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Modeling Multistream Heat Exchangers with and without Phase Changes for Simultaneous Optimization and Heat Integration

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A new equation-oriented process model for multistream heat exchangers (MHEX) is presented with a special emphasis on handling phase changes. The model internally uses the pinch concept to ensure the minimum driving force criteria. Streams capable of phase change are split into substreams corresponding to each of the phases. A novel disjunctive representation is proposed that identifies the phases traversed by a stream during heat exchange and assigns appropriate heat loads and temperatures for heat integration. The disjunctive model can be reformulated to avoid Boolean (or integer) variables using inner minimization and complementarity constraints. The model is suitable for optimization studies, particularly when the phases of the streams at the entry and exit of the MHEX are not known a priori. The capability of the model is illustrated using two case studies based on cryogenic applications. © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 190–204, 2012
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Introduction

Heat integration in the chemical process industry is usually performed by a sequential strategy. The first step in this strategy is to design and optimize the process while assuming that all the heating and cooling loads will be supplied by the utilities. Once the process conditions (pressure, temperature, and flowrates of streams) are known, heat integration can be performed in the subsequent step, using techniques such as the problem table[1] or LP/MILP transshipment model.[2] The literature also suggests an alternate simultaneous strategy that performs the heat integration while optimizing the process.[3,4] Although the simultaneous strategy is much more difficult to implement and solve, it can lead to larger economic benefits.[5]

A multistream heat exchanger (MHEX) is a single process unit in which multiple hot and cold streams exchange heat simultaneously. MHEXs are very common in cryogenic applications where heat transfer equipment need to be kept compact and well-insulated while recovering heat from streams at very small temperature driving forces.[6] Use of a MHEX to perform such heat transfer tasks often leads to substantial savings in both energy and capital cost. MHEXs are traditionally analyzed using composite curves, a thermodynamic concept used in heat integration called pinch analysis. The streams in an MHEX are multicomponent and typically undergo phase changes. An important issue concerning the use of the pinch concept (or heat integration) for design or optimization of MHEXs is how to handle the nonlinear variation in heat capacity-flowrates when a stream changes phase while exchanging heat, particularly when the phases are not known a priori.

There are a few noteworthy contributions on handling streams with phase changes. Ponce-Ortega et al.[7] proposed a new approximation to the logarithmic mean temperature difference, which handles matches involving phase changes in the heat exchanger network. Their approach assumes

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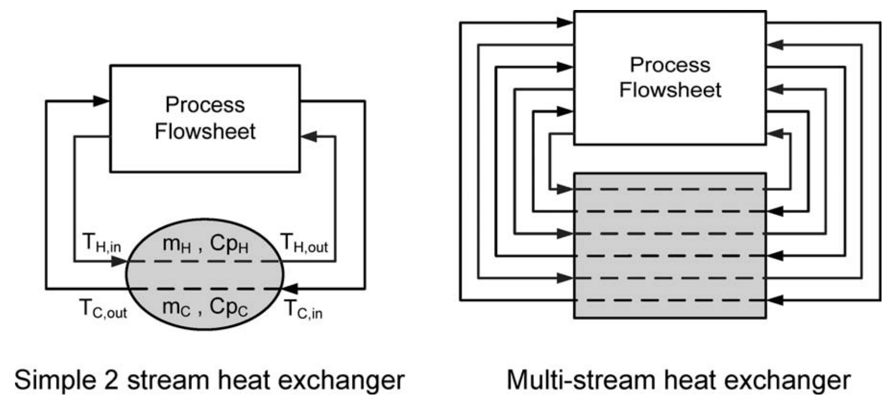

Figure 1. A two stream heat exchanger and a MHEX connected to rest of process flowsheet.

constant sensible and latent heat at isothermal phase changes, but may not be appropriate for multicomponent systems. Also, the work of Hasan et al.[8] can handle nonisothermal phase changes since they construct cubic correlations for each phase in the T-H profile of every stream involved in the heat exchanger network. However, this approach cannot be applied when the composition of stream is also being optimized and the phases traversed in the heat exchanger network are not known a priori. A general high level targeting model that focuses on process optimization while handling phase changes in the heat exchanger networks is still missing and the present work addresses this issue in the context of simultaneous optimization and heat integration of flowsheets containing MHEXs.

Figure 1 shows a simple process representation of a conventional two-stream heat exchanger, and a MHEX whose inlet and outlet streams are connected to other equipment in a process flowsheet. For process modeling, the two stream heat exchanger with hot stream i and cold stream j can be represented by a relatively straightforward model of the form,

$$\begin{aligned} F_i(T_i^{\text{in}} - T_i^{\text{out}}) &= f_j\left(t_j^{\text{out}} - t_j^{\text{in}}\right) \\ T_i^{\text{in}} &\geq t_j^{\text{out}} + \Delta T_{\min} \\ T_i^{\text{out}} &\geq t_j^{\text{in}} + \Delta T_{\min} \end{aligned} \tag{1}$$

An overall energy balance can also be written for the MHEX as

$$\sum_{i \in H} F_i\left(T_i^{\text{in}} - T_i^{\text{out}}\right) = \sum_{j \in C} f_j\left(t_j^{\text{out}} - t_j^{\text{in}}\right) \tag{2}$$

i.e., the net heat content of all the hot streams is same as that of the cold streams. However, in this case the constraints to ensure minimum temperature driving force are nontrivial and cannot be defined explicitly because the matches between multiple hot and cold streams are not known a priori. Even performing an energy balance can be nontrivial when some streams involved in the MHEX change phase during heat transfer. This is because the correlations used to calculate enthalpy depend on the phase (subcooled, superheated, or two-phase region) and since the outlet temperature is not known a priori (it is an output variable of the model), it implies that the phase is not known a priori. This is even more challenging in the context of process optimization because pressure and composition of some or all the streams in the flowsheet are treated as variables, which cause the phase boundaries to move during the optimization.

It is to be noted that a simulation-based process model for MHEX can have exactly one degree of freedom (typically the temperature of one of the outlet hot or cold streams), which is determined by the overall enthalpy balance. The minimum driving force constraint is not inherent in this calculation, and hence there is no guarantee that the solution obtained does not involve temperature crossovers or violates the minimum temperature driving force criterion. Only a feasible set of input parameters can avoid this problem. However, getting such a set of input parameters is not trivial when several hot and cold streams are involved. For example, users of process simulators like Aspen Plus[9] have reported warning and error messages when changing input parameters for simulation of flowsheets containing MHEXs (Zitney, National Energy Technology Laboratory, Morgantown, personal communication, 2009).

It is therefore not surprising that there are hardly any simulation-, or optimization-, based process models for MHEX in the open literature, which take care of these previously mentioned issues. Even the proprietary MHEATX model in Aspen Plus is simulation-based with no straightforward extension for equation-oriented optimization. As a result, design and operating conditions of many cryogenic processes like natural gas liquefaction and air separation are often based on rules of thumb or heuristics. Therefore, there is scope for optimizing the operating conditions and even the state of the streams at the entry and exit points of the MHEX to further improve the process efficiency. Optimization of flowsheets containing one or more MHEXs can be regarded as a case of simultaneous optimization and heat integration, where the inlet and outlet stream conditions of MHEXs are optimized simultaneously along with the rest of the process variables, to minimize overall cost, while satisfying the constraints imposed by the external process as well as feasible heat transfer constraints inherent for MHEXs.

In this article, we propose a general nonlinear equation-oriented model for MHEX that addresses all the issues mentioned above. The proposed model for MHEX can be easily connected to models of other process units and is suitable for use in simulation and optimization of flowsheets containing MHEXs. The process model for MHEX is based on the pinch concept,[1] which ensures that the laws of thermodynamics and minimum temperature driving force criterion are not violated. The next section presents a background on pinch analysis for heat integration and describes the Duran and Grossmann[3] model, which can perform these calculations without using temperature intervals, thereby making it suitable for simultaneous optimization and heat integration. In the third section, the basic model for the MHEX is presented as an inverse of the minimum utility cost problem encountered in heat integration and the model equations are described in the absence of phase changes.

The issue of phase change is dealt within the fourth section, by defining a priori a set of candidate streams, which are capable of phase change. The streams belonging to this set are split into three substreams corresponding to superheated, two phase, and subcooled regions. The phase detection and assignment of temperatures for heat integration are performed using a disjunctive representation involving Boolean variables.[10] The disjunctive model and its working mechanism are described in two subsections. Further extensions of the model include handling small temperature changes and pressure drops, and improving the representation of temperature-enthalpy profile for heat integration. The fifth section shows that the disjunctions can be reformulated to avoid binary variables by solving an inner minimization problem with complementarity constraints.[11,12] The capability of the model is demonstrated using two numerical examples in the last two sections. The first example involves determining optimal usage of an available liquid nitrogen stream as a cooling utility for a heat integration problem. The second example is the commercial Poly Refrigerant Integrated Cycle Operations (PRICO) process for LNG production.[13] Here, the proposed model for MHEX is used within a mathematical programming formulation of the flowsheet of the PRICO process to determine the optimal operating conditions and composition of mixed refrigerant (MR) that minimizes the shaft work required for vapor compression.

Background

Before the introduction of the pinch concept, MHEXs were analyzed graphically by plotting composite curves on the temperature-enthalpy (T–Q) diagram. The hot and cold composite curves are the cumulative heat content of all the hot and cold streams, respectively. When both curves are superimposed, the overlap between them indicates the amount of heat that can be recovered within the process. When the concept of pinch analysis was developed later on, it put forth a simple yet elegant methodology for systematically analyzing the scope of heat integration in chemical processes and the surrounding utility systems with the help of first and second laws of thermodynamics.[1,14] A typical graphical representation of the composite curves in pinch analysis is shown in Figure 2.

There are several high level targeting models that address the heat recovery task described above by solving the well-known "minimum utility" problem, i.e., "Given" a set of hot and cold streams with inlet and outlet temperatures and heat capacity flowrates, determine the minimum hot and cold utility after requirements.

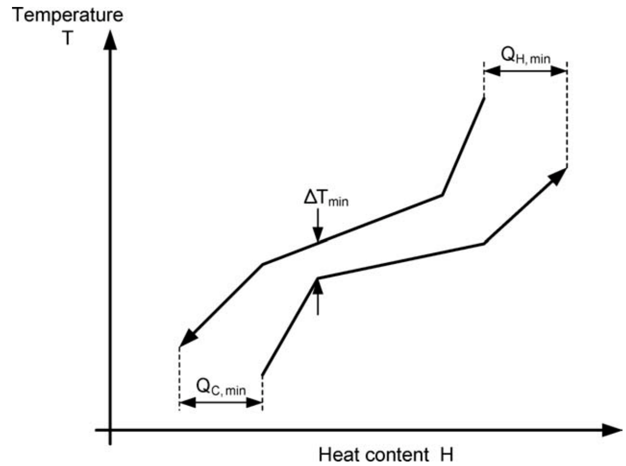

Figure 2. Graphical determination of pinch location and minimum utility loads.

Most of the tools that determine the minimum utility requirement without regard to hardware design proceed by defining temperature intervals and computing enthalpy contributions of the involved streams in each of the temperature intervals. This approach works well if the stream temperatures and flowrates are known a priori; for example, after the process has been designed or optimized. However, if the process conditions are also to be optimized simultaneously, then the process flowrates and temperatures need to be treated as variables that will change during the optimization and the construction of temperature intervals will now imply making discrete decisions. Discrete decision-making will lead to discontinuities and pose problems for nonlinear programming algorithms. Thus, the method of constructing temperature intervals fails in the case of simultaneous optimization and heat integration. To work around this issue, Duran and Grossmann[3] formulated an alternate set of constraints that locate the pinch point without the definition of temperature intervals. The heat integration constraints of their model for minimizing the energy cost allow the treatment of variable flowrates and temperatures as given by the process optimization path, and hence pose no difficulty in simultaneous optimization and heat integration.

Model for MHEX in the absence of phase changes

From the perspective of process modeling, MHEXs can be treated in the same way as heat exchanger networks through the use of high-level targeting models. Consequently, the approach of using the pinch concept in the simultaneous optimization and heat integration of chemical flowsheets can also be applied for simultaneous optimization of flowsheets containing MHEXs. However, an MHEX just exchanges heat between the involved streams and does not consume any hot or cold utilities. Thus, the model for MHEX is equivalent to the following problem statement, which is almost the inverse of minimum utility cost problem, i.e., "Given a MHEX that does not consume any heating and cooling utilities, determine feasible temperatures and heat capacity-flowrates for the involved streams."

Based on the above problem statement, we can modify the Duran and Grossmann[3] model and apply it for MHEXs. The Duran and Grossmann[3] model uses the heat integration constraints to calculate the utility targets, which are embedded with appropriate cost coefficients in the objective function of the overall nonlinear optimization problem for the flowsheet. Our proposed modification involves setting the hot and cold utility loads in their heat integration constraints to a constant value of zero. This forces the heat integration constraints to treat the MHEX as an adiabatic device, i.e., net heat lost by all the hot streams will be matched to the net heat gained by all cold streams. Also, the pinch concept that is inherent in the heat integration constraints enforces maximum heat recovery while ensuring that the minimum driving force criterion is not violated. Since the MHEX does not require hot and cold utilities, it does not contribute any utility cost to the objective function of the parent flowsheet. Thus, the final model for an MHEX is the modified set of heat integration constraints that only need to be embedded as additional constraints in the nonlinear programming model of the overall flowsheet. The problem of simultaneous optimization and heat integration of flowsheets containing MHEXs takes the form,

$$\begin{aligned}
&\min \phi(x,w)\\
&\text{s.t. } h(x,w)=0\\
&\quad g(x,w)\le 0\\
&\Omega(x)=\sum_{i\in H}F_i(T_i^{\text{in}}-T_i^{\text{out}})-\sum_{j\in C}f_j(t_j^{\text{out}}-t_j^{\text{in}})=0\\
&AP_C^p-AP_H^p\le 0,\ p\in P\\
&AP_H^p=\sum_{i\in H}F_i[\max\{0,T_i^{\text{in}}-T^p\}-\max\{0,T_i^{\text{out}}-T^p\}],\ p\in P\\
&AP_C^p=\sum_{j\in C}f_j[\max\{0,(t_j^{\text{out}}-(T^p-\Delta T_{\min})\}\\
&\qquad -\max\{0,t_j^{\text{in}}-(T^p-\Delta T_{\min})\}],\ p\in P
\end{aligned} \tag{3}$$

where H and C are index sets for the hot and cold streams that are involved with the MHEX while vector x, given by $x = (F_i, T_i^{\text{in}}, T_i^{\text{out}}$: all $i \in H$; $f_j, t_j^{\text{in}}\ t_j^{\text{out}}$: all $j \in C$) represents the corresponding temperature and flowrate of these streams. The set $P = H \cup C$ is the index set of pinch point candidates whose temperatures are defined by ($T^p = T_i^{\text{in}}$: all $p = i \in H$; $T^p = (t_j^{\text{in}} + \Delta T_{\min})$: all $p = j \in C$). The vector w represents all the other process parameters and variables that are not associated with heat integration while $\phi(w, x)$, $h(w, x)$, and $g(w, x)$ represent the objective function, mass and energy balances, design equations, and other specifications of the process. Note that the model includes the *max* function which is nondifferentiable at $T = T^p$. This deficiency can be circumvented by either a smooth approximation[3,15] or logic disjunctions.[16] Grossmann et al.[16] have shown that the use of logic disjunctions requires $3n^2$ binary variables where n is the number of streams involved in heat integration. As shown later, the mechanism of handling phase change requires additional flash calculations and substreams for heat integration. Therefore, rather than adding combinatorial complexity to an already nonlinear and nonconvex NLP, we prefer to use the smoothing approximation of Balakrishna and Biegler,[15] which has the following form:

$$\max\{0, f(x)\} = 1/2[\left(f(x)^2+\beta^2\right)^{1/2}+f(x)\Big]. \tag{4}$$

Conditioning of the smooth approximation function can also be improved in Eq. 3 by replacing the upper bound of zero used for $AP_C^p\ (x) - AP_H^p\ (x)$ by a small tolerance ε. This particular smooth approximation belongs to the well-known class of NCP functions that is used for solution of complementarity problems. More information on this problem class can be found in Baumrucker et al.[12] While the values of β and ε are determined by trial and error, we have found that the performance of the NLP solver is usually not very sensitive to this choice. Values of $\beta = 10^{-4}$ and $\varepsilon = 5 \times 10^{-7}$ seemed to work well with the NLP solver CONOPT.[17]

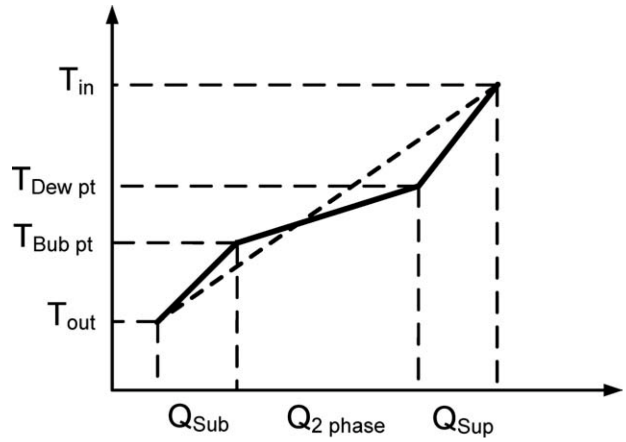

Figure 3. Representation of stream changing phase on T–Q diagram.

Dealing with Phase Changes in the MHEX

Heat integration technology relies on an important assumption of constant heat capacity flowrate. The theory of pinch analysis cannot be readily extended if the variation of heat capacity-flowrate is nonlinear with temperature. Typically, the heat capacity does not vary significantly in the subcooled and the superheated regions, which are in a single phase, and a standard assumption is that the heat capacity-flowrate remains constant in the single-phase regions. However, this assumption does not hold when a stream changes phase while exchanging heat. This is especially important for multicomponent streams, where the phase changes can occur over a large temperature range. Consider a case where a stream traverses through the two-phase region, while the inlet and outlet conditions are in the single-phase regions. On the T–Q diagram, an assumption of constant heat capacity-flowrate implies a single linear segment that joins the inlet and outlet of the stream. This is shown as the dashed segment in Figure 3. In practice, the stream behaves more like the solid lines in Figure 3, which assumes that the heat capacity-flow rate is piecewise constant in each region.

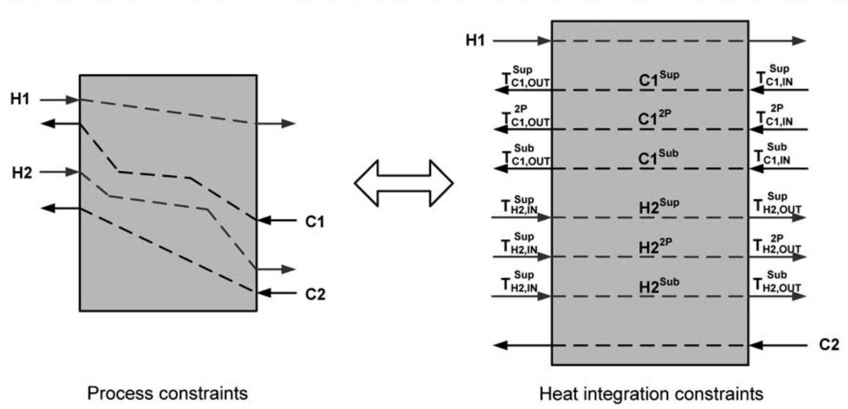

Figure 4. Integrated model for simultaneous optimization and heat integration with phase changes.

It is clear from Figure 3 that the assumption of constant heat capacity-flowrate throughout the temperature range of the stream will cut off the candidate pinch location at dew point if the stream is a hot stream or that at the bubble point if the stream is cold stream. Thus, the assumption of constant heat capacity-flowrate leads to an inaccurate representation of physical and thermodynamic properties, and also the possibility of violating the minimum driving force criterion near the phase boundaries that separate the superheated, two-phase, and subcooled regions.

An important point to be noted is that for the piecewise-linear approximation, dew and bubble points need to be calculated to track the point where the stream changes phase. In the case of simultaneous optimization and heat integration, the dew and bubble points will change during the optimization because pressure and compositions are treated as variables. Also, it is not known a priori whether the stream will indeed traverse the two-phase region or not, because inlet and outlet temperatures of the streams are also treated as variables which can be optimized. Therefore, additional modifications are needed in the previously proposed model for the MHEX so that it can handle the existence and the nonlinear behavior associated with phase changes.

In this article, we propose a new strategy for handling streams undergoing phase change in heat integration in the context of simultaneous optimization, where it is not known a priori whether the stream changes phase or not. We propose to classify a priori the streams involved in heat integration by two mutually exclusive sets of streams: those which are capable of changing phase, and those which do not change phase. Although it is not necessary to define the latter set, knowing a priori from the physical or operating constraints that the stream will remain within the same phase throughout the heat exchange operation helps to reduce the size of the problem. Streams belonging to the former set, which are denoted as parent streams, are subdivided into substreams corresponding to superheated (sup), two-phase (2p), and subcooled (sub) regions. From the point of view of heat integration, the parent stream is disregarded and instead, each of its substreams is treated as a separate stream with corresponding inlet and outlet temperatures and associated heat loads.

Figure 4 demonstrates the new integrated model for simultaneous optimization and heat integration with phase changes for a simple case of two hot streams and two cold streams. Hot stream H1 and cold stream C2 do not change phase and are treated as described in the previous section. Hot stream H2 and cold stream C1 are split into three substreams corresponding to different states. Thus, the MHEX in Figure 4 has four physical streams from the process point of view, but from the heat integration point of view there are eight independent streams. The heat integration constraints require that the substreams be assigned inlet and outlet temperatures and heat loads. As an example, if a hot stream enters as a superheated vapor and exits as a subcooled liquid then these assignments can be easily performed as follows: the substream corresponding to superheated region enters at the superheated inlet temperature of the parent stream and exits at the dew point, the substream corresponding to the two-phase region enters at the dew point and exits at the bubble point, the substream corresponding to subcooled region enters at the bubble point and exits at the subcooled outlet temperature of the parent stream.

The heat loads for each of these substreams can be assigned by evaluating the enthalpy at inlet and outlet conditions of the substreams using the assigned temperatures and selecting the appropriate correlations for the vapor and liquid phases. These calculations also involve finding the dew and bubble point temperatures and corresponding enthalpies at saturated vapor and saturated liquid, respectively. The enthalpy calculation requires the knowledge of flowrate, composition, pressure, and temperature. It is obvious that each of these substreams inherits the flowrate and the overall composition of its parent stream. We will initially demonstrate this strategy for the case where there is no pressure drop for the parent streams as they flow through the MHEX (or it is insignificant and can be ignored). In that case, the substreams also inherit the pressure from their parent streams.

As per our strategy, substreams corresponding to all three phases exist in the model irrespective of actual traversal of phases by the parent stream at any feasible solution for the problem. Obviously, when a particular phase does not exist, we need to ensure that the corresponding substream does not contribute to the heat integration calculations. This is done by setting the heat load of the substream to zero, and setting the corresponding outlet and inlet temperatures to a default value. These tasks are performed using a novel disjunctive model, which is discussed in the next section. In simple terms, this model assigns appropriate inlet and outlet temperatures and heat loads for the substreams in their presence or absence so that they are correctly represented while performing the calculations for heat integration.

Disjunctive model for phase detection

The phases traversed by the parent stream while exchanging heat can be determined if the state of this stream at the inlet and outlet of the MHEX is known. Our model detects the state of the parent stream at the inlet and the outlet by comparing its temperature with dew and bubble point temperatures. The dew and bubble point temperatures can change during the optimization since pressure, temperature, and composition of streams are treated as variables that vary between their upper and lower bounds. It is possible that the inlet and outlet states of the stream are not identical for every feasible solution and correct assignments need to be made for all possible combinations of states at the inlet and outlet. Thus, the task of phase detection and making appropriate assignments involves combinatorial decision-making and this can be best accomplished using disjunctions and logic propositions.[10] The complete model for phase detection consists of three components: disjunctions for phase detection at the inlet and outlet of the MHEX, flash calculations for the two-phase substream that integrate with the disjunctions, and enthalpy calculations and evaluation of heat loads of substreams.

The disjunction for phase detection consists of three terms corresponding to the three possible states. The disjunctions corresponding to the inlet and outlet state of the parent stream involved in the MHEX have the following form:

$$\begin{bmatrix} Y_{\mathrm{IN}}^{V} \\ T_{\mathrm{IN}} \geq T_{\mathrm{DP}} \\ T_{\mathrm{in}}^{\mathrm{sup}} = T_{\mathrm{IN}} \\ T_{\mathrm{in}}^{2p} = T_{\mathrm{DP}} \\ T_{\mathrm{in}}^{sub} = T_{\mathrm{BP}} \end{bmatrix} \vee \begin{bmatrix} Y_{\mathrm{IN}}^{VL} \\ T_{\mathrm{BP}} \leq T_{\mathrm{IN}} \leq T_{\mathrm{DP}} \\ T_{\mathrm{in}}^{\mathrm{sup}} = T_{\mathrm{DP}} \\ T_{\mathrm{in}}^{2p} = T_{\mathrm{IN}} \\ T_{\mathrm{in}}^{sub} = T_{\mathrm{BP}} \end{bmatrix} \vee \begin{bmatrix} Y_{\mathrm{IN}}^{L} \\ T_{\mathrm{IN}} \leq T_{\mathrm{BP}} \\ T_{\mathrm{in}}^{\mathrm{sup}} = T_{\mathrm{DP}} \\ T_{\mathrm{in}}^{2p} = T_{\mathrm{BP}} \\ T_{\mathrm{in}}^{sub} = T_{\mathrm{IN}} \end{bmatrix} \tag{5}$$

$$\begin{bmatrix} Y_{\mathrm{OUT}}^{V} \\ T_{\mathrm{OUT}} \geq T_{\mathrm{DP}} \\ T_{\mathrm{out}}^{\mathrm{sup}} = T_{\mathrm{OUT}} \\ T_{\mathrm{out}}^{2p} = T_{\mathrm{DP}} \\ T_{\mathrm{out}}^{sub} = T_{\mathrm{BP}} \end{bmatrix} \vee \begin{bmatrix} Y_{\mathrm{OUT}}^{VL} \\ T_{\mathrm{BP}} \leq T_{\mathrm{OUT}} \leq T_{\mathrm{DP}} \\ T_{\mathrm{out}}^{\mathrm{sup}} = T_{\mathrm{DP}} \\ T_{\mathrm{out}}^{2p} = T_{\mathrm{OUT}} \\ T_{\mathrm{out}}^{sub} = T_{\mathrm{BP}} \end{bmatrix} \vee \begin{bmatrix} Y_{\mathrm{OUT}}^{L} \\ T_{\mathrm{OUT}} \leq T_{\mathrm{BP}} \\ T_{\mathrm{out}}^{\mathrm{sup}} = T_{\mathrm{DP}} \\ T_{\mathrm{out}}^{2p} = T_{\mathrm{BP}} \\ T_{\mathrm{out}}^{sub} = T_{\mathrm{OUT}} \end{bmatrix} \tag{6}$$

where T_{IN} and T_{OUT} are the inlet and outlet temperature of the parent stream, T_{DP} and T_{BP} are the dew and bubble point temperature of the parent stream and the remaining variables correspond to temperatures of the proposed substreams as seen in Figure 4. The disjunctions work as follows: if the Boolean variable corresponding to any term of the disjunction is true, the corresponding constraints for the substreams are enforced; else the constraints are ignored by making them redundant. Since the disjunctions involve an exclusive OR, only one Boolean variable can be true. Specific examples of various cases in Eqs. 5 and 6 are given in Section 4.2. The proposed disjunctions have the following features:

(a) All constraints in terms of disjunctions are linear. Hence, it is easier to disaggregate the variables and relax the terms of the disjunctions.

(b) For special cases where the inlet or outlet of the parent stream corresponds to the dew or bubble point, two terms of the disjunction intersect at these phase boundaries. Therefore, it does not matter whether the stream is regarded as singe-phase or a two-phase stream at the phase boundaries and no special provisions are necessary to force a particular Boolean variable to be true.

(c) The disjunctions for the outlet can be obtained by simply replacing the subscript in by out in the disjunction for the inlet.

(d) The disjunctions remain the same for both hot and cold streams, and hence can be formulated for all process streams involved in heat integration.

For a hot stream, the states at the inlet and the outlet can also be related to each other using the following logic constraints:

(a) The inlet can be either superheated, two-phase, or subcooled.

(b) If the inlet is superheated, then the outlet is either superheated, two-phase, or subcooled.

(c) If the inlet is two-phase, then the outlet is either two-phase or subcooled.

(d) If the inlet is subcooled, then the outlet is subcooled.

(e) The outlet can either be superheated, two-phase, or subcooled.

(f) If the outlet is superheated, then the inlet is superheated.

(g) If the outlet is two-phase, then the inlet is either superheated or two-phase.

(h) If the outlet is subcooled, then the inlet is either superheated or two-phase or subcooled.

The above constraints can be written as logic propositions that relate the truth values of the Boolean variables in disjunctions (5) and (6),

$$\begin{aligned} & Y_{\mathrm{IN}}^{\mathrm{V}} \veebar Y_{\mathrm{IN}}^{\mathrm{VL}} \veebar Y_{\mathrm{IN}}^{\mathrm{L}} \\ & Y_{\mathrm{IN}}^{\mathrm{V}} \rightarrow Y_{\mathrm{OUT}}^{\mathrm{V}} \veebar Y_{\mathrm{OUT}}^{\mathrm{VL}} \veebar Y_{\mathrm{OUT}}^{\mathrm{L}} \\ & Y_{\mathrm{IN}}^{\mathrm{VL}} \rightarrow Y_{\mathrm{OUT}}^{\mathrm{VL}} \veebar Y_{\mathrm{OUT}}^{\mathrm{L}} \\ & Y_{\mathrm{IN}}^{\mathrm{L}} \rightarrow Y_{\mathrm{OUT}}^{\mathrm{L}} \\ & Y_{\mathrm{OUT}}^{\mathrm{V}} \veebar Y_{\mathrm{OUT}}^{\mathrm{VL}} \veebar Y_{\mathrm{OUT}}^{\mathrm{L}} \\ & Y_{\mathrm{OUT}}^{\mathrm{V}} \rightarrow Y_{\mathrm{IN}}^{\mathrm{V}} \\ & Y_{\mathrm{OUT}}^{\mathrm{VL}} \rightarrow Y_{\mathrm{IN}}^{\mathrm{V}} \veebar Y_{\mathrm{IN}}^{\mathrm{VL}} \\ & Y_{\mathrm{OUT}}^{\mathrm{L}} \rightarrow Y_{\mathrm{IN}}^{\mathrm{V}} \veebar Y_{\mathrm{IN}}^{\mathrm{VL}} \veebar Y_{\mathrm{IN}}^{\mathrm{L}} \end{aligned} \tag{7}$$

Similar logic propositions are written for the cold streams.

The substream corresponding to the two-phase region has to be treated separately. When the outlet of the parent stream lies in the two-phase region, both vapor and liquid phases exist and flash calculations are required for consistent enthalpy calculations, which will now depend on the vapor and liquid fractions and their corresponding compositions. However, flash calculations need not be executed in all cases. If a stream at outlet conditions is not within the two-phase region, then a simple enthalpy balance should be performed using the enthalpy correlation corresponding to the existing phase at outlet. This sequential procedure implies decision-making at run time and would lead to discontinuity in equation-oriented optimization. This can be taken care of by either using disjunctions[18] or by relaxing the VLE constraints using slacks.[19] However, in our proposed formulation that involves substreams, when the two-phase region is not traversed, we are free to assign any specifications for flash calculations as long as the information for the two-phase substream is correctly represented for heat integration, i.e., heat load for substream is zero, and the inlet and outlet temperature are identical. Therefore, in this work we propose a new strategy, which is tailored to integrate flash calculations with the disjunctions. It relies on the following formulation, i.e., to allow vapor liquid equilibrium (VLE) equations for flash calculation to converge to a feasible solution in case of single phase (vapor or liquid) outlet is to operate it at the boundary of the two-phase region. This implies that one of the following is true:

(a) If only vapor outlet exists, then the operating temperature for flash calculations should be same as the dew point temperature of the inlet stream.

(b) If only liquid outlet exists, then the operating temperature for flash calculations should be same as the bubble point temperature of the inlet stream.

This formulation forces the flash to operate as single saturated phase at the boundaries of the two-phase region, i.e., either at dew or bubble point conditions of the parent stream. Consequently, the VLE equations do not need to be relaxed at all, irrespective of state of the parent stream at the inlet and outlet conditions. The flash model operates in the (P,T)-mode, with the heat duty Q_{Flash} being calculated as an output variable from an enthalpy balance. The operating pressure for the flash calculations as well as the inlet flowrate and composition are derived from the parent stream. The remaining inputs, i.e., the operating temperature T_{Flash} and the enthalpy of the stream H_{Flash} inlet will depend on phases traversed by the parent stream, and are supplied by the disjunctions as follows:

$$H_{\mathrm{Flash\ inlet}} = H_{\mathrm{IN}} - H_{\mathrm{V}}(T_{\mathrm{in}}^{\mathrm{sup}}) + H_{\mathrm{DP}} + H_{\mathrm{BP}} - H_{\mathrm{L}}(T_{\mathrm{in}}^{\mathrm{sub}}) \quad (8)$$

$$T_{\mathrm{Flash}} = T_{\mathrm{out}}^{2p}$$

Here, H_{IN} is the enthalpy of the parent stream at the inlet of the MHEX and is assumed to be supplied by the upstream process unit. H_{DP} and H_{BP} are the enthalpy of the parent stream at dew and bubble point conditions, respectively. H_{V} and H_{L} are enthalpy correlations corresponding to the vapor and liquid phases. The heat load Q_{Flash} for the above mentioned flash calculations is evaluated using the energy balance:

$$Q_{\mathrm{Flash}} = VH_{\mathrm{V}}(T_{\mathrm{Flash}}, y) + LH_{\mathrm{L}}(T_{\mathrm{Flash}}, x) - H_{\mathrm{Flash\ inlet}} \quad (9)$$

Here, V and L are the vapor and liquid flowrates from the flash output, and y and x are the corresponding mole fractions. The specifications for flash calculations as given in Eq. 8 are not obvious and therefore we provide further explanation in Section 4.2.

Finally, the heat load for the substreams is given by the following set of equations:

$$Q^{\mathrm{sup}} = F[H_{\mathrm{V}}(T_{\mathrm{in}}^{\mathrm{sup}}) - H_{\mathrm{V}}(T_{\mathrm{out}}^{\mathrm{sup}})] \quad (10a)$$

$$Q^{\mathrm{sub}} = F[H_{\mathrm{L}}(T_{\mathrm{in}}^{\mathrm{sup}}) - H_{\mathrm{L}}(T_{\mathrm{out}}^{\mathrm{sub}})] \quad (10b)$$

$$Q^{2p} = -FQ_{\mathrm{Flash}} \quad (10c)$$

Equation 10 is applicable if the parent stream is a hot stream. For cold streams, we simply reverse the signs of the terms in the right hand sides of Eq. 10. The advantage of our proposed formulation is that all enthalpy calculations are performed outside the disjunctions. As a result, appropriate enthalpy correlations for the vapor and liquid phases are used without any reference to missing or nonexistent phases.

Working mechanism of the disjunctive model

It can be shown that the model proposed above can account for all possible combinations of states for the inlet and the outlet. The working principle of the model is demonstrated with some of these cases.

Case 1: Inlet Is Superheated and Outlet Is Subcooled. For this case, it is clear that the hot stream is traversing all the three states and we expect heat loads for all the substreams to be positive. In this case, $Y_{\mathrm{IN}}^{\mathrm{V}}$ and $Y_{\mathrm{OUT}}^{\mathrm{L}}$ are true and the constraints corresponding to those terms in disjunctions (5) and (6) are enforced so that

$$T_{\mathrm{in}}^{\mathrm{sup}} = T_{\mathrm{IN}} \quad (11a)$$

$$T_{\mathrm{in}}^{2p} = T_{\mathrm{DP}} \quad (11b)$$

$$T_{\mathrm{in}}^{\mathrm{sub}} = T_{\mathrm{BP}} \quad (11c)$$

$$T_{\mathrm{out}}^{\mathrm{sup}} = T_{\mathrm{DP}} \quad (12a)$$

$$T_{\mathrm{out}}^{2p} = T_{\mathrm{BP}} \quad (12b)$$

$$T_{\mathrm{out}}^{\mathrm{sub}} = T_{\mathrm{OUT}} \quad (12c)$$

Equations 11a and 12a imply that the substream corresponding to superheated state enters at the superheated inlet temperature of the parent stream and exits at the dew point temperature. Similarly, Eqs. 11b and 12b point out that the substream corresponding to two-phase region enters and exits at dew and bubble point temperature, respectively. Finally, from Eqs. 11c and 12c, we can conclude that the substream corresponding to subcooled state enters at its bubble point temperature and exits at subcooled outlet temperature of parent stream. Thus, it is clear that inlet and outlet temperatures of the substreams corresponding to the superheated, two-phase, and subcooled regions have been correctly assigned.

If the temperature of the substreams in Eq. 8 are substituted with values given in Eqs. 11 and 12, then the enthalpy of the inlet stream and operating temperature for flash calculations is given by

$$H_{\mathrm{Flash\ inlet}} = H_{\mathrm{IN}} - H_{\mathrm{V}}(T_{\mathrm{IN}}) + H_{\mathrm{DP}} + H_{\mathrm{BP}} - H_{\mathrm{L}}(T_{\mathrm{BP}}) \quad (13)$$

$$T_{\mathrm{Flash}} = T_{\mathrm{BP}}$$

Since $H_{\mathrm{IN}} = H_{\mathrm{V}}(T_{\mathrm{IN}})$ and $H_{\mathrm{BP}} = H_{\mathrm{L}}(T_{\mathrm{BP}})$, it follows that $H_{\mathrm{Flash\ inlet}} = H_{\mathrm{DP}}$. Since $T_{\mathrm{Flash}} = T_{\mathrm{BP}}$, the flash calculations will force an ''only-liquid'' outlet with the same flowrate and composition as that of the inlet. The enthalpy of this liquid outlet will now be given by $H_L(T_{Flash}, x) = H_{BP}$. Substituting the above specifications and output variables of flash calculations in Eq. 9, we get $Q_{Flash} = H_{BP} - H_{DP}$. Thus Eq. 10c becomes

$$Q^{2p} = F(H_{DP} - H_{BP}) \tag{14}$$

The heat load for the substream corresponding to two-phase region as given by Eq. 14 is appropriate since this substream enters as saturated vapor at dew point and exits as saturated liquid at bubble point. If the inlet and outlet temperatures of the substreams corresponding to the superheated and subcooled phases given in Eqs. 11 and 12 are substituted in Eqs. 10a and 10b, we get,

$$Q^{sup} = F[H_V(T_{IN}) - H_{DP}] \tag{15}$$

$$Q^{sub} = F[H_{BP} - H_L(T_{OUT})]$$

which correctly represent the enthalpy of superheating and subcooling for the substreams corresponding to the superheated and subcooled regions, respectively.

Case 2: Inlet Is Superheated and Outlet Is Two-phase (Either Within or on Boundary). For this case, the hot stream is traversing through only two phases, i.e., superheated and the two-phase region. The two-phase region can be either partially or fully traversed depending on the exit temperature of the parent stream. In this case, Y_{IN}^{V} and Y_{OUT}^{VL} are true and the constraints corresponding to those term in disjunctions (5) and (6) are enforced so that

$$T_{in}^{sup} = T_{IN} \tag{16a}$$

$$T_{in}^{2p} = T_{DP} \tag{16b}$$

$$T_{in}^{sub} = T_{BP} \tag{16c}$$

$$T_{out}^{sup} = T_{DP} \tag{17a}$$

$$T_{out}^{2p} = T_{OUT} \tag{17b}$$

$$T_{out}^{sub} = T_{BP} \tag{17c}$$

Equations 16a and 17a imply that the substream corresponding to superheated state enters at the superheated inlet temperature of the parent stream and exits at the dew point temperature. Similarly, Eqs. 16b and 17b point out that the substream corresponding to two-phase region enters at dew point temperature and exits at the two-phase temperature given by the outlet temperature of parent stream. Finally, the nonexistent substream corresponding to the subcooled region is made redundant by assigning identical dummy values of bubble point temperature to both its inlet and outlet using (16c) and (17c), respectively. Thus, it is clear that inlet and outlet temperatures of the substreams corresponding to the superheated and two-phase are correctly assigned, whereas the subcooled substream is rendered redundant.

If the temperature of the substreams in Eq. 8 are substituted with values given in Eqs. 16 and 17, then as demonstrated in the previous case, $H_{Flash\ inlet} = H_{DP}$ whereas the operating temperature for the flash calculation is now given $T_{Flash} = T_{OUT}$. With these specifications, the flash calculations (which are done separately) will enforce correct liquid and vapor outputs at the outlet temperature of the parent stream (since it is already a specification for the flash). The heat load for the two-phase substream will be the difference in enthalpy of inlet and outlet streams of the flash calculations, which is calculated correctly by the energy balance (9).

If the inlet and outlet temperatures of the substreams corresponding to the superheated and subcooled states given in Eqs. 16 and 17 are substituted in Eqs. 10a and 10b, we get,

$$Q^{sup} = F[H_V(T_{IN}) - H_{DP}] \tag{18}$$

$$Q^{sub} = F[H_L(T_{BP}) - H_L(T_{BP})] = 0$$

While Q^{sup} correctly represents the enthalpy of the superheated substream, Q^{sub} takes a value of zero since the subcooled substream does not exist in reality.

Thus, the mechanism proposed in this work assigns correct inlet and outlet temperatures to the existing substreams and makes the nonexistent subcooled substream redundant by forcing its heat load to zero and inlet and outlet temperatures to be identical and equal to some dummy value (in this case, it is bubble point temperature). Similarly, arguments can be made to show that the model works as expected for all the other cases.

Extension for handling streams with small temperature changes

Sometimes, streams involved in heat integration have a significant heat load while undergoing very small temperature changes. Examples are evaporating liquids or condensing vapors, where the temperature change approaches zero as composition approaches that of a single pure component. In conventional heat integration, such streams are usually handled by defining a fictitious temperature drop of one degree for the stream to use well-defined (not unbounded) values for heat capacity-flowrate in the pinch calculations. Although solutions obtained using this approach are only approximate, they provide a tractable way of handling such streams when there are no scaling or numerical issues during enthalpy calculations. We propose a similar approach for handling such streams, and our framework easily allows assigning fictitious temperatures since this information is decoupled from that used for process calculations. We systematize this approach further by defining a small number α as the fictitious temperature drop rather than using a fixed value of one degree. Here, α is user-defined and can be tuned based on the numerical values of heat loads, accuracy, and scalability.

We illustrate below the modifications in temperature assignments in the event of small temperature changes for a general hot substream. We define T_{in}^{PC} and T_{out}^{PC} as the right hand side variables in Eqs. 5 and 6, respectively. We also define T_{in}^{HI} and T_{out}^{HI} as the corresponding left hand side variables in Eqs. 5 and 6, respectively. Our goal is to relax the assignments in Eqs. 5 and 6 for the case when $\Delta T = T_{in}^{PC} - T_{out}^{PC} \leq \alpha$. For this case, we define the heat integration variables T_{in}^{HI} and T_{out}^{HI} through the following disjunction:

$$\begin{bmatrix} \Delta T \geq \alpha \\ T_{\text{in}}^{\text{HI}} = T_{\text{in}}^{\text{PC}} \\ T_{\text{out}}^{\text{HI}} = T_{\text{out}}^{\text{PC}} \end{bmatrix} \vee \begin{bmatrix} \Delta T \leq \alpha \\ T_{\text{in}}^{\text{HI}} = \frac{T_{\text{in}}^{\text{PC}}+T_{\text{out}}^{\text{PC}}}{2} + \frac{\alpha}{2} \\ T_{\text{out}}^{\text{HI}} = \frac{T_{\text{in}}^{\text{PC}}+T_{\text{out}}^{\text{PC}}}{2} - \frac{\alpha}{2} \end{bmatrix} \tag{19}$$

It can be seen that for a special case when ΔT and α are equal, both the terms of the disjunctions are identical and it does not matter which term is selected as true. Cold substreams are dealt with in the same manner except that the sign of ΔT and $\alpha/2$ are reversed. Obviously, the use of this disjunction will lead to an additional integer (or Boolean) variable for every substream considered in the model. One way to avoid these integer variables is to use the max operator as follows:

$$\begin{aligned} T_{\text{in}}^{\text{HI}} &= \max\left(T_{\text{in}}^{\text{PC}}, \frac{T_{\text{in}}^{\text{PC}} + T_{\text{in}}^{\text{PC}} + \alpha}{2}\right) \\ T_{\text{out}}^{\text{HI}} &= \min\left(T_{\text{in}}^{\text{PC}}, \frac{T_{\text{in}}^{\text{PC}} + T_{\text{in}}^{\text{PC}} - \alpha}{2}\right) \end{aligned} \tag{20}$$

along with the smooth approximation of Balakrishna and Biegler.[15] Clearly, knowing a priori that temperature drops for certain substreams are not small will help in reducing the number of such disjunctions or smooth approximations. It is worth mentioning that the model of Grossmann et al.[16] which uses disjunctions for handling isothermal two-phase streams by directly assigning heat loads rather than using heat capacity-flowrates is still recommended when it is known a priori that only a few such streams are traversed. In such cases, a hybrid method based on pinch location can be used, where only substreams with very small temperature changes are handled using the disjunctions of Grossmann et al.,[16] while the rest of the substreams are handled as described in the third section. This is the approach used in the first numerical example presented later. However, the approach of using fictitious temperature change which is modeled using Eq. 19 or 20 is more practical when there are several streams where neither temperature change nor phases traversed are known a priori.

Handling pressure drop

The proposed model for handling phase changes was demonstrated to work effectively under the assumption of no pressure drops for the streams involved in the MHEX. The model can be suitably modified if pressure drops also need to be accounted. Pressure drops are generally complex functions of the thermodynamic and transport properties of the fluid, velocity, and flow pattern of the fluid and the hardware geometry of the heat exchanging device. In practice, pressure drops in the cryogenic streams are usually based on heuristics and operational experience. Also, our intention in this work is to develop a process model with the least possible dependence on hardware design information. The simplest way of including pressure drops is to prespecify the pressure drop for the entire length of MHEX and assume that pressure varies linearly across the length. Since our model is based on heat integration and does not use length or volume of the MHEX, an alternate approach for handling pressure drop would be to assume that the pressure varies linearly with the heat load of the stream. If we define $s \in S = \{\text{sup, 2p, sub}\}$ as set of phases and assume that each phase contributes in an identical manner to the overall pressure drop, the pressure drop for individual phases can be given by

$$\Delta P^s = \frac{Q^s}{\sum_{s\in S} Q^s} \Delta P^{\text{tot}}, \ s \in S \tag{21}$$

If a particular phase does not exist, our model, as discussed earlier, forces the heat load for the corresponding substream to be zero. In this case, Eq. (21) automatically forces the corresponding pressure drop to be zero. The pressures at the inlet and outlet of each substream can be related to pressure drops across individual phases as shown in Eq. 22,

$$\begin{aligned} P_{\text{in}}^{\text{sup}} &= P_{\text{IN}} \\ P_{\text{out}}^{\text{sup}} &= P_{\text{IN}} - \text{DP}^{\text{sup}} \\ P_{\text{in}}^{2p} &= P_{\text{out}}^{\text{sup}} \\ P_{\text{out}}^{2p} &= P_{\text{in}}^{2p} - \Delta P^{\text{2p}} \\ P_{\text{in}}^{\text{sub}} &= P_{\text{out}}^{2p} \\ P_{\text{out}}^{\text{sub}} &= P_{\text{in}}^{\text{sub}} - \Delta P^{\text{sub}} \end{aligned} \tag{22}$$

The pressures given by Eq. 22 are analogous to temperatures for the substreams and are used in the calculations of corresponding inlet and outlet enthalpies. An important point to be noted is that the dew point enthalpy now uses P_{in}^{2p} while the bubble point enthalpy uses P_{out}^{2p} since the dew and bubble point conditions correspond to the two boundaries of the two-phase region. It is clear from Eqs. 21 and 22, and the previously proposed model that there is an implicit relationship between the enthalpies and the pressures.

Improving the approximation for nonlinear T-Q representation

The discretization scheme proposed earlier for handling the nonlinearity in T–Q profile is essentially dividing each phase into only one segment. Depending on the application, a better approximation may sometimes be needed. One way of improving the approximation is to change the discretization scheme from one segment per phase to a larger number of segments, i.e., each of the phases can be further split into piecewise linear segments. This discretization is influenced by the composition and phase characteristics of the heat integrated streams over the range of the optimization variables. This behavior is hard to assess a priori, as it is problem dependent and usually must be determined by trial and error.

Stream discretization can be based either on temperature or heat load. Splitting based on temperature is not advisable because for the special case where a stream has a single pure component the temperature is constant in the two-phase region, and yet, the substream will have a positive heat load. Hence, it is better to subdivide individual phases into segments of equal heat loads. The number of segments used for the approximation need not be the same in each phase. In fact, a good strategy is to use more segments in the two-phase region as compared to single-phase regions, which are expected to be less nonlinear.

For modeling purposes, we define n^s as the number of segments used for phase s. The disjunctions written for inlet and outlet temperatures for the substreams in Eqs. 5 and 6 still apply but with a slight modification. In the disjunction for phase detection at the inlet, i.e., Eq. 5, the inlet temperatures of substreams are replaced by the inlet temperature of the first segment of the corresponding states. Similarly, in the disjunction for phase detection at the outlet, i.e., Eq. 6, the outlet temperatures of the substreams are replaced by the outlet temperature of the last segment of the corresponding state. Thus, the disjunctions now assign inlet and outlet temperature to the first and last segments, respectively, for each state. As before, each of these segments again act as independent streams for heat integration and their inlet and outlet temperatures and heat loads need to be evaluated. The pressures determined at the inlet and outlet of each phase as given by Eq. 22 still apply. Using this information, the inlet and outlet pressure for each segment of each phase can be calculated using Eq. 23,

$$\begin{aligned} & P_{\text{in}}^{s,1} = P_{\text{in}}^{s}, \quad s \in S \\ & P_{\text{out}}^{s,j} = P_{\text{in}}^{s,j} - \frac{\Delta P^s}{n^s}, \quad j=1,\ldots n^s, \quad s \in S \\ & P_{\text{in}}^{s,j} = P_{\text{out}}^{s,j-1}, \quad j=1,\ldots n^s, \quad s \in S \end{aligned} \tag{23}$$

The total heat load corresponding to the states, i.e., Q^s can be calculated using Eq. 10, except that P_{in}^s, P_{out}^s, T_{in}^s, and T_{out}^s are replaced by $P_{\text{in}}^{s,1}$, $P_{\text{out}}^{s,ns}$, $T_{\text{in}}^{s,1}$, and $T_{\text{out}}^{s,ns}$, respectively. Based on a uniform distribution of the heat loads among the segments, the heat load for individual segments j is given by,

$$q^{s,j} = \frac{Q^s}{n^s}, \quad j = 1, \ldots n^s, \quad s \in S \tag{24}$$

The unknown inlet and outlet temperatures for the segments is calculated implicitly through $n^s - 1$ energy balance equations for each state. These energy balance equations have the form,

$$F[H_{\text{in}}^{s,j}(T_{\text{in}}^{s,j}, P_{\text{in}}^{s,j}) - H_{\text{out}}^{s,j}(T_{\text{out}}^{s,j}, P_{\text{out}}^{s,j})] = q^{s,j}, \quad j = 2, \ldots n^s, \quad s \in S \tag{25}$$

along with the additional constraints that the inlet temperature and enthalpy of any segment equals the outlet temperature and enthalpy of the preceding segment.

Reformulation of Disjunctions

The disjunctions for phase detection can be reformulated as a mixed-integer nonlinear programming (MINLP) problem.[20] However, it is also possible to reformulate them as a nonlinear programming problem and thus avoid the use of binary variables. This reformulation is based on the concept of picking the correct function in piecewise smooth domains. The composite function can be represented by the following inner minimization problem and the associated equations[11,12]:

$$\min_y \sum_{i=1}^{N} (x - a_i)(x - a_{i-1}) y_i \tag{26a}$$

$$\text{s.t.} \sum_{i=1}^{N} y_i = 1 \tag{26b}$$

$$y_i \geq 0 \tag{26c}$$

$$z = \sum_{i=1}^{N} f_i(x) y_i \tag{27}$$

where N is the number of piecewise linear segments, $f_i(x)$ is the function defined over the interval $x \in [a_{i-1}, a_i]$, and z represents the value of the piecewise function. Problem (26) is an LP and will set $y_i = 1$ and $y_{j \neq i} = 0$ when $x \in [a_{i-1}, a_i]$. This inner minimization problem can be embedded within an outer optimization problem by writing the optimality (KKT) conditions:

$$\sum_{i=1}^{N} y_i = 1 \tag{28a}$$

$$(x - a_i)(x - a_{i-1}) - \mu_i + \lambda = 0 \tag{28b}$$

$$0 \leq y_i \perp \mu_i \geq 0 \tag{28c}$$

where λ and μ_i are multipliers corresponding to Eqs. 26b and 26c, respectively. For our problem, it is evident that the first constraint in each term of the disjunction given in Eq. 5 or 6 defines intervals in which the temperature of inlet or outlet stream lies. Consequently, we can formulate an inner minimization formulation analogous to Eq. 26 that sets the Boolean variable corresponding to a term of the disjunction to be true when inlet or outlet temperature of the stream lies in the interval generated by that term. The inner minimization problem for phase detection is given by the following equation:

$$\min - [Y^{\text{V}}(T - T_{\text{DP}}) + Y^{\text{VL}}(T_{\text{DP}} T)(T - T_{\text{BP}}) + Y^{\text{L}}(T_{\text{BP}} - T)] \tag{29a}$$

$$\text{s.t.} \qquad Y^{\text{V}} + Y^{\text{VL}} + Y^{\text{L}} = 1 \tag{29b}$$

$$Y^{\text{V}} \geq 0, \quad Y^{\text{VL}} \geq 0, \quad Y^{\text{L}} \geq 0 \tag{29c}$$

The optimality conditions corresponding to Eq. 29 are given by the following constraints:

$$Y^{\text{V}} + Y^{\text{VL}} + Y^{\text{L}} = 1 \tag{30a}$$

$$-(T - T_{\text{DP}}) - \mu^{\text{V}} + \lambda = 0 \tag{30b}$$

$$-(T_{\text{DP}} - T)(T - T_{\text{BP}}) - \mu^{\text{VL}} + \lambda = 0 \tag{30c}$$

$$-(T_{\text{BP}} - T) - \mu^{\text{L}} + \lambda = 0 \tag{30d}$$

$$0 \leq Y^{\text{V}} \perp \mu^{\text{V}} \geq 0 \tag{30e}$$

$$0 \leq Y^{\text{VL}} \perp \mu^{\text{VL}} \geq 0 \tag{30f}$$

$$0 \leq Y^{\text{L}} \perp \mu^{\text{L}} \geq 0 \tag{30g}$$

Equations 30e–30g are complementarity constraints and they are handled using the penalty formulation.[12] Note that subscripts IN and OUT have been omitted in Eqs. 29 and 30

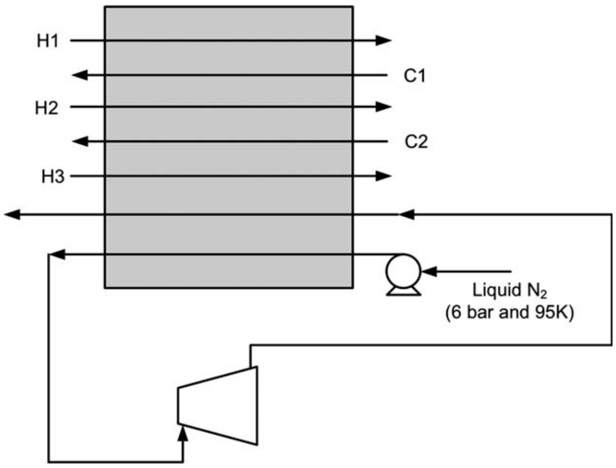

Figure 5. Flowsheet for motivating example.

for the sake of clarity, as the same formulation can be used in an identical manner for phase detection at both inlet and outlet. Logic Eqs. 7 are reformulated as linear constraints with continuous variables and combined with Eq. 30 to complete the formulation.

A Motivating Example

The decoupling of stream information for process calculations and heat integration as proposed in this article allows for flexible process design and optimization of flowsheets having MHEXs. This is first demonstrated using a simple example that combines a classical heat integration task with a flowsheet optimization problem. The schematic of the flowsheet is shown in Figure 5 where several streams from a process flowsheet are exchanging heat in a MHEX. Although hot streams H1 to H3 and cold streams C1 and C2 are allowed to exchange heat, their flow conditions (flowrates, inlet and outlet temperatures, and pressures) are governed by the process and hence are fixed with no available degrees of freedom. The information about these streams that is relevant to heat integration is shown in Table 1. A simple pinch analysis reveals that the above set of process streams requires additional cooling and this is met using a nitrogen stream that is available as a resource within the process.

The auxiliary nitrogen stream is available as a pressurized liquid at 6 bar and 95K and can be exhausted at any pressure as low as the ambient pressure. Although this stream can be used as a conventional cold stream with a single pass through the MHEX to satisfy the overall energy balance, the difference in inlet and exit pressures and along with additional degrees of freedom in the form of flexible inlet and outlet temperatures implies that there is scope to further reduce the operating (energy and material flow) cost. The concept of pressure-based energy can be combined with pinch analysis to derive several types of alternative structural configurations involving compression or expansion of process streams before or after heat exchange.[21]

To illustrate the concepts proposed in this work, we consider the option of pumping the nitrogen stream as a liquid to a higher pressure prior to heat exchange, followed by expansion as a gas, to recover work and add cooling, and finally another heat exchange before it leaves the MHEX at a lower pressure. Increasing the pressure due to pumping reduces the latent heat during heat exchange, thereby providing less cooling for a fixed nitrogen flow. However, it also allows better use of the utility in matching the composite curves (cold utility need not be supplied at the lowest available temperature) with greater extraction of work and cooling in the expander. The objective is to minimize the net cost which includes the material cost (flow of N2 stream) and power (supplied by the expander and consumed by the pump).

The above problem is solved using the strategy of simultaneous optimization and heat integration as described in the previous sections. From the point of view of heat integration, the nitrogen stream during its first pass through the MHEX is subdivided into three substreams corresponding to subcooled, two-phase and superheated regions. During the second pass, it is known a priori that the stream enters the MHEX as a vapor (as it exits the expander as a superheated vapor) and also leaves as a vapor since it is receiving heat. Thus, only the substream corresponding to the superheated phase is considered for the second pass. For this problem, we consider only one segment per phase. Thus, the nitrogen process stream will contribute four cold streams to the heat integration. Although phases traversed and the disjunctions to be chosen are known a priori which simplifies the problem, the temperatures and heat loads of the newly constructed cold stream are unknown and will vary during the optimization. Furthermore, it is known a priori that the two-phase region exists during the first pass and the substream corresponding to it will have identical inlet and outlet temperature, since dew point and bubble point temperatures are identical for pure component nitrogen. As recommended earlier, since there is only one such stream for heat integration that exchanges heat under two-phase conditions at a constant temperature, we use the approach of Grossmann et al.[16] for this substream and the rest of the streams are handled as described in the third section.

The degrees of freedom in this optimization problem are the nitrogen flow rate (F_{N_2}), discharge pressure of pump (P_1), temperature at the exit of first pass through the MHEX (T_1), pressure at exit of expander (P_2) and temperature at the exit of the second pass through the MHEX (T_3). The rest of the output variables can be calculated using mass, energy and performance equations for the involved process equipment such as the pump, expander and the MHEX. The process models use ideal thermodynamics. In terms of physical and thermodynamic properties, only correlations for saturation pressure, specific heat and latent heat are required, which were retrieved from Aspen Plus.[9] Some of the

Table 1. Data for the Fixed Process Streams in the Motivating Example

Stream	T_{in} (K)	T_{out} (K)	F_{cp} (kW K^{-1})
H1	298	250	3.0
H2	265	180	4.0
H3	195	150	2.0
C1	220	245	3.0
C2	255	280	3.5

Table 2. Model Equations, Constraints, and Specifications for the Motivating Example

Expander	Pump
Performance: $\frac{P_1}{P_2} = \left(\frac{T_1}{T_2}\right)^{\frac{\gamma}{\gamma-1}}$	Work: $W_P(\text{kW}) = \frac{(P_1-6)F_{N_2}\eta_P}{\rho_{N_2}}$
Work: W_E (kW) = $F_{N_2}\,\eta_E \int_{T2}^{T1} Cp dT$	Efficiency: $\eta_P = 0.75$
Efficiency: $\eta_E = 0.7$	Liquid density: $\rho_{N_2} = 0.8086$ kg/l
Process constraints	Costs
Minimum approach temperature: $\Delta T_{\min} = 4$ K	Liquid nitrogen streams: $c_F = 0.50$ \$/l
Only vapor phase in expander: $T_2 \geq T_{\text{sat}}\ (P_2)$	Electricity: COE = 0.12 \$/kWhr
Upper bound on pump discharge pressure: $P_1 \leq 15$ bar	Objective
Lower bound on exit pressure: $P_2 \geq 1.01325$ bar	Minimize: $\frac{28.013 c_F F_{N_2}}{\rho_{N_2}} + \frac{\text{COE}(W_P - W_E)}{3600}$ (\$/s)

important process equations and constraints are shown in Table 2. The above problem is modeled as a MINLP and solved within the GAMS equation-oriented environment[22] by using a branch and bound algorithm coupled with the NLP solver CONOPT. The optimization problem results in a system of 129 continuous variables, nine binary variables (corresponding to nine streams for heat integration) and 170 constraints. The optimal solution for the problem is shown in Table 3. As can be seen, it is advantageous to pressurize the nitrogen liquid inlet stream from 6 to 7.25 bar, before it undergoes heat exchange during the first pass. It is interesting to note that the extent of superheat at entry and exit of the expander are 166 K and 74 K respectively. Although the constraint to force only-vapor phase in the expander did not force the exit temperature to reach its lower bound, the optimal exit pressure does reach its lower bound of ambient pressure. Thus, significant work is extracted while ensuring a good match between the composite curves. Finally, the exit temperature of 294 K after the second pass differs from the maximum temperature in the system (inlet temperature of hot stream H1) by 4 K, the value of $\Delta T_{\min}$ prespecified for heat integration.

Industrial Case Study: Natural Gas Liquefaction

We demonstrate our proposed model for MHEXs using the commercial PRICO process for natural gas liquefaction.[23] The PRICO process, shown in Figure 6 uses a single-stage mixed refrigerant (MR) system. The natural gas stream enters at 55 bar and ambient temperature and is liquified by cooling to −155°C. This cooling task is accomplished by using MR, which circulates in a closed loop refrigeration cycle. The objective is to determine the operating conditions and composition of the MR that minimizes the compressor work. The posed problem involves several challenges, which are noted below:

- Outlet of the sea-water cooler (stream S5) can be either in the superheated or two-phase conditions.
- High pressure refrigerant outlet (stream S6) can be either in the two-phase or subcooled conditions.
- Outlet of the throttle valve (stream S7) can be either in the two-phase or subcooled conditions.
- All pressures and temperatures in the flowsheet are free to be varied and can be optimized.
- The MR may include the following components: nitrogen, methane, ethane, propane and butane. Since the refrigerant composition can also be varied, dew and bubble point conditions change accordingly, and hence phase boundaries will move during the optimization.
- Nonlinear thermodynamics are in form of the SRK cubic equation of state, where the appropriate (vapor or liquid) root needs to be selected for existing and nonexistent phases. We refer to Kamath et al.,[24] who describe an equation-based optimization model to accomplish this objective.

As discussed earlier, the number of segments chosen for each phase is a trade-off between a more accurate representation of the temperature-enthalpy nonlinearity and a much larger size of the model. The reduction in error due to an increased number of segments used for each of the phases is shown in Figure 7 for the natural gas stream. We see that two to three segments seem enough to capture the nonlinear effects in the single phase (superheated and subcooled)

Table 3. Optimal Solution for the Motivating Example

Variable	Optimal Value
Nitrogen flow rate, F_{N_2}	0.03 kmol/s
Discharge pressure of pump, P_1	7.253 bar
Exit temperature after first pass through MHEX, T_1	265.735 K
Discharge pressure of expander, P_2	1.10325 bar
Exit temperature after second pass through MHEX, T_3	293.997 K

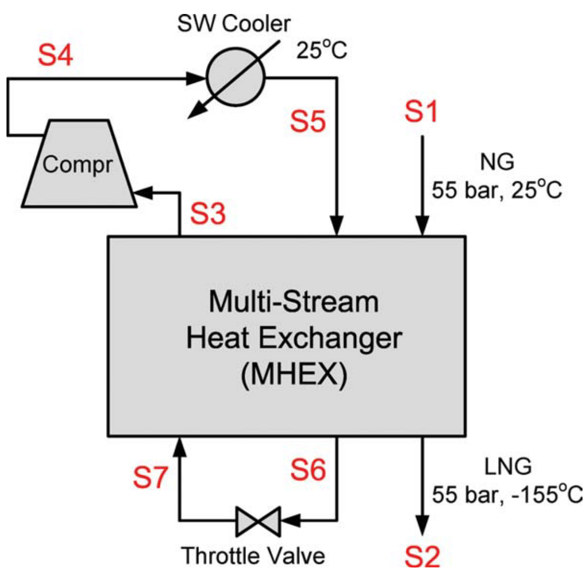

Figure 6. PRICO process for liquefaction of natural gas.

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

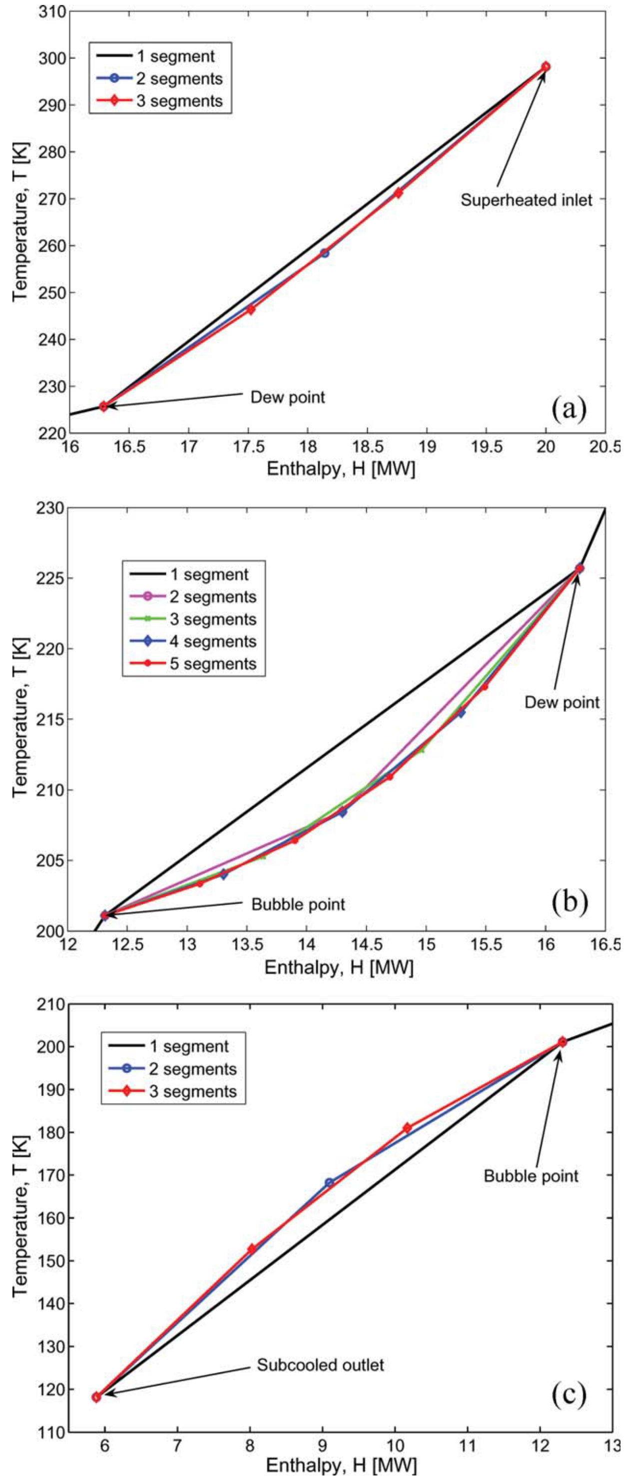

Figure 7. Effect of increasing the number of linear segments used for representing temperature-enthalpy profile.

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

regions. For the two-phase region, the fraction of vapor and liquid changes as the stream loses or gains heat and hence more than three segments may be needed. The nonlinear effects for the refrigerant streams may be slightly different from the natural gas stream because of different pressures and compositions selected for the refrigerant during the optimization. For this case study, the number of segments selected for the superheated, two-phase, and subcooled regions are three, five and three, respectively. We expect that this discretization scheme should be reasonably accurate for most other systems.

Minimizing the compression work in the PRICO process has been studied previously by Del Nogal et al.[25] Their strategy involves two steps. In the first step, a genetic algorithm proposes a set of candidate solutions over a discretized space, which is assessed and refined using an in-house simulator. In the second step, this set of solutions is used as initial guess for determining the optimal solution over the continuous space using standard NLP optimization methods. On the other hand, our formulation allows the use of an equation-oriented strategy for heat integration, phase detection as well as handling of non-existent phases. Consequently, we can solve the same problem as a single medium-size equation-oriented NLP problem using the complementarity formulation described in the fifth section. Although the flowsheet is small, the phase detection and the discretization scheme along with cubic equations for all sub-streams results in a medium-scale problem. The model has 3366 variables and 3426 constraints, and it is implemented and solved using GAMS/CONOPT. Although the problem structure is sparse, it is nonlinear and nonconvex and the solution is aided by bootstrapping initialization based on generating feasible points from the individual units.

The comparison of our optimization results with that of Del Nogal et al.[25] is shown in Table 4. As can be seen, our new methodology is able to find a better optimal solution that features more than 12% reduction in power consumption. It is also worth mentioning that our equation-oriented optimization strategy requires only two CPU minutes as compared to 410 CPU minutes by the integrated genetic optimizer-simulator framework of Del Nogal et al.[25] on similar computer hardware. The key findings about the phases at the optimal solution are

(a) The outlet of sea-water cooler is two-phase.

(b) The high pressure refrigerant at the outlet is subcooled.

(c) The low pressure refrigerant at the inlet is two-phase.

(d) The inlet to compressor is superheated.

In particular, (d) is nonintuitive because simple refrigeration systems are found to be most efficient when the degree of superheat is minimized. However, the PRICO process can be regarded as a refrigeration cycle with internal heat exchange where a certain degree of superheating can sometimes be optimal.[26]

Conclusions

Developing a process model for MHEXs is not trivial owing to issues such as ensuring minimum driving force criteria and accounting for heat load of streams with or without phase changes, particularly when the matches between the streams are not known a priori. This article describes a new equation-oriented process model for MHEX that addresses all of these issues. The process modeling is based on the fact that a MHEX can be regarded as a special case of a heat exchanger network that does not require any utilities. Consequently, the model by Duran and Grossmann[3] for

Table 4. Comparison of Optimization Results for the PRICO Problem

	$\Delta T_{min} = 1.2\%$		$\Delta T_{min} = 5\%$	
	Del Nogal's Work	This Work	Del Nogal's Work	This Work
Power (MW)	24.53	21.51	33.49	28.63
Flow (kmol/s)	3.53	2.928	3.47	3.425
P_{lower} (bar)	4.84	2.02	2.4	1.68
P_{upper} (bar)	43.87	17.129	36.95	26.14
Refrigerant (mol %)				
N_2	10.08	5.82	15.32	12.53
CH_4	27.12	20.62	17.79	19.09
C_2H_6	37.21	39.37	40.85	32.96
C_3H_8	0.27	0.0	0.41	0.0
n-C_4H_{10}	25.31	34.19	25.62	35.42

simultaneous optimization and heat integration can be tailored for modeling MHEXs in the absence of phase changes.

To handle phase changes, a novel strategy is proposed in which the streams involved in the MHEX are split into three substreams corresponding to the superheated, two-phase, and subcooled regions. This is accomplished by using a disjunctive formulation that automatically detects phases and performs the appropriate flash and enthalpy calculations irrespective of the actual phases traversed by the streams. The model was demonstrated using a small motivating example and an industrial case study involving liquefaction of natural gas with mixed refrigerant. It is shown that this equation-oriented optimization strategy can lead to a significant reduction in computation time and even provide better solutions as compared to strategies used in previous work. It is expected that this model will find useful applications in process simulation and optimization of flowsheets that have one or more MHEXs, where the state of the streams entering and/or leaving the MHEX are not known a priori and can be optimized to achieve a desired objective.

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Notation

Roman letters

AP = pinch inequality
Cp = heat capacity
C = set of cold streams
F/f = molar flowrate of hot/cold stream
H = set of hot streams; enthalpy when subscripted
L = molar flowrate of liquid stream
P = pressure
Q = heat duty
T/t = hot/cold stream temperature
V = molar flowrate of vapor stream
w = process variables
x = liquid mole fraction
y = vapor mole fraction
Y = Boolean variable

Greek letters

α = temperature tolerance
β = relaxation in smoothing function
ΔT = temperature difference
ε = relaxation tolerance on pinch inequalities
ϕ = objective function
λ = Lagrange multiplier
μ = bound multiplier
Ω = enthalpy balance function

Subscripts

BP = bubble point
DP = dew point
IN/in = index/properties at stream inlet
Flash = property from flash
OUT/out = index/properties at stream outlet

Superscripts

2p = two phase
HI = for heat integration formulation
L = liquid phase
PC = from process conditions
V = vapor phase
VL = vapor/liquid phase
S/s = set/index of phases
sub = subcooled phase
sup = superheated phase

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