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Refrigerant Selection and Cycle Design for Industrial Heat Pump Applications exemplified for Distillation Processes

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ABSTRACT

Mechanical compression heat pumps are indispensable to facilitate the transition from thermally driven processes to renewable energy by electrification, upgrading low-temperature waste heat to recycle it at a higher temperature level. However, the implementation of such heat pumps up to date encounters limitations, due to equipment limitations and a lack of tools for the design of process concepts for the application of high-temperature heat pumps. The optimal design of heat pumps relies heavily on the selection of an appropriate refrigerant, as the thermodynamic properties significantly affect the heat pump cycle design and performance. While existing methods are capable of identifying thermodynamically beneficial refrigerants, they do not directly account for practical constraints such as limitations on the compressor discharge temperature, compression ratio, and vacuum operation. The current study proposes a fast-screening approach for arbitrary heat pump applications, considering a large set of established refrigerants. The method automatically assesses the performance of the refrigerants for a specified set of heat sink and source, adjusting the heat pump design with an optional internal heat exchanger in case of necessary superheating prior to compression. The approach is illustrated for the evaluation of heat pump-assisted distillation processes.

Keywords: Heat pump, Refrigerant, Screening tool, Energy integration, Distillation

INTRODUCTION

In the context of global warming and increasing costs of CO_2 emissions, the transition to renewable energy sources and the improvement of energy efficiency are essential objectives for the chemical industry. One potential approach to achieve both of these goals in a single step is the implementation of heat pumps, which recover low-temperature waste heat that would otherwise be lost to the environment through cooling water and elevate the heat to a higher temperature level at which it can be reused or recycled within the process [1]. Heat pumps present a distinctive and transformative opportunity for the electrification of industrial processes, which can immediately improve the sustainability through an expanded share of renewable electricity generation. Furthermore, the integration of heat pumps may not even require significant modifications to the existing equipment, thereby rendering them a versatile solution for both new processes and retrofitting of existing processes. This allows for significant energy savings in existing plants without the need for extensive modifications [1]. While a variety of heat pump concepts can be used to upgrade the available heat, compression heat pumps are used in most applications [2].

The left-hand Clausius-Rankine cycle, which is employed to describe the thermodynamic process associated with a closed-cycle compression heat pump, is illustrated in **Figure 1 (a-c)**. The initial step of this cycle involves an irreversible pressure increase within the vapor phase, which is subsequently followed by an isobaric energy exchange in the form of heat as the refrigerant undergoes condensation. The condensed refrigerant is expanded during the isenthalpic pressure reduction, and subsequently, heat is exchanged during the evaporation of the refrigerant.

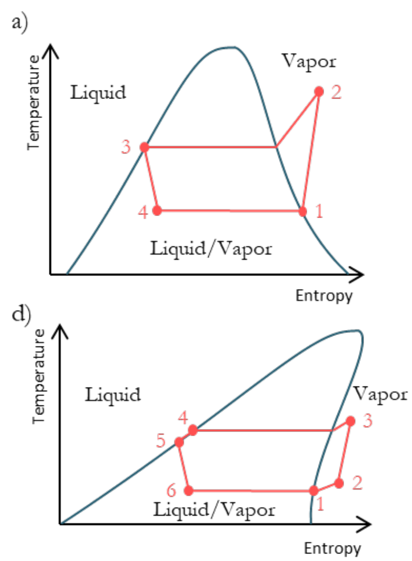

Figure 1: T-s diagram without a) and with d) superheating, heat pump cycle without b) and with e) superheating and p-h diagram without c) and with f) superheating

In the event that the refrigerant exhibits a hanging two-phase envelope the vapor needs to be superheated before entering the compressor to ensure that no liquid droplets form during compression which can cause damage to the compressor. For superheating the vapor, an additional heat exchanger and heat source are required. The additional heat exchanger can be implemented in the form of an internal heat exchanger (IHX), as shown in **Figure 1 (d-f)**. This configuration ensures the superheating through subcooling the refrigerant at higher pressure prior to expansion, thereby eliminating the need for external heating. However, this approach results in more complex behavior during start-up and limited operational flexibility for different temperature levels [3].

Today the implementation of heat pumps in industry is still limited due to a limited availability and experience on the use of high-temperature heat pumps, as well as the large investment costs, required for the expensive compressor [4]. In addition to these economic challenges, there are also persistent technical limitations to the application of compressors for industrial applications. Post-compression temperatures exceeding 160 °C and temperature lifts beyond 95 °C are still regarded as technically limitations [5], while exceeding these limits to yield sink temperatures up to 200 °C is expected to enable a huge range of applications [6]. Another important limitation dependent on the compressor type is the compression ratio, which is typically in the range of 2-4 with a practical limit of approximately 8 for the majority of compressor types [1]. However, some reciprocating compressors are reportedly capable of compression ratios as high as 12 at low flow rates [1]. High compression ratios can better be achieved by means of multistage compression cycles [7], or multiple cascade heat pumps with individual working fluid cycles, but these solutions are more complex and require significant investment costs, rendering them practically uneconomic [1].

The performance of external heat pumps depends largely on the specific refrigerant, which due to its thermal properties mandates the design of the compression cycle and the required work. The selection of an appropriate refrigerant for a given process depends on a number of criteria, including thermodynamic suitability, environmental compatibility, safety, efficiency and cost-effectiveness [4]. As no single refrigerant dominates all of these criteria, a trade-off must be made.

Various methods have been proposed to identify an appropriate refrigerant for a given process. Some methods focus on the thermodynamic properties and safety aspects of a range of different refrigerants, such as the work of Mateu-Royo et al. [8] and Koundinya and Seshadri [9], who evaluate refrigerants and cycle configurations quantitatively based on energy and exergy requirements, environmental impact, and economic considerations. Other authors, such as Kiss et al. [10] and Jiang et al. [11], propose general heuristics for the selection and assessment of heat pumps and refrigerants. The most general and recent methods investigate the sensitivity of refrigerants and heat pump configurations across a wide range of operating conditions [12] or solve the inverse problem, seeking an optimal refrigerant for a given application and cycle configuration based on continuous molecular targeting [13]. All these methods provide valuable tools for the identification of suitable refrigerants and heat pump designs, given that the specific application has been fixed. However, none of these methods was integrated in conceptual process design studies.

The present study proposes a computationally efficient methodology for the rapid screening and identification of a suitable refrigerant and heat pump cycle design that can be integrated in process design studies. The method considers a wide range of established pure refrigerants to provide practical solutions, automatically evaluating heat pumps with adaptive use of IHX, required in case of superheating of the refrigerant prior to compression. The case study illustrates the application for a combined refrigerant selection and conceptual design of heat pump-assisted distillation processes, based on the shortcut screening approach proposed by Skiborowski [14].

CALCULATION PROCEDURE OF A HEAT PUMP CYCLE

The calculations for the external heat pumps are based on the cycle designs and state diagrams illustrated in **Figure 1**. The computations only require the specification of the refrigerant's property parameters, as well as the temperature levels and heat duties of the source and sink. First, the lower pressure level of the heat pump is determined such that the saturated vapor temperature of the refrigerant has a pre-defined approach temperature to the minimum temperature of the heat source. Subsequently, the pressure after the compression is determined on the basis of flash calculations, ensuring that the refrigerant's saturated liquid temperature has the same approach temperature to the maximum temperature of the heat sink. In case the resulting pressure exceeds the critical pressure of the refrigerant, it is deemed thermodynamically unsuitable for this particular application, as it would create a trans- or supercritical heat pump process.

In case isentropic compression results in partial condensation, superheating prior to compression is facilitated by an IHX, which mitigates the need for an external heat source while simultaneously enhancing the specific enthalpy difference during the evaporation of the refrigerant. The degree of superheating is set such that the temperature of the refrigerant subsequent to isentropic compression must be at least equal to its saturated vapor temperature at the higher pressure level.

In this scenario, the specific enthalpy of the refrigerant on the higher pressure level after the IHX and prior to the throttle $h_5(T_5, p_{high})$ is determined based on the enthalpy balance of the IHX that is reduced to

$$h_5 = h_4 - (h_2 - h_1) \tag{1}$$

based on the specific enthalpy after the condensation in the heat exchanger with the external sink $h_4(T_{p_{high}}^{saturated\ liquid}, p_{high})$, and the difference between the specific enthalpy of the refrigerant at the low pressure level after the IHX and prior to the compressor $h_2(T_2, p_{low})$ and after the evaporation due to heat exchange with the source prior to the IHX $h_1(T_{p_{low}}^{saturated\ vapor}, p_{low})$. The specific enthalpy at the compressor inlet $h_2(T_2, p_{low})$ is calculated based on the temperature after superheating, which exceeds the saturated vapor temperature at the lower pressure by the degree of superheating. The specific enthalpy after compression

$$h_3(T_3, p_{high}) = \frac{h_{isentropic} - h_2}{\eta_{isentropic}} + h_2 \tag{2}$$

is calculated on the basis for the specific enthalpy for an isentropic compression $h_{isentropic}(T_{isentropic}, p_{high})$ and the isentropic efficiency $\eta_{isentropic}$, which results in an additional temperature increase due to the inefficiencies. Subsequently, the required refrigerant flow rate

$$\dot{n}_{Ref,sink} = \frac{\dot{Q}_{original,sink}}{|h_4 - h_3|} \tag{3}$$

for complete integration of the heat duty of the sink $\dot{Q}_{original,sink}$, and the refrigerant flow rate

$$\dot{n}_{Ref,source} = \frac{|\dot{Q}_{original,source}|}{h_1 - h_6} \tag{4}$$

for complete integration of the heat duty of the source $\dot{Q}_{original,source}$ are calculated. Note that the absolute value is considered, since heat duties for the sink are defined as negative values. The smaller of the two flow rates is then selected as the refrigerant flow rate $\dot{n}_{Ref}$, in order to guarantee complete integration of the smaller evaporation or condensation duty.

Adiabatic expansion results in the specific enthalpy of the refrigerant prior to evaporation at the lower pressure $h_6(T_6, p_{low})$ being equivalent to the specific enthalpy at the IHX outlet at the higher pressure $h_5(T_5, p_{high})$. In the absence of superheating, the specific enthalpy at the compressor inlet $h_2(T_2, p_{low})$ is equivalent to the saturated vapor enthalpy at lower pressure $h_1(T_{p_{low}}^{saturated\ vapor}, p_{low})$. Additionally, $h_5(T_5, p_{high})$ is equal to the saturated liquid enthalpy at the higher pressure $h_4(T_{p_{high}}^{saturated\ liquid}, p_{high})$.

In the following step, the remaining heat that is not covered by the heat pump is determined. In case the heat pump does not provide the full heat duty required by the heat sink

$$\dot{Q}_{sink} = \dot{Q}_{original,sink} - \dot{n}_{Ref} \cdot |(h_4 - h_3)| \tag{5}$$

must be provided by an external heat source, while an additional external cooling source with

$$\dot{Q}_{source} = \dot{Q}_{original,source} + \dot{n}_{Ref} \cdot |(h_1 - h_6)| \tag{6}$$

is required in case the heat pump cannot use all of the heat from the heat source. Finally, the electrical compressor duty is determined as,

$$\dot{W}_{el} = \frac{h_3 - h_2}{\eta_{mechanical}} \quad (7)$$

taking into account a mechanical efficiency, $\eta_{mechanical}$.

SHORTCUT-BASED SCREENING OF ALTERNATIVE PROCESS CONFIGURATIONS

The proposed method for the design of external heat pumps can directly be linked with a shortcut-based screening method for distillation-based processes, as presented by Skiborowski [14]. This shortcut method screens various distillation column configurations, including direct, indirect, and intermediate split configurations, as well as their thermally coupled versions on the basis of minimum energy demand calculations, building on the Rectification Body Method [15]. This provides the minimum energy demand and temperature levels of the condensers and reboilers of each configuration for a specified separation task. The proposed screening tool for external heat pumps can further evaluate the design of external heat pumps for any combination of heat source or sink from the respective process configurations, if not already utilized for another type of heat integration.

CASE STUDY

The case study investigates the combination of the external heat pump evaluation and the shortcut-based screening for distillation-based process, for the separation of a zeotropic mixture of hexanol, octanol, and decanol. The mixture is fed with equimolar composition and a flow rate of 10 mol/s in the column, assuming saturation conditions at the operating pressure of the column, where it is separated into pure products under isobaric and adiabatic conditions at 80 mbar. The further discussion focuses exemplarily on the comparison of the two simple sequences, the direct split (DS) and indirect split (IS), and a thermally coupled dividing-wall column (DWC). For the purpose of this study, an isentropic efficiency of 85 % and a mechanical efficiency of 95 % are assumed for the compressor of the heat pumps. All computations are based on the extended Antoine equation in combination with the UNIQUAC model for the nonideality of the liquid and the Redlich-Kwong equation of state for the nonideality of the vapor phase. Additionally, DIPPR correlations are employed for the specific heat capacity and heat of vaporization. The respective property parameters are extracted from the AspenPlus PURE39 and NIST-TRC databases.

The temperatures in the heat exchangers and the energy demand of the different sequences without heat pumps are presented in **Table 1**. The dividing wall column has the lowest energy demand, 22 %/ 35 % lower than the DS/ IS sequence, since the thermal coupling reduces the internal mixing losses.

Table 1: Temperature in heat exchangers and energy demand of the different sequences without heat pumps.

	DS	IS	DWC
T_{Top} [°C]			
- Column 1	92.26	103.32	92.26
- Column 2	122.78	92.26	
T_{Bottom} [°C]			
- Column 1	132.84	151.70	151.70
- Column 2	151.70	122.78	
Energy demand [kW]			
- Column 1	368.64	597.89	592.80
- Column 2	386.62	322.03	
- Net total	755.26	919.91	592.80

For each of the possible heat sources and sinks possible implementations of external heat pumps are evaluated. The refrigerant screening is exemplary discussed for the DWC column. This configuration has the largest temperature difference between the reboiler and condenser of 59.44 K. Considering an approach temperature of 5 K requires the refrigerant condensation temperatures in the heat pump of 156.7 °C and the heat pump to perform a temperature lift of 69.44 K.

Half of the initial set of 38 refrigerants are discarded as the required high-level pressure exceeds their critical pressure. The individual heat pump design for the remaining 19 refrigerants and the respective minimum energy demands are listed together with the respective pressure levels and compressor discharge temperature in **Figure 2**. For all refrigerants, complete electrification of the DWC column is feasible, requiring only external cooling. The net energy demand can be reduced with a heat pump by 54 % with R1233zd and even 76 % with water (R718). Yet, water as refrigerant is practically infeasible in a single-stage heat pump due to the sub-atmospheric operation, and a compressor discharge temperature of 377 °C, which would mandate multi-stage compression with interstage cooling. Practical limitations of ambient pressure (dotted line) and 170 °C (dashed line) are indicated in **Figure 2**, in order to identify unpractical refrigerants.

The selection of the preferred refrigerant, among the practical suitable ones, focuses solely on the lowest net energy demand, which identifies acetone as the preferred choice, despite the additional heat exchanger required for superheating. While R1130 has a comparable energy demand without this additional heat exchanger, there are concerns about its toxicity and ozone depletion potential, underscoring important safety and environmental factors that were not considered in the current selection process and should be addressed in future

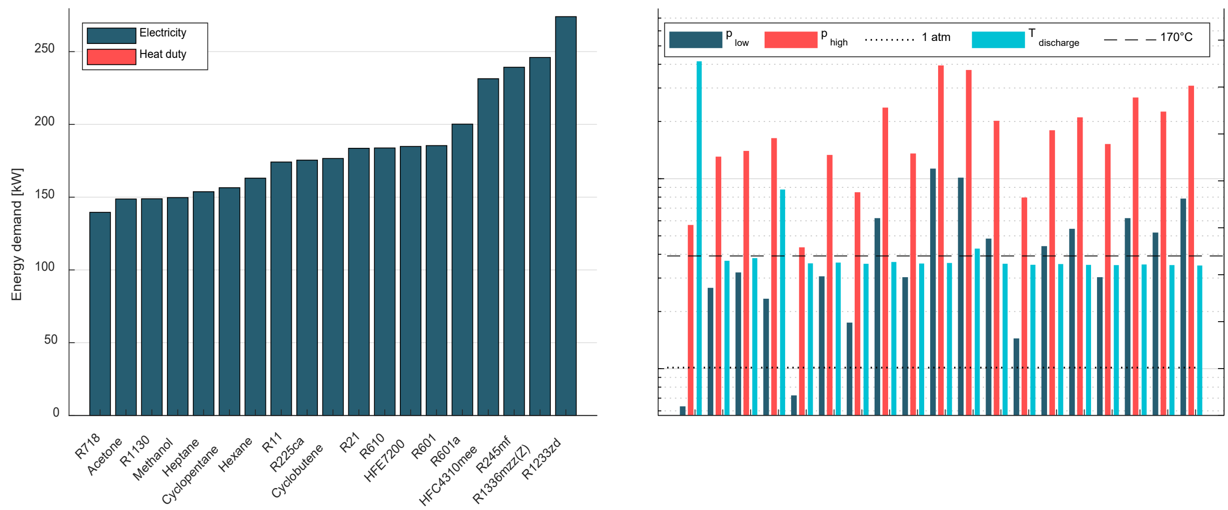

Figure 2: Energy demand (left) of DWC with heat pump and pressure levels (right) for thermodynamically feasible refrigerants.

evaluations.

As acetone is also among the preferred refrigerants in terms of total energy demand for DS and IS, it is utilized as a representative refrigerant for further performance comparison of the different sequences with heat pumps. Due to the fact that DS and IS possess two columns, four different configurations with a single heat pump, as well as two configurations with two heat pumps are possible, resulting in 16 different (heat pump-assisted) process variants for this separation task. The energy demand of the process variants and the potential energy saving of the best heat pump configuration compared to their process without heat pump are summarized in **Figure 3**.

With 83 % net energy savings the heat pump-assisted DS with two heat pumps does not only provide the largest saving potential but also shows the lowest net energy requirement overall. The study does not only highlight the potential of the integrated approach, but also illustrates that the heat pump-assisted simple sequence may require less energy that the heat pump-assisted DWC, which however requires only a single column shell and a single compressor and may be cost-beneficial.

The heat pump-assisted IS variants 11 and 14 in **Figure 3** employ a heat pump to utilize the heat from the condenser of column 2 to provide the necessary heat for the reboiler of column 1. These variants require additional

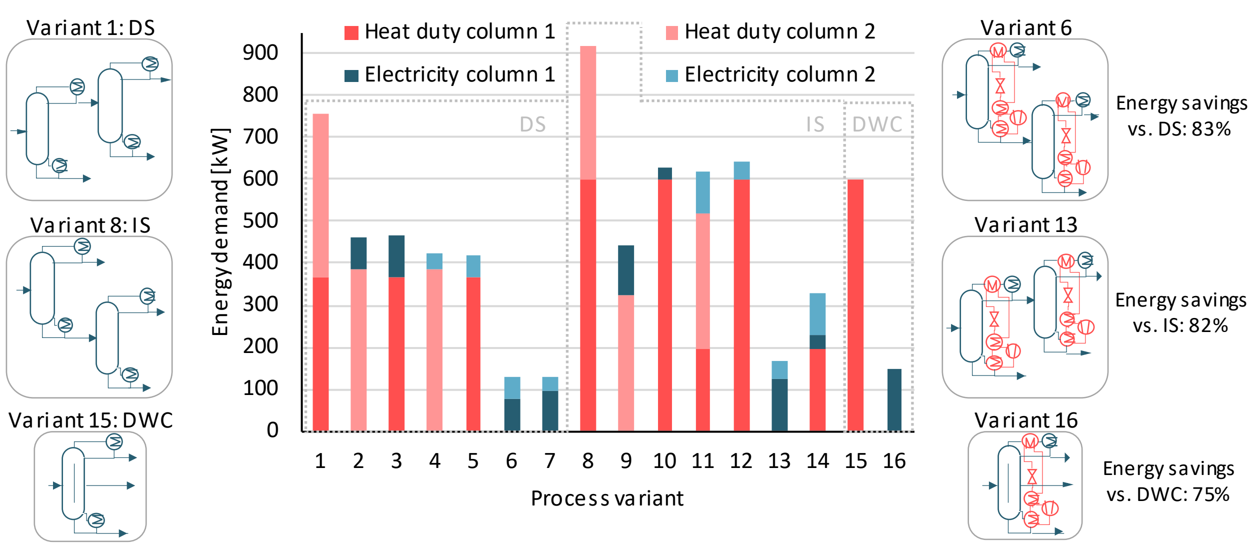

Figure 3: Energy demand for a selection of process alternatives and energy saving potential of intenfication with compression heat pumps with acetone as refrigerant.

heating for column 1, as the discrepancy in energy demand between the two columns (see **Table 1**) leads to the upgraded heat being insufficient to fully integrate the required energy demand of the reboiler. Consequently, the full electrification of process variant 14 is not feasible.

CONCLUSION

The present study introduces a novel methodology for the efficient screening of heat pump cycles and refrigerants based on knowledge of the heat sink and source of the specific application, thereby facilitating its applicability to a wide range of industrial processes. The current implementation of the method assesses the heat pump design, energy demand, as well as thermodynamic and practical constraints of 38 pure refrigerants for a given application which is further showcased for the evaluation of heat pump-assisted distillation processes. As illustrated by the case study, the integration of heat pumps in distillation processes can be complemented by other energy integration methods, thus further reducing the energy demand, whereas possible combinations should be explored quantitatively on a case-specific basis. The scope of the study will be extended in further work to consider other energy-integrated distillation processes and additional heat sources and sinks.

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