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Excess-Heat Recovery and Promotion through Organic Chemical Heat Pumps

Heat recovery and promotion is essential to decarbonization, and chemical heat pumps based on reversible organic reactions can aid to fulfil this. This paper studied the isopropanol/acetone/hydrogen (IAH) and the *tert*-butanol/isobutene/water (tB/iB) systems regarding their performance and economic competitiveness through simulation and found that the IAH presents satisfactory performance and has the potential to be a very promising solution in increasing the overall energy efficiency while also preventing the emission of massive amounts of CO₂ and other greenhouse gases released during energy production and transformation. This system presents enough arguments to become a very successful solution if proper politico-economic support and incentives are established and put into practice.

Keywords: Chemical heat pump, Economic analysis, Entransy efficiency, Excess heat, Reversible organic reactions

Received: May 29, 2021; accepted: September 29, 2021

DOI: 10.1002/ceat.202100242



Supporting Information
available online

1 Introduction

It is well-known that sizeable amounts of heat are wasted each year. This so-called low-grade thermal energy is released in the process industries mainly through cooling water and air coolers, at temperatures up to around 475 K, meaning it must be upgraded to useful levels before it can be reused [1–3]. Adopting innovative and advanced systems, such as chemical heat pumps (CHPs), to upgrade this low-temperature heat to higher temperatures, can provide considerable energy savings, increase overall process efficiency, and reduce greenhouse gas (GHG) emissions through fossil fuel displacement [4, 5].

The critical levels of atmospheric GHG concentrations is one of the big motivators behind the world's current need to turn away from raw energy consumption, focusing on efficient utilization and recovery/reuse [1, 6]. Although their overall emissions trend has slowed, through the shift toward less carbon-intensive solutions [7], and an increase in renewables in the energy mix [8, 9], the, relatively recent, abnormally accelerated rise results in a series of problems such as atmospheric pollution [10], ocean acidification [11, 12], and global warming [10], which ultimately give rise to higher intensity wildfires, floods, droughts, storms, among many others [13]. These increasingly more severe, and frequent, natural disasters result in progressively heavier capital costs and human life endangerment, having affected more than 68 million people worldwide and resulting in losses of over \$130 billion in 2018 alone [14].

Seeing as how most GHG emissions result from energy production, transformation, and consumption [15], recycling low-grade energy, e.g., through excess-heat recovery and promotion, is extremely appealing to industries worldwide [16, 17].

Industrial excess-heat recovery is of such importance, in fact, that it is considered one of the most valuable research topics in energy utilization [18, 19].

Organic reaction chemical heat pumps (ORCHPs) are a particularly interesting technology within the CHP family. These can upgrade heat from various sources (industrial, solar, geothermal, etc.) to higher temperatures by taking advantage of catalytically reversible coupled endo-exothermic chemical reaction cycles [1, 3, 20, 21]. In addition to requiring almost no mechanical work, these systems can operate in much higher and broader temperature ranges, allowing for higher flexibility and adaptability of the operating conditions to a situation's particular requirements [1, 3, 19, 22]. Apart from these, this technology also has the added benefits of using mostly harmless chemical species, requiring little thermal isolation since the energy is stored in the chemical bonds, occupying relatively small volumes due to their usually high energy density, and the fact that the most common existing systems' reactions are fairly

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commonplace in the commercial chemical industries, meaning the handling technology and knowledge are well established [1, 2, 17, 23].

The purpose of this paper is to explore two well-known CHPs systems regarding the effect of the operatory variables in the performance of the system and evaluating the cost to implement and operate this type of solutions. Sect. 2 presents an overview of the isopropanol/acetone/hydrogen (IAH) system, and of the *tert*-butanol/isobutene/water (tB/iB) system investigated in this work with the objective to study the excess-heat recovery and promotion through the selected organic heat pumps. This section also describes the main metrics used to measure a CHP's performance namely the effectiveness and the entransy efficiency and the economic metrics to evaluate the two systems. Sect. 3 presents the process simulation models of the systems implemented for the CHPs used to promote excess heat. The results of the study are presented in Sect. 4 and finally the main conclusions of the work, are presented along with the future work and contribution to practice.

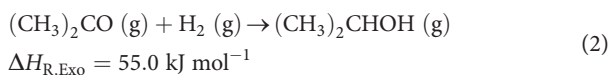
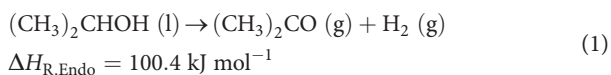
2 Chemical Heat Pumps and Metrics to Compare the Systems

The CHPs systems are briefly described as well as the main metrics used to compare the systems, namely the performance and economic metrics related to implementation and system operation.

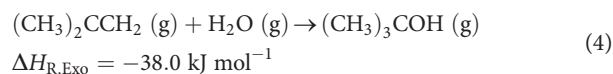
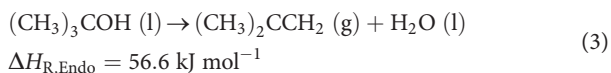
2.1 Overview of the Systems

This section focuses on two of the most well-known and established CHP systems to date, the IAH system (Eq. (1)), and the tB/iB system (Eq. (3)).

Regarding the IAH system, the endothermic reaction (Eq. (1)) consists of the dehydrogenation of isopropanol into acetone and hydrogen, which occurs catalytically in the liquid-phase at temperatures up to around 355 K. The exothermic reaction (Eq. (2)) consists of the reverse and typically occurs between 453 K and 493 K [20, 21].



Regarding the tB/iB system, the endothermic reaction (Eq. (3)) consists of the dehydration of *tert*-butanol into isobutene and water, and the exothermic reaction (Eq. (4)) consists of the reverse. This system operates in the same temperature ranges as the previous system [21, 24].



Both these systems follow a fairly simple flowsheet (Fig. 1) where low-temperature (T_L)¹⁾ excess heat is supplied to the endothermic reactor (R_L), promoting the decomposition reaction (Eqs. (1) and (3)). The resulting mixture is separated in some separation equipment (SU), such as a flash separator (FS), distillation column (DC), or similar. Afterwards, the gaseous mixture is fed to the exothermic reactor (R_H) where the recombination reaction (Eqs. (2) and (4)) yields the original reactant and releases high temperature (T_H) upgraded heat. The heat exchanger (HX) present in the system is responsible for preheating the exothermic reactor's feed stream. The excess heat utilized in these systems serves two purposes, driving the endothermic reaction and the separation process, the latter being the driving-force for the continuously operating system [3, 21, 22].

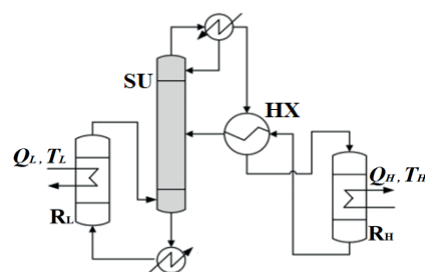


Figure 1. Organic reaction chemical heat pump diagram.

2.2 Performance Metrics

There are several metrics available to gauge a CHP's performance [21, 23, 25], however, this work will only make use of two of these, the effectiveness, which translates the system's enthalpy efficiency and the entransy efficiency, which translates its entropy efficiency.

Starting with the effectiveness (Eq. (5)), this is written as [26, 27]

$$\xi = \frac{\eta}{\eta_{\text{max}}} \quad (5)$$

where η is the system's coefficient of performance (COP; Eq. (6)), given by

$$\text{COP} = \frac{Q_H}{Q_L + Q_r} \quad (6)$$

and η_{max} is the system's maximum COP value (Eq. (7)), given by

$$\eta_{\text{max}} = \frac{1 - [T_c/T_L]}{1 - [T_c/T_H]} \quad (7)$$

1) List of symbols at the end of the paper.

where Q_H is the high-temperature heat released by the exothermic reactor, Q_L is the low-temperature heat supplied to the endothermic reactor, Q_r is the heat load of the distillation column's reboiler, and T_c is the condenser's temperature.

Despite providing very important information, the effectiveness does not account for the quality differences between the low and high-temperature heats, meaning another metric which contemplates this detail is needed. One such metric is the entransy efficiency (G^* ; Eq. (8)), which is expressed as [25, 28]

$$G^* = \frac{Q_H T_H}{Q_L T_L + Q_r T_r} \quad (8)$$

where the numerator and the denominator give the entransy produced and absorbed by the system.

2.3 Economic Metrics

The main purpose of the economic metrics is to provide some information needed to make a judgement or decision to evaluate and compare both systems. The economic analysis of the systems will be performed in two distinct ways. The first, used during the optimization studies, does not account for any monetary depreciation over time, interest rates, or the like. It is given by taking the system's investment costs (IC), as given by Aspen HYSYS' APEA (Aspen Process Economic Analyzer) and dividing it by the project's amortization period, which, in this case, is 20 years (20 a). This is known as the project's amortization and adding the system's annual operating costs (OC) to this value gives its total annual cost (TAC; Eq. (9)).

$$CHP_{TAC} [\text{€a}^{-1}] = \frac{IC}{20 \text{ a}} + OC \quad (9)$$

This TAC can be compared with the cost of utilizing natural gas (NG) to produce the same amount of heat as that recovered in the exothermic reactor to gauge the competitiveness associated with a given CHP solution. Calculating the CHP's excess cost (EC; Eq. (10)), in relation to NG, is a simple way to quantify this competitiveness.

$$EC [\%] = \frac{CHP_{TAC} - NG \text{ cost}}{CHP_{TAC}} \times 100 \quad (10)$$

The natural gas price used in this work was 0.030 € kWh⁻¹ (source: Eurostat [29]). Tab. 1 presents the carbon tax (CT) [30, 31] values used in this work.

Table 1. Carbon tax values used in this work.

Rate used in	Value [€ t ⁻¹ CO ₂]
(European average)	35.85
Finland	62.18
Sweden	108.81

The second economic analysis method is more complex and accounts for the system's yearly cash flow (YCF; Eq. (11)), which is equal to the yearly savings obtained when shifting from the use of natural gas to a chemical heat pump, the internal rate of return (IRR), the CHP's maintenance costs (MC), which are equal to 1% of the system's IC, and its overall lifecycle (20 years). This more detailed method uses the project's updated cash flows (UCF; Eq. (12)) to determine its associated payback time through the accumulated cash flows (ACF; Eq. (13)), which reflects how promising the investment can be.

$$YCF = NG \text{ cost} - CHP_{TAC} \quad (11)$$

$$UCF = \frac{YCF + \text{Amortization}_{0 \leq y \leq 20} - MC}{(1 + IRR)^y} \quad (12)$$

$$ACF = UCF_y + UCF_{y-1} \quad (13)$$

3 Simulation Study

Models of the IAH and tB/iB chemical heat pump systems were developed in the Aspen HYSYS software (Figs. S1 and S2 in the Supporting Information, SI) by following the generic design presented in Fig. 1. In addition, the UNIQUAC-Virial property package model was used for physical property calculations.

The IAH system's endothermic reaction was modeled using the kinetic data available in the work of Xu et al. [32], whereas the exothermic reaction was modeled as an equilibrium reaction. Both reactions in the tB/iB system were modeled as conversion reactions with 60% approach to equilibrium. In practice, since these systems operate in a closed-loop, convergence will only be obtained when both reactions present very similar conversions since only these conditions will be able to preserve the continuous operation's overall steady-state equilibrium.

The first significant difference between these chemical heat pump systems appears in this flowsheet development stage where the tB/iB system forces the use of an advanced distillation technique due to the binary azeotrope formed between *tert*-butanol and water. This led to the addition of an azeotropic distillation column (ADC), and its pre-concentrator, a three-phase separator (3PS), as well as a fourth chemical species (benzene) which acts as the entrainer in the heterogeneous azeotropic distillation. These additions to the generic design increased its complexity substantially, which will have repercussions in this system's future studies.

Given the large number of process variables that can be studied and optimized, factorial experiments were used instead of the one-factor-at-time method due to the efficiency at evaluating the effects and possible interactions of the several factors [33, 34]. The results of the sequential factorial experimentation performed are presented in Sect. 4 without details related to factorial experimentation which objective was to select the best control levels of the factors. The reactors' operating pressures, as well as their inlet and working temperatures, and the SU's working pressure and temperature are some of the factors considered in this work. Tabs. S1 and S2 present the detailed information regarding all considered factors and Tabs. S3

and S4 present the ranges used throughout the present work (see SI).

4 Results and Discussion

Fig. 2 presents the results obtained from the study conducted on the IAH system. Although the first experiment succeeded in identifying the system's operating ranges, half of its results were inoperable solutions, which is why they are not presented.

Fig. 2a shows the system's cost and performance variations throughout the different experiments, as well as the constant that represents the cost of producing the same amount of heat through the use of natural gas. As expected, the performance increases as the study narrows in on the set of operating conditions that produces the best results, and it can also be seen that the entransy efficiency undergoes a greater increase than the enthalpy efficiency, indicating that the former is more sensitive to changes in the operating conditions. Regarding the system's cost variation, the first thing to note is that its behavior is very similar to that of the performance, meaning the cost is heavily influenced by the amount of low-temperature heat needed to generate the same amount of high temperature heat (Fig. 2b),

which is understandable since this directly affects the utilities needed throughout the flowsheet.

Although the system's competitiveness is best in experiment 3, the cost/performance ratio improved throughout the study, meaning the operating conditions in experiment 5 produce the best cost-benefit relation since it is possible to obtain more high-temperature heat through the same excess heat input.

Fig. 3 presents the results of the study conducted on the tB/iB system. Similar to what occurred for the previous system, the first experiment's results are not presented. Fig. 3a shows the system's cost and performance variations throughout the different experiments, as well as the constant that represents the cost of producing the same amount of heat using natural gas. As earlier, the performance increases as the study progresses, however it is important to take note of the effectiveness values. These are higher than 1, i.e., this system is operating at an enthalpy efficiency above 100 %, which, for this technology, is impossible. In reality, this is consequence of Eq. (7) not accounting for the excess-heat input through the ADC's reboiler, causing the system's actual *COP* to be higher than its theoretical maximum *COP*, consequence of the discrepancy between Eqs. (6) and (7). This situation perfectly illustrates the need to review and update the performance metrics surrounding this type of CHP.

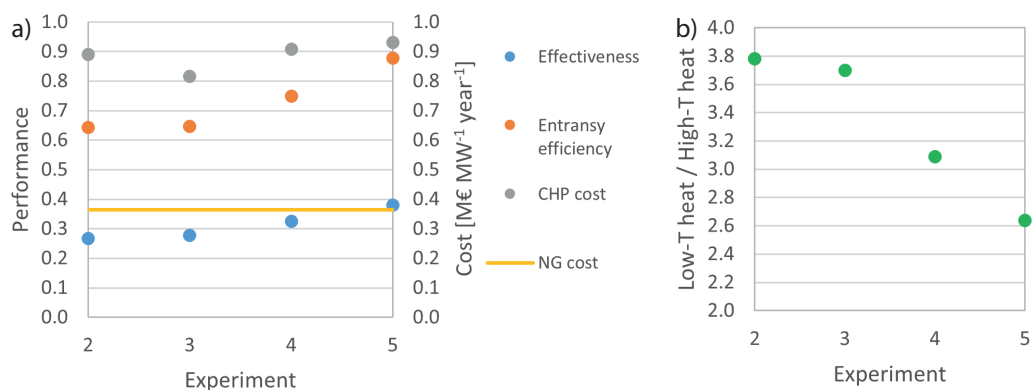


Figure 2. Results obtained from the study conducted on the IAH system. (a) System, and natural gas, costs to produce the same amount of high-temperature heat; (b) ratio between the needs of excess heat at Q_L and the released heat at Q_H .

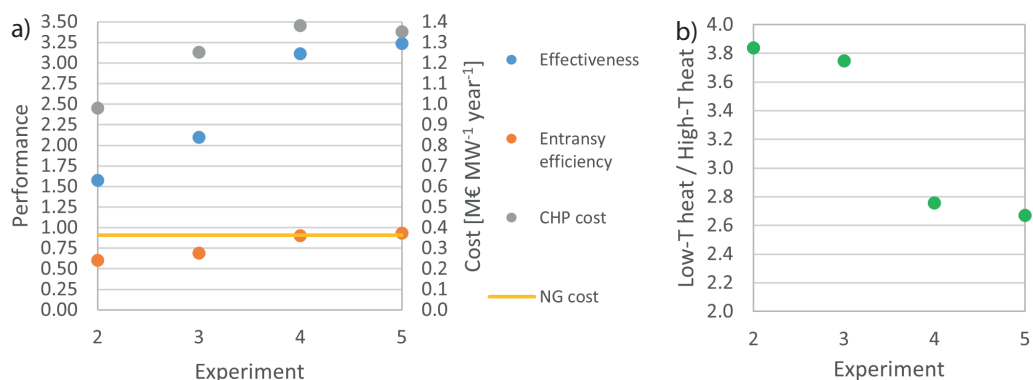


Figure 3. Results obtained from the study conducted on the tB/iB system. (a) System, and natural gas, costs to produce the same amount of high-temperature heat; (b) ratio between the needs of excess heat at Q_L and the released heat at Q_H .

This system's cost variation follows a pattern almost identical to its performance, meaning the latter experiments present a better cost/performance relation, however, since experiment 2 presents the lowest total cost, the operating conditions in this experiment produce the most competitive solution but with a high need of excess heat to promote the same amount of high temperature heat.

Overall, despite their similarities, this system's flowsheet's higher complexity resulted in much less competitive solutions as the cost is around 30 % higher than the IAH system.

4.1 IAH and tB/iB Systems Comparison

From a comparative standpoint, both systems' studies produced many of the same findings, which is understandable since they are fundamentally identical. Despite the many similarities between them, and even though they are still considerably more expensive than the use of natural gas, Tab. 2 shows that whereas the IAH system saw a decrease in excess cost, i.e., an increase in attractiveness, in experiment 3, the tB/iB system's competitiveness only worsened as the study progressed. Ultimately, this, along with it presenting a simpler flowsheet, led to the selection of the IAH system to undergo further experimentation.

Table 2. Excess cost variation for both the IAH and the tB/iB systems throughout the optimization studies.

Experiment	System	
	IAH [%]	tB/iB [%]
2	59.08	62.85
3	55.26	70.89
4	59.82	73.59
5	60.77	73.03

4.2 Further Experimentation on the IAH System

Even though the IAH system is the most attractive, its results are still far from appealing, meaning it must be studied, and optimized, in greater detail. This section presents the studies conducted on this basis, where the focus was turned to some operational aspects not yet considered, such as the excess hydrogen in circulation and the use of a distillation column as the main separation unit.

4.2.1 Hydrogen Excess

Tab. 3 shows the results obtained from the study conducted on the system's hydrogen excess. As expected, decreasing the amount of hydrogen in circulation also cuts the system's overall cost

since the equipment's dimensions, and utilities needed throughout the flowsheet, will be reduced, however, it is important to pay close attention to the balance between the system's cost, performance and heat capacity.

Focusing on the performance, both metrics decrease as the hydrogen available also decreases, most likely due to the decrease in high-temperature heat released in the exothermic reactor. It is, however, interesting to note that this behavior indicates that the hydrogen in this system may play a stabilization role regarding its entransy efficiency and a heat absorption role regarding its enthalpy efficiency.

Reducing the H₂ excess from scenarios 1 to 2 led to an increase in the system's low-temperature heat capacity since the amount of products entering the endothermic reactor will be lower, thus allowing for an increase in the reaction's conversion.

Focusing on the system's excess cost, the most notable observation is that scenario 4 offers almost no benefits in comparison with scenario 3, meaning the former can be swiftly discarded. This leaves only scenarios 2 and 3. Given that these offer fairly similar solutions, even though scenario 2 presents slightly better results, both from a performance and heat capacity standpoints, the most cost competitive solution, scenario 3, is chosen moving forward.

4.2.2 Parametric Study on the Reactors' Operating Pressures

Fig. 4 shows the results obtained from conducting a study on both reactors' operating pressures, to better understand how these affect the system's responses and the balance that exists between them. This study is particularly important given these factors' influence on the system's heat capacity and cost, undoubtedly its most significant aspects.

The first thing to note is that the exothermic reactor's operating pressure results in more costly solutions as it increases (Figs. 4a and 4d), and that this parameter does not appear to impact the system's performance (Fig. 4b) and heat capacity (Fig. 4c) in any notable extent, although a clear upswing trend can be noted in both cases, for increasing pressure values.

Going into a more in-depth analysis, and focusing on the endothermic reactor's operating pressure, the most noticeable observation is the significant impact that this parameter has on the system; cost variations reach more than 350 k€ and energy variations almost reach 0.9 MW. The most notable observation,

Table 3. IAH system's cost, performance, heat capacity ratio, and excess cost results for the excess hydrogen study.

Scenario	Cost		Performance		Q _L /Q _H ratio	Excess cost [%]
	[M€ a ⁻¹]	[M€ MW ⁻¹ a ⁻¹]	Effectiveness	Entransy		
1	2.15	0.78	0.31	0.72	3.32	53.06
2	1.77	0.67	0.29	0.68	3.56	45.03
3	1.44	0.61	0.27	0.60	3.87	39.67
4	1.24	0.60	0.24	0.56	4.29	38.53

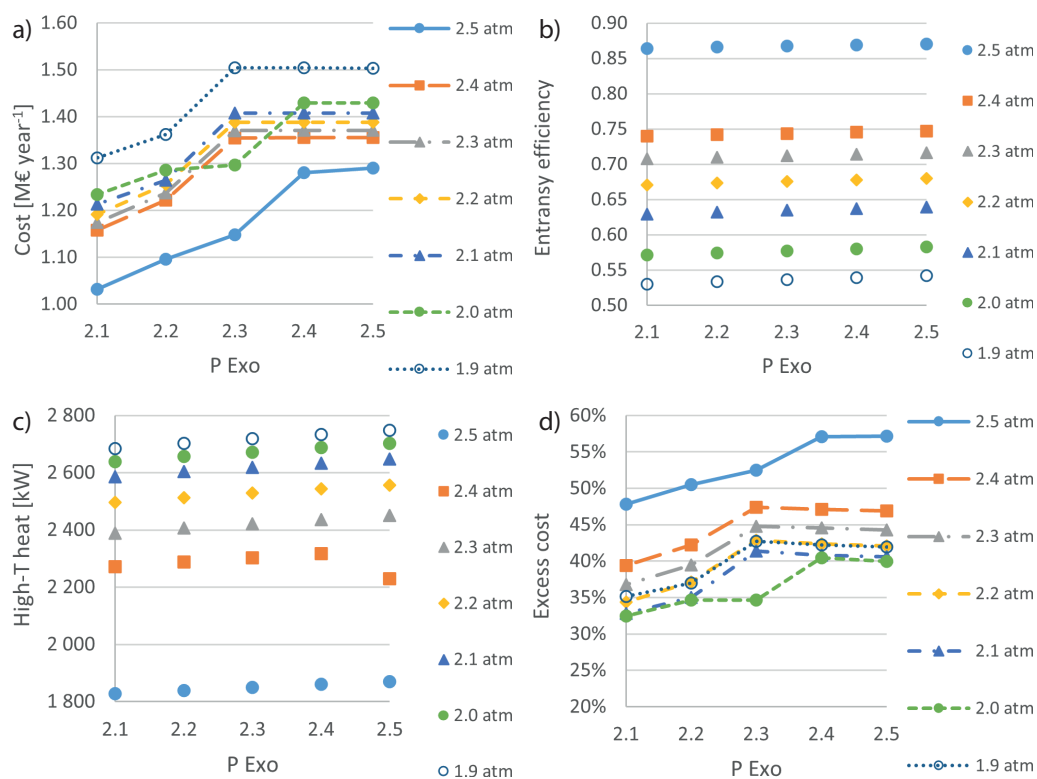


Figure 4. Results obtained from the parametric study conducted on the IAH system's reactors. (a) System's costs; (b) entransy efficiency; (c) high-temperature heat capacity; (d) excess cost.

however, is related to the divergent trends between the system's total cost and heat capacity (Figs. 4a and 4c, respectively), which, in turn, lead to divergent trends between these and the system's performance and excess cost (Figs. 4b and 4d, respectively).

Beginning with the system's total cost, Fig. 4a shows that this increases with decreasing pressure, which would mean lower pressures produce better results, however, the decrease in heat capacity (Fig. 4c) with increasing pressure gives rise to a divergent behavior directly affecting its cost-competitiveness, as can be seen in Fig. 4d where higher pressures result in less competitive solutions. This disagreement is also present between the system's performance and heat capacity where the former's increase comes at the cost of a decrease in the latter's values.

Ultimately, these divergent trends lead to the need for a balance between all of the system's responses and this equilibrium is best attained when the reactors' operating pressures are around 2.1/2.2 atm.

4.2.3 Distillation Column vs Flash Separator

The third and final study conducted on the IAH system posed the questions of "What would happen if a distillation column was used instead of a flash separator? Will the increased separation efficiency, and consequently lower compression work,

offset the additional investment costs? Will the system become far too expensive or will the increased heat capacity, through the reboiler, lead to even more cost competitive solutions?"

Fig. 5a shows that the system's cost did increase, from an average of around 1.23 M€ a^{-1} to around 1.52 M€ a^{-1} , a 24% increase, however, the 64% increase in high-temperature heat released by the exothermic reactor (Fig. 5c), from around

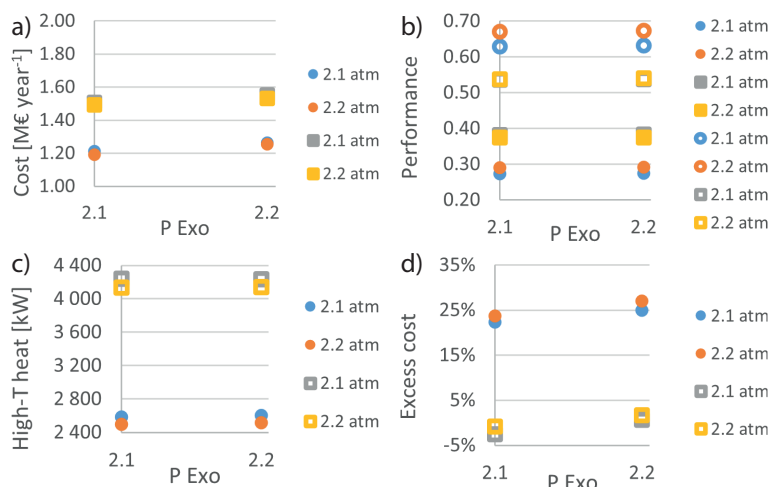


Figure 5. Results obtained from the study conducted on the IAH comparing a flash separator (circles) and a distillation column (squares). (a) System's costs; (b) performance (effectiveness {filled} and entransy efficiency {no fill}); (c) high-temperature heat capacity; (d) excess cost.

2.55 MW to 4.19 MW, was enough to create two solutions in which this IAH system can be considered cost competitive with the use of natural gas (Fig. 5d).

Fig. 5b shows the system's performance when using a flash separator and a distillation column. This figure is interesting as it helps visualize an intriguing phenomenon. The naturally more energy-efficient distillation column leads to an increase in the system's enthalpy efficiency, which relates to the overall heat losses, however, the greater entropy associated with a distillation process leads to a decrease in the system's overall entransy efficiency.

Considering there are two scenarios that can be considered cost competitive with the use of natural gas, it is possible to determine their payback period, which effectively translates their economic robustness. Tab. 4 presents the payback time for the best solution, under different IRR values, however, with payback periods of 14 and 16 years when considering extremely low IRRs of 3 % and 5 %, respectively, it becomes incredibly arduous to argue in favor of these solutions. These results are, unfortunately, a good illustrator of the poor economic performance that still plagues these systems. Nonetheless, a strong case can be made, and special attention should be paid, to the CO₂ emissions that could be prevented, which can reach over 7500 t a⁻¹.

Table 4. Payback time variation, for the most cost-competitive solution, under different IRR values.

Internal rate of return [%]	Payback time [a]
3	14
5	16
7	21
10	23

5 Conclusions

It is undeniable that heat recovery and promotion is an invaluable asset on the road to decarbonization. Organic reaction chemical heat pumps, in particular, present enough arguments to become a very successful solution, if proper politico economic support and incentives are established and put into practice. This technology can effectively be considered as an emerging alternative to other heat pump solutions, and, as such, its adoption is heavily dependent on the existence, or not, of government-funded programs, namely those which involve some form of financial backing/assistance.

This work found that the IAH chemical heat pump system based on reversible organic endo exothermic reactions is both technically and economically feasible, meaning it is an excellent candidate to focus on when considering future research paths, namely the improvement of the catalysts involved, especially those in the endothermic reaction, the development of reactive distillation setups, and, perhaps most importantly, carrying out actual implementation studies.

One of this work's most significant findings was that this technology appears to become more competitive with increasing heat capacity. This indicates it will be a good solution where large amounts of heat are needed, as is the case with many industrial distillation columns, where the column's condenser can feed the endothermic reactor and its reboiler is then fed by the CHP's exothermic reactor, thus possibly enabling the creation of a self-sustaining distillation system.

The authors have declared no conflict of interest.

Supporting Information

Supporting Information for this article can be found under DOI: <https://doi.org/10.1002/ceat.202100242>. This section includes additional information about the simulation study performed.

Symbols used

ΔH	[kJ mol ⁻¹]	Reaction enthalpy
G^*	[-]	Entransy efficiency
P	[atm]	Pressure
Q	[kW]	Heat power
T	[K]	Temperature

Greek letters

η	[-]	Coefficient of performance
ξ	[-]	Effectiveness

Sub- and Superscripts

c	Condenser
Endo	Endothermic
Exo	Exothermic
H	High-temperature
In	Inlet
L	Low-temperature
max	Maximum
R	Reaction
r	Reboiler

Abbreviations

3PS	Three-phase separator
ACF	Accumulated cash flow
ADC	Azeotropic distillation column
APEA	Aspen process economic analyzer
CHP	Chemical heat pump
COP	Coefficient of performance
DC	Distillation column
EC	Excess Cost
FS	Flash separator
GHG	Greenhouse gases
HX	Heat exchanger
IAH	Isopropanol/Acetone/Hydrogen
IC	Investment costs

IRR	Internal rate of return
OC	Operating costs
ORCHP	Organic reaction chemical heat pump
R _H	Exothermic reactor
R _L	Endothermic reactor
SU	Separation unit
TAC	Total annual cost
tB/iB	Tert-butanol/Isobutene/Water
UCF	Updated cash flow
YCF	Yearly cash flow

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