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Utilization of Waste Heat Stream in Distillation

Zbigniew T. Fidkowski and Rakesh Agrawal*

Air Products & Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, Pennsylvania 18195-1501

Cost of separation can be reduced by utilizing all available energy streams at various temperature levels. In the simplest case a waste energy heat stream can be used to partially vaporize a liquid feed stream. A more beneficial process involves an entire evaporation of a portion of the feed and introducing it into a column below the liquid portion of the feed. One can also use the waste energy stream as a heating medium in an intermediate reboiler in the column. There is, however, a limit to the amount of the waste energy that can be utilized in each case, beyond which this approach is no longer beneficial. Detailed analysis of the waste heat utilization enables us to determine this limit and compare each of these flowsheet options.

Introduction

The energy requirements for distillation can be decreased by utilizing an available "waste energy" stream. A "waste energy" stream can be a heat source which is inexpensive (in comparison with the heating medium used in reboiler), or it may even be available at no cost from a process stream. We assume that the temperature of this waste heat stream is usually lower than the temperature at the bottom of the column, so that it cannot be simply applied as a heating medium in the reboiler, but it still can be used to boil process streams at a lower temperature. Considerable work has been done to exploit waste energy in distillation through the use of an inter-reboiler or a feed heater (Patterson and Wells, 1977). It has been shown that, in most systems, the reduction in the reboiler heat requirement is substantially less than the heat used to vaporize a portion of the feed. In some cases, the reboiler heat duty can actually increase if more waste heat is used to preheat the feed (Liebert, 1993).

The fact that preheating the total feed is not very efficient has been known in cryogenic air separation for quite some time (Ruhemann, 1949; Latimer, 1967). Air is distilled in a three-column system to produce nitrogen, argon, and oxygen product streams, as shown in Figure 1. In the first step, air feed (78.12% nitrogen, 0.93% argon, and 20.95% oxygen) near its dew point is distilled in a high pressure rectifier to produce a liquid nitrogen stream at the top of the column and a crude liquid oxygen bottoms stream. The bottoms stream generally has about 35% oxygen and 1.5% argon and the rest is nitrogen. The crude liquid oxygen stream then forms the feed to a lower pressure column. It is in this column that final distillation is performed to produce nitrogen at the top and oxygen from the bottom. A side rectifier is used with the low pressure column to produce argon. Use of a side rectifier with a main distillation column to separate a ternary feed mixture is widely known (King, 1980). The early designers of air separation plants realized that the condensing duty at the top of the side rectifier can be provided by heat exchange with the crude liquid oxygen prior to feeding it to the low pressure column. Indeed, the earlier air distillation plants were designed by preheating all the crude liquid oxygen resulting in a two-phase feed to the low pressure column (Ruhemann, 1949). However, it has been known for quite some time that by splitting the crude liquid oxygen into two streams and nearly

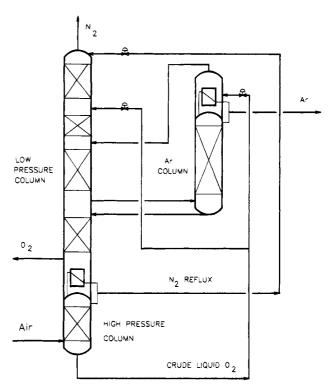


Figure 1. Cryogenic distillation of air to produce nitrogen, oxygen, and argon.

totally vaporizing one of the streams in the side rectifier condenser and feeding the vaporized stream, a couple of stages below the other stream results in an increased argon recovery. Latimer (1967) has discussed in detail the benefit of matching the concentration ratios of the key components of each of the two streams with the corresponding ratios on the stages where they are fed. Most modern cryogenic air separation plants exploit this enhanced distillation by feeding a portion of the crude liquid oxygen directly to the low pressure column and nearly totally vaporizing the second portion by preheating and then feeding it a couple of stages below the other feed. Wankat and Kessler (1993) have recently discussed the same phenomenon of having two feeds of the same composition but with different enthalpies to a distillation column.

It is clear that there are at least three possible ways in which waste heat can be supplied to a distillation column. In the first, a fraction of the feed stream is vaporized so that it is introduced into the column as a two-phase stream. The second option is to split the feed into two streams, vaporize one of them and introduce

^{*} Author to whom correspondence should be addressed.

this portion a couple of stages below the liquid portion of the feed. The third possibility is to use an additional reboiler at an intermediate location of the stripping section in the column.

It should be noted that a similar set of options exists in case when surplus refrigeration is available at a temperature warmer then the overhead condenser.

Various types of heat exchangers can be used. Heat transfer where ΔT is minimized utilizes the waste energy more effectively, which may also decrease the number of stages in a distillation column (this happens when we move the intermediate reboiler further down the column), but capital cost of the heat exchanger increases due to increased surface area. If the same type of additional heat exchanger is used in each considered distillation configuration, then the biggest mean ΔT will be in the exchanger used for the two-feed column, where one portion of a stream is completely vaporized. Although the type of the heat exchanger used in either of these configurations will have a significant impact on the economy of the process, we will assume in our analysis that the waste heat can be supplied into each configuration with approximately similar effort.

There seems to be some confusion about the relative merits of each of the three options. The objective of this work is to determine when and how the waste heat stream should be utilized, and the advantages or disadvantages of each of the three flowsheet options.

We assume that minimizing vapor flow from the reboiler minimizes energy input to the process. However, excessive waste heat input will eventually need to be removed from the overhead condenser, resulting in an uneconomical design. We will point out circumstances leading to such cases.

Due to simplicity a detailed analysis has been performed for binary distillation with the classical assumption of constant molar overflow in each section of the column. We will also exclude mixtures exhibiting inflection points on their y-x equilibrium diagrams, so there is no possibility for a tangent pinch to occur, although similar effects can be observed for these mixtures as well. Ternary or higher mixtures are not easily amenable to analysis performed for binary mixtures. Therefore we first present the analysis for the binary distillation in detail, and this is followed by a brief discussion of results from the computer simulations for ternary mixtures.

Column with a Single Two-Phase Feed

The schematic of the column is shown in Figure 2a. Assuming constant molar overflow we have

$$L_{\rm TI} = L_{\rm I} + qF \tag{1}$$

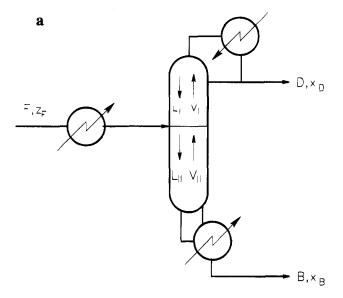
$$V_{\rm II} + V_{\rm I} - (1 - q)F$$
 (2)

The expression for minimum vapor flow can easily be derived by writing balance equations for the rectifying section of the column, i.e.,

$$V_{\rm I} = L_{\rm I} + D \tag{3}$$

$$V_{\rm L} y^* = L_{\rm L} x^* + D x_{\rm D} \tag{4}$$

where x^* and y^* satisfy the "feed line" equation (5) and the equilibrium relation (6):



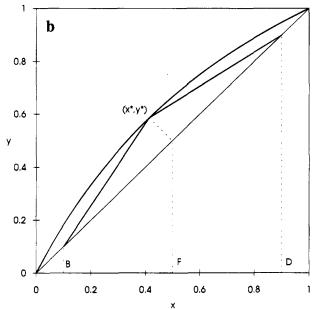


Figure 2. (a) Schematic of a distillation column with a single, two-phase feed. (b) Operating lines on y-x diagram for a column with a single, two-phase feed, at minimum reflux conditions.

$$qx^* + (1 - q)y^* = z_F \tag{5}$$

$$y^* = f_{eq}(x^*) \tag{6}$$

From eqs 2-4 we obtain a formula for the minimum vapor flow rate as a function of feed flow rate (F), feed composition (z_F) and quality (q), and distillate flow rate (D) and composition (x_D) .

$$V_{\rm II} = D \frac{x_{\rm D} - x^*}{v^* - x^*} - (1 - q)F \tag{7}$$

A similar expression can be derived for the stripping section.

The y-x diagram for this case is shown in Figure 2b.

Column with Two Feeds

A liquid feed at its boiling point can be split into two streams.

$$F = F_{\rm L} + F_{\rm V} \tag{8}$$

One of them, $F_{\rm V}$, is then vaporized by the "waste heat", and both feeds are introduced into a column in different locations. This situation is shown in Figure 3a.

For constant molar overflow, the internal flows of the phases in particular sections are related as follows:

$$L_{\rm II} = L_{\rm I} + F_{\rm L} \tag{9}$$

$$V_{\rm II} = V_{\rm I} \tag{10}$$

$$L_{\rm III} = L_{\rm II} \tag{11}$$

$$V_{\rm III} = V_{\rm II} - F_{\rm V} \tag{12}$$

At minimum reflux conditions, assuming that tangent pinches cannot occur, the operating line may pinch the equilibrium line at the upper feed level (Figure 3b), at the lower feed level (Figure 3c), or at both places at once.

If the upper pinch occurs, the minimum vapor flow from the reboiler $(V_{\rm III}^{\rm up})$ can be calculated from a material balance on the rectifying section

$$V_{t} = L_{t} + D \tag{13}$$

$$V_{\rm I} y(z_{\rm F}) = L_{\rm I} z_{\rm F} + D x_{\rm D} \tag{14}$$

together with the equilibrium relation

$$y(z_{\mathbf{F}}) = f_{\mathbf{eq}}(z_{\mathbf{F}}) \tag{15}$$

From eqs 10-14 we obtain

$$V_{\text{III}}^{\text{up}} = D \frac{x_{\text{D}} - z_{\text{F}}}{y(z_{\text{F}}) - z_{\text{F}}} - F_{\text{V}}$$
 (16)

Note that if the upper pinch controls, we can reduce the minimum vapor flow from the reboiler by increasing the flow rate of the vapor feed, i.e., by increasing utilization of the waste energy stream.

When minimum vapor flow from the reboiler is determined by the lower pinch, we can write the material balance equation for the rectifying and middle sections of the column

$$V_{\rm II} + F_{\rm L} = L_{\rm II} + D \tag{17}$$

$$V_{\mathrm{II}}z_{\mathrm{F}} + F_{\mathrm{I}}z_{\mathrm{F}} = L_{\mathrm{II}}x(z_{\mathrm{F}}) + Dx_{\mathrm{D}}$$
 (18)

where

$$x(z_{\rm F}) = f_{\rm eq}^{-1}(z_{\rm F})$$
 (19)

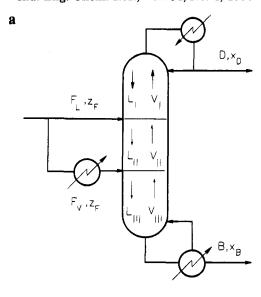
From eqs 12, 17, and 18 we calculate the minimum vapor flow rate from the bottom reboiler determined by the lower pinch $(V_{\text{III}}^{\text{lo}})$:

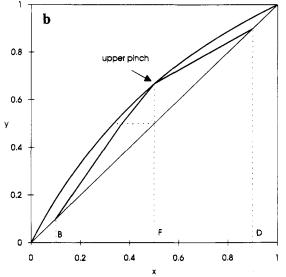
$$V_{\rm III}^{\rm lo} = D \frac{x_{\rm D} - x(z_{\rm F})}{z_{\rm F} - x(z_{\rm F})} - F$$
 (20)

In this case, an increase of the waste energy stream has no effect on the minimum vapor flow.

The minimum vapor flow from the reboiler which is required for a given separation depends on which pinch controls, and

$$V_{\rm III} = \max\{V_{\rm III}^{\rm up}, V_{\rm III}^{\rm lo}\} \tag{21}$$





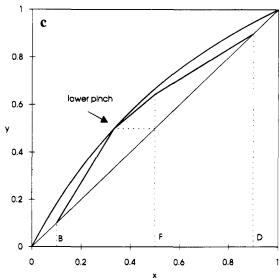


Figure 3. (a) Schematic of a distillation column with two feeds: liquid and vapor of the same composition. (b) Operating lines on y-x diagram for a column with two feeds at minimum reflux conditions. Upper pinch controls. (c) Operating lines on y-x diagram for a column with two feeds at minimum reflux conditions. Lower pinch controls.

When stream F_{V} is only a small portion of the total feed, the upper pinch controls the vapor flow from the

reboiler, i.e., $V_{\rm III}^{\rm up} > V_{\rm III}^{\rm lo}$, and reboiler duty can be reduced by utilizing more of the waste energy to increase the flow rate of the vapor feed. As this vapor feed flow rate increases, the value of $V_{\rm III}^{\rm up}$ drops and eventually becomes equal to $V_{\rm III}^{\rm lo}$. Up to this point the total heat input, which is the sum of the used waste heat and the reboiler heat, remains unchanged. A further increase in the utilization of waste energy is not beneficial, as it will not decrease the heat input to the reboiler and would only contribute toward increasing the condenser duty.

Column with Two Reboilers

Feed is introduced to the column as a boiling liquid stream, and an additional reboiler is used in the stripping section to utilize waste energy. The column is shown in Figure 4a. Note that the intermediate reboiler does not have to be physically contained in the column—we can withdraw a side stream of liquid from the column, boil it, and return the vapor into the column. Therefore an implementation of an intermediate reboiler is no more difficult than splitting a feed into two streams, vaporizing one of them, and introducing them in two places into the column.

For purposes of comparison, we can make the two-reboiler case equivalent to two-feed distillation: we assume that (1) the same amount of the waste heat—sufficient to vaporize $F_{\rm V}$ moles of liquid—is used in both cases and (2) the intermediate reboiler is introduced at the level of the stripping section where vapor stream composition is equal to the overall (liquid in this case) feed composition $z_{\rm F}$.

For a constant molar overflow internal flows of phases in particular sections are related as follows:

$$L_{\rm II} = L_{\rm I} + F \tag{22}$$

$$V_{II} = V_{I} \tag{23}$$

$$L_{\rm III} = L_{\rm II} - F_{\rm V} \tag{24}$$

$$V_{\rm III} = V_{\rm II} - F_{\rm V} \tag{25}$$

Comparing these balances with eqs 9-12, we see that the column with an intermediate reboiler does not work exactly in the same way as the two-feed column, since the liquid flow rates in the intermediate section are different. The operating line for the intermediate section (II) can be expressed as

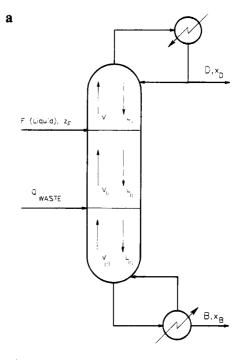
$$y = \frac{L_{\rm II}}{V_{\rm II}}x - B\frac{x_{\rm B}}{V_{\rm II}} \tag{26}$$

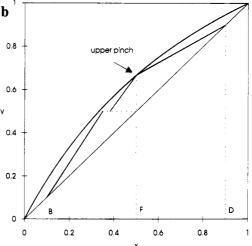
whereas the operating line for the stripping section (III) is given as

$$y = \frac{L_{\text{III}}}{V_{\text{III}}}x - B\frac{x_{\text{B}}}{V_{\text{III}}}$$
 (27)

It can be shown that both operating lines pass through point (x_B, x_B) on the y-x diagram and if $F_V > 0$ then the slope of operating line III is always greater than the slope of line II.

$$\frac{L_{\rm III}}{V_{\rm III}} > \frac{L_{\rm II}}{V_{\rm II}} \tag{28}$$





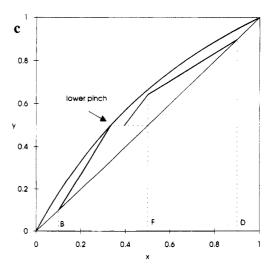


Figure 4. (a) Schematic of a distillation column with an intermediate reboiler. (b) Operating lines on y-x diagram for a column with an intermediate reboiler at minimum reflux conditions. Upper pinch controls. (c) Operating lines on y-x diagram for a column with an intermediate reboiler at minimum reflux conditions. Lower pinch controls.

The operating line for the part of the column below the feed is discontinuous at the level where the intermediate reboiler is located.

Since we have assumed that tangent pinches will not occur, the operating line may pinch the equilibrium line at the feed level (upper pinch, Figure 4b), at the intermediate reboiler level (lower pinch, Figure 4c), or simultaneously in both places.

In case where upper pinch controls we can use the same equations as for the two-feed case (eqs 10, 12, 13, and 14) to calculate the minimum vapor flow from the bottom reboiler

$$V_{\text{III}}^{\text{up}} = D \frac{x_{\text{D}} - z_{\text{F}}}{y(z_{\text{F}}) - z_{\text{F}}} - F_{\text{V}}$$
 (29)

and the minimum vapor flow for the column with an intermediate reboiler (eq 29) is the same as for the twofeed column (eq 16).

If the lower pinch controls, it is only possible for line III (not for line II) to pinch the equilibrium line at the intermediate reboiler level (Figure 4c). The expression for minimum vapor flow can be derived from the following balances:

$$V_{\rm III} + F = L_{\rm III} + D \tag{30}$$

$$V_{\rm III}z_{\rm F} + Fz_{\rm F} = L_{\rm III}x(z_{\rm F}) + Dx_{\rm D} \tag{31}$$

where

$$x(z_{\rm F}) = f_{\rm eq}^{-1}(z_{\rm F})$$
 (32)

obtaining

$$V_{\rm III}^{\rm lo} = D \frac{x_{\rm D} - x(z_{\rm F})}{z_{\rm F} - x(z_{\rm F})} - F \tag{33}$$

Note that this is the same formula as for the double feed column (eq 20). Therefore, at minimum reflux conditions, the energy requirements for a column with two feeds and a column with an intermediate reboiler are the same, and can be calculated from equations 16, 20 and 21.

Comparison and Discussion

Consider an example of an ideal mixture with $\alpha =$ $2.0, z_{\rm F} = 0.5, x_{\rm B} = 0.1, \text{ and } x_{\rm D} = 0.9.$ Minimum vapor flow from the bottom reboiler as a function of the waste heat supplied to the column (for all the discussed cases) is shown in Figure 5. Waste heat has been expressed in terms of the fraction of feed that it can produce by vaporization of a boiling liquid feed:

$$F_{\rm V} = (1 - q)F = Q_{\rm waste}/\lambda \tag{34}$$

We see that minimum vapor flow for a column with a single, two-phase feed is always higher than for the other cases. This can be easily proved by the geometrical construction shown in Figure 6 (see also Pratt,

By partial vaporization of a liquid feed with a waste heat and introducing it into a column as a single, twophase stream, we are able to reduce minimum vapor flow from the bottom reboiler required for the separation. However, the net reduction in bottom reboiler heat consumption is smaller than the amount of additional

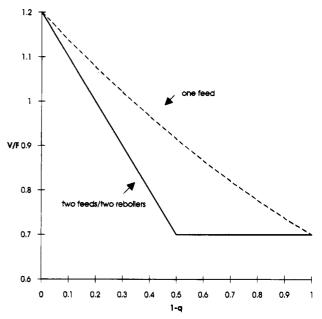


Figure 5. Minimum vapor flow from the bottom reboiler as a function of waste heat for a column with a single, two-phase feed, a column with two feeds, and a column with an intermediate reboiler. Example for ideal mixture with $\alpha = 2.0$, $z_F = 0.5$, $x_B =$ 0.1, and $x_D = 0.9$.

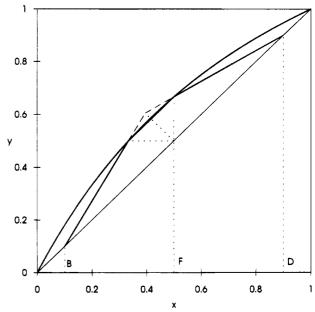


Figure 6. Simple geometrical proof that minimum vapor flow (and minimum reflux ratio) for a column with a single, two-phase feed is always higher than minimum vapor flow for a two-feed column.

heat provided for partial vaporization of the liquid feed, owing to the change in pinch composition when $F_{\rm V}$ increases. The benefit will become even smaller if there is any cost associated with a waste heat. Since the additional energy supply cannot be fully compensated by a reduction in the minimum vapor flow, the reflux ratio (or condenser duty) has to increase in this case, which makes this option even less attractive (especially for cryogenic separations).

The minimum vapor flows for the column with two feeds and for the column with two reboilers are the same.

When the upper pinch controls the vapor flow in the rectifying section of the column, the vapor flow generated in the bottom reboiler can be reduced by exactly

Table 1. Comparison of Number of Theoretical Stages Required to Separate an Ideal Mixture, Where $\alpha = 2.0$, z_F = 0.5, x_B = 0.1, x_D = 0.9, and q = 0.5 at Various Reflux

reflux ratio	column with one two- phase feed	column with two feeds	column with intermediate reboiler	column with one liquid feed
1.93	21	18	16	14
2.02	19	17	16	14
2.21	15	16	15	14

^a Minimum reflux for the two-phase feed column is $R_{\min} = 1.84$. Reflux ratios were chosen by multiplying this minimum reflux by a factor 1.05, 1.1, and 1.2, correspondingly.

the amount of the waste energy provided, either with the vaporized feed or through an intermediate reboiler. Because the total amount of energy provided to the column remains unchanged, the reflux ratio also does not change. We are able to replace a part of the reboiler duty with the (less valuable) waste stream energy.

Obviously there is an upper limit to this approach, otherwise we could swap all the reboiler energy with waste energy. By increasing the waste heat stream we increase the slope of the operating line in the stripping section, until finally it pinches equilibrium line. At this point both (upper and lower) pinches are active. This determines the highest amount of waste energy that can beneficially be supplied to a column. Further increase of waste heat relieves the upper pinch, but the lower pinch remains active and vapor flow generated in the bottom of the column remains unchanged. This unnecessarily increases condenser duty.

The greatest amount of waste heat that can be beneficially supplied to a column can be calculated from eqs 16 and 20 as

$$Q_{\text{waste}}^{\text{max}} = \lambda \left\{ F - D \left[\frac{x_{\text{D}} - x(z_{\text{F}})}{z_{\text{F}} - x(z_{\text{F}})} - \frac{x_{\text{D}} - z_{\text{F}}}{y(z_{\text{F}}) - z_{\text{F}}} \right] \right\}$$
(35)

Although the minimum energy requirements for a column with two feeds and a column with two reboilers are the same, there is a significant difference between these two configurations. For values of the reflux ratio higher than minimum, the column with an intermediate reboiler will require fewer stages in the intermediate section than the two-feed column to perform the same separation. This can be seen by comparing a distance between the operating line and the equilibrium line in the intermediate section of the column in Figure 3 and Figure 4. We calculated number of stages in our example, for each column configuration at q = 0.5; see Table 1. Surprisingly, for this example, at small reflux ratios the column with two feeds requires less stages than the column with one, two-phase feed. In Table 1 we included additionally results for a column with one liquid feed, which can be treated as a column where the waste heat is not utilized. Separation in this column requires of course the smallest number of stages.

The other advantage of a column with an intermediate reboiler is that we have more flexibility to place the waste heat stream in the proper location, i.e., to place the intermediate reboiler as low as possible, thus minimizing the irreversibility of heat exchange and decreasing the number of stages.

An important assumption in all these considerations was that the waste heat temperature is high enough to entirely vaporize the feed stream; i.e., this temperature must be greater than the dew point of the feed. This is not a necessary condition, however. We might be able to utilize a waste heat stream (without any heat pumping) even if its temperature is lower (but not lower than the boiling point of the feed). This observation is especially important for widely boiling mixtures, where instead of vaporizing entirely one of the feed streams, we will be able to vaporize it only partially. Our benefits decrease in this case, but remain the same for the twofeed column and the column with two reboilers.

All these conclusions are simply an interpretation of analytical equations derived for binary mixtures. In order to verify if the results can be extended to multicomponent mixtures, we made detailed computer simulations for all the discussed cases, i.e., the column with feed preheating, the column with two feeds, and the column with two reboilers for the following ternary mixtures:

> benzene, toluene, o-xylene, methanol, ethanol, propanol-2, ethanol, propanol-2, isobutanol nitrogen, argon, oxygen

These systems represent a variety of mixtures with correspondingly easy/easy, easy/difficult, difficult/easy, and easy/difficult separation, roughly judging by comparison of equilibrium diagrams for all the binary pairs. We assumed various feed compositions and various splits, i.e., direct split (where the most volatile component is obtained almost pure in distillate), indirect split (where the least volatile component is obtained almost pure as the bottom product), and transition split (where intermediate component is distributed between the distillate and the bottom product so that liquid feed composition is the same as liquid composition on the feed plate). Our conclusions, based on these simulations, are similar to the conclusions for binary cases. Partial vaporization of the feed reduces reboiler duty, but increases condensing duty in comparison with a liquid feed case. Using the column with two feeds or the column with two reboilers allows us to reduce reboiler duty exactly by the amount of waste heat provided. There is always an upper limit on the amount of the waste heat that can be introduced to a column without increasing the condenser duty. This limit is caused by the fact that a pinch point appears on the composition profile when the amount of the waste heat introduced to the column reaches a certain value. For a ternary mixture this is usually a saddle-type pinch point located in the vicinity of the vapor feed or intermediate reboiler. Conditions for the occurrence of this pinch point are determined by the composition of the bottom product, equilibrium relation, amount of the waste heat introduced, and its temperature. For more information about pinch point calculations see Fidkowski et al. (1991). Therefore, there is no simple recipe for determination of the maximum amount of the waste heat that can be introduced to the column without increasing the condenser duty.

For example, for the indirect split of a boiling liquid mixture of benzene (30 mol %), toluene (30%), and o-xylene (40%), where o-xylene is produced with recovery 99.75% and purity 95%, it is possible to introduce an amount of the waste heat sufficient to vaporize 50% of the feed, reducing the reboiler duty by 48% and with the condenser duty remaining unchanged. Further increase of the vapor feed (or the waste heat) up to 60% of the total feed increases the condenser duty by 7.5%, reducing the reboiler duty by an additional 3%.

In another example, which is the indirect split of a boiling liquid mixture containing 30 mol % methanol, 30% ethanol, and 40% propanol-2, where propanol-2 is produced with 95% recovery and 95% purity, a much higher reflux ratio is required to perform this difficult separation and consequently internal column flow rates are much higher than the feed flow rate. In this case it is possible to vaporize almost the entire feed stream with the waste heat which reduces the reboiler duty by 15%, without a significant increase in the condenser duty.

Energy savings are the same for the column with two feeds and the column with two reboilers. However, if temperature of the waste heat is higher than the dew point of the feed (plus a given ΔT in the heat exchanger), then using the intermediate reboiler is much more beneficial than vaporizing a portion of the feed. These conclusions for ternary mixtures are based only on the results of our simulations, and contrary to a binary mixture case we do not have a general proof.

It also should be pointed out that although in some circumstances energy requirements of the plant decrease when the waste heat is used, the capital cost of the plant increases, since the additional heat exchanger is needed and number of stages in the column may increase. We considered only energy requirements of the distillation plant, because the energy cost of distillation exceeds usually the capital cost of the plant. However, practical application of one of these methods must be based on economical evaluation of available designs.

Finally, it can be noted that all the considerations here can be symmetrically reversed for a situation where instead of a waste heat stream there is a "waste cooling medium" available.

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Nomenclature

B =bottoms flow rate D = distillate flow rateF = feed flow ratef = functionL =liquid flow rate

q = feed quality

Q = heat stream

R = reflux ratio

V =vapor flow rate

x =liquid mole fraction

y =vapor mole fraction

z = overall composition of a two phase stream

 α = relative volatility λ = heat of vaporization

Subscripts

I, II, III = section of a column

B = bottoms

D = distillate

eq = equilibrium

F = feed

min = minimum

waste = waste heat stream

Superscripts

* = pinch composition for a two-phase feed

lo = lower pinch controls

max = maximum

up = upper pinch controls

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