulated conventional distillation configuration was used as a benchmark for comparison with the alternative configurations.

Thermal coupling process

In this study, thermally coupled distillation sequences were simulated as an alternative process to reduce the energy required to achieve the same effective separation as the conventional distillation process. Thermally coupled distillation sequences are reconfigurations of the Petyluk distillation sequence. In a typical conventional distillation configuration for a ternary mixture, the lightest component is separated at the top of the first column. The intermediate component reaches a maximum concentration near the feed stage and decreases toward the bottom of the column as remixing of the mixture occurs before feeding into the second column. Additional energy is then required to re-purify and separate the re-mixed mixture (Saxena et al. 2017).

A Petyluk distillation sequence aims to achieve energy savings by using a pre-fractionator to reduce the energy requirement for the remixing of the intermediate component. The *partially* separated mixture is fed into one main column, in which the light and heavy components can be separated at the top and bottom of the column, respectively, whilst the intermediate component can be separated at the stage of highest concentration. This distillation sequence has the potential to achieve energy reductions through the use of a pre-fractionator and one main column. Notwithstanding, the main operational challenge with this configuration is the requirement to maintain the upper and lower parts of both the pre-fractionator and main column at different pressures, simultaneously, for a bi-directional vapor flow. However, it has been discussed that such a pressure profile is not always feasible and

renders this configuration nearly impractical (Saxena et al. 2017).

Thermally coupled systems aim to achieve similar energy reductions whilst circumventing the operational challenge by maintaining unidirectional vapor flows between two columns as recycle streams. The recycle streams are drawn from the feed stage where the concentration of the intermediate component is the highest, and fed to the subsequent column for further separation before remixing. The total duty required for the distillation separation is reduced by eliminating either a reboiler or condenser in each column and the use of the intermediate recycle streams to achieve the desired separation. Previous studies have achieved energy savings of approximately 35%, with respect to a conventional distillation configuration, through thermally coupled configurations (Saxena et al. 2017). The arrangements of the thermally coupled systems as shown in the study by Saxena et al. (2017) to achieve energy duty reductions, were used in this study. The thermally coupled configurations differed by the directions of the vapor flows between the two columns.

Two thermally coupled systems were simulated (Thermal Couples 1 and 2) as shown in Figures 4 and 5. In Thermal Couple 1, column C1 is

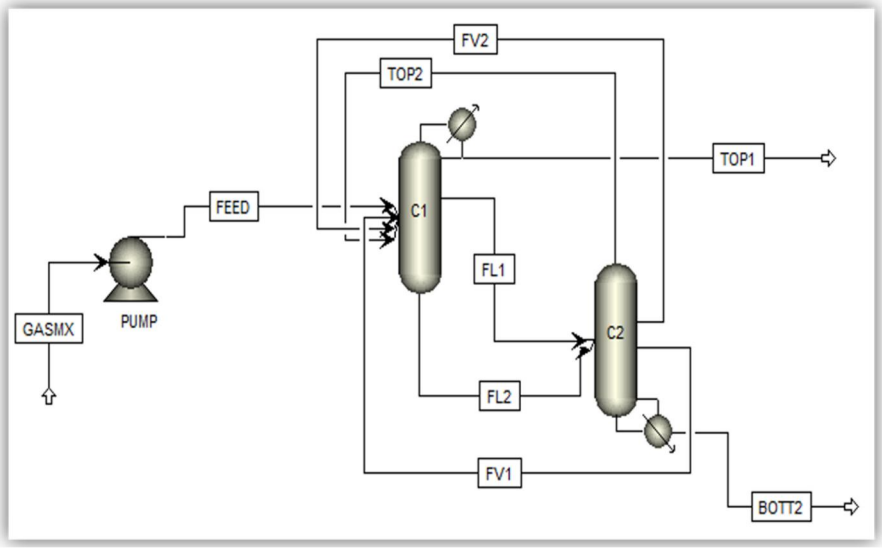


Figure 4. Simulated process Thermal Couple 1.

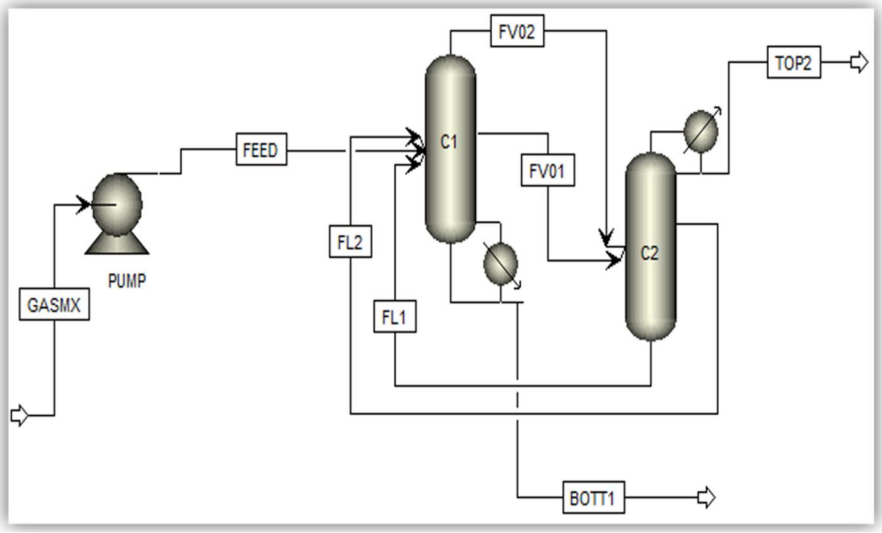


Figure 5. Simulated process Thermal Couple 2.

without a reboiler and column C2 is without a condenser. The Xe-rich stream is recovered as the bottom stream of column C2. The unidirectional flow of the streams of the same phase required for the operation of such thermally coupled systems is maintained by recycling the vapor streams FV1, FV2, and TOP2 to column C1. The liquid streams FL1 and FL2 are fed to column C2. For these thermally coupled systems, both columns were operated at the same high pressure to circumvent operational challenges associated with the pressure profile across the two columns for a unidirectional flow of the vapor intermediate streams.

Similarly, Thermal Couple 2 was simulated with column C1 without a condenser and C2 without a reboiler. The liquid intermediate streams FL1 and FL2 are recycled back to column C1 for more separation of the Xe, and vapor streams FV01 and FV02 were fed into column C2 with substantially low concentrations of Xe. The Xe-rich stream was recovered as the bottom stream of column C1. In both these thermally coupled systems, the key process parameters were identified as the total duty of each column, molar reflux (RR) and boil-up reflux ratios (BR), and the feed stages. Table 3 displays the optimal reflux and boil-up ratios identified from the sensitivity analyses.

Table 3. Thermally coupled system's main specifications.

		Column C1	Column C2
Thermal Couple 1	Molar RR*	1	–
	Molar BR**	–	4
Thermal Couple 2	Molar RR	–	0.05
	Molar BR	3	–

*Reflux Ratio (RR).
**Boil-up Ratios (BR).

Gas hydrates separation method

The separation method by the gas hydrates as a potential alternative was simulated based on the experimental work of Matizakurima (2020). Figure 6 displays a concept for Xe separation from the mixture of Ar, Kr, and Xe, using gas hydrates technology. As shown in the figure, after hydrate formation, Xe is concentrated in the hydrate phase because of the lower hydrate dissociation condition of Xe compared to Ar and Kr. Then, the gas phase which is concentrated with Ar, and Kr can be separated by vacuuming. Finally, using gas hydrate dissociation, Xe is concentrated in the gas phase.

The concentration of Xe from 0.257 to 0.613 mol/mol was demonstrated at the lab scale under conditions of low temperature and high pressure over one hydrate stage in the study by Matizakurima (2020). The experimental results indicated that the concentration of xenon had the most significant increase in the first and second hydrate stages, with a 20% energy cost reduction over cryogenic distillation. The experimental conditions for the separation demonstrated by Matizakurima are summarized in Table 4.

The separation by formation and dissociation of gas hydrates is understood to be a physical separation. In this study, only a simplified simulation of the gas hydrate separation was conducted. In this simulation, the separation was represented as a gas-solid extraction process in

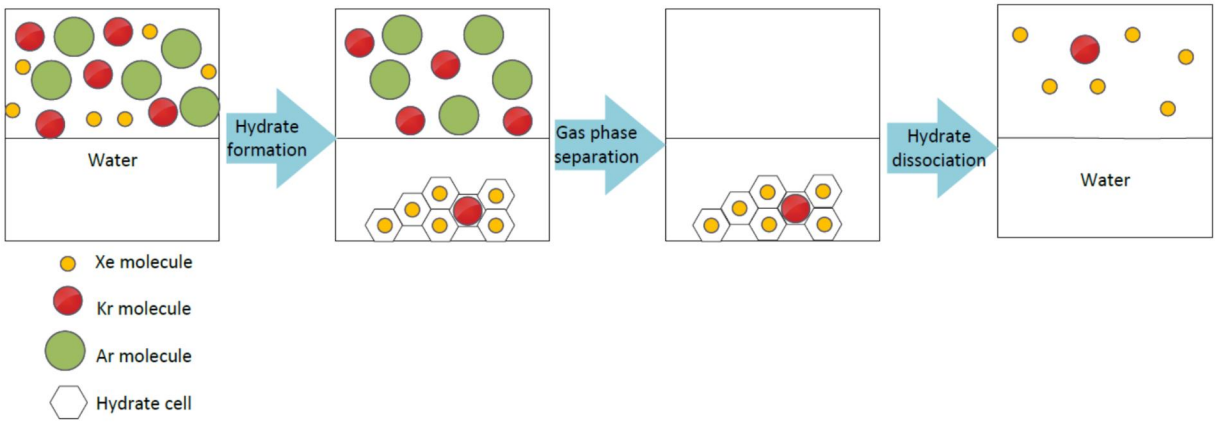


Figure 6. A concept of Xe separation from the mixture of Ar, Kr, and Xe using the gas hydrate method.

Aspen, with specifications (temperature, pressure, concentration changes, and duty requirements) directly based on the hydrate formation and dissociation conditions experimentally validated in the study by Matizakurima (2020). This allowed this approximate simulation to be representative of actual experimental conditions and outcomes for the gas hydrate separation considered in this study.

The process was heat-integrated by implementing heat exchangers between the reactor outlet streams and the gas feed mixture, effectively eliminating the energy required to raise the inlet temperature from −185 °C to −0.99 °C (272.16 K) for the hydrate formation. Gas hydrate formation is exothermic (Babaee 2015), releasing an amount of energy equivalent to that required for dissociation (Matizakurima 2020). This improves the thermodynamic efficiency of the process by allowing for a potential adiabatic operation through heat exchange between the hydrate formation and hydrate dissociation reactors. For the simulation, energy duties were specified in both reactors to represent the required cooling and heating loads. In the overall duty evaluation after simulations, an ideal net duty of zero was assumed, based on an assumed complete heat exchange between the reactors during the exothermic and endothermic formation and dissociation processes, respectively. As such, compression to meet the hydrate formation pressure remained the main operation consuming significant amounts of energy in the process.

Through the separation method of gas hydrates, the Xe concentration in the inlet gas mixture (stream GASFEED0) was increased from 0.257 to 0.613 mol/mol. The Xe-concentrated gas mixture is released from hydrate dissociation and can be used to pre-heat the gas feed, thus being liquefied (stream FEED) before being fed into the distillation section, as shown in Figure 7.

Table 4. Conditions for the separation of Xe by gas hydrates.

	Temperature (K)	Pressure (bar)
Hydrate formation conditions	272.16	20.6 bar
Gas Mixture Composition		
	*Feed Composition	*Concentrated composition
Xe (mol/mol)	0.257	0.613
Kr (mol/mol)	0.336	0.281
Ar (mol/mol)	0.407	0.106

*Streams in the simulated hydrate separation, Figure 7.

Hybrid process

A Hydrate–Hybrid process was proposed as a separation method to achieve further energy savings by combining the Gas Hydrate process with the Thermally Coupled distillation configuration. The idea was to use the hydrate separation to pre-concentrate the Xe in the feed gas mixture, before being fed to the cryogenic distillation section for further high-purity separation. This

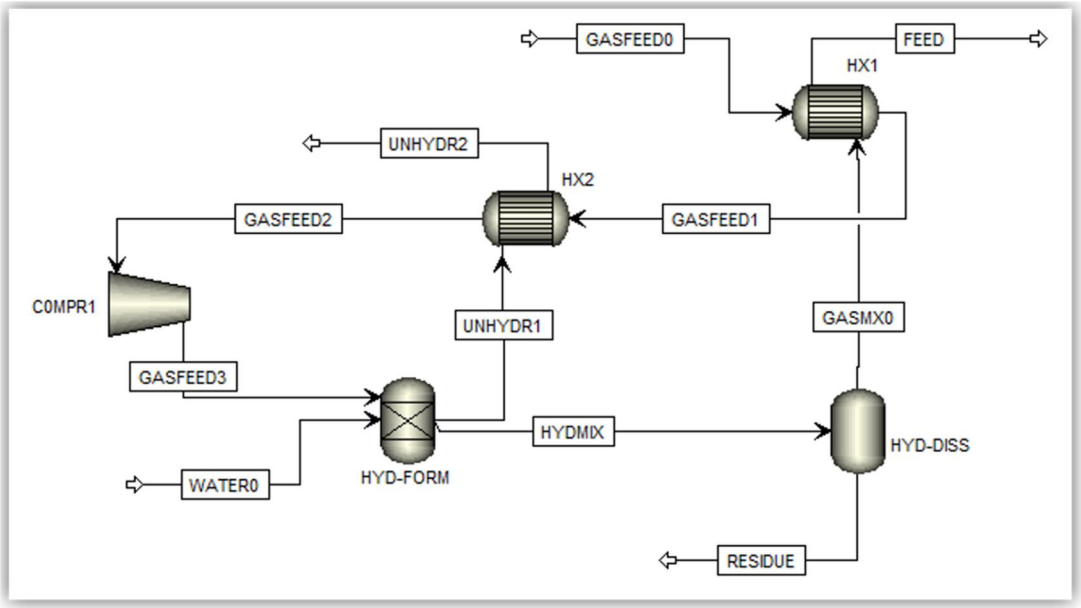


Figure 7. Simulated gas hydrate separation process as an extraction process.

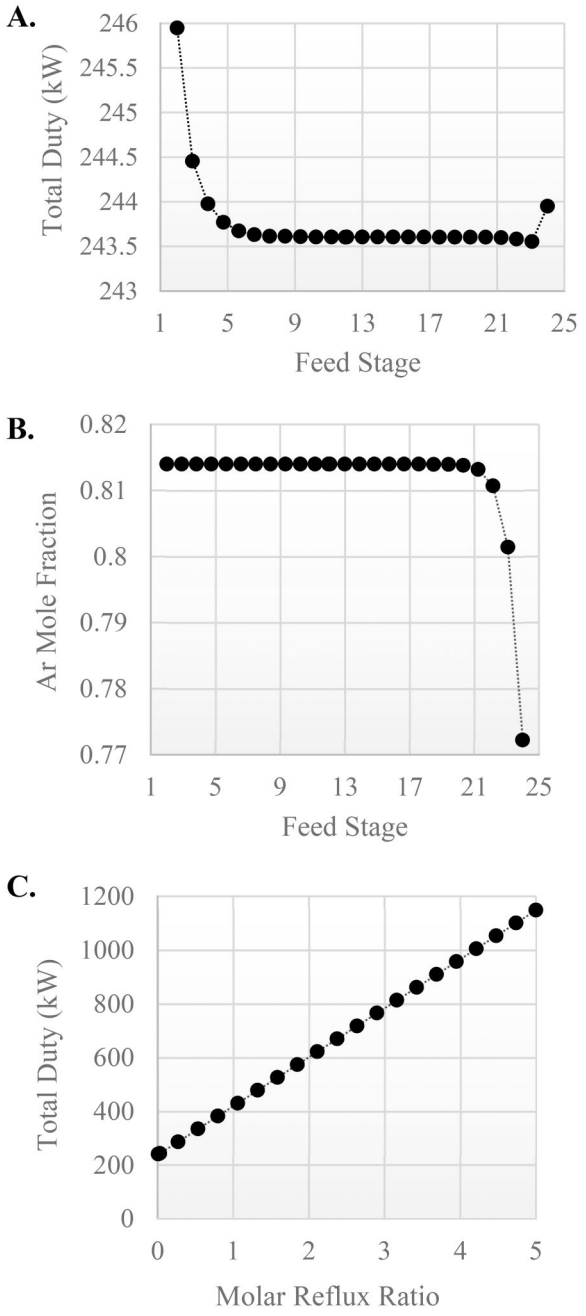


Figure 8. Sensitivity analysis results for column C1.

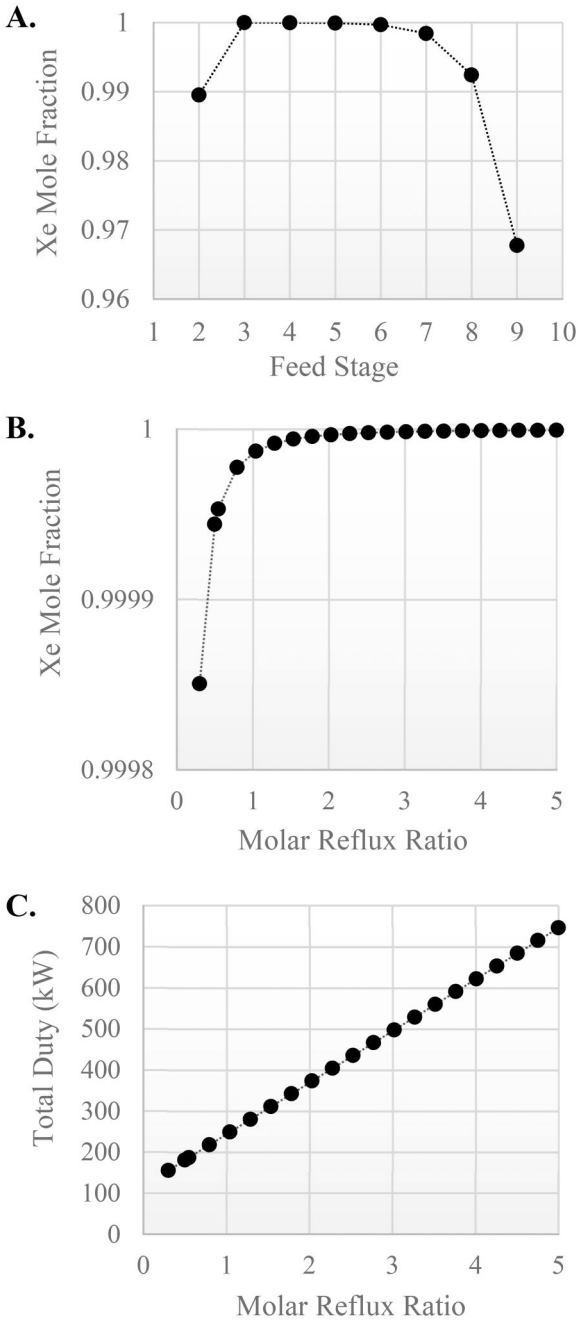


Figure 9. Sensitivity analysis results for column C2.

approach was anticipated to further reduce the total distillation duty by making the separation easier, owing to a higher concentration of the key component, Xe, present in the feed.

In this study, two Hybrid processes were simulated—Hybrid 1 and Hybrid 2. The Hybrid processes 1 and 2, were simulated by combining the simulated Hydrate separation with the systems Thermal Couple 1 and 2, respectively. These configurations aimed to reduce the energy duty required for the separation with the Hydrate section serving the purpose of pre-concentrating the Xe in the gas mixture, before being fed into the distillation section to achieve further separation to the higher target concentration.

Results and discussion

Sensitivity analyses for optimal column parameters

Figures 8 and 9 demonstrate the sensitivity analysis results for columns C1 and C2, respectively,

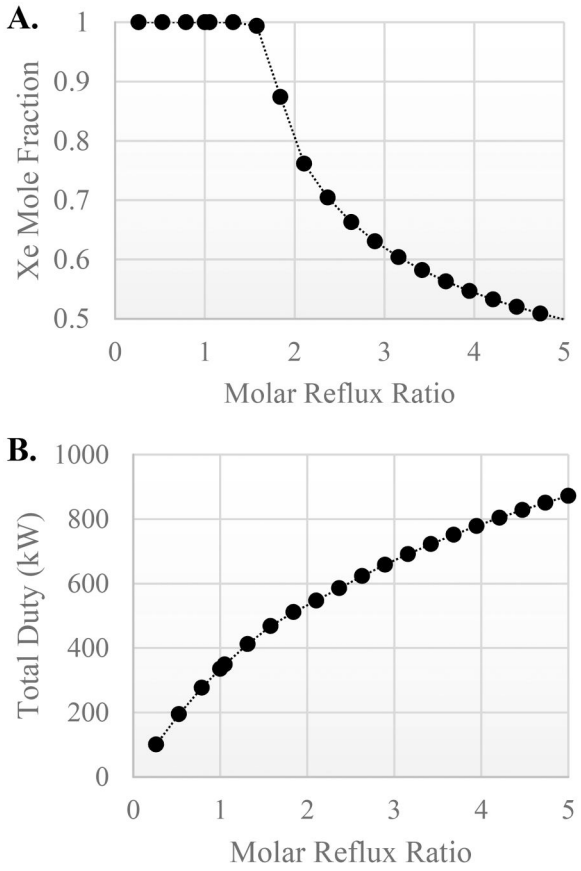


Figure 10. Thermal Couple 1, column C1 sensitivity analysis.

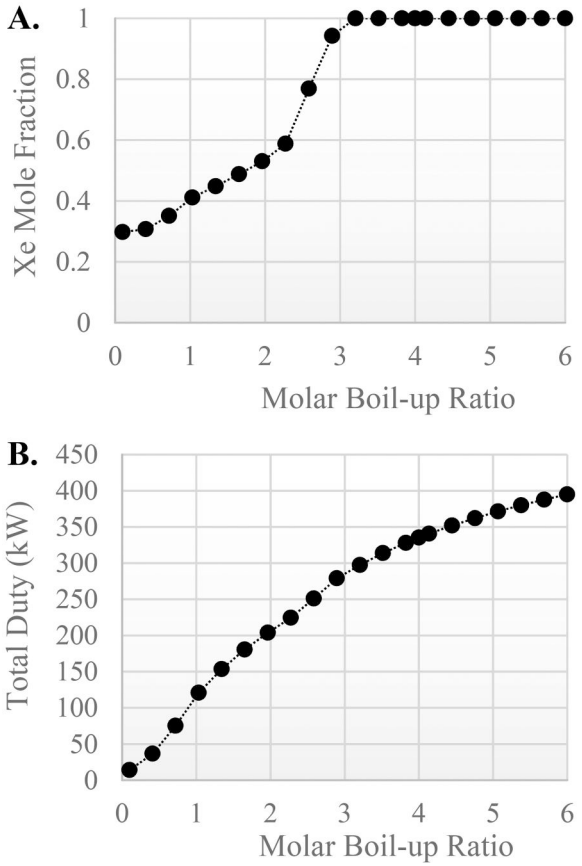


Figure 11. Thermal Couple 1, column C2 sensitivity analysis.

in the conventional distillation process. The sensitivity analysis results shown in Figure 8(C) indicated a directly proportional relationship between the total duty of column C1 and the molar reflux ratio. This was congruent with the expected relationship between the two parameters. Saxena et al. (2017) found a similar proportional relationship between the molar reflux ratio and the column heat duty. It is understood that increasing the reflux ratio increases the amount of the distillate condensed and fed back into the column causing the reboiler to heat more liquid, thus increasing the overall duty required. Therefore, the lowest feasible reflux ratio required to meet an effective separation was desired—which was 0.031. Below this identified optimal reflux ratio, insufficient distillate was fed back into the column, leading to the drying of stages.

Figure 8(A and B) showed that introducing the gas mixture feed at stage 23 simultaneously allowed operation at the lowest total duty whilst effectively separating Ar as the lightest component in the first column (C1), reaching a concentration of approximately 0.8 mol/mol. A separation of Ar in the first column is crucial to ease the separation in the second column (C2) for obtaining a Xe-rich stream as the bottom stream of column 2. In Figure 9(C), a similar proportional relationship between the molar reflux ratio and the total duty for column C2 was observed. As such, the lowest possible reflux ratio for an effective separation was desired. Figure 9(B) communicates that the target concentration of Xe in the bottom stream of column C2 could be achieved at the lowest reflux ratio of approximately 0.5. The bottom stream from column C1 was fed onto stage 3 of column C2 to achieve the most effective separation (>0.9999 mol/mol Xe), as supported by Figure 9(A).

Figures 10 and 11 show the sensitivity analysis results for columns C1 and C2 in the thermal couple method, respectively. In Figures 10 and 11(B) proportional relationships between the ratios (boil-up and reflux ratios) and the total column duty, similar to the conventional process, were observed. The lowest possible boil-up and reflux

ratios to achieve the separation of Xe were desired, as the objective of the optimization was to minimize the total duty required for the separation. The same principle applies as with the conventional distillation configuration, the total column duty rises with an increase in the reflux/boil-up ratios as more mixture is fed back into the column demanding greater cooling and heating duties in the condenser and reboiler, respectively.

Figure 10(A) shows that a minimum reflux ratio of approximately 0.3 was required to reach the target Xe concentration of 99.99 mol%. However, it was found that at such a low reflux ratio, the overall flow rate of the Xe-recovery stream (stream BOTT2 in Figure 4) was significantly reduced. This indicated a tradeoff between achieving high-purity separations and maintaining sufficient flow rates. The lowest reflux ratio to achieve the target Xe concentration without compromising the overall flow rate of the Xe-recovery stream was found to be 1. For column C2, a minimum boil-up ratio of 3.2 was required to achieve the targeted high Xe concentration. Similar to column C1, a minimum boil-up ratio of 4 was found to simultaneously reach the high Xe concentration and avoid substantially low flow rates of the Xe-rich stream as the bottom stream of column C2. The system of Thermal Couple 2 was also optimized similarly, selecting the optimal feed stages and reflux/boil-up ratios from sensitivity analyses (Figure 11).

Performance comparisons of the optimized alternative configurations

In total, five separation processes were simulated and optimized through sensitivity analyses as discussed in the above sections. The total duties computed by the software after the simulation of each optimized configuration were collected and compared. The configurations were compared based on the total energy savings in the distillation section and the performance of the overall system, with the conventional distillation configuration as the benchmark.

The energy savings were determined as the percentage decrease of the total duty demand relative to that of the Conventional process. An overall Xe system recovery parameter was defined as the ratio of the mole amount of Xe in the recovered Xe-rich stream of each process and that in the inlet gas mixture.

$$Energy\ savings\ (\%) = \frac{Alternative\ process\ total\ duty\ (kW) - Conventional\ process\ total\ duty\ (kW)}{Conventional\ process\ total\ duty\ (kW)} \quad (1)$$

$$Xe\ system\ recovery\ (\%) = \frac{Xe\ amount\ in\ Xe-recovery\ stream(mol)}{Xe\ amount\ in\ gas\ mixture\ feed(mol)} \quad (2)$$

In Figure 12, the total energy duty required in the distillation section to achieve the separation is represented for each process. Both the thermally coupled processes achieved the Xe separation with a total duty demand of less than 400 kW, lower than the duty demand for the conventional distillation configuration. The saving in the total duty demand was consequential to the elimination of a reboiler or condenser in each column, as this reduced the total heating and cooling duty required during the separation. The use of intermediate recycle streams between the columns also contributed to these observed energy savings by reducing the total flow to the reboiler and condenser, reducing the heating and cooling duty demands, respectively.

In addition to reducing the total duty demand, the recovery of Xe was another important consideration in the performance of each system. Table 5 displays that although Thermal Couple 1 (23%) achieved greater energy savings than Thermal Couple 2 (7.5%), this was at the expense of the system Xe recovery. The low Xe recovery (0.61) in Thermal Couple 1 was attributed to the substantial loss of Xe in the distillate stream of column C1 (see Figure 4). This observation

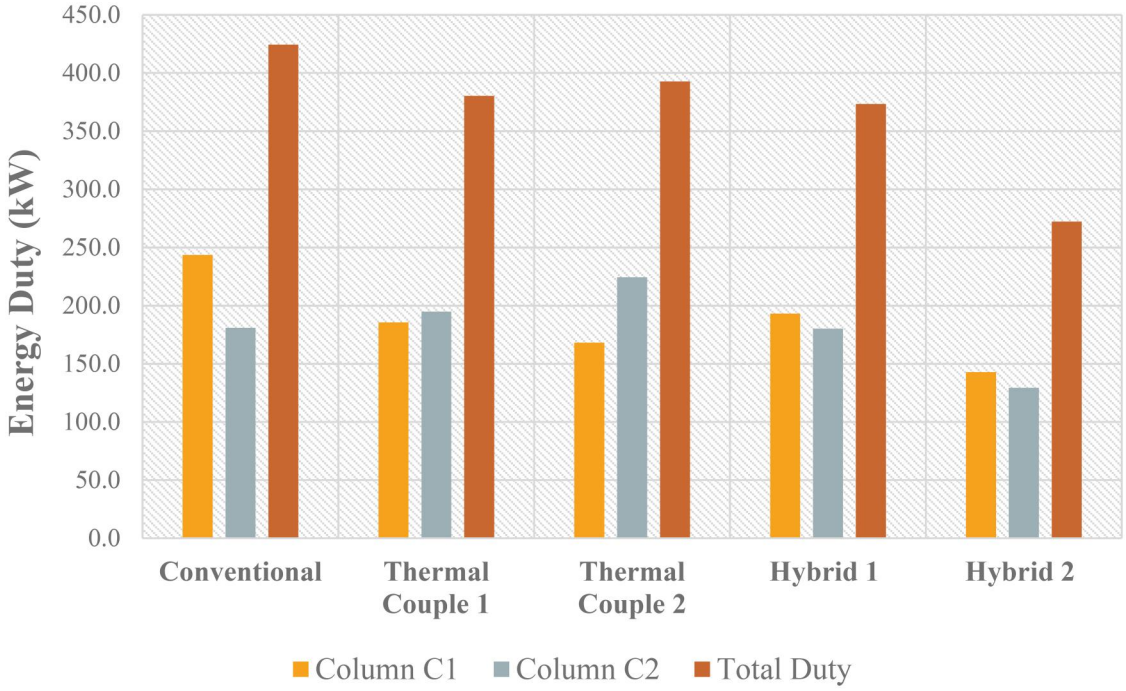


Figure 12. Energy comparisons of suggested processes (Hybrids 1 and 2—a combination of Thermal Couple 1 and 2, respectively, with the hydrate separation).

Table 5. Energy savings and Xe recovery comparisons of simulated processes.

Configuration	Xe system recovery	*Total energy savings (%)
Conventional	0.98	–
Thermal Couple 1	0.61	23
Thermal Couple 2	0.94	7.5
Hybrid 1	0.97	12.0
Hybrid 2	0.99	35.8

*Energy savings in the distillation system.

indicated that at the selected optimal reflux ratio of 1 for column C1 of Thermal Couple 1, insufficient distillate was recycled back into the column, leading to a less efficient separation and Xe losses in the top distillate stream.

In Thermal Couple 2 (Figure 5), column C1 does not have a condenser, and the column-top stream is fed into column C2 to achieve further Xe separation. This configuration minimized Xe losses as evidenced by a substantially greater Xe-recovery (0.94). Therefore, Thermal Couple 2 trumps Thermal Couple 1, regardless of having lower energy savings, due to a higher Xe recovery achieved, as the primary aim of this study.

Table 5 indicates that the configuration of Hybrid 2 was found to be the most efficient system, achieving a Xe recovery (0.99) marginally greater than that for the Conventional process (0.98), and all the other considered configurations. Hybrid 2 also achieved a high Xe system recovery with the lowest energy consumption (35.8% energy savings) in the distillation section compared to the other considered configurations. The simulation process for the Hybrid 2 method is shown in Figure 13. This configuration is a combination of the gas hydrate separation, to pre-concentrate Xe in the gas feed, and a thermally-coupled distillation configuration similar to Thermal Couple 2, for an energy-efficient high-purity separation.

A high-level economic evaluation was performed based on the total cooling, heating, and electric duties computed in the simulation of each optimized configuration. Utility price rates ($/kJ) obtained from the Aspen software and an assumed operation heuristic of 8000 h/year were used to determine annual operating costs (AOC). The economic evaluation was primarily based on the AOC as the key economic factor directly related to the energy-intensiveness of the process.

Consequential to the energy savings achieved, the thermally coupled systems and hybrid processes exhibited lower operating costs compared to the conventional configuration. Figure 14 illustrates that, whilst the other configurations

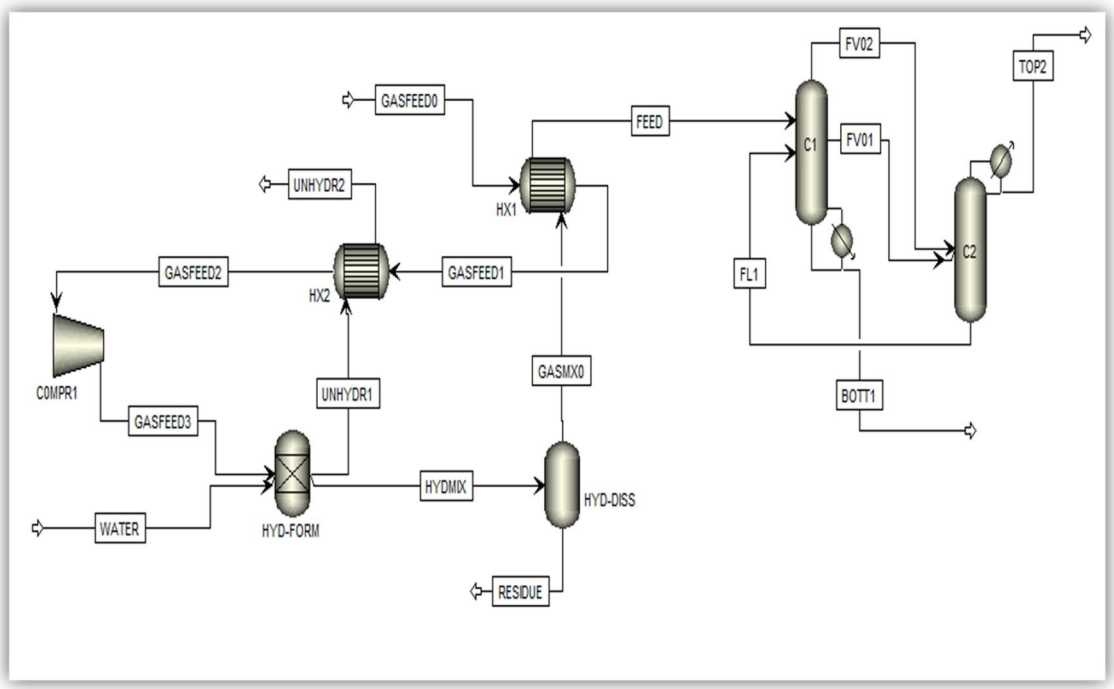


Figure 13. Hydrate–Hybrid 2 process with the highest Xe recovery and energy savings for the distillation system.

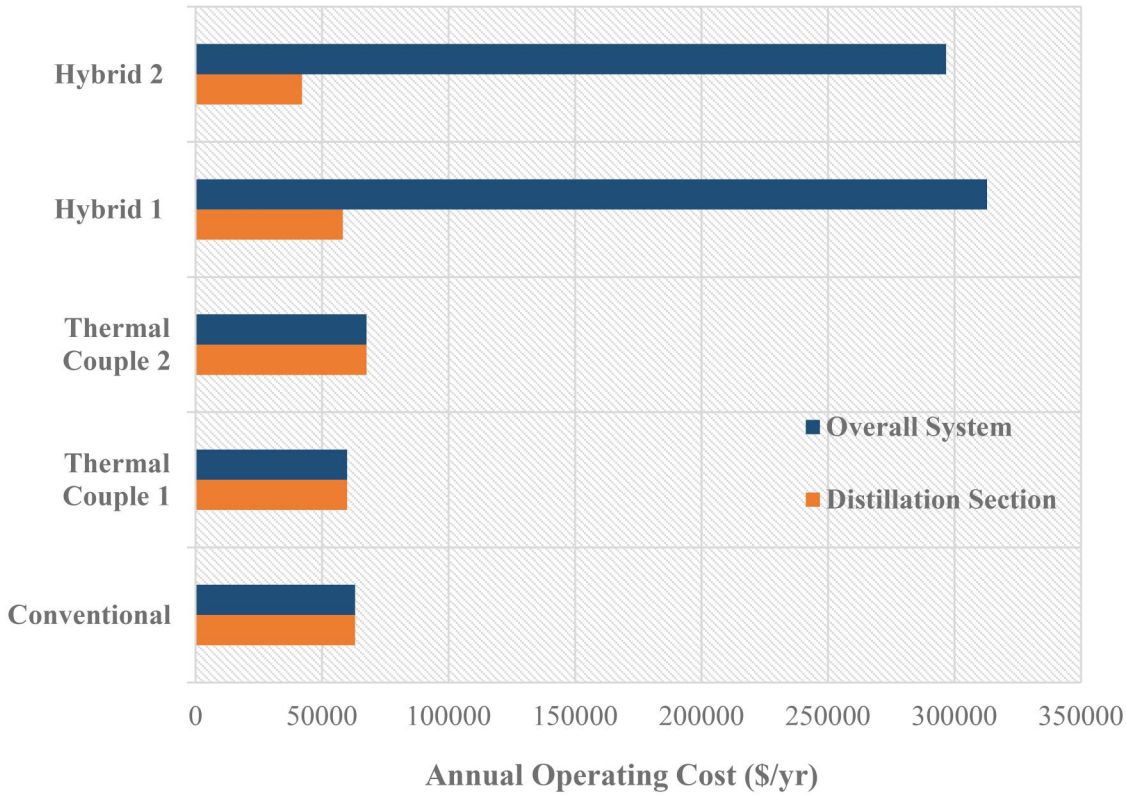


Figure 14. Annual operating costs (AOC) of the simulated separation processes.

demonstrated only moderate savings in operating costs—less than 10% relative to the conventional process—Hybrid 2 achieved the most substantial reduction, with operating costs for the distillation section decreased by approximately 33%. Hybrid 2 (Figure 13) achieves the most energy savings by pre-concentrating Xe in the gas mixture, which *eases*, by reducing energy requirements, the

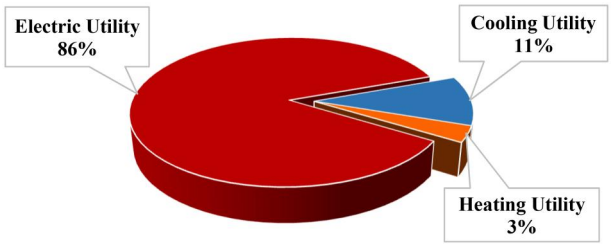


Figure 15. Distribution of AOC for the overall process of Hybrid 2.

separation performed by the distillation section due to the mixture compositions being closer to the target purity levels. Additionally, eliminating a reboiler and condenser in the columns through the use of intermediate streams reduces the total heating and cooling duties required in the system.

The intermediate stream (FV01) allows for a high Xe recovery in the bottom of column C1, by feeding into column C2 before the remixing of the intermediate component (Kr) with the mixture toward the bottom of column C1 (Saxena et al. 2017). Purging the intermediate component from the stage of highest concentration (close to the feed stage) in column C1 to column C2 for further separation minimizes the remixing whilst reducing the load to the reboiler, and maintaining a high concentration of Xe in the bottom stream of column C1.

However, it can be seen that for the overall system, the operating costs were escalated for the Hybrid processes. This was attributed to the inclusion of the operating costs associated with the Hydrate section. A net duty of zero was assumed between the hydrate formation and dissociation reactors as supported by the postulation that the hydrate formation–dissociation process can be achieved adiabatically through heat integration (Matizakurima 2020). The breakdown of the AOC for the overall system of Hybrid 2 was considered. Figure 15 shows that approximately 86% of the total operating costs arise from electric utility expenses, which were mainly attributed to the compressor (COMPR1) in the hydrate section of the Hybrid process. This was due to the intense gas compression from 1.2 bar (GASFEED2) to 20.6 bar (GASFEED3) required to meet the pressure conditions for gas hydrate formation, as shown in Figure 13.

Conclusion

The present work demonstrated the separation of Xe from a noble gas mixture of Xe, Kr, and Ar by cryogenic distillation through Aspen Plus simulations. Thermally coupled distillation sequences, Thermal Couple 1 and 2, were simulated as alternative distillation configurations to achieve a high-purity Xe separation with reduced energy consumption relative to a conventional cryogenic distillation sequence. Separation through gas hydrates was also considered as an alternative separation method. In this study, an approximate simulation of the gas hydrate separation process was conducted, directly based on experimentally validated data from a previous study demonstrating the concentration of Xe in Xe + Kr + Ar gas mixture through gas hydrates.

In total, five two-column distillation configurations were simulated viz.; a Conventional distillation sequence, two Thermally Coupled configurations, and Hybrid configurations which combined a gas hydrate separation with the thermally coupled sequences. All configurations were optimized through sensitivity analyses for an efficient Xe separation at reduced duty demands. The optimized configurations were compared based on total duty demand and Xe recovery, with the conventional process as the benchmark.

Hybrid 2, a combination of the Hydrate separation and Thermal Couple 2, was proposed as the most efficient configuration for the Xe separation. This was motivated by the configuration Hybrid 2 achieving the highest Xe recovery of 99 mol% with energy savings of ≈36% and annual operating costs reduction of ≈33% for the cryogenic distillation separation, compared to the conventional distillation sequence. The use of gas hydrate separation to pre-concentrate Xe in the feed gas mixture reduced the total duty demand for the high-purity separation achieved by the distillation section in this hybrid configuration.

A net-zero duty demand for the gas hydrate separation was assumed based on the postulation that hydrate formation and dissociation can be carried out adiabatically through heat integration. It was also found that through heat exchange with the outlet streams after hydrate formation and dissociation, the additional heating duty

required to raise the feed gas mixture to the temperature level for gas hydrate separation could be eliminated. However, it was found that the intense compression of the feed gas mixture (1.2 to 20.6 bar) required to meet gas hydrates formation conditions dramatically escalated the overall operating costs of the hybrid configuration, which can be an economic disincentive.

Gas hydrate promoters, such as TBAB, are recommended as a potential solution to moderate, by decreasing the pressure and increasing temperature conditions required for the formation of gas hydrates (Babaee 2015). This would eliminate the intense compression in the hydrate section and reduce the total operating costs for the overall system of Hybrid 2, making it more economically attractive as an alternative process for Xe separation and recovery. Since Aspen Plus does not offer dedicated packages for gas hydrate simulations, a comprehensive simulation of the gas hydrate separation process is recommended for future work. This is to capture the thermodynamic behavior more accurately relative to the simplified simulation conducted in this study based on experimental data, and potentially corroborate the findings.

The proposed hybrid separation methods show the potential to substantially reduce energy consumption and operating costs, which directly contribute to lowering greenhouse gas emissions and reducing reliance on nonrenewable energy sources. By achieving high xenon recovery rates efficiently, these methods promote resource efficiency, minimize waste, and maximize the utility of raw materials. Such advancements in separation technology align with sustainable practices, making industrial processes more environmentally friendly and economically viable.

Disclosure statement

No potential conflict of interest was reported by the author(s).

References

Abedini R, Nezhadmoghadam A. 2010. Application of membrane in gas separation processes: its suitability and mechanisms. Petrol Coal. 52(2):69–80.

Aneke M, Wang M. 2015. Potential for improving the energy efficiency of cryogenic air separation unit (ASU) using binary heat recovery cycles. Appl Therm Eng. 81: 223–231. doi: 10.1016/j.applthermaleng.2015.02.034.

Babaee S. 2015. Hydrate phase equilibrium studies for Xe, Ar, Kr and CF4 in the presence of TBAB aqueous solutions. Durban: School of Engineering, University of KwaZulu-Natal.

Babaee S, Hashemi H, Mohammadi AH, Naidoo P, Ramjugernath D. 2015. Experimental measurements and thermodynamic modeling of hydrate dissociation conditions for the xenon + TBAB+ water system. J Chem Eng Data. 60(5):1324–1330. doi: 10.1021/je5010092.

Babaee S, Hashemi H, Naidoo P, Ramjugernath D.,. 2021. Application of gas hydrates in the separation and purification of xenon from a mixture of xenon and argon. J Chem Eng Data. 66(10):3815–3825. doi: 10.1021/acs.jced.1c00435.

Baker RW. 2002. Membrane technology and applications (3rd Edition). Wiley Publications.

Banerjee D, Simon CM, Elsaidi SK, Haranczyk M, Thallapally PK. 2018. Xenon gas separation and storage using metal-organic frameworks. Chem. 4(3):466–494. doi: 10.1016/j.chempr.2017.12.025.

Benali M, Aydin B. 2010. Ethane/ethylene and propane/propylene separation in hybrid membrane distillation systems: optimization and economic analysis. Sep Purif Technol. 73(3):377–390. doi: 10.1016/j.seppur.2010.04.027.

Bernardo P, Clarizia G. 2013. 30 years of membrane technology for gas separation. Chem Eng Trans. 32:1999–2004.

Czaja AU, Trukhan N, Müller U. 2009. Industrial applications of metal–organic frameworks. Chem Soc Rev. 38(5): 1284–1293. doi: 10.1039/b804680h.

Eslamimanesh A, Mohammadi AH, Richon D, Naidoo P, Ramjugernath D. 2012. Application of gas hydrate formation in separation processes: a review of experimental studies. J Chem Thermodyn. 46:62–71. doi: 10.1016/j.jct.2011.10.006.

Forster P, et al. 2014. Characterization and modeling of materials for Kr–Xe separations. U. S. D. o. Energy. Las Vegas: University of Nevada.

FortuneBusinessInsights. 2020. Xenon Market Size, Share & COVID-19 Impact Analysis, By Type (N3, N4.5, and N5), By Application (Imaging & Lighting, Satellite, Electronics & Semiconductors, Medical, and Others), and Regional Forecast, 2022–2029. https://www.fortunebusinessinsights.com/xenon-market-101965.

Jensen NK, Rufford TE, Watson G, Zhang DK, Chan KI, May EF.,. 2012. Screening zeolites for gas separation applications involving methane, nitrogen, and carbon dioxide. J Chem Eng Data. 57(1):106–113. doi: 10.1021/je200817w.

Kang Z, Fan L, Sun D.,. 2017. Recent advances and challenges of metal–organic framework membranes for gas

separation. J Mater Chem A. 5(21):10073–10091. doi: 10.1039/C7TA01142C.

Kim E, Ko G, Seo Y., 2017. Greenhouse gas (CHF3) separation by gas hydrate formation. ACS Sustain Chem Eng. 5(6):5485–5492. doi: 10.1021/acssuschemeng.7b00821.

Kosinov N, Gascon J, Kapteijn F, Hensen EJM.,. 2016. Recent developments in zeolite membranes for gas separation. J Membr Sci. 499:65–79. doi: 10.1016/j.memsci.2015.10.049.

Kostoglou N, Koczwara C, Prehal C, Terziyska V, Babic B, Matovic B, Constantinides G, Tampaxis C, Charalambopoulou G, Steriotis T, et al. 2017. Nanoporous activated carbon cloth as a versatile material for hydrogen adsorption, selective gas separation and electrochemical energy storage. Nano Energy. 40:49–64. doi: 10.1016/j.nanoen.2017.07.056.

Kukulka W, Cendrowski K, Michalkiewicz B, Mijowska E. 2019. MOF-5 derived carbon as material for CO2 absorption. RSC Adv. 9(32):18527–18537. doi: 10.1039/c9ra01786k.

Larijani MA, Bayat M, Afshin H. 2019. Simulation and performance improvement of cryogenic distillation column, using enhanced predictive Peng–Robinson equation of state. Fluid Phase Equilib. 489:117–130. doi: 10.1016/j.fluid.2019.01.022.

Leiva CA, Poblete DA, Aguilera TL, Acuña CA, Quintero FJ. 2020. Air separation units (ASUs) simulation using Aspen Hysys® at Oxinor I of air liquid Chile S.A. plant. Polish J Chem Technol. 22(1):10–17. doi: 10.2478/pjct-2020-0003.

Linde. 2020. History and technological progress, cryogenic air separation.

Matizakurima F. 2020. Separation of noble gas mixtures of (Xe, Ar and Kr) using gas hydrate. Durban: Chemical Engineering Technology, University of KwaZulu-Natal.

Miandoab ES, Mousavi SH, Kentish SE, Scholes CA.,. 2021. Xenon and krypton separation by membranes at sub-ambient temperatures and its comparison with cryogenic distillation. Sep Purif Technol. 262:118349. doi: 10.1016/j.seppur.2021.118349.

Omer QM, et al. 2017. Simulation study for energy minimization and performance enhancement using cryogenic plate and packed bed column networks for air separation. Aust Chem Eng. 4(2):1–6.

Rizk J, Nemer M, Clodic D., 2012. A real column design exergy optimization of a cryogenic air separation unit. Energy (Oxford). 37(1):417–429. doi: 10.1016/j.energy.2011.11.012.

Saxena N, Mali N, Satpute S. 2017. Study of thermally coupled distillation systems for energy-efficient distillation. Sadhana (Bangalore). 42(1):119–128. doi: 10.1007/s12046-016-0580-x.

Sircar S, Golden TC, Rao MB. 1996. Activated carbon for gas separation and storage. Carbon. 34(1):1–12. doi: 10.1016/0008-6223(95)00128-X.

Sloan ED. 2010. Natural gas hydrates in flow assurance. Gulf Professional Publishing. Hardback ISBN: 9781856179454.

Vorotyntsev VM, Malyshev VM. 2011. Calculating the separation coefficients in argon, krypton and xenon gas mixture separation by gas hydrate crystallization. Russ J Phys Chem. 85(11):1990–1994. doi: 10.1134/S0036024411110343.

Vorotyntsev VM, Malyshev VM, Vorotyntsev IV, Battalov SV. 2016. Improving the efficiency of gas hydrate crystallization due to the application of gas separation membranes. Theor Found Chem Eng. 50(4):459–468. doi: 10.1134/S0040579516040473.

Yan R, Wang Z, Cui X, Ju Y, Sha H, Li S, Huang P, Wang X, Ma W, Fan Y, et al. 2021. PandaX-4T cryogenic distillation system for removing krypton from xenon. Rev Sci Instrum. 92(12):123303–123303. doi: 10.1063/5.0065154.

Zhang C, Dong X, Chen Y, Wu H, Yu L, Zhou K, Wu Y, Xia Q, Wang H, Han Y, et al. 2022. Balancing uptake and selectivity in a copper-based metal–organic framework for xenon and krypton separation. Sep Purif Technol. 291:120932. doi: 10.1016/j.seppur.2022.120932.

Zhou H-CJ, Kitagawa S. 2014. Metal–organic frameworks (MOFs). Chem Soc Rev. 43(16):5415–5418. doi: 10.1039/c4cs90059f.