Chapter 20

Heat Integration of Reactors

20.1 The Heat Integration Characteristics of Reactors

The heat integration characteristics of reactors depend both on the decisions that have been made for the removal or addition of heat and the reactor mixing characteristics. In the first instance, adiabatic operation should be considered since this gives the simplest design.

1) *Adiabatic operation.* If adiabatic operation leads to an acceptable temperature rise for exothermic reactors or an acceptable decrease for endothermic reactors, then this is the option that would normally be chosen. If so, then the feed stream to the reactor requires heating and the effluent stream requires cooling in most cases. The heat integration characteristics are thus in most cases a cold stream (the reactor feed) if the feed needs to be increased in temperature or vaporized and a hot stream (the reactor effluent) if the product needs to be decreased in temperature or condensed. The heat of reaction appears as increased temperature of the effluent stream in the case of an exothermic reaction or decreased temperature in the case of an endothermic reaction.
2) *Heat carriers.* If adiabatic operation produces an unacceptable rise or fall in temperature, then the option discussed in Chapters 6 and 14 is to introduce a heat carrier. The operation is still adiabatic, but an inert material is introduced with the reactor feed as a heat carrier. The heat integration characteristics are as before. The reactor feed is in most cases a cold stream and the reactor effluent a hot stream. The heat carrier serves to increase the heat capacity flowrate of both streams.
3) *Cold shot and hot shot.* Injection of cold fresh feed for exothermic reactions or preheated feed for endothermic reactions to intermediate points in the reactor can be used to control the temperature in the reactor. Again, the heat integration characteristics are similar to adiabatic operation. The feed is most often a cold stream if it needs to be increased in temperature or vaporized and the product a hot stream if it needs to be decreased in temperature or condensed. If heat is provided to the cold shot or hot shot streams, these are additional cold streams.
4) *Indirect heat transfer with the reactor.* Although indirect heat transfer with the reactor tends to bring about the most complex reactor design options, it is often preferable to the use of a heat carrier. A heat carrier creates complications elsewhere in the flowsheet. A number of options for indirect heat transfer were discussed earlier in Chapter 6.

The first distinction to be drawn, as far as heat transfer is concerned, is between the plug-flow and mixed-flow reactor. In the plug-flow reactor shown in Figure 20.1, the heat transfer can take place over a range of temperatures. The shape of the profile depends on the following:

- Inlet feed concentration
- Inlet temperature
- Inlet pressure and pressure drop (gas-phase reactions)
- Conversion
- Byproduct formation
- Heat of reaction
- Rate of cooling/heating
- Presence of catalyst diluents or changes in catalyst through the reactor.

Figure 20.1a shows two possible thermal profiles for exothermic plug-flow reactors. If the rate of heat removal is low and/or the heat of reaction if high, then the temperature of the reacting stream will increase along the length of the reactor. If the rate of heat removal is high and/or the heat of reaction is low, then the temperature will decrease. Under conditions between the two profiles shown in Figure 20.1a, a maximum can occur in the temperature at an intermediate point between the reactor inlet and exit.

Figure 20.1b shows two possible thermal profiles for endothermic plug-flow reactors. This time, the temperature decreases for low rates of heat addition and/or high heat of reaction. The temperature increases for the reverse conditions. Under conditions between the profiles shown in Figure 20.1b, a minimum can occur in the temperature profile at an intermediate point between the inlet and exit.

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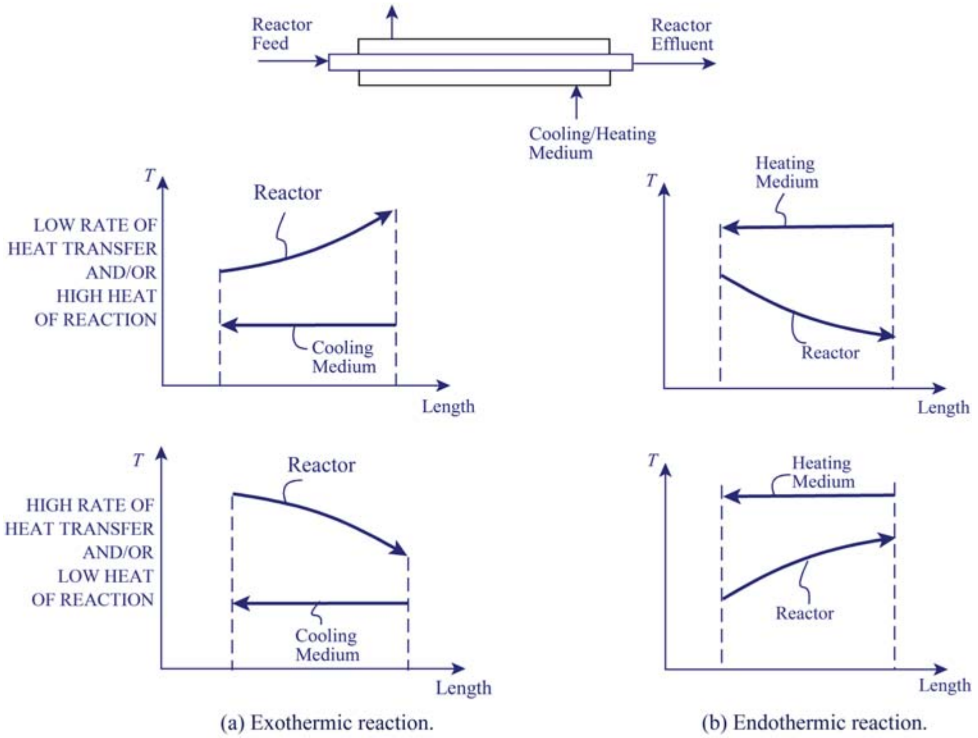


(a) Exothermic reaction. (b) Endothermic reaction.

Figure 20.1
The heat transfer characteristics of plug-flow reactors.

The thermal profile through the reactor will, in most circumstances, be carefully optimized to maximize selectivity, extend catalyst life, and so on. Because of this, direct heat integration with other process streams is almost never carried out. The heat transfer to or from the reactor is instead usually carried out by a heat transfer intermediate. For example, in exothermic reactions, cooling might occur by boiling water to generate steam, which, in turn, can be used to heat cold streams elsewhere in the process or across the site.

By contrast, if the reactor is mixed-flow, then the reactor is isothermal. This behavior is typical of stirred tanks used for liquid-phase reactions or fluidized-bed reactors used for gas-phase reactions. The mixing causes the temperature in the reactor to be effectively uniform.

For indirect heat transfer, the heat integration characteristics of the reactor can be broken down into the following three cases:

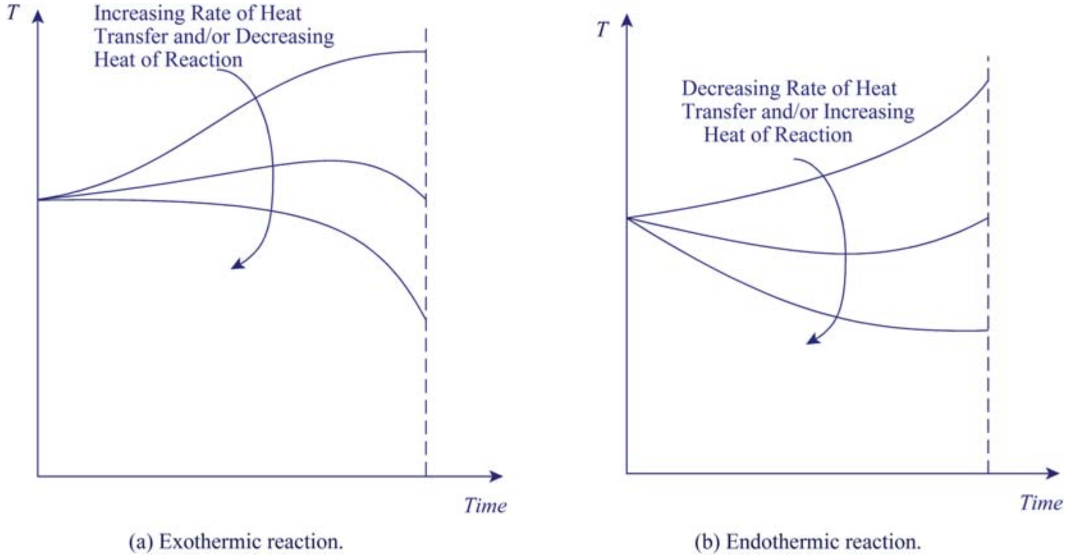
a) If the reactor can be matched directly with other process streams (which is unlikely), then the reactor profile should be included in the heat integration problem. This would be a hot stream in the case of an exothermic reaction or a cold stream in the case of an endothermic reaction.

b) If a heat transfer intermediate is to be used and the cooling/heating medium is fixed, then the cooling/heating medium should be included and not the reactor profile itself. Once the cooling medium leaves an exothermic reactor, it is a hot stream requiring cooling. Similarly, once the heating medium leaves an endothermic reactor, it is a cold stream requiring heating. For cooling and heating media such as heat transfer oils and molten salts, these will be returned directly to the reactor once the heat has been removed or added.

c) If a heat transfer intermediate is to be used but the temperature of the cooling/heating medium is not fixed, then both the reactor profile and the cooling/heating medium should be included. The temperature of the heating/cooling medium can then be varied within the content of the overall heat integration problem to improve the targets, as described in Chapter 19.

In addition to the indirect cooling/heating within the reactor, the reactor feed is an additional cold stream, if it needs to be increased in temperature or vaporized, and the reactor product an additional hot stream, if it needs to be decreased in temperature or condensed.

For the ideal-batch reactor, the temperature can be assumed to be uniform throughout the reactor at any instant in time for the purposes of heat integration. Figure 20.2a shows typical variations in temperature with time for an exothermic reaction in a batch reactor. A family of curves illustrates the effect of increasing the rate of heat removal and/or decreasing heat of reaction. Each individual curve assumes the rate of heat transfer to the cooling medium to be constant for that curve throughout the batch cycle. Figure 20.2b shows typical curves for endothermic reactions. Again, each individual curve in Figure 20.2b assumes the rate of heat addition from the heating medium to be constant throughout the batch process.



(a) Exothermic reaction.

(b) Endothermic reaction.

Figure 20.2

The heat transfer characteristics of batch reactors.

Fixing the rate of heat transfer in a batch reactor is often not the best way to control the reaction. The heating or cooling characteristics can be varied with time to suit the characteristics of the reaction (see Chapter 16). Because of the complexity of batch operation and the fact that operation is usually on a small scale, it is rare for any attempt to be made to recover heat from a batch reactor, or supply heat by recovery. Instead, utilities are normally used.

The heat duty on the heating/cooling medium is given by

$$Q_{REACT} = -(\Delta H_{STREAMS} + \Delta H_{REACT}) \qquad (20.1)$$

where

Q_{REACT} = reactor heating or cooling required
$\Delta H_{STREAMS}$ = enthalpy change between feed and product streams
ΔH_{REACT} = reaction enthalpy (negative in the case of exothermic reactions)

5) *Quench.* As discussed in Chapter 6, the reactor effluent may need to be cooled rapidly (quenched). This can be by indirect heat transfer using conventional heat transfer equipment or by direct heat transfer by mixing with another fluid.

If indirect heat transfer is used with a large temperature difference to promote high rates of cooling, then the cooling fluid (e.g. boiling water) is fixed by process requirements. In this case, the heat of reaction is not available at the temperature of the reactor effluent. Rather, the heat of reaction becomes available at the temperature of the quench fluid. Thus, the feed stream to the reactor is a cold stream, the quench fluid is a hot stream and the reactor effluent after the quench is also a hot stream. This was discussed under data extraction in Chapter 19.

The reactor effluent might require cooling by direct heat transfer because the reaction needs to be stopped quickly, or a conventional heat exchanger would foul, or the reactor products are too hot or corrosive to pass to a conventional heat exchanger. The reactor product is mixed with a liquid that can be recycled, cooled product or an inert material such as water. The liquid vaporizes partially or totally and cools the reactor effluent. Here, the reactor feed is a cold stream and the vapor and any liquid from the quench are hot streams.

Now consider the placement of the reactor in terms of the overall heat integration problem.

20.2 Appropriate Placement of Reactors

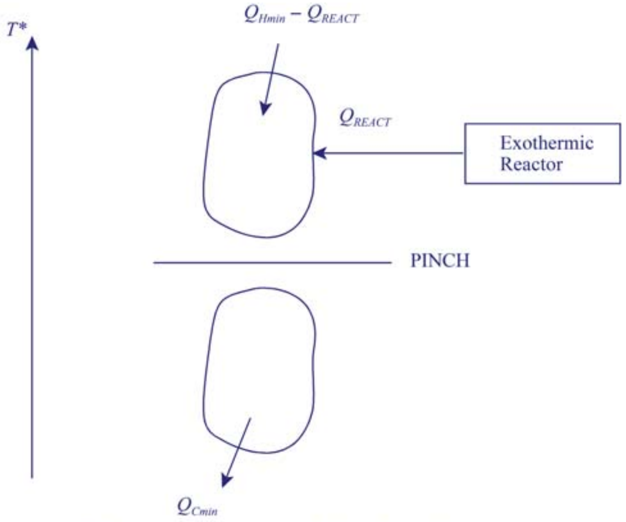
In Chapter 17, it was seen how the pinch takes on fundamental significance in improving heat integration. Now consider the consequences of placing reactors in different locations relative to the pinch.

Figure 20.3 shows the background process represented simply as a heat sink and heat source divided by the pinch. Figure 20.3a shows the process with an exothermic reactor integrated above the pinch. The minimum hot utility can be reduced by the heat released by reaction.

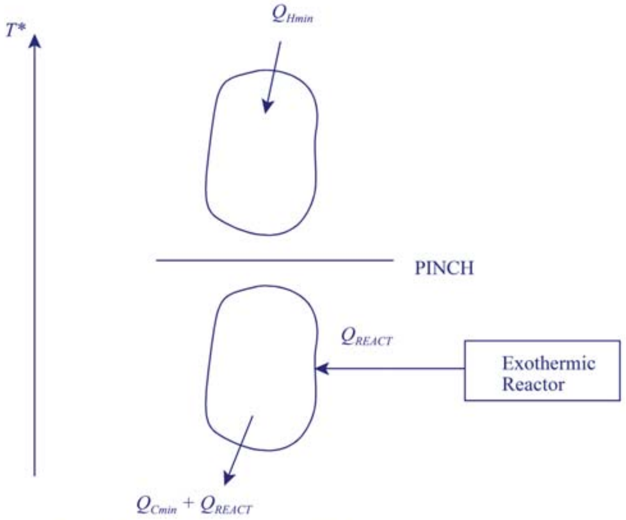
By comparison, Figure 20.3b shows an exothermic reactor integrated below the pinch. Although heat is being recovered, it is being recovered into part of the process, which is a heat source. The hot utility requirement cannot be reduced, since the process above the pinch needs at least Q_{Hmin} to satisfy its enthalpy imbalance.

There is no benefit by integrating an exothermic reactor below the pinch. The appropriate placement for exothermic reactors is above the pinch (Glavic, Kravanja and Homsak, 1988).

Figure 20.4a shows an endothermic reactor integrated above the pinch. The endothermic reactor removes Q_{REACT} from the process above the pinch. The process above the pinch needs at least Q_{Hmin} to satisfy its enthalpy imbalance. Thus, an extra Q_{REACT} must be



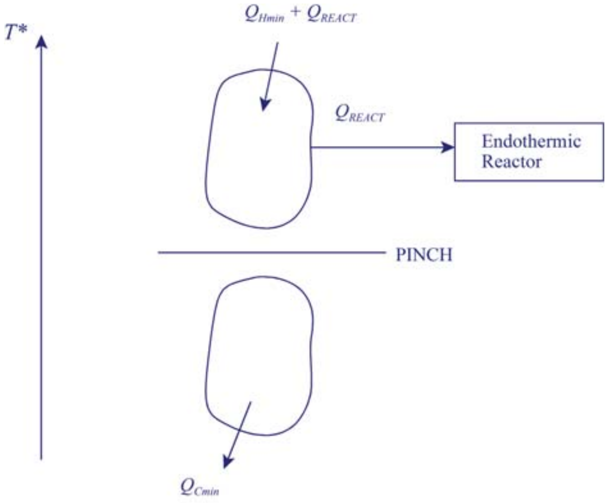
(a) Exothermic reactor integrated above the pinch.



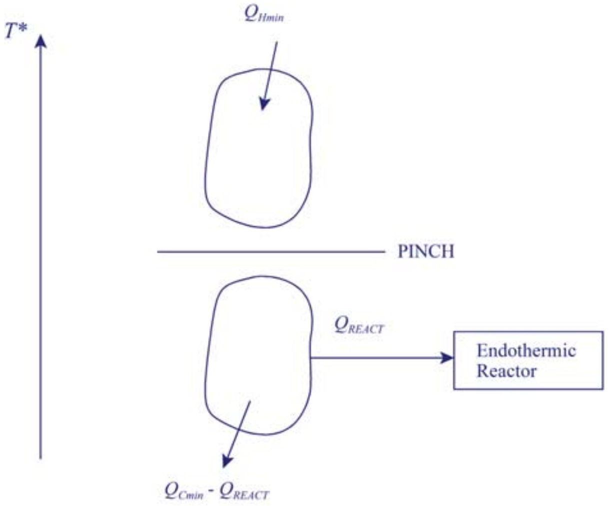
(b) Exothermic reactor integrated below the pinch.

Figure 20.3

Appropriate placement of an exothermic reactor.



(a) Endothermic reactor integrated above the pinch.



(b) Endothermic reactor integrated below the pinch.

Figure 20.4

Appropriate placement of an endothermic reator.

imported from hot utility to compensate. There is no benefit in integrating an endothermic reactor above the pinch. Locally, it might seem that a benefit is being derived by running the reaction by recovery. However, additional hot utility must be imported elsewhere to compensate.

By contrast, Figure 20.4b shows an endothermic reactor integrated below the pinch. The reactor imports Q_{REACT} from part of the process that needs to reject heat anyway. Thus, integration of the reactor serves to reduce the cold utility consumption by Q_{REACT}. There is an overall reduction in hot utility because, without integration, the process and reactor would require $(Q_{Hmin} + Q_{REACT})$ from the utility.

There is no benefit in integrating an endothermic reactor above the pinch. The appropriate placement for endothermic reactors is below the pinch (Glavic, Kravanja and Homsak, 1988).

20.3 Use of the Grand Composite Curve for Heat Integration of Reactors

The above appropriate placement arguments assume that the process has the capacity to accept or give up the reactor heat duties at the given reactor temperature. A quantitative tool is needed to assess the capacity of the background process. For this purpose, the grand composite curve is used and the reactor profile treated as if it was a utility, as explained in Chapter 17.

The problem with representing a reactor profile is that, unlike utility profiles, the reactor profile might involve several streams. The reactor profile involves not only streams such as those for indirect heat transfer shown in Figure 20.1, but also the reactor feed and effluent streams that can be an important feature of the reactor heating and cooling characteristics. The various streams associated with the reactor can be combined to form a grand composite curve for the reactor. This can then be matched against the grand composite curve for the rest of the process. The following example illustrates the approach.

Example 20.1 Consider again the process for the manufacture of phthalic anhydride discussed in Example 19.1. The data was extracted from the flowsheet in Figure 19.10 and listed in Table 19.1. The composite curves and grand composite curve are shown in Figure 19.11.

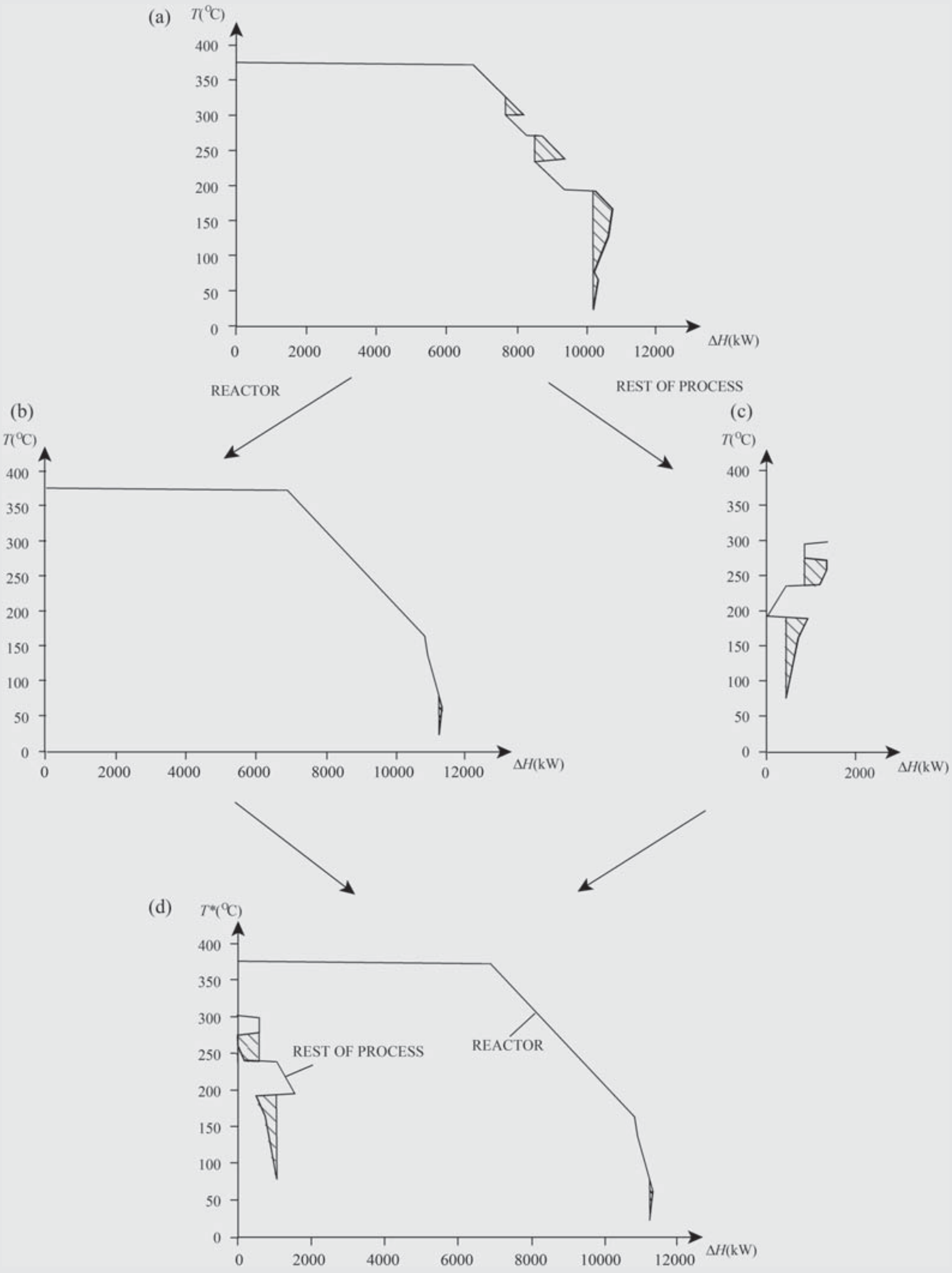


Figure 20.5

The problem can be divided into two parts, one associated with the reactor and the other with the rest of the process ($\Delta T_{min} = 10\,^{\circ}\mathrm{C}$) and then superimposed.

a) Examine the placement of the reactor relative to the rest of the process.
b) Determine the utility requirements of the process.

Solution

a) The stream data used to construct the grand composite curve in Figure 20.5a include those associated with the reactor and those for the rest of the process. If the placement of the reactor relative to the rest of the process is to be examined, those streams associated with the reactor need to be separated from the rest of the process. Figure 20.5b shows the grand composite curves for the two parts of the process. Figure 20.5b is based on Streams 1, 2, 6 and 7 from Table 19.1 and Figure 20.5c is based on Streams 3, 4, 5, 8, 9, 10 and 11.

In Figure 20.5d, the grand composite curves for the reactor and that for the rest of the process are superimposed. To obtain maximum overlap, one of the curves must be taken as a mirror image. It can be seen in Figure 20.5d that the reactor is appropriately placed relative to the rest of the process. Had the reactor not been appropriately placed, it would have been extremely unlikely that the reactor would have been changed to make it so. Rather, to obtain appropriate placement of the reactor, the rest of the process would more likely have been changed.

b) Figure 20.6 shows the grand composite curve for all the streams with a steam generation profile matched against it. The process cooling demand is satisfied by the generation of high-pressure (41 bar) steam from boiler feedwater, which is superheated to 270 °C. High-pressure steam generation is preferable to low-pressure generation. There is apparently no need for cooling water.

A greater amount of steam would be generated if the noncondensible vent was treated using catalytic thermal oxidation (see Chapter 25) rather than absorption. The exotherm from catalytic thermal oxidation would create an extra hot stream for steam generation.

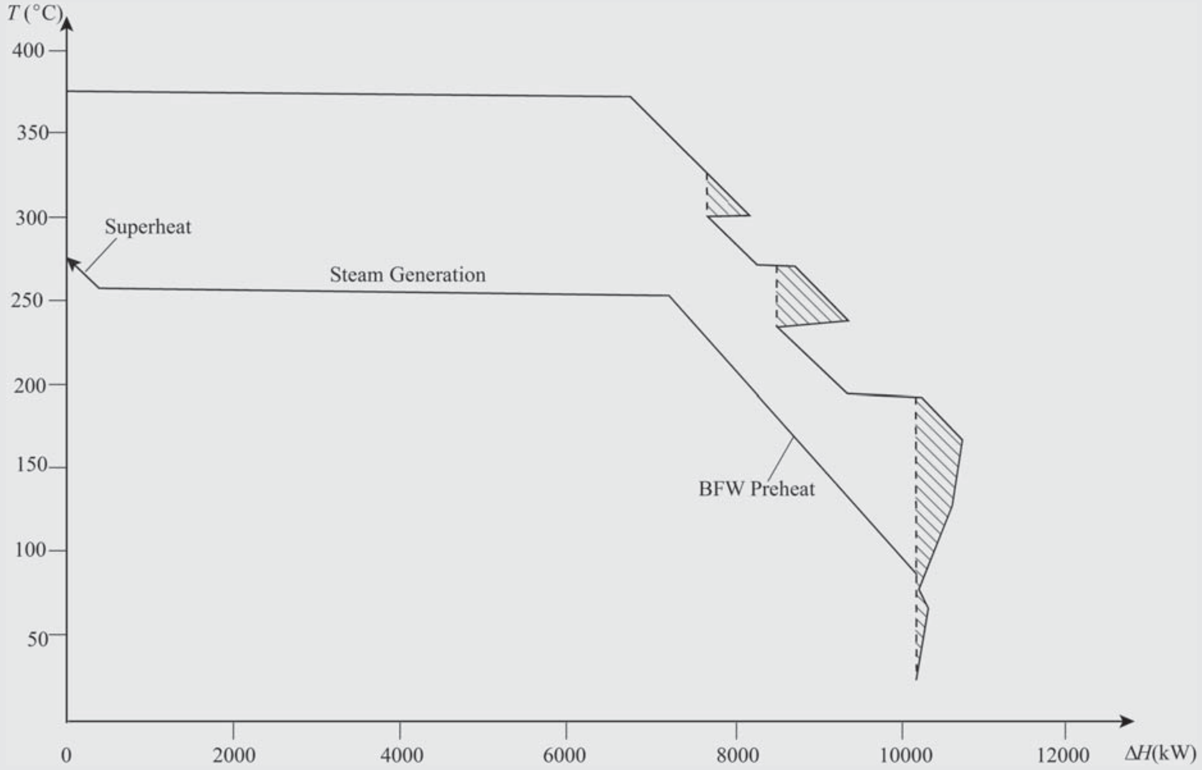


Figure 20.6

The grand composite curve for the whole process apparently requires only high-pressure steam generation from boiler feedwater.

20.4 Evolving Reactor Design to Improve Heat Integration

If the reactor is inappropriately placed, then the process changes might make it possible to correct this. One option would be to change the reactor conditions to bring this about. Most often, however, the reactor conditions will probably have been optimized for selectivity, catalyst performance, and so on, which, taken together with safety, materials-of-construction constraints, control, and so on, makes it unlikely that the reactor conditions would be changed to improve heat integration. Rather, to obtain appropriate placement of the reactor, the rest of the process would most likely be changed.

If changes to the reactor design are possible, then the simple criteria introduced in Chapter 19 can be used to direct those changes. Heat integration will always benefit by making hot streams hotter and cold streams colder. This applies whether the heat integration is carried out directly between process streams or through an intermediate such as steam. For example, consider the exothermic reactions in Figure 20.1a. Allowing the reactor to work at a higher temperature improves the heat integration potential if this does not interfere with selectivity or catalyst life or introduce safety and control problems, and so on. However, if the reactor must work with a fixed intermediate cooling fluid, such as steam generation, then the only benefit will be a reduced heat transfer area in the reactor. The steam becomes a hot stream available for heat integration after leaving the reactor. If the pressure of steam generation can be increased, then there may be energy or heat transfer area benefits when it is integrated with the rest of the process.

Care should be taken when preheating reactor feeds within the reactor using the heat of reaction. This is achieved in practice simply by passing the cold feeds directly to the reactor and allowing them to be preheated by mixing with hot materials within the reactor. However, if the exothermic reactor is appropriately placed above the pinch and the feeds start below the pinch, then the preheating within the reactor is cross-pinch heat transfer. In this case, feeds should be preheated by recovery using streams below the pinch before being fed to the reactor. This increases the heat generated within the reactor and heat integration will benefit from the increased heat available for recovery from the reactor.

20.5 Heat Integration of Reactors – Summary

The appropriate placement of reactors, as far as heat integration is concerned, is that exothermic reactors should be integrated above the pinch and endothermic reactors below the pinch. Care should be taken when reactor feeds are preheated by heat of reaction within the reactor for exothermic reactions. This can constitute cross-pinch heat transfer. The feeds should be preheated to pinch temperature by heat recovery before being fed to the reactor.

Appropriate placement can be assessed quantitatively using the grand composite curve. The streams associated with the reactor can be represented as a grand composite curve for the reactor and then matched against the grand composite curve for the rest of the process.

If the reactor is not appropriately placed, then it is more likely that the rest of the process would be changed to bring about appropriate placement rather than changing the reactor. If changes to the reactor design are possible, then the simple criterion of making hot streams hotter and cold streams colder can be used to bring about beneficial changes.

Table 20.1

Stream data for a process with an exothermic chemical reactor.

Stream		Enthalpy change (kW)	T_S (°C)	T_T (°C)
No.	Type			
1	Hot	7000	377	375
2	Hot	3600	376	180
3	Hot	2400	180	70
4	Cold	2400	60	160
5	Cold	200	20	130
6	Cold	200	160	260

20.6 Exercises

1. The stream data for a process involving a highly exothermic chemical reaction are given in Table 20.1.
   - **a)** Sketch the composite curves for $\Delta T_{min} = 10\,°C$, confirm that it is a threshold problem and determine the cold utility requirements.
   - **b)** It is proposed to use steam generation as cold utility. Assume saturated boiler feedwater is available and that the steam generated is saturated in order to calculate how much steam can be generated by the process at a pressure of 41 bar. The temperature of saturated steam at the pressure is 252 °C and the latent heat is 1706 $kJ\cdot kg^{-1}$.
   - **c)** If the steam is superheated to a temperature of 350 °C, calculate how much steam can be generated at 41 bar. Assume the heat capacity of steam is 4.0 $kJ\cdot kg^{-1}\cdot K^{-1}$.
   - **d)** Describe what would happen if the steam was generated from boiler feedwater at 100 °C with a heat capacity of 4.4 $kJ\cdot kg^{-1}\cdot K^{-1}$. How would the steam generation be calculated under these circumstances?

Reference

Glavic P, Kravanja Z and Homsak M (1988) Heat Integration of Reactors: I. Criteria for the Placement of Reactors into Process Flowsheet, *Chem Eng Sci*, **43**: 593.