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Synthesis of Heat Exchanger Networks at Subambient Conditions with Compression and Expansion of Process Streams

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This article presents an optimization formulation for the synthesis of heat exchanger networks where pressure levels of process streams can be adjusted to improve heat integration. Especially important at subambient conditions, this allows for the interconversion of work, temperature, and pressure-based exergy and leads to reduced usage of expensive cold utility. Furthermore, stream temperatures and pressures are tuned for close tracking of the composite curves yielding increased exergy efficiency. The formulation is showcased on a simple example and applied to a case study drawn from the design of an offshore natural gas liquefaction process. Aided by the optimization, it is demonstrated how the process can extract exergy from liquid nitrogen and carbon dioxide streams to support the liquefaction of a natural gas stream without additional utilities. This process is part of a liquefied energy chain, which, supplies natural gas for power generation while facilitating carbon dioxide sequestration. *AIChE J,* 57: 2090–2108, 2011
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Introduction

The design of energy-efficient processes received a lot of attention during the energy crises of the 1970s and has recently attracted new attention because of the current high cost of energy as well as the new goal of reduced CO_2 emissions to mitigate global warming. Consequently, researchers have studied methodologies for the optimal design of heat exchanger networks.[1–4] One of the most successful tools to optimize energy integration during process design is pinch analysis. By providing a rigorous lower bound for the utilities needed by a given process design, it serves as a guideline for achievable process integration during flowsheet synthesis.[5–9]

The decomposition of the design process for chemical plants has been previously illustrated by the Onion Diagram, which indicates the levels of process design as well as the natural sequence of decisions. Commonly, at the core of the Onion Diagram is the reactor system (R), followed by the separation system (S), the heat recovery system (H), and the utility system (U). In the first version of the Onion Diagram, however, Linnhoff et al.[9] did not include the utility level, but more important, they included compression and

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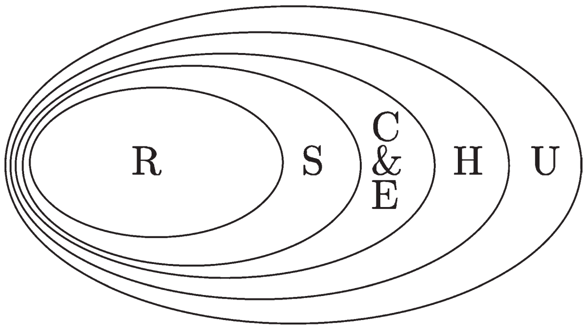


Figure 1. Illustration of the natural sequence in process design (reactor system, separation system, compression and expansion, heat exchanger system, and utilities).

The R of reaction, the s of separation, the c and e of compression and expansion, the h of heat and the u of utilities.

expansion (C&E) inside the heat recovery system (see Figure 1). This is interesting and highly relevant to this article, because expanders and compressors play a significant role in the proposed methodology. However, important "feedbacks" from outer to inner layers exist, which complicate the simplified flow of information in one direction indicated in Figure 1. One of these feedbacks is related to the interaction between setting the pressure of separation equipment, such as distillation columns and evaporators, and the design of the heat recovery system. By changing the pressure levels of such separators, the corresponding temperature levels of important (large duties) heat sources and sinks will change. This may have a significant impact on the scope for direct heat integration or heat pumping. Figure 1 shows an extended version of the traditional Onion Diagram where compression and expansion of the process streams are taken to be separate operations isolated from the utility system. Use of the concepts underlying this extended Onion Diagram is a central part of the ExPAnD methodology presented by Aspelund et al. in 2007.[10]

Pinch analysis (PA) covers the interface between the basic process (R, S) and the utility system (U) with special focus on the heat recovery system (H). This methodology has reached a mature level of industrial application over the years and has been successfully applied to improve heat recovery, to design better heat and power systems and utility systems, as well as in many other aspects of process design. An introduction to and overview with references to original research are given in the textbook of Smith.[6] The major limitation with this methodology is that only temperature is used as a quality parameter, thus neglecting pressure and composition. Over the last decades, PA has been a source of physical insights, which have led to advances in the synthesis of heat exchanger networks. Two thorough reviews of heat exchanger network synthesis (HENS) were published by Gundersen and Naess in 1988[1] and by Jezowski in 1994.[2,3] More recently in 2002, Furman and Sahinidis contributed a critical review and annotated bibliography of 461 articles on the design of HENs.[4]

Exergy analysis (EA)[11] can be used in all stages of process synthesis (PS), and the advantage is the inherent capability of including all stream properties (temperature, pressure, and composition); however, a limitation is its focus on the equipment units, rather than the flowsheet level. In addition, there is no obvious conversion from exergy to cost; in fact, there is often a conflict between reducing exergy losses and reducing cost. Nevertheless, Anantharaman et al.[12] tried to combine PA and EA in drawing so-called energy level composite curves. The new energy level parameter was proposed by Feng and Zhu.[13] Homšak and Glavič[14] suggested power availability curves to visualize the effect of pressure changes, which are not taken into account in the traditional composite curves of PA, to guide the appropriate placement of compressors and expanders.

Optimization techniques, usually referred to as mathematical programing (MP), are widely used in PS. One of the main challenges in their application is the fact that most problems in process design feature discrete decisions between process alternatives in addition to nonlinear process models as well as economic models with continuous variables. Thus, these problems need to be cast as mixed integer nonlinear programs (MINLP). An inherent property of such problems, even for problems of relatively small size, is the difficulty to guarantee that the global optimal solution has been found. Simultaneous optimization and heat integration of chemical processes can be formulated using MP, and several authors have contributed ideas.[15–26] The reader is referred to Furman and Sahinidis review for additional references on the sequential and simultaneous synthesis of HEN.[4]

Although there have been extensive efforts to optimize heat exchanger networks, very few articles have been published describing how the pressure of process streams can be manipulated to achieve more energy- and cost-effective processes. This is especially important in energy-intensive cryogenic processes, such as the liquefaction of natural gas or hydrogen, where the temperature of process streams is very sensitive to changes in pressure as the boiling or condensation temperature is a function of pressure. Furthermore, expansion or compression of process streams changes both temperature and pressure and converts stream enthalpy into work or vice versa. For example, a pressurized stream can be expanded to produce both thermal (cold) exergy and work from pressure exergy. Earlier, efforts have been made to develop an extended pinch analysis and design procedure (ExPAnD) and study the attainable regions (AR) for expansion of process streams at subambient temperatures.[10,27] However, these procedures rely on heuristics and a graphical interpretation of pressure exergy. It would be beneficial to formulate the problem using MP. Holiastos and Manousiouthakis[28] have shown the theoretical potential for moving the composite curves closer together by using ideal heat and power processes based on the second law of thermodynamics. This may provide interesting theoretical insights; however, such processes cannot be implemented as real engineered systems.

This article presents a process design tool that combines PA, EA, and MP to find heat exchanger networks with minimal irreversibility by varying pressure levels of process streams. It is structured as follows. First, the problem statement is given. Then, the state space approach for modeling the problem is described providing a detailed formulation of the pressure operator, the pinch operator, and the exergy operator. Two examples highlight the application of the formulation: First, a simple example with one hot stream and two cold streams is considered, where the pressure of one of the cold streams can be manipulated. Then, the methodology is applied to achieve a better design in a novel process for liquefaction of natural gas using liquid CO_2 (LCO_2) and liquid inert nitrogen (LIN) as cold carriers.[29]

Problem Statement

The problem statement can be formulated as follows:

Given a set of process streams with a supply state (temperature, pressure, and the resulting phase) and a target state, as well as utilities for power, heating, and cooling; design a system of heat exchangers, expanders, pumps, and compressors in such a way that an objective is minimized.

It should be emphasized that this problem definition is significantly more complex than the standard heat recovery problem in PA. First, the issue of soft target temperatures is now expanded to include also soft target pressures. Second, the thermodynamic process from the initial to the final state is not specified, and the change in temperature and pressure as well as phase may follow a large set of different routes. Third, the distinction between process streams and utilities, as well as between hot and cold streams, is no longer obvious. In fact, streams may change identity; for example, a cold process stream may temporarily change to a hot stream, and vice versa. Some process streams act like utilities by providing energy sources or sinks at temperatures outside the range spanned by the available utilities. Additionally, stream properties such as phase can be changed by manipulating the pressure. Finally, note that the actual problem considered will suggest the objective. Typically, it will correspond to some representation of operating cost, but an example will show that minimization of utility cost may be meaningless in some cases. Another possible choice for the objective is the exergy efficiency of the process.

In this article, the typical assumptions that are made in PA are used. Process streams are considered to have constant heat capacity, and pressure drops across heat exchangers are neglected. Because the heat capacity varies with temperature, the assumption of constant heat capacity may lead to significant error. This can be mitigated by splitting a stream into several piecewise segments with different heat capacities depending on the temperature interval. Recently, a formulation that allows for nonconstant heat capacities was presented in Ref. 25, where an empirical cubic correlation is used. It should be pointed out that this formulation is significantly more complex as it requires more variables and constraints. When combined with varying process conditions (flow rates, temperatures, and pressures), the problem cannot be solved in reasonable time. Expansion and compression of streams are modeled as isentropic processes, while an isentropic efficiency factor is introduced to adjust for unavoidable losses in real processes. To model the thermodynamic behavior of the fluid as the pressure changes, any equation of state can be used in principle[30]; here, for simplicity, the ideal gas model is used.

Description of the Process Model

A state space approach for design of heat exchanger networks including compressors and expanders

The state space approach to mass and heat transfer network design was presented by Bagajewicz et al. in 1998.[23] The article describes a way to divide the operations into mass and heat transfer. On a similar basis, the state space realization of a HEN and compressor/expander network is shown in Figure 2.

The pinch operator locates the pinch point and thus infers the minimum utility requirements for the process streams. These are divided into two categories, fixed and variable. The pressure of fixed streams is constant, while it can be changed through expansion and compression for variable streams. The former will contribute to the pinch operator as in standard PA, whereas the latter also interacts with the pressure operator. Typically, fixed streams are represented using a constant heat capacity flow rate and the inlet and outlet temperatures. To model phase changes occurring in single-component streams, the phenomena can be represented by dividing the stream into three substreams: two streams with a constant heat capacity and a third with the latent heat of the phase change at constant temperature. As shown in Figure 2, the pressure of variable streams is allowed to change through compressors and expanders. This has several implications. First, inlet and outlet temperatures will vary so that the standard transhipment formulation will not be able to solve the problem.[18] Instead, a nonlinear and nonconvex model needs to be applied. Second, one stream can result in up to four contributions to the pinch operator if a maximum of three pressure manipulation stages (compressors and/or expanders) is allowed for each stream. This increases the complexity of the problem considerably as the number of binary variables in the pinch operator scales with the square of the number of streams.

A PA approach for the structure of the HEN and C&E system

In this section, arguments for the most favorable routes for compression and expansion relative to heating and cooling are presented. It will be argued later in this article that the appropriate placement of compression and expansion is above and below the pinch, respectively, and with both pressure manipulations preferably starting at the pinch temperature. As a result, an exit stream from a compressor should be cooled to the pinch temperature if expansion (or another compression) is considered as the next step, thus it is a hot stream. Similarly, an exit stream from an expander should be heated to pinch temperature if compression (or another expansion) is considered as the next step, thus it is a cold stream. This is illustrated in Figure 3 that shows the graphical representation of the problem statement for one hot and one cold process stream where a total of three pressure manipulations (e.g., one compressor and two expanders) are allowed for each stream. The hot stream can be cooled, compressed, cooled, expanded, heated, compressed, and cooled. Similarly, the cold stream can be heated, expanded, heated, compressed, cooled, expanded, and heated.

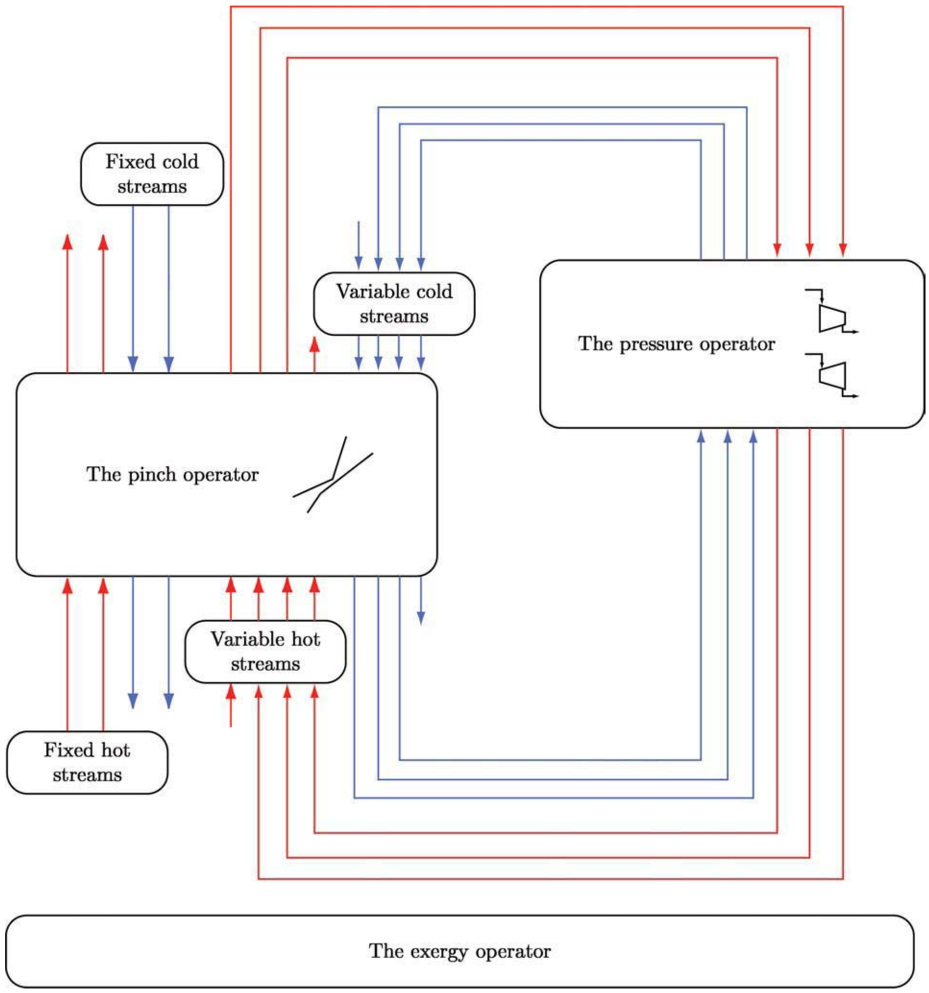


Figure 2. State space realization of a heat exchanger and compressor/expander network including the exergy operator that transforms energies into exergies to quantify irreversibilities.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

When supply and target temperatures and pressures of a stream are fixed, there are eight additional variables: three intermediate inlet temperatures, three intermediate outlet temperatures, and two intermediate outlet pressures. However, intermediate inlet temperatures, or equivalently exit temperature of the expanders or compressors, are related to the exit pressure of the expanders or compressors. Therefore, there are five independent variables for each stream. The chosen route for compression and expansion of hot and cold streams in Figure 3 is not arbitrary. The pressure manipulations can be treated as a series of process modifications. In PA, the general approach used to identify process modifications that reduce the energy requirements is called the "plus–minus" principle,[31] which states that in general the hot and cold utility targets will be reduced by:

- increasing hot stream (heat source) duty above the pinch or decreasing hot stream duty below the pinch, and
- decreasing cold stream (heat sink) duty above the pinch or increasing cold stream duty below the pinch.

Furthermore, to avoid cross-pinch heat transfer that would result in an increase in consumption of utilities beyond the target, the following applies:

- heat must not be transferred across pinch (from above to below),
- hot utility must not be used below pinch, and
- cold utility must not be used above pinch.

One example that applies to the plus–minus principle is a heat pump. A heat pump, if implemented correctly, will transfer heat from below pinch to above pinch, either through an open cycle, such as vapor recompression in distillation, or in a closed heat pump with an external working fluid. In this way, heat is removed below pinch and added above pinch, and will, according to the plus–minus principle, decrease the need for both hot and cold utilities at the expense of the work required in the compressor. Similar to the open cycle heat pump, compression of a gas will increase the temperature of the gas, and thereby either increase the duty of a heat source or decrease the duty of a heat sink. Therefore, by applying the principles above, a stream should always be compressed above pinch temperature. However, compression of a gas at a higher temperature will increase the required work for the same pressure ratio. Although not incorporated here, it should be noted that, from a capital cost point of view, it is beneficial to compress the

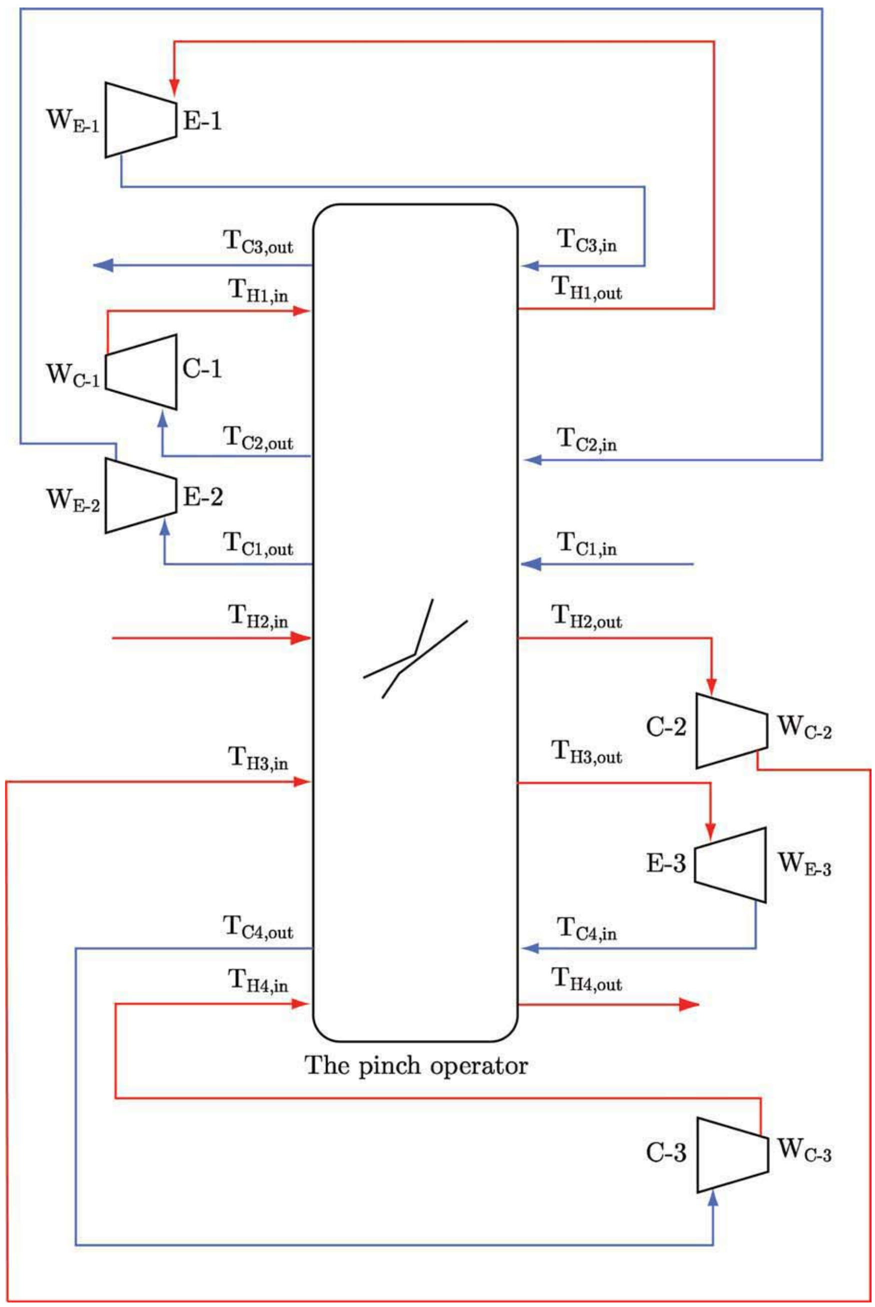


Figure 3. Superstructure with heat exchangers, compressors, and expanders for a hot and a cold stream split into segments showing intermediate temperatures.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

gas at as low temperature as possible, as the density is higher, and therefore the compressor can be made smaller and less expensive. In some cases, a higher pressure ratio can also be obtained, as the exit temperature will be lower.

An example that demonstrates the principles above is shown in Figure 4. A hot stream with a heat capacity flow rate of 2 kW/K is to be cooled from 130 to −75°C and compressed from 0.1 to 0.2 MPa. Two cold streams are to be heated. The first cold stream has a heat capacity flow rate of 5 kW/K and is to be heated from 15 to 140°C. The other cold stream has a heat capacity flow rate of 1 kW/K and is to be heated from −50 to 140°C. The hot stream is divided into two segments, H1 and H2, and a compressor is inserted. In addition to the supply and target temperature of the hot stream, two additional intermediate temperatures are introduced: the outlet temperature of segment H1, $T_{H1,out}$, and the inlet temperature of segment H2, $T_{H2,in}$. The former corresponds to the temperature at the intake of the compressor, whereas the latter is the exit temperature of the compressor. In this example, the compressor intake temperature for the divided hot stream, $T_{H1,out}$, is varied systematically from the lowest possible temperature (−75°C) to the highest possible temperature (130°C) in

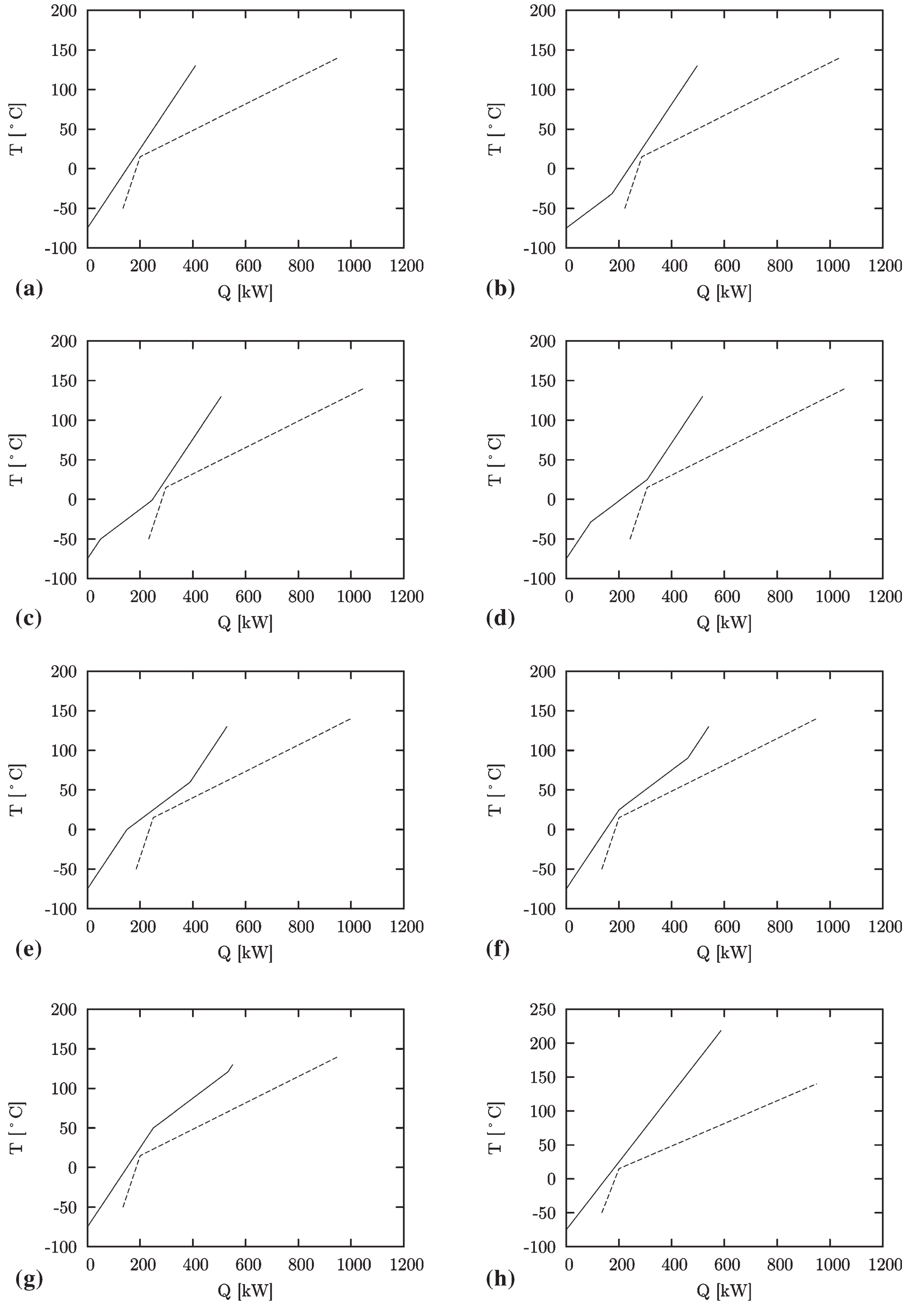


Figure 4. Composite curves resulting from compression of a hot stream at varying compressor intake temperatures.

(a) Case 1: No compression. (b) Case 2: compression at $T_{H1,out} = -75°C$. (c) Case 3: compression at $T_{H1,out} = -50°C$. (d) Case 4: compression at $T_{H1,out} = -28.5°C$. (e) Case 5: compression at $T_{H1,out} = 0°C$. (f) Case 6: compression at $T_{H1,out} = 25°C$. (g) Case 7: compression at $T_{H1,out} = 50°C$. (h) Case 8: compression at $T_{H1,out} = 130°C$.

appropriate intervals. In Figure 4, the composite curves for each of the eight considered cases are shown. In Table 1, the temperature after compression $T_{H2,in}$, the work W, the hot and cold utilities, Q_H and Q_C, respectively, and the exergy efficiency ψ, which will be formally defined in Section "The Exergy Operator," are given. Figure 5 shows the variation of W, Q_H, Q_C, and ψ as a function of compressor intake temperature $T_{H1,out}$. In the calculations, a minimum temperature approach $\Delta T_{min} = 10°C$ and isentropic compression of an ideal gas with a polytropic exponent of $\kappa = 1.4$ are assumed.

Table 1. **Effect of Compression of a Hot Stream at Varying Compressor Intake Temperatures on Utility Requirements and Exergy Efficiency**

Case	$T_{H1,out}$ (°C)	$T_{H2,in}$ (°C)	Q_H (kW)	Q_C (kW)	W (kW)	ψ (%)
1	—	—	540.0	135.0	—	56.3
2	−75.0	−31.6	540.0	221.7	86.7	66.4
3	−50.0	−1.2	540.0	232.7	97.7	63.1
4	−28.5	25.0	540.0	242.0	107.1	61.1
5	0.0	59.8	470.4	185.0	119.6	67.0
6	25.0	90.3	409.5	135.0	130.5	73.2
7	50.0	120.7	398.5	135.0	141.5	71.8
8	130.0	218.3	363.5	135.0	175.5	67.6

The first case (Figure 4a) shows the composite curves (CCs) for the three streams without compression. As can be seen from Table 1, the hot and cold utilities are 540 and 135 kW, respectively, and the exergy efficiency is 56.3% for a hot stream pressure of 0.1 MPa (pressure-based exergy is not included). Because the heat capacity flow rate of the CC for the cold streams is always larger than the CC for the hot streams above pinch, the pinch temperature (15°C/25°C) does not change throughout the example.

In the second case, the hot stream is compressed at the lowest possible temperature. As can be seen from Table 1, the required work is only 86.7 kW; however, as it is compressed solely below the pinch point, it leads to an increase in cold utility, which is in accordance with the plus–minus principle. In contrast to the previous case, the pressure exergy is used so that exergy efficiency is increased to 66.4%.

In Case 3, the compression temperature is increased to −50°C. As a result, the work is increased to 97.7 kW, and because the compressor exit temperature is below the pinch, there is an equal increase in cold utility. It can therefore be concluded that if a stream has to be compressed below the pinch, it should be compressed at as low temperature as possible.

In Case 4, the exit temperature (25°C) is exactly equal to the hot pinch temperature resulting in the worst possible placement of the compressor and an exergy efficiency of only 61.1%. This can be explained by the maximum amount of heat resulting from the compression delivered below the pinch. It increases the cold utility without reducing the hot utility, with an increase in work from Case 3.

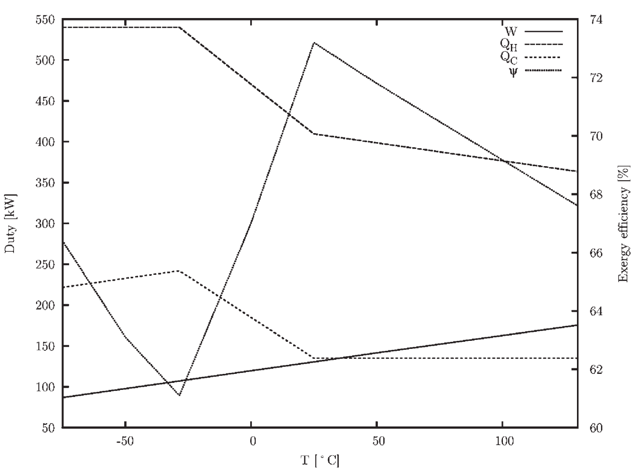


Figure 5. **Exergy efficiency, required work, and utilities for the example.**

In Case 5, the compression is performed across the pinch (from below to above), and the temperatures before and after compression are 0 and 59.8°C, respectively, which means that a portion of the heat because ofcompression is provided above pinch. This will reduce the hot and cold utilities duties, as the plus–minus principle states, and increase the exergy efficiency when compared with Case 4.

Case 6 is the optimal configuration with an exergy efficiency of 73.2%. Here, the hot stream is cooled to hot pinch temperature (25°C) before it is compressed to 0.2 MPa and 90.3°C. Although the work has increased to 130.5 kW, all the heat from the compressor is now provided above pinch and will therefore reduce the hot and cold utilities duty to 409.5 and 135 kW, respectively. As can be seen, the cold utility is now the same as in Case 1 where no compression took place. Furthermore, note that the CCs are close over a large interval, which is an indication of the small irreversibilities in the HEN.

Increasing the compressor intake temperature further requires additional work, which will be recovered as heat. However, because work is always worth more than heat above ambient temperature, this process leads to a degradation of exergy. Therefore, the exergy efficiency continues to decrease in Case 7 and is at its lowest value for compression above pinch in Case 8. It could be argued that in the last case the hot utility could be provided at a lower temperature because the temperature after compression is higher than the cold stream outlet temperature plus the minimum internal temperature approach of 10°C. However, even when accounting for this effect, the exergy efficiency will still be lower than for Case 6.

As demonstrated in Figure 5, it is best to compress the hot stream beginning from the pinch point than from any temperature below the pinch point if one strives for high exergy efficiency. Cases 2–5 violate the plus–minus principle, they increase the hot stream duty below the pinch. On the other hand, Cases 7 and 8 lead to a degradation of exergy, that is, conversion from work to heat.

As already mentioned, for this example, the heat capacity flow rate for the cold CC above the pinch is larger than the heat capacity flow rate for the hot stream. Hence, the pinch point remains the same throughout the example. In the opposite situation, the pinch point will coincide with the compressor exit temperature and actually increase as the intake temperature to the compressor is increased, thereby reducing the benefit of compression above the pinch point. In addition, because in most problems several streams are involved, the pinch point is likely to ''jump'' from one location to another when the pressure of process streams is manipulated.

A similar analysis can be performed for the case of expansion. It will decrease the temperature of the process stream, and thereby either decrease the duty of a heat source or increase the duty of a heat sink. Applying the plus–minus principle, a stream should always be expanded to an expander exit temperature that is below the pinch. This is certainly the fact for all refrigeration cycles. However, similar to compression, the expansion work will be greater at higher temperatures. Furthermore, a larger cold duty will be produced. Therefore, it is obvious that expansion of a gas should start at the pinch temperature and end below the pinch temperature. If the sole purpose of the expansion is to produce work, it is favorable to expand the gas at as high temperature as possible, which is clearly the case for power production plants. Nevertheless, in many processes where heat integration is important, and especially for processes that require refrigeration, generation of work is secondary for providing heat sinks. An example and a discussion of expansion of a cold stream below the pinch can be found in Ref. 10.

In general, a stream without phase change and with a supply pressure equal to the target pressure should not be compressed or expanded. However, in some cases, it may be beneficial to expand, compress, and expand (or vice versa) the same stream with intermediate cooling and heating to take advantage of heat pockets created by other process streams at higher or lower temperatures. To do so work must be available, of course. One example of such a refrigeration cycle is the inverse Brayton cycle (expander cycle) commonly used in air separation and peak-shave LNG plants.

For a liquid stream, there is no reason for manipulating the pressure as the effect is marginal. However, for a stream with phase change, pumping in the liquid phase and expansion in the gas phase is a very interesting option that should be investigated. A more thorough discussion with heuristics for how to use pressure manipulations in process design can be found in Ref. 10.

From the previous discussion, it can be concluded that the most beneficial way of manipulating the pressure of a hot stream is to cool, compress, cool, expand, heat, compress, and cool it. Furthermore, the stream should always be compressed to temperatures above the pinch point and expanded to temperatures below the pinch point. Compression and expansion of a hot stream should preferably start at the hot pinch temperature. Therefore, as shown in Figure 3, an expanded stream will always be a cold stream, whereas a compressed stream will always be a hot stream when further pressure changes are to be made. Similarly, a cold stream can be heated, expanded, heated, compressed, cooled, expanded, and heated. Compression and expansion of a cold stream should preferably start at the cold pinch temperature. Note that during this process, a hot stream may temporarily change to be a cold stream, and a cold stream may temporarily change to be a hot stream. It is also worth noticing that the location of the pinch point is very likely to change once pressure manipulations are introduced, because the shape of the composite curve will change. This suggests the use of an optimization model to find the best trade-off as even small problems become intractable.

Model Formulation

The model consists of four parts: the pinch operator, the pressure operator, the exergy operator, and the objective function, recall Figure 2. The pinch operator is responsible for locating the pinch point and subsequently determining the minimum required utilities. In the case of constant heat capacity flow rates, the pinch operator is linear. The pressure operator uses equations of state in combination with isentropic changes of state to connect streams at different pressure levels. With the thermodynamic model, nonconvex constraints are introduced that cannot be reformulated. Typically, objective functions corresponding to variable costs are linear. Together these operators form an MINLP involving nonconvex functions.

The pinch operator

At the heart of the optimization model is the pinch operator, which calculates the minimum required hot and cold utilities. Because stream pressure is allowed to change through compressors and expanders, the inlet temperatures to the pinch operator will vary, thus creating difficulties for the temperature interval model as first proposed by Linnhoff and Flower in 1978[32] and modeled as a transhipment problem by Papoulias and Grossmann in 1983.[16] Restructuring the temperature intervals implies making discrete changes that lead to nondifferentiabilities in the model.

Duran and Grossmann proposed an optimization formulation to find the minimum utility requirement for cases with variable stream data in 1986.[18] The pinch location method was developed to optimize and heat integrate chemical processes simultaneously, and therefore allows for variable inlet temperatures and heat capacity flow rates to the pinch operator. The presented formulation locates the pinch point by comparing the hot utility required for the subsystem of streams above each pinch candidate. It yields a small model without binary variables but uses nonsmooth functions. Thus, the problem cannot be solved with standard optimization algorithms, and smooth approximations were introduced. A reformulation of this model based on disjunctive programing was presented by Grossmann et al. in 1998.[19] This reformulation removes the nonsmooth constraint at the expense of binary variables, which distinguish if a stream is always below a candidate pinch point, above it, or crosses it. A candidate pinch point can be any stream inlet temperature. Hence, each hot or cold stream is regarded as a possible pinch candidate. This model is a MILP if heat capacity flow rates are nonvarying; otherwise, it leads to a MINLP.

Another pinch operator that allows variable temperatures was presented in a series of three articles by Yee et al. in 1990.[20–22] Here, a superstructure is proposed that matches each hot and cold stream at different stages. It uses binary variables to assign a possible heat exchange between hot and cold streams in addition to heat balances and temperature constraints. Although more complex than the pinch point location model, this pinch operator has the advantage of calculating the required area as part of the optimization routine. Unfortunately, this leads to a very large number of binary variables, and the model can therefore not be used for the considered purposes.

Recently, the model by Yee et al. was extended by Ponce-Ortega et al.[26] to include isothermal process streams and by Hasan et al.[25] for process streams with nonconstant heat capacity. In the latter case, a significant number of binary variables is added to the model rendering it too complicated for this application.

It has been found in this present research that the formulation given by Grossmann et al.[19] is the most tractable MINLP formulation currently available for the pinch operator. Their model can also include the case of isothermal streams, which is neglected in the presentation here. As in the original article, the big M formulation is used. For completeness, it can be described as follows.

Given is a set of hot process streams H and a set of cold process streams C. Let $S = H \cup C$ be the set of all process streams. For each $s \in S$, $T_{s,\text{in}}$, $T_{s,\text{out}}$, F_s, and $c_{p,s}$ denote the inlet and outlet temperature, the flow rate, and the heat capacity of the stream, respectively. Let $k \in H$ and $l \in C$ be indices of pinch candidates. Let Q_{HOT_i} be the energy to be transferred from hot stream i, and Q_{COLD_j} the energy to be transferred to cold stream j. Let q_{ki}^{hp} and q_{li}^{cp} be the energy available from hot stream i above hot pinch candidate k and cold pinch candidate l, respectively. Likewise, let q_{kj}^{hp} and q_{lj}^{cp} be the energy required by cold stream j above pinch candidate k and l, respectively. The hot and cold utilities used are Q_{H} and Q_{C}. The minimum approach temperature between hot and cold streams is given by $\Delta T_{\min}$. Lastly, binary variables w_{ki}^1, w_{ki}^2, and w_{ki}^3 denote if hot stream i is completely above, crosses or is completely below hot pinch candidate k, respectively. z_{kj}^1, z_{kj}^2, z_{kj}^3, u_{li}^1, u_{li}^2, u_{li}^3, v_{lj}^1, v_{lj}^2, and v_{lj}^3 denote analogous cases for the other combinations of streams and pinch candidates as indicated by the indices. U and M are upper bounds on the heat transfer and temperatures, and ε is a small parameter introduced to distinguish numerically if a stream crosses the pinch candidate or is below the pinch candidate.

$$Q_{\text{H}} + \sum_{i \in H} Q_{\text{HOT}_i} = Q_C + \sum_{j \in C} Q_{\text{COLD}_j},$$
$$Q_{\text{H}} \geq \sum_{j \in C} q_{kj}^{hp} - \sum_{i \in H} q_{ki}^{hp}, \quad \forall k \in H,$$
$$Q_{\text{H}} \geq \sum_{j \in C} q_{lj}^{cp} - \sum_{i \in H} q_{li}^{cp}, \quad \forall l \in C,$$
$$Q_{\text{HOT}_i} = F_i c_{p,i}(T_{i,\text{in}} - T_{i,\text{out}}), \quad \forall i \in H,$$
$$Q_{\text{COLD}_j} = F_j c_{p,j}(T_{j,\text{out}} - T_{j,\text{in}}), \quad \forall j \in C,$$
$$q_{ki}^{hp} - Q_{\text{HOT}_i} \leq U(1 - w_{ki}^1), \quad \forall (i,k) \in H \times H,$$
$$T_{i,\text{in}} \geq T_{k,\text{in}} - M(1 - w_{ki}^1), \quad \forall (i,k) \in H \times H,$$
$$T_{i,\text{out}} \geq T_{k,\text{in}} - M(1 - w_{ki}^1), \quad \forall (i,k) \in H \times H,$$
$$q_{ki}^{hp} - F_i c_{p,i}(T_{i,\text{in}} - T_{k,\text{in}}) \leq U(1 - w_{ki}^2), \quad \forall (i,k) \in H \times H,$$
$$T_{i,\text{in}} \geq T_{k,\text{in}} - M(1 - w_{ki}^2), \quad \forall (i,k) \in H \times H,$$
$$T_{i,\text{out}} \leq T_{k,\text{in}} - \varepsilon + M(1 - w_{ki}^2), \quad \forall (i,k) \in H \times H,$$
$$q_{ki}^{hp} \leq U(1 - w_{ki}^3), \quad \forall (i,k) \in H \times H,$$
$$T_{i,\text{in}} \leq T_{k,\text{in}} - \varepsilon + M(1 - w_{ki}^3), \quad \forall (i,k) \in H \times H,$$
$$T_{i,\text{out}} \leq T_{k,\text{in}} - \varepsilon + M(1 - w_{ki}^3), \quad \forall (i,k) \in H \times H,$$
$$w_{ki}^1 + w_{ki}^2 + w_{ki}^3 = 1, \quad \forall (i,k) \in H \times H,$$
$$q_{kj}^{hp} - Q_{\text{COLD}_j} \geq -U(1 - z_{kj}^1), \quad \forall (j,k) \in C \times H,$$
$$T_{j,\text{in}} \geq T_{k,\text{in}} - \Delta T_{\min} - M(1 - z_{kj}^1), \quad \forall (j,k) \in C \times H,$$
$$T_{j,\text{out}} \geq T_{k,\text{in}} - \Delta T_{\min} - M(1 - z_{kj}^1), \quad \forall (j,k) \in C \times H,$$
$$q_{kj}^{hp} - F_j c_{p,j}(T_{j,\text{out}} - (T_{k,\text{in}} - \Delta T_{\min})) \geq -U(1 - z_{kj}^2), \quad \forall (j,k) \in C \times H,$$
$$T_{j,\text{in}} \leq T_{k,\text{in}} - \Delta T_{\min} + M(1 - z_{kj}^2), \quad \forall (j,k) \in C \times H,$$
$$T_{j,\text{out}} \geq T_{k,\text{in}} - \Delta T_{\min} - \varepsilon - M(1 - z_{kj}^2), \quad \forall (j,k) \in C \times H,$$
$$q_{kj}^{hp} \leq U(1 - z_{kj}^3), \quad \forall (j,k) \in C \times H,$$
$$T_{j,\text{in}} \leq T_{k,\text{in}} - \Delta T_{\min} - \varepsilon + M(1 - z_{kj}^3), \quad \forall (j,k) \in C \times H,$$
$$T_{j,\text{out}} \leq T_{k,\text{in}} - \Delta T_{\min} - \varepsilon + M(1 - z_{kj}^3), \quad \forall (j,k) \in C \times H,$$
$$z_{kj}^1 + z_{kj}^2 + z_{kj}^3 = 1, \quad \forall (j,k) \in C \times H,$$
$$q_{li}^{cp} - Q_{\text{HOT}_i} \leq U(1 - u_{li}^1), \quad \forall (i,l) \in H \times C,$$
$$T_{i,\text{in}} \geq T_{l,\text{in}} + \Delta T_{\min} - M(1 - u_{li}^1), \quad \forall (i,l) \in H \times C,$$
$$T_{i,\text{out}} \geq T_{l,\text{in}} + \Delta T_{\min} - M(1 - u_{li}^1), \quad \forall (i,l) \in H \times C,$$
$$q_{li}^{cp} - F_i c_{p,i}(T_{i,\text{in}} - (T_{l,\text{in}} + \Delta T_{\min})) \leq U(1 - u_{li}^2), \quad \forall (i,l) \in H \times C,$$
$$T_{i,\text{in}} \geq T_{l,\text{in}} + \Delta T_{\min} - M(1 - u_{li}^2), \quad \forall (i,l) \in H \times C,$$
$$T_{i,\text{out}} \leq T_{l,\text{in}} + \Delta T_{\min} - \varepsilon + M(1 - u_{li}^2), \quad \forall (i,l) \in H \times C,$$
$$q_{li}^{cp} \leq U(1 - u_{li}^3), \quad \forall (i,l) \in H \times C,$$
$$T_{i,\text{in}} \leq T_{l,\text{in}} + \Delta T_{\min} - \varepsilon + M(1 - u_{li}^3), \quad \forall (i,l) \in H \times C,$$
$$T_{i,\text{out}} \leq T_{l,\text{in}} + \Delta T_{\min} - \varepsilon + M(1 - u_{li}^3), \quad \forall (i,l) \in H \times C,$$
$$u_{li}^1 + u_{li}^2 + u_{li}^3 = 1, \quad \forall (i,l) \in H \times C,$$
$$q_{lj}^{cp} - Q_{\text{COLD}_j} \geq -U(1 - v_{lj}^1), \quad \forall (j,l) \in C \times C,$$
$$T_{j,\text{in}} \geq T_{l,\text{in}} - M(1 - v_{lj}^1), \quad \forall (j,l) \in C \times C,$$
$$T_{j,\text{out}} \geq T_{l,\text{in}} - M(1 - v_{lj}^1), \quad \forall (j,l) \in C \times C,$$
$$q_{lj}^{cp} - F_j c_{p,j}(T_{j,\text{out}} - T_{l,\text{in}}) \geq -U(1 - v_{lj}^2), \quad \forall (j,l) \in C \times C,$$
$$T_{j,\text{in}} \leq T_{l,\text{in}} + M(1 - v_{lj}^2), \quad \forall (j,l) \in C \times C,$$
$$T_{j,\text{out}} \geq T_{l,\text{in}} - \varepsilon - M(1 - v_{lj}^2), \quad \forall (j,l) \in C \times C,$$
$$q_{lj}^{cp} \leq U(1 - v_{lj}^3), \quad \forall (j,l) \in C \times C,$$
$$T_{j,\text{in}} \leq T_{l,\text{in}} - \varepsilon + M(1 - v_{lj}^3), \quad \forall (j,l) \in C \times C,$$
$$T_{j,\text{out}} \leq T_{l,\text{in}} - \varepsilon + M(1 - v_{lj}^3), \quad \forall (j,l) \in C \times C,$$
$$v_{lj}^1 + v_{lj}^2 + v_{lj}^3 = 1, \quad \forall (j,l) \in C \times C.$$

The pressure operator

Let p_s be the pressure of stream s where $s \in S$. The pair $(s_1, s_2) \in \text{EX} \subset (S \times C)$ denotes that the outlet of stream s_1 from the pinch operator is connected to the inlet of stream s_2 to the pinch operator with an expander. Likewise, the pair $(s_1, s_2) \in \text{CO} \subset (S \times H)$ denotes connection with a compressor. Note that inlet and outlet of the streams refer to the heat exchanger, not the compressor or expander. $\tilde{T}_{s_2}$ denotes the exit temperature of a reversible process, κ is the polytropic exponent, and η_C and η_E are the isentropic efficiencies of the compressors and expanders, respectively. W_{s_1} denotes the work required or released by compression or expansion of stream s_1. The reversible and adiabatic compression or expansion of an ideal gas can be formulated as follows.

$$
\begin{aligned}
(\kappa-1)\ln p_{s_1} + \kappa \ln \tilde{T}_{s_2} &= (\kappa-1)\ln p_{s_2} + \kappa \ln T_{s_1}, \\
&\qquad \forall (s_1, s_2) \in \mathrm{CO} \cup \mathrm{EX}, \\
\left(T_{s_1} - \tilde{T}_{s_2}\right) &= (T_{s_1} - T_{s_2})\eta_{\mathrm{C}}, \quad \forall (s_1, s_2) \in \mathrm{CO}, \\
\left(T_{s_1} - \tilde{T}_{s_2}\right)\eta_{\mathrm{E}} &= (T_{s_1} - T_{s_2}), \quad \forall (s_1, s_2) \in \mathrm{EX}, \\
W_{s_1} &= F_{s_1} c_{\mathrm{p},s_1}(T_{s_2} - T_{s_1}), \quad \forall (s_1, s_2) \in \mathrm{CO}, \\
W_{s_1} &= F_{s_1} c_{\mathrm{p},s_1}(T_{s_1} - T_{s_2}), \quad \forall (s_1, s_2) \in \mathrm{EX}.
\end{aligned} \tag{1}
$$

The logarithmic terms in Eq. 1 involve positive, physical quantities for which tighter bounds are established to avoid the logarithm becoming undefined. Note that compressor and expander work are both defined as nonnegative quantities. Hence, the net work produced equals the sum of the expansion work minus the sum of the compression work. In the general case when the thermodynamic properties of the streams are described with a volume-explicit equation of state, the equations are to be rewritten accordingly. A detailed discussion on how to compute the unknown exit temperature and the work for an isentropic process can be found in Ref. 30. Lastly, it should be noted that in the case studies no pressure drop is considered in the heat exchangers, although a constant pressure drop can be easily considered in the given model.

The exergy operator

The exergy operator has two purposes: to calculate the exergy of the process streams and the utilities and to find the exergy conversion efficiency. According to Ref. 11, work is defined as 100% exergy, whereas the exergy of the hot and cold utilities depends on the ambient temperature as well as the utility temperature and duty. For a utility with constant temperature, the Carnot efficiency can be used to find the exergy content. Note that we have assumed the hot utility to be above the ambient temperature and the cold utility to be below ambient temperature. Let T_0 and p_0 be ambient temperature and pressure, respectively. T_U^h and T_U^c are the temperatures at which hot and cold utilities are provided. One can interpret the exergy operator as a pricing tool to derive cost coefficients for the different utilities thermodynamically so that the optimal solution corresponds to minimum irreversibility.

$$
\begin{aligned}
ExW &= \sum_{(s_1,s_2)\in CO} W_{s_1} - \sum_{(s_1,s_2)\in \mathrm{EX}} W_{s_1} \\
ExQhu &= Q_{\mathrm{H}}\left(1 - \frac{T_0}{T_U^h}\right) \\
ExQcu &= Q_{\mathrm{C}}\left(\frac{T_0}{T_U^c} - 1\right)
\end{aligned}
$$

The thermomechanical exergy of the process streams consists of the temperature-based exergy and the pressure-based exergy. Because we assume that the process streams are nonisothermal, a logarithmic expression must be used to calculate the exergy content as shown in Eq. 2. The pressure exergy is defined by Eq. 3. The expressions can be derived using the first and second laws of thermodynamics and the ideal gas model with constant heat capacities. A derivation of the exergy expressions can be found in Ref. 11.

$$
E_s^{(\mathrm{T})} = F_s c_{\mathrm{p},s}\left[T_s - T_0\left(1 + \ln\left(\frac{T_s}{T_0}\right)\right)\right] \tag{2}
$$

$$
E_s^{(\mathrm{p})} = F_s T_0 R \ln\left(\frac{p_s}{p_0}\right) = F_s\left(\frac{\kappa-1}{\kappa}\right) c_{p,s} T_0 \ln\left(\frac{\mathrm{p}_s}{p_0}\right). \tag{3}
$$

When calculating the exergy conversion efficiency it is important to exclude contributions that do not change during the process to get a representative measure. The chemical exergy is therefore excluded from the calculations and only the thermomechanical exergy is included.

$$
E_s^{(\mathrm{tm})} = E_s^{(T)} + E_s^{(p)}.
$$

A more thorough discussion about thermomechanical exergy for subambient process streams can be found in Ref. 10. The exergy conversion efficiency is defined as the useful outlet exergy divided by the inlet exergy. The inlet exergy is defined as the sum of the thermomechanical exergy of inlet process streams and utilities and the net work required, whereas the outlet useful exergy is the sum of the thermomechanical exergy in the outlet streams and the net work produced as stated in Eq. 4.

$$
\psi = \frac{E^{(\mathrm{tm})}_{\text{outlet streams}} + \sum_{(s_1,s_2)\in \mathrm{EX}} W_{s_1}}{E^{(\mathrm{tm})}_{\text{inlet streams}} + \sum_{(s_1,s_2)\in \mathrm{CO}} W_{s_1} + ExQcu + ExQhu}. \tag{4}
$$

Streams with fixed temperatures contribute only temperature-based exergy as the pressure remains constant throughout the process, whereas the streams with variable temperature include both the pressure- and temperature-based exergy, that is, the total thermomechanical exergy. The exergy input from the utilities is included in Eq. 4. The net required work and net generated work are also included in the exergy efficiency. If the heat capacity flow rates, supply, and target temperatures and pressures of the process streams are fixed, the highest exergy efficiency can be found by minimizing the exergy input of the required work, hot and cold utilities.

The objective function

The objective function combines the results from pinch, pressure, and exergy operators into one measure. For example, when the stream heat capacity flow rates and the inlet and outlet pressure and temperatures are constant, the exergy required by the design can be minimized resulting in a solution with minimal irreversibilities.

Table 2. Given Information for Streams in Simple Example

Stream	$F_s c_{p,s}$ (kW/K)	$T_{s,\text{in}}$ (K)	$T_{s,\text{out}}$ (K)	p_s (MPa)
H1	3	288	123	0.1
C1	2	213	288	0.1
C2	1.7	113	—	0.4
C3	1.7	—	—	—
H2	1.7	—	—	—
C4	1.7	—	288	0.1

$$\min\ ExW + ExQhu + ExQcu \tag{5}$$

If flow rates are allowed to vary, more care needs to be taken to ensure that the exergy of the streams with variable flowrate is accounted for.

Alternatively, it is possible to assign different costs for the utilities and work than those obtained from thermodynamical considerations.

Examples

All problems were solved in GAMS 23.2 using BARON with CPLEX and SNOPT on a Intel Xeon W3570 workstation using one core at 3.20 GHz and 4 GB RAM under Linux 2.6.28. The relative termination tolerance in GAMS, OptCR, was set to 10^{-4}, while the absolute termination tolerance in GAMS, OptCA, was not changed and the default value given by BARON, 10^{-9}, was used. No deviating tolerances were set for either SNOPT or CPLEX. As BARON is used, bounds on the variables need to be given. Bounds on temperatures are given by the available utility temperatures, and bounds on pressures are specified individually in the examples.

A simple example

In this example, the benefits of using the model formulation presented in this article are illustrated. One hot stream (H1) and one cold stream (C1) are at constant pressure, a second cold stream (C2) is to be expanded from 0.4 to 0.1 MPa. In light of the discussion earlier, C2 could potentially be expanded, compressed, and expanded with necessary cooling and/or heating. In this example, the heat capacity flow rates of all streams are constant. The data for each stream are given in Table 2, and the connection and labeling of streams are shown in Figure 6.

Furthermore, $\Delta T_{min} = 4\text{K}$, $T_0 = 288\text{K}$, $p_0 = 0.1\text{MPa}$, $T_U^h = 383\text{K}$, $T_U^c = 93\text{K}$, $\kappa = 1.352$, and $\eta_C = \eta_E = 1$. Unknown inlet temperatures can be varied between 103 and 373 K, the pressure of stream C3 is restricted to 0.1–0.4 MPa, and the pressure of H2 to 0.1–0.6 MPa.

Several different cases are studied. First, no expanders and compressors are used. Then, to contrast the possible benefits of adjusting pressure levels of intermediate streams, three additional cases are presented where the objective and some constraints are modified.

The CCs and GCC for the base case without pressure manipulation are shown in Case 1 in Figure 7. No work is produced and the heating and cooling utilities are 64.5 and 112 kW, respectively, giving a thermomechanical exergy efficiency of 68.1%. The change in pressure exergy for stream C2 is ignored in these initial calculations. If a valve is used and the pressure change in C2 is accounted for, the exergy efficiency will be as low as 39.2%. As can be seen from the GCC, the pinch point is at 217 K/213 K.

In Case 2, the model formulation is used to find the minimum irreversibilities given the possible path from Figure 6. This is formulated using the objective function given by Eq. 5. It is found to be optimal that stream C2 is expanded to 0.183 MPa, recompressed to 0.382 MPa, and finally expanded down to 0.1 MPa. The net work produced by the process is 92.96 kW, the hot utility requirement is reduced to 45.46 kW, and no cold utility is necessary. The resulting exergy efficiency is 91.4% if one assumes that the net work produced can be used elsewhere. Results for the intermediate state variables are listed in Table 3. The problem was solved in 4 h and 42 min. There are four pinch points, at 130.85 K/126.85 K, at 168.37 K/164.37 K, at 217 K/213 K, and at 244.21 K/240.21 K. Note that the GCC seems to indicate an additional pinch point at 117 K/113 K. However, this is a result of the fact that the designed process requires no cold utility and, therefore, it does not indicate the existence of an additional pinch point. This large number of pinch points corresponds to the objective of minimizing irreversibilities and therefore decreasing the gap between hot and cold composite curves as far as possible. It is worth mentioning that this configuration and the most favorable intermediate temperature for expanding this stream could also have been found by the ExPAnD methodology.[10] The advantage of the optimization approach of this article is time saving and assurance of optimality. It is also worth noticing that the result from Case 2 is in agreement with the proposed model in Figure 6. At first sight, this example seems innocuous. However, it is indeed a difficult global optimization problem as the ideal gas model introduces nonconvexities and the pinch operator introduces 108 binary variables. Furthermore, the existence of multiple pinch points at the optimal solution introduces degeneracy that slows the solution algorithm significantly.

In Case 3, the system is evaluated on an energy basis where hot and cold utility duties as well as the work

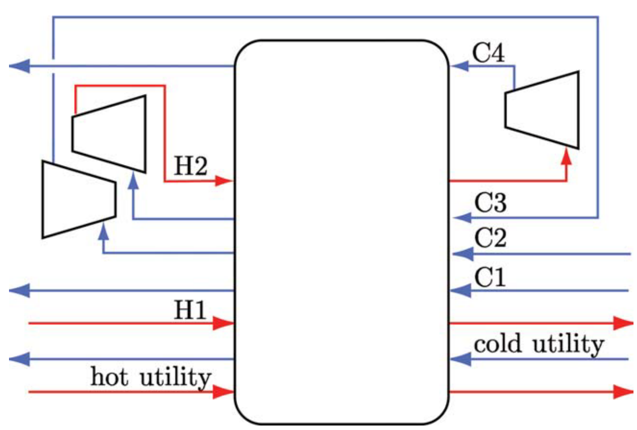


Figure 6. Possible arrangement of streams in the simple example.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

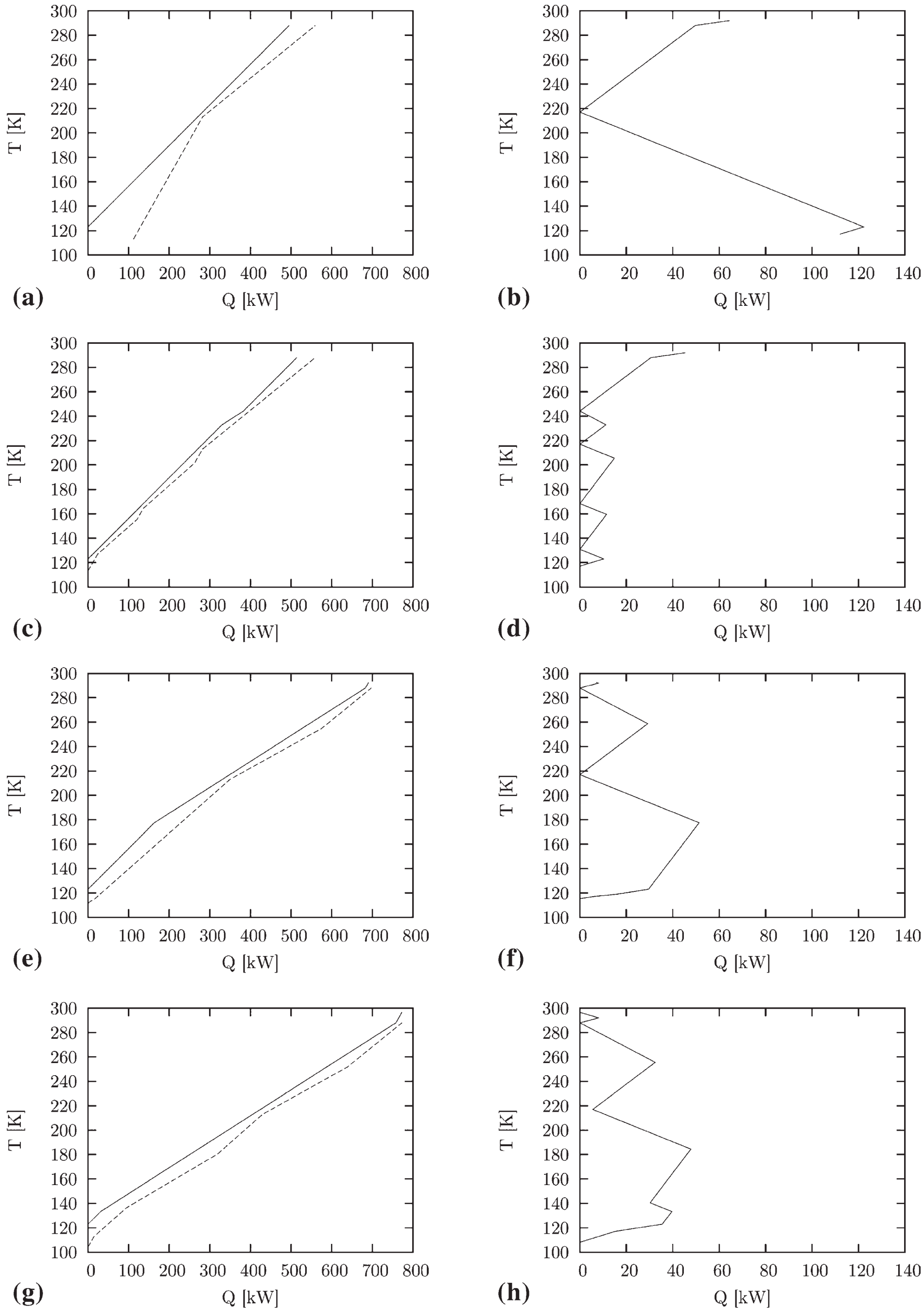


Figure 7. Composite and grand composite curves for the different cases in the simple example.

(a) Composite curves for Case 1. (b) Grand composite curves for Case 1. (c) Composite curves for Case 2. (d) Grand composite curves for Case 2. (e) Composite curves for Case 3. (f) Grand composite curves for Case 3. (g) Composite curves for Case 4. (h) Grand composite curves for Case 4.

provided to the process are minimized. The objective function is given by

$$\min W + Q_{\mathrm{H}} + Q_{\mathrm{C}}. \tag{6}$$

Here, it is optimal to expand stream C2 to 0.116 MPa, recompress to 0.201 MPa, and then expand to 0.1 MPa. Results for the intermediate-state variables are listed in

Table 3. Result for Decision Variables for Case 2 of the Simple Example

Stream	$T_{s,\mathrm{in}}$ (K)	$T_{s,\mathrm{out}}$ (K)	p_s (MPa)
C2	—	155.56	—
C3	126.85	201.56	0.183
H2	244.21	233.00	0.382
C4	164.39	—	—

Table 4. Result for Decision Variables for Case 3 of the Simple Example

Stream	$T_{s,\mathrm{in}}$ (K)	$T_{s,\mathrm{out}}$ (K)	p_s (MPa)
C2	—	197.18	—
C3	142.71	263.99	0.116
H2	304.76	123.47	0.201
C4	103.00	—	—

Table 5. Result for Decision Variables for Case 4 of the Simple Example

Stream	$T_{s,\mathrm{in}}$ (K)	$T_{s,\mathrm{out}}$ (K)	p_s (MPa)
C2	—	180.07	—
C3	125.52	251.65	0.100
H2	296.71	121.44	0.188
C4	103.00	—	—

Table 4. The total net work produced is 58.08 kW, and the cold and hot utilities are 0 and 10.58 kW, respectively, giving an exergy efficiency of 84.9%. The problem was solved in 7 s. In this case, there are two pinch points, one at 217 K/213 K and one at 288 K/284 K.

In Case 4, the minimal irreversibilities are found while fixing the hot and cold utilities to zero. In this case, minimizing irreversibilities is the same as maximizing net work produced. Stream C2 is expanded from 0.4 to 0.1 MPa, recompressed to 0.188 MPa, and expanded to 0.1 MPa. Results for the intermediate temperatures are listed in Table 5. The total net work produced is 47.5 kW, and the hot and cold utilities are both 0 kW, giving an exergy efficiency of 83.2%. In this case, the problem is completely balanced by the hot and cold streams and substreams so that there is no need for hot or cold utilities. The problem was solved in less than 2 s. There exists one pinch point at 288 K/284 K and a near pinch at 217 K/213 K. Again, the GCC touches the temperature axis two additional times at both ends, which indicates that neither cold nor hot utility is required.

By adding additional passes of C2 through the heat exchanger, expanders, and compressors, the exergy efficiency can be further increased; however, the investment cost would be increased significantly while the benefits diminish. It is also possible to set the isentropic efficiencies for the compressors and expanders to a value less than 100%. This will reduce the exergy efficiency but lead to a more realistic process model. Furthermore, the model allows for changes in the heat capacity flow rate of the process streams. In this way, constraints on the utilities as well as the net produced work can be set, forcing them to be zero. This is done in the next example, where an LNG process, which is self-supporting with power and utilities using the cold exergy from liquid carbon dioxide and liquid nitrogen, is optimized.

Design of an LNG process using LCO_2 and LIN as cold carriers

The liquefied energy chain (LEC)[33] is a novel energy- and cost-effective transport chain for stranded natural gas that is used for onshore power production with CO_2 capture and offshore enhanced oil recovery (EOR). It includes an offshore section, a combined gas carrier, and an integrated receiving terminal, see Figure 8. In the offshore section, natural gas is liquefied to produce LNG, while liquid carbon dioxide (LCO_2) and liquid inert nitrogen (LIN) act as cold carriers. The reheated nitrogen is emitted to the atmosphere at ambient conditions, while the CO_2 is transferred at high pressure to an offshore oilfield for EOR. LNG is transported to the receiving onshore terminal in the combined carrier. There, the cold exergy of the LNG is recovered in a liquefaction process for carbon dioxide and nitrogen. In this transport chain, CO_2 can be provided by industrial sources such as cement production, petrochemical plants, or any power plant with CO_2 capture.

In a fully integrated energy chain, the onshore process is connected to an air separation unit that produces nitrogen for the offshore process and oxygen for an oxy-fuel power plant where natural gas is combusted to produce electricity as well as carbon dioxide and water. Water is removed from the flue gas. The CO_2 is compressed to a pressure above the triple point and liquefied by vaporization of the remaining LNG.

The LEC has better exergy efficiency and it is reasonable to believe that it will have lower investment costs than existing technology for dedicated transport of LNG and LCO_2. Furthermore, the concept shows potential for utilization of stranded natural gas with CO_2 sequestration on a commercially sound basis.[29,33]

In this example, it is shown how the ExPAnD methodology[10] and the previously discussed optimization formulation can be used to improve the design and optimize the operation of the offshore LNG process shown in Figure 9. The goal is to design a process that is self-sufficient in the sense

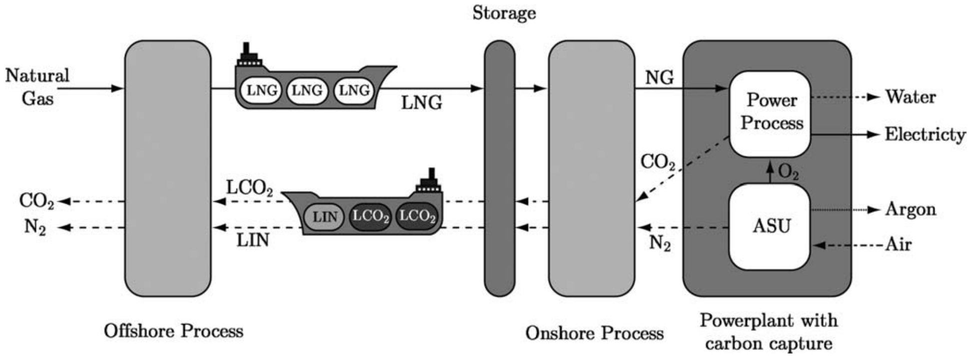


Figure 8. The liquefied energy chain.

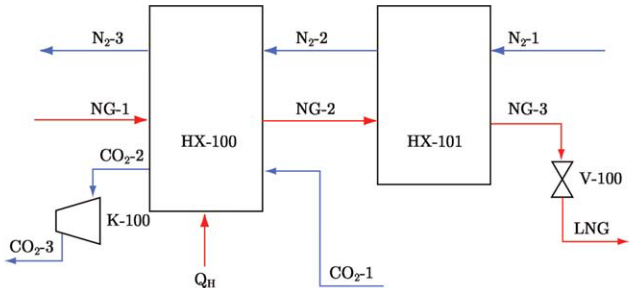


Figure 9. Process flow diagram of the base case offshore LNG process before pressure manipulation.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

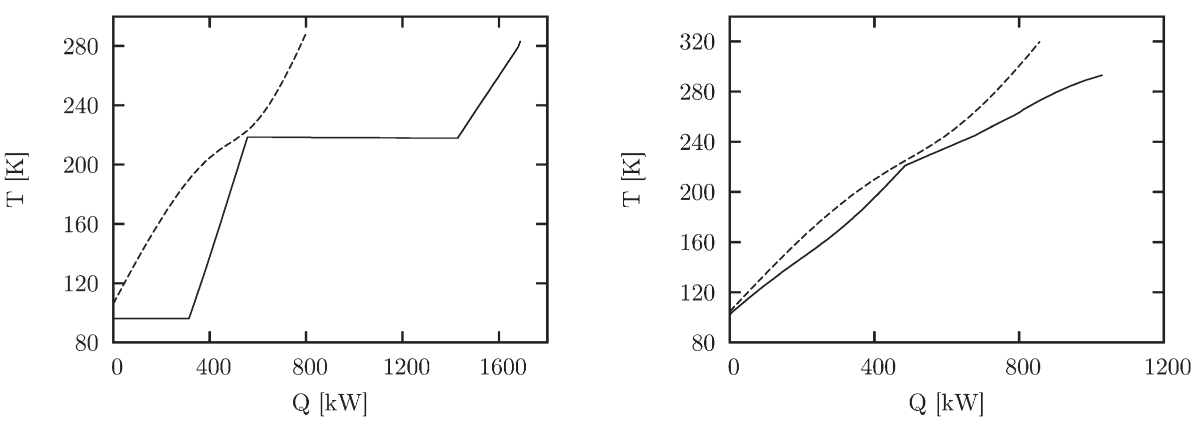
that it does not require the supply of utilities or work because space is at a premium in any offshore process.

Natural gas at 7 MPa and 15°C is to be liquefied and let down to 0.1 MPa and −164.1°C. The state of LCO_2 is to be changed from 0.55 MPa and −54.5°C to 15 MPa and 10°C, whereas LIN at 0.6 MPa and −177°C is to be heated, vaporized, and vented to the atmosphere at 0.1 MPa; the outlet temperature is not specified. The gas composition of the natural gas stream, ambient conditions, and equipment data are as in Ref. 29. The process design calculations are based on a production rate of 1 kg/s LNG. In the case of complete carbon capture, combustion of this natural gas stream will result in 2.73 kg/s CO_2. If one assumes that a practically feasible solution may capture 90% of the generated carbon dioxide, the flow rate of LCO_2 to the offshore LNG process is equal to 2.46 kg/s.

The process is simulated with HYSYS using the SRK equation of state. Figure 10a shows the composite curves (CCs) for the process before any pressure manipulation is performed, which is referred to as Case I. Note that it is necessary to supply hot utility, which is provided by sea water available at ambient conditions. At 57.9%, the exergy efficiency of this process is low because of the large driving forces between the CCs and the energy intensive compression of CO_2 in the gas phase. The flow rate of LIN is minimized while meeting the requirement of no cold utility usage. Two reasons lead to this change in the considered objective. First, the process is to operate on an offshore platform where space restrictions favor a process design that does not require utilities. These constraints, which are introduced in the studied cases below, lead to a meaningless objective if Eq. 5 was still used. Second, the only task liquid nitrogen performs in this process is to provide exergy to the liquefaction train, but, at the same time, it takes up space in the cold carrier that could otherwise be used to ship CO_2. Additionally, a lot of power is required to produce liquid nitrogen in the onshore process. Thus, minimizing the nitrogen flow rate while meeting utility constraints leads to the most economical solution.

For completeness, the flow rates of the various streams, the required or produced work, as well as the exergy conversion efficiency are shown in Table 6. Note the sign convention for W: A positive value indicates that work needs to be supplied, whereas a negative value means that work is generated.

The first step in the design procedure is to use the ExPAnD methodology[10] for streams that undergo a phase transition to develop an improved initial design, referred to as Case II. The heuristics suggest that LCO_2 should be pumped to avoid compression. Likewise, the LIN should be pumped to 10 MPa to avoid the large driving forces in the heat exchanger, thereby transforming temperature-based exergy to pressure-based exergy. The nitrogen stream is then expanded and fed back to the heat exchanger to transform the pressure exergy into work and cold duty at a more appropriate temperature level. Finally, it can be shown that the natural gas should be compressed to 10 MPa before entering the heat exchangers to decrease the heat capacity flow rate of the natural gas stream in the pinch region. The new PFD and CCs are found in Figures 11 and 10b, respectively. Again, the process is simulated with HYSYS using the SRK equation of state. The required amount of LCO_2 and LIN, the net work produced, and the exergy conversion efficiency are found in Table 6. As the composite curves show, the varying heat capacity curve of the natural gas can be tracked much more efficiently leading to a steep increase in exergy efficiency to 74.4% while decreasing the nitrogen



(a) CC before pressure manipulation (Case I) (b) CC after application of ExPAnD (Case II)

Figure 10. Composite curves for the offshore LNG process before pressure manipulation (a) and after application of the ExPAnD methodology (b).

Table 6. Main Results for LNG Case Study

Case	LNG (kg/s)	LIN (kg/s)	LCO_2 (kg/s)	W (kW)	Q_H (kW)	Q_C (kW)	ψ (%)
I	1.0	1.83	2.46	820.2	888.6	0.0	57.9
II	1.0	1.29	2.46	−15.43	172.8	0.0	74.4
IIIa	1.0	0.0	2.46	114.05	15.99	467.76	52.1
IIIb	1.0	0.30	2.46	0.0	136.19	385.19	59.3
IIIc	1.0	0.90	2.46	0.0	24.359	0.0	84.9
IIId	1.0	0.90	2.46	0.0	0.0	0.0	84.6

I refers to the base case design, II after application of the ExPAnD methodology, IIIa–d refer to the different optimization scenarios. $W > 0$ indicates that work needs to be supplied whereas $W < 0$ means that work is generated.

flow rate by 29.5%. For future reference, it should be noted that pumps P-100, P-101, and P-102 require 15.32 kW, 17.61 kW/(kg/s) F_{N_2} and 40.04 kW, respectively, and compressor K-101 uses 58.69 kW.

In the next step, the expansion of N_2 will be optimized to provide cold utility at the temperature levels necessary in order to reduce the required nitrogen flow rate again (Case III). Following the discussion earlier in this article, a cold stream with varying pressure levels is to be heated, expanded, heated, compressed, cooled, expanded, and heated, as this will result in the best trade-off between increases in capital investment and process efficiency. The presented optimization formulation will be used to find the intermediate temperatures and pressures that will result in the smallest nitrogen flow rate.

The stream data for this initial design (inlet and outlet temperatures as well as averaged heat capacity values) are collected from the HYSYS model for Case II. Because the natural gas consists of several components, mostly methane, ethane, and propane, condensation will occur over a temperature interval. In the process, the natural gas stream is cooled at a pressure that is above the critical point. The temperature/enthalpy curve will therefore not have the flat condensation region normally found when condensing a single-component fluid. However, the heat capacity is still far from constant. Therefore, the stream is divided into three individual streams (H1–H3), which yield a reasonably good fit to the actual cooling curve. Similarly, the heat capacity flow rate of the high-pressure liquid nitrogen and liquid CO_2 streams are not constant either. The liquid carbon dioxide stream is divided into two individual streams (C1 and C2). Its inlet and outlet temperatures as well as the pressure and flow rates remain fixed. The high-pressure nitrogen stream to be expanded is treated as a variable stream according to Figure 3 allowing for two expansion cycles and one compression cycle with intermediate heating and cooling, resulting in three possible cold streams and one possible hot stream. The initial cold nitrogen stream is split into three streams (C3–C5) to get more accurate fit of the averaged heat capacities. Expansion, compression, and expansion result in streams C6, H4, and C7, respectively. The outlet temperature of the nitrogen stream is variable. Overall, the process is modeled using a total of four hot and seven cold streams with three possible pressure manipulations, see Figure 12.

Because of the high pressure and low temperature of the nitrogen stream, the first expansion is far from ideal; hence, a nonideal polytropic exponent of $\kappa = 1.51$ together with an efficiency factor for the work of $\eta_C = 0.7$ are used for the first expansion, based on a comparison with the HYSYS simulation. For the possible expansions and compressions below 4 MPa the pressure operator, which is based on the ideal gas model, is accurate. The hot and cold utility temperatures are set to 383.15 and 93.15K, respectively. Here, $\Delta T = 4$K, $\kappa = 1.352$, $\eta_C = \eta_E = 1.0$, $M = 400$K, $U = 1300$kW, and $\varepsilon = 0.1$K. The pressure of C6 is constrained to be between 0.3 and 1 MPa, while the one of H4 can vary between 1.0 and 3.5 MPa. The flow rates of the nitrogen streams are equal throughout the flow sheet; similarly, streams consisting of carbon dioxide have equal flow rate. Table 7 shows the stream data for the optimization model. There are seven decision variables: the nitrogen flow rate (F_{N_2}), the intermediate outlet temperatures ($T_{H4,out}$, $T_{C5,out}$, and $T_{C6,out}$), and pressures (p_{H4}, p_{C6}) of the nitrogen

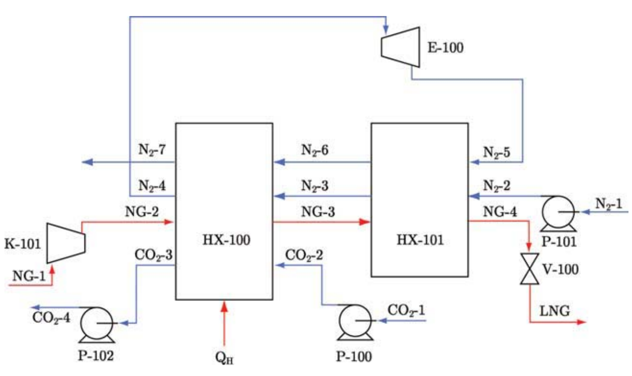


Figure 11. Process flow diagram of the offshore LNG process after applying the ExPAnD methodology.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

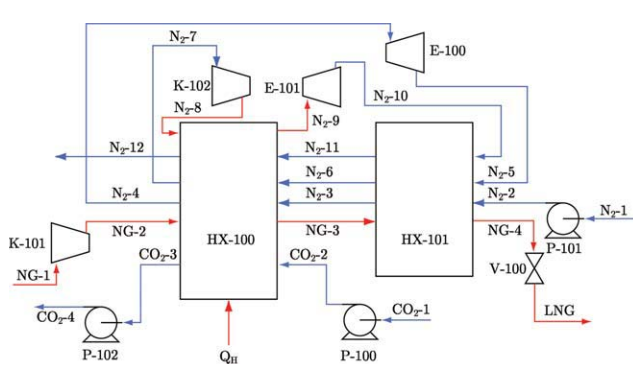


Figure 12. Final process flow diagram for the offshore LNG process.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 7. Given Data for the Optimization of the Offshore LNG Process

Stream	F_s (kg/s)	$c_{p,s}$ (kJ/kg)	$T_{s,\mathrm{in}}$ (K)	$T_{s,\mathrm{out}}$ (K)	p_s (MPa)
H1 (NG-2–NG-4)	1.0	3.46	319.8	265.15	10.0
H2 (NG-2–NG-4)	1.0	5.14	265.15	197.35	10.0
H3 (NG-2–NG-4)	1.0	3.51	197.35	104.75	10.0
H4 (N_2-8–N_2-9)	—	1.15	—	—	—
C1 (CO_2-2–CO_2-3)	2.46	2.11	221.12	252.55	6.0
C2 (CO_2-2–CO_2-3)	2.46	2.48	252.55	293.15	6.0
C3 (N_2-2–N_2-4)	—	2.48	103.45	171.05	10.0
C4 (N_2-2–N_2-4)	—	1.80	171.05	218.75	10.0
C5 (N_2-2–N_2-4)	—	1.18	218.75	—	10.0
C6 (N_2-5–N_2-7)	—	1.07	—	—	—
C7 (N_2-10–N_2-12)	—	1.04	—	—	0.1

streams as well as the outlet temperature of the nitrogen stream ($T_{C7,\mathrm{out}}$). The goal is to design a process that is self-sustained, i.e., that does not require utilities or work, with the minimal nitrogen flow rate. Thus, the objective function is to minimize the flowrate of nitrogen.

The following cases are investigated:

- Case IIIa: minimize flow rate of nitrogen,
- Case IIIb: minimize flow rate of nitrogen so that $W \leq 0$,
- Case IIIc: minimize flow rate of nitrogen so that $Q_C = 0$ and $W \leq 0$,
- Case IIId: minimize flow rate of nitrogen so that $Q_C = Q_H = 0$ and $W \leq 0$.

In Case IIIa, the minimal N_2 flow rate is found using one hot and one cold utility available at 383.15 and 93.15 K, respectively, in accordance with the previously described optimization model. As can be expected in the presence of utilities and external sources of work, no nitrogen is required to support the process. As can be seen from the composite curves, which are not balanced with utilities, in Figure 13a, CO_2 provides only a very narrow temperature interval heat sink for the natural gas stream. Because there is no N_2 stream, no work is produced by expanding it and the process requires that 114.05 kW of work is supplied. Overall, these factors lead to a low exergy efficiency of 52.1%, see Table 6. The problem was solved in 5 s. It should be pointed out that the optimization formulation in this case does not find the given utilities. Instead, because of degeneracy with respect to the objective of minimizing the nitrogen flow rate, it reports results that are increased by an arbitrary constant. However, the minimum utility needed can be calculated easily. The values of the decision variables for all Cases IIIa–IIId are shown in Table 8.

In Case IIIb, an additional constraint is added requiring that the process does not require work, i.e., $W \leq 0$. As a result, the flow rate of nitrogen at the optimal solution is

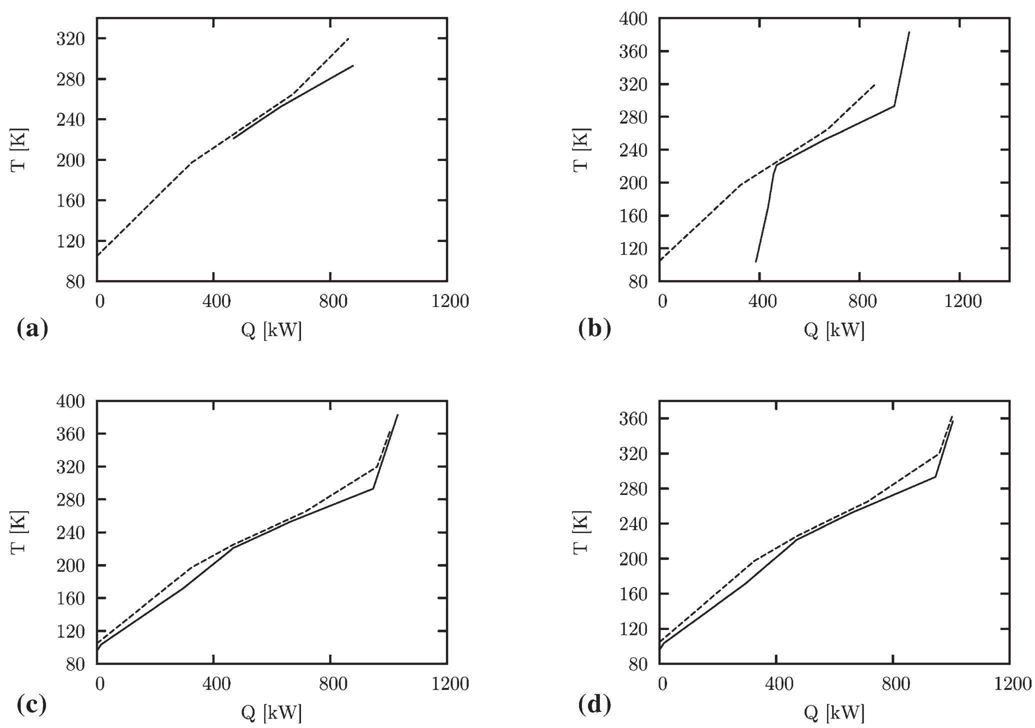


Figure 13. Compositive curve for the offshore LNG process resulting from the different optimization cases.

(a) Case IIIa: minimum N_2 flow rate. (b) Case IIIb: minimum N_2 flow rate with $W \leq 0$. (c) Case IIIc: minimum N_2 flow rate with $W \leq 0$ and $Q_C = 0$. (d) Case IIIc: minimum N_2 flow rate with $W \leq 0$ and $Q_C = Q_H = 0$.

Table 8. Results for the Decision Variables for Case III of the LNG Offshore Process Design

Variable	Unit	Case IIIa	Case IIIb	Case IIIc	Case IIId
F_{N_2}	kg/s	0.0	0.296	0.898	0.898
$T_{H4,in}$	K	319.9	383.15	365.01	365.00
$T_{H4,out}$	K	319.8	383.15	225.12	226.56
p_{H4}	MPa	3.50	3.50	2.677	2.743
$T_{C5,out}$	K	218.75	383.15	222.55	221.11
$T_{C6,in}$	K	97.89	210.39	95.66	95.66
$T_{C6,out}$	K	188.23	383.15	221.12	221.15
p_{C6}	MPa	0.457	1.00	0.390	0.400
$T_{C7,in}$	K	123.73	210.39	95.66	95.66
$T_{C7,out}$	K	315.7	261.05	383.15	357.05

increased though still only a fraction of what had been found in Cases I and II. The required cold utility is decreased in comparison to the previous result, see Table 6. In this case, at the found solution, both p_{C6} and p_{H4} are at their upper bounds, see Table 8. To provide the required work, the inlet temperature of the second expander on the nitrogen stream is chosen as large as possible. This is achieved by heating C5 with utility and by not cooling stream H4. Overall, the exergy efficiency of the design increases to 59.3%, which is still below the results found in Cases I and II. The solution was found in 143 s.

Case IIIc solves the problem with an additional constraint forcing $Q_C = 0$. To make up for the lack of cold utility, the flow rate of N_2 supplied to the process is increased over the previous two cases. Only a small amount of hot utility is required, which is basically used only to heat the vented nitrogen stream to its high outlet temperature. As can be seen from Figure 13, the cold composite curve is able to track the cooling curve of the natural gas nicely. Additionally, the exergy efficiency is increased to 84.9% and surpassed the values found in the early designs (Cases I and II). The solution was found in 13 h and 8 min.

Case IIId adds the constraint that no hot utility may be used, i.e., $Q_H = 0$. The resulting process design is very similar to the results from the previous case, as can be seen in Table 8. This can be explained as follows: The objective function is not impacted when $T_{C7,out}$ is varied within a certain range, but the necessary hot utility Q_H changes, thus creating a degenerate optimal solution. Fixing $Q_H = 0$ removes this degeneracy from the problem and reduces the computational effort, too. The solution was found in 3 h and 26 min. Note that the exergy efficiency is slightly smaller than in the previous result. This results from the reduced exhaust temperature of the vented N_2 stream, which exergy content can be considered lost anyway and is only included for completeness. In comparison to Case II, the nitrogen flow rate could be reduced by 30.4%; in comparison to Case I, it is reduced by 50.8%. Furthermore, the process does not require any supplied utility or work, see Table 6.

Because of the simplifications used in the model formulation, the results cannot directly be implemented in HYSYS when a more rigorous physical property model is selected in the process simulator. For example, given the same pressure difference across an expander and the same temperature at the expander inlet, a reversible process with an ideal gas will result in a different outlet temperature than a reversible process modeled with a cubic equation of state. Similarly, the hot and cold streams are modeled to have constant heat capacities, while HYSYS models the streams more accurately where heat capacity is a function of temperature. Thus, it is necessary to change the intermediate temperatures and pressures found by the model slightly to obtain a feasible result upon implementation of the optimization results in HYSYS.

Discussion

It is shown that by expanding and compressing process streams appropriately (according to the plus–minus principle in PA) the requirements for hot and cold utilities may be significantly reduced. A superstructure for such pressure manipulations is developed, showing that a hot stream may change to a cold stream after expansion and that a cold stream may shift to a hot stream upon compression. If possible, a process stream should be compressed or expanded from the pinch temperature given that the pinch point does not change. As it is likely that the pinch point will change, however, optimization is required.

Allowing for compression and expansion of the process streams will increase the complexity of traditional PA significantly as one stream will result in several streams with the possibility for expansions and compressions. Furthermore, as the inlet temperatures to the pinch operator will vary, it is necessary to use the pinch operator suggested by Grossmann et al.[19] This pinch operator is nonlinear in the case of varying heat capacity flow rates. To model the second-law constraints in the pinch operator, it requires a large number of binary variables leading to a nonconvex MINLP. In addition, a pressure operator and an exergy operator are developed, both are based on ideal gas assumptions. The pressure operator introduces additional nonlinear and nonconvex terms, hence combining the operators (pinch, pressure, and exergy) forms a nonconvex MINLP, which needs to be solved by a global solver. By combining the operators, the minimal irreversibilities for a heat exchanger network that allows for compression and expansion can be solved. Because of the nonconvexity of the MINLP formulation, however, only small problems can be solved at present.

In the examples, a maximum of three pressure manipulations are allowed; however, by adding more heat exchanger passes, compressors, and expanders, even higher thermodynamic efficiencies can be obtained. The marginal effect of adding additional expanders and compressors is not expected to justify the additional capital investments. If the process inlet and outlet specifications are constant, it is possible to find the minimal irreversibilities by minimizing the net exergy input from the hot and cold utilities and maximizing the work produced, as done in the first example. If the heat capacity flow rates of the process streams are allowed to vary, the exergy conversion efficiency including the inlet and outlet exergy of the process streams must be maximized to obtain good results.

From the first studied example, it can be seen that it is possible to obtain a solution (Case 4) where both hot and cold utilities are avoided; such a solution cannot be expected for every problem, though. If ΔT_{min} in Case 2 had been increased it would not have been possible to find a solution without hot or cold utilities and no net work. The exergy efficiency would decrease because of the increased temperature differences (and thereby larger irreversibilities); however, the costs (area) of the heat exchangers would also decrease. For ideal expansions and compressions it is difficult to obtain a solution without utilities and with no net work without changing the flow rate of the process streams. This is easier to achieve with compressor and expander isentropic efficiencies less than 100%, as there will be losses in each compressor/expansion cycle, which are dependent on the inlet temperature.

As can be seen from Table 6, the proposed process of using liquid nitrogen and liquid CO_2 to liquefy natural gas will have a very low thermodynamic efficiency if the pressures of the process streams are not manipulated. The most important contribution to increase the efficiency comes from using sound engineering knowledge formalized in the ExPAnD methodology. However, the selection of the intermediate pressure and temperature levels in the nitrogen loop is not so straightforward. It is here where the optimization formulation delivers additional value. It suggests a process design that satisfies the constraints of no utility usage and further lowers the N_2 flow rate.

Producing hot and cold utilities as well as work can be very expensive in an offshore process; hence, it is shown how these utilities can be avoided by compression and expansion of process streams. Also, because the net work produced cannot necessarily be used at a field site location, it should not be accounted for as useful exergy. Therefore, in Case IIId, constraints are added so that the process is to be self-sustained, that is, without hot or cold utilities and without producing or consuming power. A more thorough description of the processes in the liquefied energy chain can be found in Ref. 29.

There are three main challenges with the proposed model. First, because the problem is a nonconvex MINLP, a global solver, such as BARON or nonconvex outer approximation,[34] must be used to find the global optimum. This has the implication that only small problems such as those considered here can be solved within a reasonable time at present, even with reasonable upper and lower bounds for the variables. Second, it is not easy to set appropriate bounds without having in-depth knowledge of the process to be optimized; hence, the design tends to be an iterative process. Finally, because of the simplifications required for the model, e.g., constant heat capacity flow rate and ideal gas assumptions, the solution found by the global solver may prove not to be feasible in HYSYS simulations, as HYSYS has access to more rigorous thermodynamic models, and thereby gives a more accurate estimate for the process to be designed in the real world. On the other hand, minor adjustments can be made to eliminate this infeasibility.

Conclusions

An optimization formulation for heat and power integration is developed and implemented in GAMS using BARON as the global solver. In this extended problem definition, the process streams are allowed to undergo pressure changes as well as phase and temperature changes. The procedure is particularly suited for subambient processes where pressure-based exergy can be transformed into temperature-based exergy and vice versa by expansion and compression. The resulting design consists of heat exchangers, pumps, compressors, and expanders integrated in a way that minimizes total irreversibilities. To design less complex and less costly processes, constraints can be added that disallow (if at all possible) the use of external heating and cooling as well as external power. The proposed approach combines pinch analysis, exergy analysis, and mathematical programming (a nonconvex MINLP model). It should be stressed that the problem addressed and solved by this new process synthesis tool is significantly more complex than the traditional heat exchanger network synthesis problem. The examples show that manipulation of stream pressures can significantly reduce the total irreversibilities in heat exchanger networks. An industrial application related to LNG shows that the optimization formulation is capable of suggesting a reasonable initial design for realistic problems.

Although the proposed optimization model can give a reasonable design for new processes, the formulation can be improved and expanded to be even more general. First of all a more sophisticated pressure operator based on more accurate equations of state, for example, SRK, should be implemented to achieve more accurate results for nonideal gases. Also, equations for liquid pumping and liquid expansion should be included. Finally, equations for phase transitions should be added. However, as the model already has reached the limit for how large problems one can solve, this is not considered at the current stage.

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Notation

C = set of cold streams
CO = set of stream pairs connected with a compressor
$c_{p,s}$ = heat of capacity of stream s, kJ/kg K
$E_s^{(p)}$ = pressure-based exergy of stream s, kW
$E_s^{(T)}$ = Temperature-based exergy of stream s, kW
$E_s^{(tm)}$ = thermomechanical exergy of stream s, kW
EX = set of stream pairs connected with an expander
$ExQcu$ = exergy of the cold utility, kW
$ExQhu$ = exergy of the hot utility, kW
ExW = exergy of the work provided to the process, kW
F_s = flow rate of stream s, kg/s
H = set of hot streams
i = index of a particular hot stream
j = index of a particular cold stream
k = index of a particular hot stream pinch candidate
l = index of a particular cold stream pinch candidate
M = upper bound on temperature, K
P_0 = ambient pressure, MPa
p_s = pressure of stream s, MPa
Q_H = hot utility used, kW
Q_C = cold utility used, kW
Q_{HOT_i} = heat to be transferred from hot stream i, kW
Q_{COLD_j} = heat to be transferred to cold stream j, kW
q_{ki}^{hp} = heat available from hot stream i above hot pinch candidate k, kW
q_{li}^{cp} = heat available from hot stream i above cold pinch candidate l, kW
q_{kj}^{hp} = heat required from cold stream j above hot pinch candidate k, kW
q_{lj}^{cp} = heat required from cold stream j above cold pinch candidate l, kW

S = set of all process streams
s, s_1, s_2 = indices of particular streams
T_0 = ambient temperature, K
T_U^c = temperature of cold utility, K
T_U^h = temperature of hot utility, K
$T_{s,\text{in}}$ = heat exchanger inlet temperature of stream s, K
$T_{s,\text{out}}$ = heat exchanger outlet temperature of stream s, K
T_{s_2} = temperature of stream s_2 exiting a reversible turbo machine, K
$\Delta T_{\min}$ = minimum approach temperature between hot and cold streams, K
U = upper bounds on the heat transfer, kW
u_{li}^n = binary variable denoting if hot stream i is completely above ($n = 1$), crosses ($n = 2$), or is completely below ($n = 3$) cold pinch candidate l
v_{lj}^n = binary variable denoting if cold stream j is completely above ($n = 1$), crosses ($n = 2$), or is completely below ($n = 3$) cold pinch candidate l
W_s = work required or released by compression or expansion of stream s, kW
w_{ki}^n = binary variable denoting if hot stream i is completely above ($n = 1$), crosses ($n = 2$), or is completely below ($n = 3$) hot pinch candidate k
z_{kj}^n = binary variable denoting if cold stream j is completely above ($n = 1$), crosses ($n = 2$), or is completely below ($n = 3$) hot pinch candidate k
ε = small parameter to distinguish numerically if a stream crosses or is below a pinch candidate, K
κ = polytropic exponent
η_C = isentropic efficiency of the compressors
η_E = isentropic efficiency of the expanders
ψ = exergy efficiency

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