2

Simulation of cryogenic processes

Process simulation is a widely used technique in the design, analysis, and optimization of process plants. Simulators are computer programs that simulate the behavior of the process plants using appropriate mathematical models. Simulators are used for a variety of purposes:

- to perform material balance and energy balance of processes,
- to determine the detailed specifications of all units of a process,
- to troubleshoot startup and shut-down operations,
- to determine performance under off-design conditions,
- to design and troubleshoot control strategies.

Simulators are also extremely useful teaching tools to understand the behavior of individual units as well as interconnected units, namely a complete plant.

Cryogenic processes differ somewhat from general chemical processes. Some of the features special to cryogenic processes include multistream heat exchangers, the possibility of internal pinch points in heat exchangers, large variation in thermophysical properties across the heat exchanger length, operation close to critical temperatures, and double distillation columns. General-purpose commercial process simulators such as Aspen Plus or Hysim have features that accommodate many of these special requirements and therefore can be used to simulate most cryogenic liquefaction and refrigeration processes, including the mixed refrigerant processes studied in this monograph. Cubic equations of state such as the Peng–Robinson or Soave–Redlich–Kwong used in general-purpose simulators, however, do not predict properties of helium, hydrogen, or neon accurately at low temperatures. Higher-order equations of state such as the modified Benedict–Webb–Rubin equation of state need to be used for the simulation of helium, hydrogen, and neon.

Process simulators can be divided into three types based on their architecture, namely

- sequential modular,
- equation-oriented,
- simultaneous modular.

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2.1 Sequential modular simulators

Sequential modular simulators are the most widely used simulators in the industry. The mathematical models representing individual units are coded separately as subroutines in these simulators. The mathematical models are developed so that the output stream data including pressure, temperature, enthalpy, entropy, etc. can be calculated for given input stream data and equipment operating parameters such as pressure ratio, outlet pressure, efficiency of the equipment, etc. While simulating the performance of a process plant, the subroutines representing different units are called in succession, with the output of one unit serving as the input of the next. The computation proceeds unit by unit from the feed to the product streams. When there are recycle loops in the process, the recycle loops are torn at suitable points and estimated values are assigned to these streams. Recycle loops are sequentially solved until the assumed values of the tear streams match the computed stream information.

2.1.1 Example: Open-cycle Linde–Hampson nitrogen liquefier

The sequential modular approach can be better understood by considering a simple example of an open-cycle Linde–Hampson nitrogen liquefier (Fig. 2.1). The design conditions for different equipment of the liquefier are shown in Table 2.1. The simulation starts with the heat exchanger. The conditions of outlet streams 3 and 5 can be determined from that of inlet streams 2 and g and the operating characteristic of the heat exchanger given the effectiveness or temperature approach between the streams at the warm or cold end of the heat exchanger. The temperature and flow rate of one of the two input streams of the heat exchanger (stream 2) are known. The temperature and flow rate of the second input stream, stream g in Fig. 2.1, are, however, not known. The temperature of streams 3 and 5 can be determined only when that of stream g is known. The flow rate of stream g, however, is dependent on the temperature of stream 3 entering the J-T valve. Thus, the conditions of stream 3 and g are interdependent. Streams that are interdependent are known as recycle streams. In such cases, the recycle is broken by tearing a recycle stream as shown in Fig. 2.2. The flow rate, pressure, and temperature of stream g' in Fig. 2.2, are assumed. With the enthalpy and flow rate of the two input streams known, the temperature (enthalpy) of the two outlet streams of the heat exchanger (3, 5) can be calculated from the specified heat

Table 2.1. Design specifications for a Linde–Hampson liquefier shown in Fig. 2.1

Compression process	Isothermal
Compressor outlet pressure	200 bar
Heat exchanger effectiveness	95%
Pressure drop in heat exchanger	0 bar
Valve outlet pressure	1 bar
Pressure drop in phase separator	0 bar

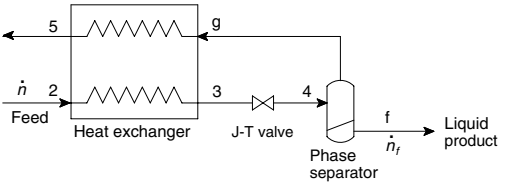

Fig. 2.1. Open-cycle Linde–Hampson liquefier.

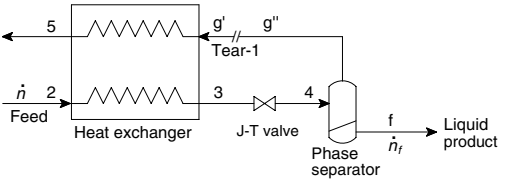

Fig. 2.2. Sequential modular simulation model of an open-cycle Linde–Hampson liquefier with tear stream g.

exchanger effectiveness or temperature approach between the streams at the warm or the cold end of the heat exchanger [see Eq. (1.50)].

The relationship between the mole flow rate of the tear stream g′ and that calculated after solving the governing equations of the heat exchanger, J-T valve, and the phase separator (stream g″) can be mathematically expressed as follows:

$$\dot{n}_{g''} = f(\dot{n}_{g'}). \tag{2.1}$$

The assumed mass flow rate $\dot{n}_{g'}$ will be the same as that calculated ($\dot{n}_{g''}$) when only the tear streams g″ and g′ are converged. The Wegstein method or a gradient method can be used to revise $\dot{n}_{g'}$ so that $\dot{n}_{g'} = \dot{n}_{g''}$. Convergence of any tear stream is assumed to have occurred when the enthalpy, flow rate, and concentration of the different components of the tear streams are about the same.

The temperature and vapor fraction at the exit of the J-T valve can be determined from the enthalpy of the inlet stream ($h_3 = h_4$). The determination of flow rates of the liquid (stream f) and vapor outlet stream (stream g″) of the phase separator is straightforward in the case of pure fluids. An isothermal flash calculation needs to be performed to determine the composition and flow rates of the liquid and vapor outlet streams in the case of mixtures (see refs. [67, 95] for the possible methods). The assumed stream information (in this case, the mass flow rate of g′) is altered at the end of each computation cycle to achieve convergence between assumed stream g′ and computed streams g″. The simulation procedure is shown in Fig. 2.3.

Table 2.2 shows the input file for the simulation of the open-cycle Linde–Hampson nitrogen liquefaction process shown in Fig. 2.2 using CRYOSIM, a process simulator developed by the author and his students [53, 74, 85]. When the converged stream g′ does not match stream g″, the computation shifts to the heat exchanger block *hx* with a new (revised) g′. The stream numbers need to be preceded by any letter/word (s in the present example) with CRYOSIM.

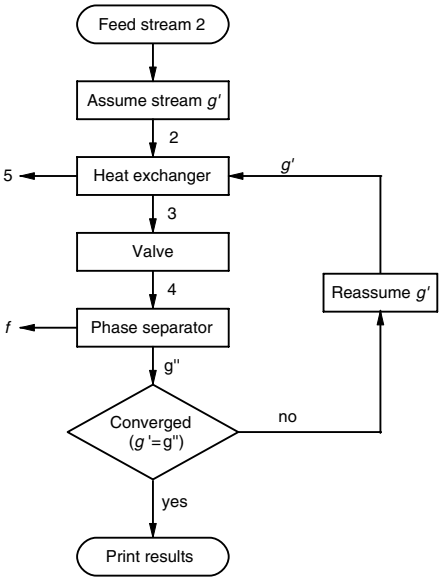

Fig. 2.3. Sequential modular simulation model for an open-cycle Linde–Hampson liquefier shown in Fig. 2.2.

Table 2.2. Input file for the simulation of a Linde–Hampson liquefier shown in Fig. 2.2 using the CRYOSIM process simulator.

```
Linde_Hampson_liquefier flowsheet {
        prop_pack = thermopack
        eos_type=peng_robinson
        components=n2 }
s2 = stream {
        flowrate = 100 kmol/hr
        pressure = 200 bar
        temperature = 300 K
        composition = (n2=1) }
sg' = stream {
        flowrate = 95 kmol/h
        pressure = 1 bar
        vapor_fraction = 1.0
        composition = (n2 = 1) }
hx = heatex2(s2:in, sg':in, s3:out, s5:out) {
        effectiveness = 1 }
jt = jt_valve(s3:in,s4:out) {
        pressure = 1 bar }
ps = phase_sep(s4:in, sf:liquid, sg':vapor)
c1 = converge(sg'':computed, sg':assumed) {
        go_to = hx
        convergence_method = wegstein }
```

Both graphical user interface and text-based inputs such as that shown in Table 2.2 can be used in commercial process simulators such as Aspen Plus. Consider an open-cycle Kapitza nitrogen liquefier (Fig. 2.4). There are two heat exchangers in the process. Hence, there must be two tear streams. The cold streams entering the heat exchanger (11, 12) are torn as shown in Fig. 2.4. Figure 2.5 shows the procedure to be followed for the simulation of the Kapitza open cycle using the sequential modular approach. The two tear stream convergence loops are nested, resulting in a large number of iterations when the estimated values of the tear streams are far from the converged values. The maximum number of nested convergence loops among the processes discussed in Chapter 1 occurs in the case of the Collins helium liquefaction process due to the presence of five heat exchangers.

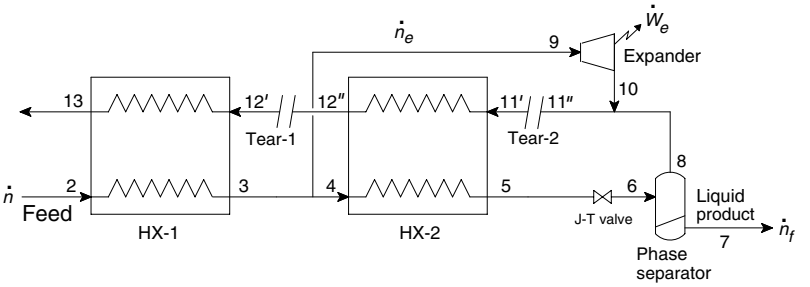

Fig. 2.4. Schematic of a Kapitza liquefaction process.

Advantages

The sequential modular method offers the following advantages:

- Process computations follow the material flow through the process. It is therefore easy to debug convergence failures.
- The mathematical models of different units (multistream heat exchangers, distillation columns, etc.) can be developed and coded separately with different solution procedures for different equipment modules.
- New types of equipment modules can be easily added. The only criterion that needs to be kept in mind while developing the new module is that the output stream information should be calculated for given input stream information and operating conditions of the equipment.
- The overall solution procedure is not affected by the complexities incorporated in each module.

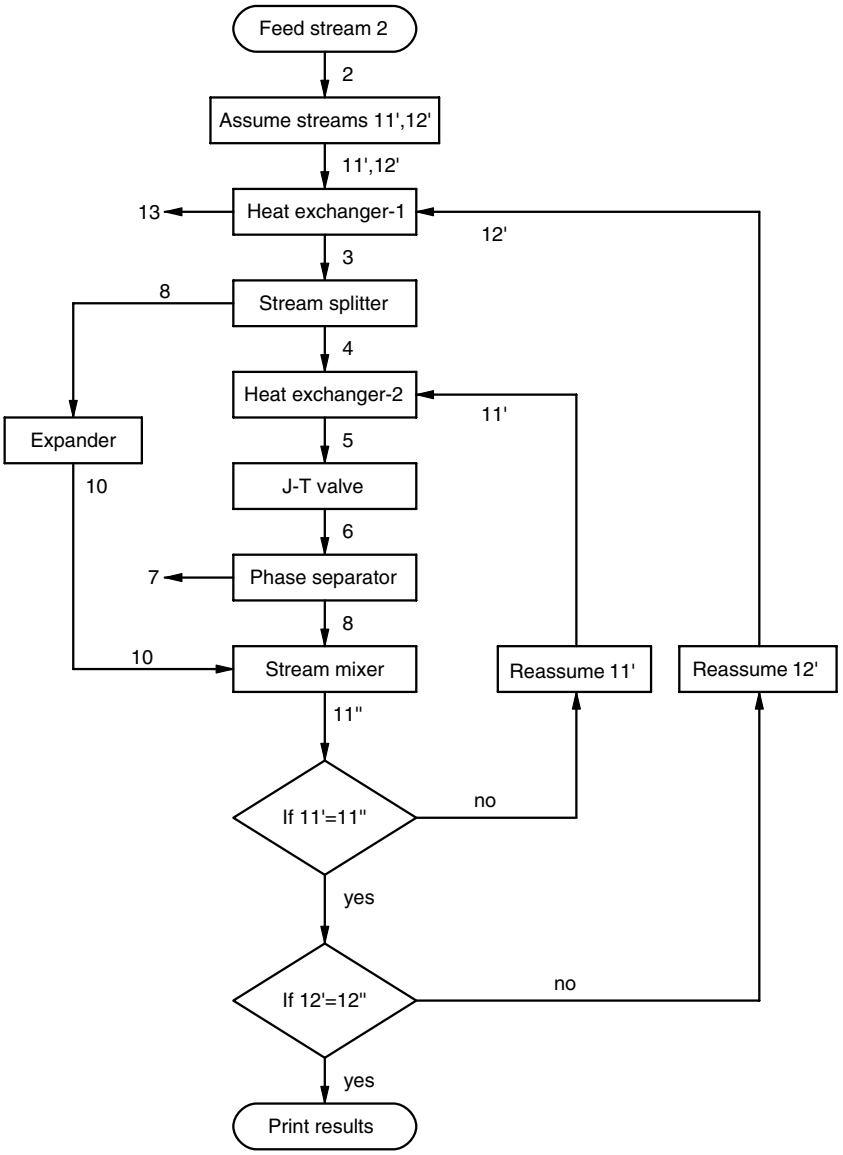

Fig. 2.5. Sequential modular simulation model for an open-cycle Kapitza liquefier (Fig. 2.4).

Disadvantages

The sequential modular approach, however, has two disadvantages:

- Computations can sometimes fail to converge when the process is strongly interconnected or when the number of tear streams is large.
- The computation time is high when the number of tear streams is large.

2.1.2 Tearing of recycle streams

Heat exchangers in which the cold stream is derived from the hot stream are sometimes known as regenerative heat exchangers. These are different from heat exchangers known as regenerators, in which heat transfer takes place between a solid and only one fluid at any point of time. One recycle stream needs to be torn for each regenerative heat exchanger. There is one recycle stream in the open-cycle Linde–Hampson liquefier shown in Fig. 2.2, and two in the closed-cycle Linde–Hampson liquefier (Fig. 1.18): one due to recycling of heat in the heat exchanger, and another due to recycling of mass (stream 5). There are two recycle streams for an open-cycle Kapitza liquefier (Fig. 2.4) and six for a closed-cycle Collins liquefier (Fig. 1.48).

Recycle streams need to be torn at appropriate locations in sequential modular simulators. The theory for automatic tearing of complex flowsheets is well developed (see Ref. [91]). Most modern process simulators tear the recycle streams automatically without the need for any user intervention. However, convergence problems do arise in some cases, and it is helpful to specify the tear streams manually. Tearing of the cold streams entering each regenerative heat exchanger has usually been found to be effective in our studies [74, 85]. If more than one cold stream exists in any heat exchanger, only one cold stream needs to be torn. The stream leaving the condenser (or aftercooler) can be torn in the case of closed-cycle systems.

2.2 Equation-oriented simulators

The governing equations of each process unit is solved one at a time, sequentially, in the case of a sequential modular approach, while the governing equations of all the units are solved together simultaneously in an equation-oriented approach. In the equation-oriented approach, each equipment module contributes the governing equations to be solved. Tearing of streams is not necessary in the equation-oriented approach since all the governing equations are solved simultaneously.

The equation-oriented approach offers the following advantages over the sequential modular method:

- As all equations are solved simultaneously, there is no need for nested iteration loops, which makes it suitable for simulation of strongly interconnected processes with many recycle loops.
- It is best suited for design optimization and dynamic simulation studies where the process needs to be simulated thousands of times.

The equation-oriented approach, however, has the following demerits:

- Good initial estimates are required for all variables for convergence.
- It is hard to handle errors when there is inconsistency in specifications.
- The addition of new equipment modules is not simple.
- A general-purpose, robust, nonlinear equation solver is required.
- Inequality constraints involving design variables are harder to implement in design optimization studies compared to sequential and simultaneous modular approaches.

While the sequential modular approach continues to be the workhorse of the industry, process simulators that have both sequential modular and equation-oriented capabilities such as the Aspen Plus are now commercially available. A few iterations in the sequential modular mode are normally needed to estimate the initial values of all variables, before the equation-oriented method can be used to reach convergence.

2.3 Simultaneous modular simulators

Consider a process with multiple tear streams. In a sequential modular approach, all tear stream convergence loops are nested one inside the other, as shown in Fig. 2.5. Only one tear stream is revised in each of these loops. This leads to a large number of iterations for convergence of all the tear streams in a sequential modular approach. In the simultaneous modular method, also known as the two-tier method, the sequential modular method is used as the basic technique for the solution of process flowsheets, with simultaneous reassumption of all tear streams as in the equation-oriented method (during convergence). The simultaneous modular approach thus combines the good features of both the sequential modular and equation-based approaches. Simultaneous modular approach is also favored for design optimization studies. In this approach, the tear stream convergence becomes an additional equality constraint in the optimization problem. The design variables and tear stream variables are varied at the end of each iteration simultaneously to reach the maxima (or minima) of the objective function while converging the tear streams simultaneously. A combination of simultaneous and sequential modular approaches is sometimes preferred. The first few iterations of the optimization problem are solved to converge the tear streams in a sequential modular approach, and the final convergence is achieved using the simultaneous modular approach. The simultaneous modular approach is also used in CRYOSIM [74] for optimization studies.

Most cryogenic processes discussed in this monograph have fewer than 10 recycle streams, and convergence is fairly rapid with the sequential modular approach. Hence, both the sequential modular and equation-oriented approach can be used to simulate mixed refrigerant processes. The simultaneous modular approach is recommended for design optimization studies.

2.4 Simulation of heat exchangers with pinch points

Pinch points form in cryogenic heat exchangers due to the large variation of specific heat or enthalpy with temperature as discussed in Section 1.16. Consider a Kapitza nitrogen liquefaction process (Fig. 1.42). The cold box that excludes the compressor and aftercooler can be simulated separately, as shown in Fig. 2.4. The flowsheet needs to be torn at two places (streams 11 and 12). While the design effectiveness or the temperature approach at the warm end can be specified for the first heat exchanger, the heat exchanger effectiveness cannot be specified for the second heat exchanger because of the possibility of an occurrence of a pinch point (Figs. 1.50 and 1.51). It is customary to specify the minimum temperature approach between the streams in the heat exchangers with pinch points. In this section, the methods to simulate the performance of a heat exchanger with a pinch point are described.

Consider a heat exchanger shown in Fig. 2.6. The temperatures of the hot and cold streams $T_{h,o}$, $T_{c,o}$, and $T_{c,n}$ are specified, along with the mass flow rates of the two streams. The temperature of the hot stream leaving the heat exchanger $T_{h,n}$ can be determined from an energy balance across the entire heat exchanger. The subscripts o refers to the warm end and n refers to the cold end.

The heat exchanger is divided into n parts such that the heat transferred across each part is the same, or the temperature change of the maximum heat capacity rate fluid stream $(\dot{m}c_p)_{\max}$ across each part is the same. The heat transfer rate across any ith part $(d\dot{Q}_i)$ will be known when either of these methods is adopted.

Consider any ith part of the heat exchanger (Fig. 2.7). The temperatures of the hot and cold streams entering the heat exchanger are designated as $T_{h,i-1}$ and $T_{c,i}$, respectively. The temperatures of the hot and cold fluid streams leaving the heat exchanger are designated as $T_{h,i}$ and $T_{c,i-1}$, respectively, as shown in Fig. 2.7. The simulation of a heat exchanger with pinch begins at the warm end of the heat exchanger (part 1). The temperatures of the streams at the warm end of part 1 ($T_{h,o}$ and $T_{c,o}$) are known. Since the heat transferred across part 1 ($d\dot{Q}_1$) is also known, the temperature of the hot and fluid streams at the cold end of part 1 ($T_{h,1}$ and $T_{c,1}$) can be estimated from a simple energy balance across part 1. With the temperature of the hot and cold fluid streams at the warm end of part 2 (cold end of part 1) now known, the procedure is repeated from parts 2 to n. The smallest of the temperature approaches between the streams ($T_{h,i} - T_{c,i}$) gives the minimum temperature approach between the

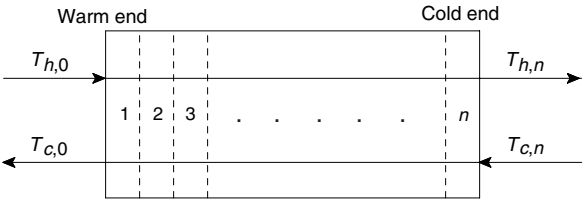

Fig. 2.6. Model of a two stream heat exchanger divided into n parts.

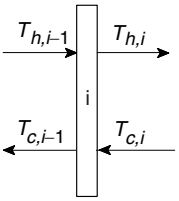

Fig. 2.7. Temperatures at the entry and exit of the ith part of a two-stream heat exchanger divided into n parts.

streams. If there are points of inflection in the temperature approach-heat load curves, the relevant parts are subdivided to determine the minimum temperature approach. CRYOSIM uses the Brent method [26] to subdivide the parts and determine the minimum temperature approach.

The above method can also be extended to multistream heat exchangers. All but one stream temperature needs to be specified to determine the minimum temperature approach in a multistream heat exchanger. Similar methods are used in the MHeatX module of the Aspen Plus process simulator, the heatexm module of the CRYOSIM process simulator, and the LNG heat exchanger module of some other simulators.

Consider the second heat exchanger of the open-cycle Kapitza nitrogen liquefaction process shown in Fig. 2.4. When only the minimum temperature approach between the streams is specified as the operating condition, the outlet temperature of the hot stream (T_5 in Fig. 2.4) is changed iteratively to meet the desired minimum temperature approach. For the second heat exchanger in Fig. 2.4, this relationship between the temperature of the hot stream leaving the heat exchanger (T_5) and the minimum temperature approach between the streams is shown in Fig. 2.8.

A minimum temperature approach of 5 K can be obtained when T_5 is 105.1 K. The desired pinch point temperature can thus be obtained by varying T_5. The minimum temperature approach condition is solved using the following expression:

$$f(T_5) = \Delta T_{\min} - \Delta T_{\min,\,\text{specified}} = 0. \tag{2.2}$$

The Newton method can be used to converge the function $f(T_5) = 0$. Most commercial process simulators have provisions for similar functions to be specified as design specifications.[1] Alternately, one can converge $f(T_5)$ and the tear streams simultaneously in the case of the simultaneous modular approach. $f(T_5)$ becomes an additional equation to be solved in the case of the equation-oriented approach.

Figure 2.9 shows the pinch point in the second heat exchanger of a Kapitza nitrogen liquefier operating at 30/1 bar for different values of temperature of the high-pressure fluid leaving the second heat exchanger (T_5). It can be seen that one or more temperature crossovers is observed at low values of T_5. Pinch point occurs in this case due to the specific heat becoming infinite during the constant temperature condensation process. The large variation of the specific heat (c_p) at temperatures close to the

[1] Design Spec in Aspen Plus.

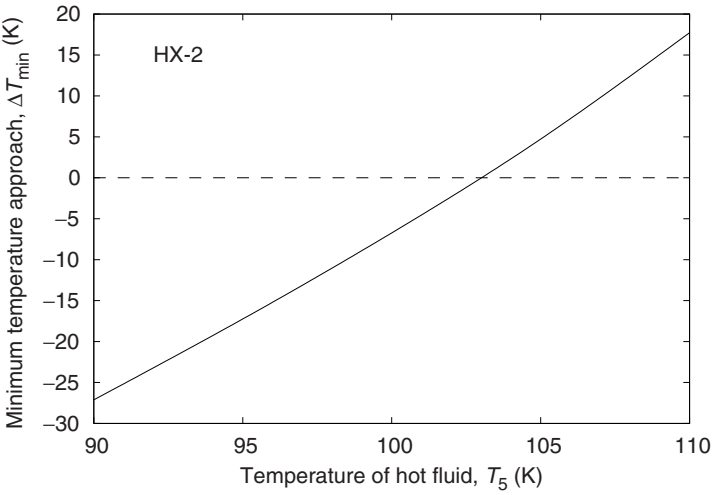

Fig. 2.8. Variation of the minimum temperature approach between the streams with temperature of the hot stream leaving the second heat exchanger (T_5) of the Kapitza nitrogen liquefaction process shown in Fig. 2.4.

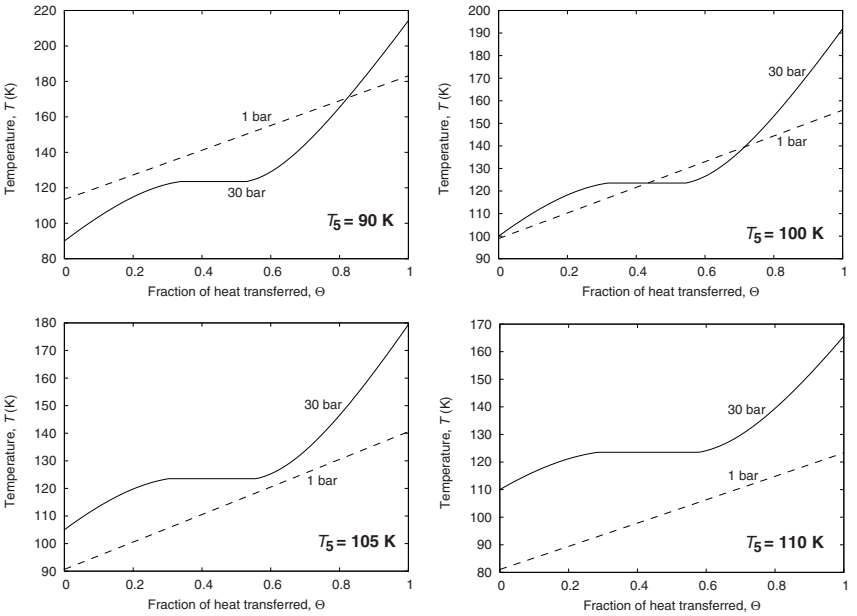

Fig. 2.9. Variation of the temperature of the hot (30 bar) and cold (1 bar) streams in the second heat exchanger of a Kapitza nitrogen liquefier at different temperatures of the hot stream leaving the heat exchanger (T_5).

critical temperature results in pinch points when the operating pressure is above the critical pressure, as discussed in Section 1.16.

2.5 Optimization of a Kapitza nitrogen liquefier

Consider the open-cycle Kapitza nitrogen liquefaction process shown in Fig. 2.4. The exergy efficiency of the process is strongly dependent on the minimum temperature approach between the streams in the two heat exchangers and the flow rate through the turbine. The simultaneous modular approach can also be used effectively for optimization studies. Table 2.3 shows the approach to be used to optimize an open-cycle Kapitza nitrogen liquefier (Fig. 2.4) operating at operating pressures of 40/1 bar using the simultaneous modular approach. The adiabatic efficiency of the turbine was assumed as 80%. The temperature approach between the streams was assumed to be 5 K in the first heat exchanger and 3 K in the second heat exchanger. The flow rate through the turbine ($\dot{n}_9$), the temperature of the cold stream leaving the first heat exchanger (T_{13}), and the temperature of the hot stream leaving the second heat exchanger (T_5) are assumed as the design variables of the optimization study. The minimum temperature approach between the streams of the heat exchanger is constrained to be greater than or equal to the specified values. The temperature at the exit of the turbine expander is constrained to prevent occurrence of two-phase flow conditions in the turbine.

Both sequential modular and simultaneous modular approaches can be used to optimize the performance of the Kapitza process. The tear streams are converged separately, as a part of each simulation run with the sequential modular approach,

Table 2.3. Method for the optimization of a Kapitza nitrogen liquefier.

Objective function: Maximize exergy efficiency, η_{ex}

Subject to constraints:
- Minimum temperature approach between the streams in the first heat exchanger, $\Delta T_{\text{min, hx}-1} \geq \Delta T_{\text{min, hx}-\text{I, specified}}$
- Minimum temperature approach between the streams in the second heat exchanger, $\Delta T_{\text{min, hx}-2} \geq \Delta T_{\text{min, hx}-\text{II, specified}}$
- No two-phase condition in the turbine or $T_{10} > T_{\text{dew, 10}}$
- Convergence of tear stream 11, $\dot{n}_{11'} - \dot{n}_{11''} = 0$, $h_{11'} - h_{11''} = 0$
- Convergence of tear stream 12, $\dot{n}_{12'} - \dot{n}_{12''} = 0$, $h_{12'} - h_{12''} = 0$

Design variables:
- Flow through the turbine, $\dot{n}_9$
- Temperature of the cold stream leaving the first heat exchanger, T_{13}
- Temperature of the hot stream leaving the second heat exchanger, T_5

Constants:
- Specified pressure drop of the high- and low-pressure streams of the first heat exchanger
- Specified pressure drop of the high- and low-pressure streams of the second heat exchanger
- Specified adiabatic efficiency of the turbine

while the tear streams are converged together with other constraints in the case of optimization using the simultaneous modular approach.

In the simultaneous modular approach, the flow rate and enthalpy of the two tear streams are also considered equality constraints, as shown in Table 2.3.

Figure 2.10 shows the convergence of the design variables during the optimization process using the Aspen Plus process simulator. The Sequential Quadratic Programming (SQP) method was used to optimize the exergy efficiency of the process.

The optimization of the performance of other cryogenic processes operating with pure fluids is similar to that described above for the Kapitza liquefaction process. The optimization of mixed refrigerant processes additionally involves a choice of refrigerants and their composition, as well as the operating pressures. The methods for the optimization of mixed refrigerant processes are discussed in Chapter 5 with practical examples.

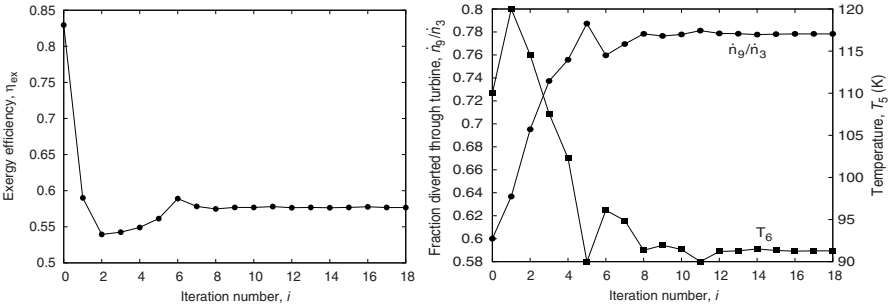

Fig. 2.10. Convergence of the design variables and objective function during the optimization of a Kapitza nitrogen liquefaction process operating at 40/1 bar, and a turbine adiabatic efficiency of 80%. The temperature approach between the streams was assumed to be 5 K in the first heat exchanger and 3 K in the second heat exchanger.

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