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REVIEW

Thermodynamic Analysis of Separation Systems

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ABSTRACT

Separation systems mainly involve interfacial mass and heat transfer as well as mixing. Distillation is a major separation system by means of heat supplied from a higher temperature level at the reboiler and rejected in the condenser at a lower temperature level. Therefore, it resembles a heat engine producing a separation work with a rather low efficiency. Lost work (energy) in separation systems is due to irreversible processes of heat, mass transfer, and mixing, and is directly related to entropy production according to the Gouy-Stodola principle. In many separation systems of absorption, desorption, extraction, and membrane separation, the major irreversibility is the mass transfer process. In the last 30 years or so, thermodynamic analysis had become popular in evaluating the efficiency of separation systems. Thermodynamic analysis emphasizes the

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use of the second law of thermodynamics beside the first law, and may be applied through (i) the pinch analysis, (ii) the exergy analysis, and (iii) the equipartition principle. The pinch analysis aims a better integration of a process with its utilities. It is one of the mostly accepted and utilized methods in reducing energy cost. Exergy analysis describes the maximum available work when a form of energy is converted reversibly to a reference system in equilibrium with the environmental conditions; hence, it can relate the impact of energy utilization to the environmental degradation. On the other hand, the equipartition principle states that a separation operation would be optimum for a specified set of fluxes and a given transfer area when the thermodynamic driving forces are uniformly distributed in space and time. Thermodynamic analysis aims at identifying, quantifying, and minimizing irreversibilities in a separation system. This study presents an overview of the conventional approaches and the thermodynamic analysis to reduce energy cost, thermodynamic cost, and ecological cost in separation systems with the main emphasis on distillation operations. Some case studies of cost reduction based on the thermodynamic analysis are also included.

Key Words: Distillation; Thermodynamic analysis; Pinch analysis; Exergy analysis; Equipartition principle; Thermoeconomics.

INTRODUCTION

Distillation is a major separation system in chemical process industries. It uses heat supplied at higher temperature levels, and rejects almost equal amount of heat in the condenser at lower temperature levels yielding a separation work of mixtures. Therefore, it is an energy intensive system, and accounts more than 3% of the energy dissipation in the United States.^[1] In the last 50 years, reduction of energy consumption in distillation attracted intensive research. Earlier research is mainly concentrated on optimum reflux ratio and column pressure. Beside that, the retrofits, such as heat-integrated columns, application of heat pumps, changing feed stage location, and using feed splitting have also been popular. Later, researchers explored the use of principles of thermodynamics in reducing the cost of separation systems, particularly in distillation operations. The excessive cost of separation systems results partly because of energy dissipation or lost work, and combination of the first and second laws of thermodynamics can identify and quantify the lost work due to irreversible processes. Efforts to minimize the entropy production have become popular since, according to the Gouy-Stodola principle, the lost separation work is directly related to entropy production resulting from irreversible heat, mass transfer, and mixing. This

innovative approach is called the thermodynamic analysis, and started with the pinch analysis, which integrates a process with its utilities in a way to reduce the cost of energy. Later exergy analysis was developed to identify the parts of systems with excessive irreversibilities and, hence, to control the lost work. Some researchers have recently combined the pinch analysis and the exergy analysis, and related thermodynamic imperfections with environmental concerns. Based on the developments in nonequilibrium thermodynamics (NET), some recent research has reported the implications of the rate of entropy production on the use of available energy in separation systems.^[2] Equipartition principle is one result of such research, and it states that the uniform distribution of thermodynamic forces in space and time can improve the thermodynamic effectiveness of separation systems. The thermodynamics approach may have wide implications in reducing the energy cost, thermodynamic cost (imperfections), and environmental deterioration. With this in mind, this study presents a critical evaluation of various approaches for reducing the cost of energy in separation systems with the emphasis on distillation. Within the next sections, some of the conventional approaches and relatively recent innovative approaches of thermodynamic analysis are presented. Some case studies on reducing the energy cost by several approaches are also presented. Finally thermoeconomics are briefly presented.

SOME CONVENTIONAL APPROACHES

Approaches for energy saving in distillation systems may vary according to the number of components, nature of mixtures, and utility constraints. Most of the conventional approaches involve internal and external modifications and a better integration of columns with the rest of energy exchanging systems. For well-balanced, nearly ideal mixtures, the most useful configuration is to separate pure components in each column in successive order of decreasing volatility. However, for mixtures, such as those containing large proportions of less volatile components, each case must be considered in detail to save energy, which may be substantial.^[3] Large concentration changes in multi-component mixture separations may lead to considerable energy losses, therefore, the key components should be removed from the feed mixture. As seen in Fig. 1, light-nonkey components can be removed by using an absorber, and the bottom products of the absorber provide the feed to the main distillation column. Similarly, heavy-nonkey components are removed by using a prestripper, and the over products of the stripper become the feed of the main distillation column. These modifications can reduce the load of the column for debottlenecking and the required number of stages.^[4,5] A recent work considers the feed composition and relative volatilities for sequencing columns

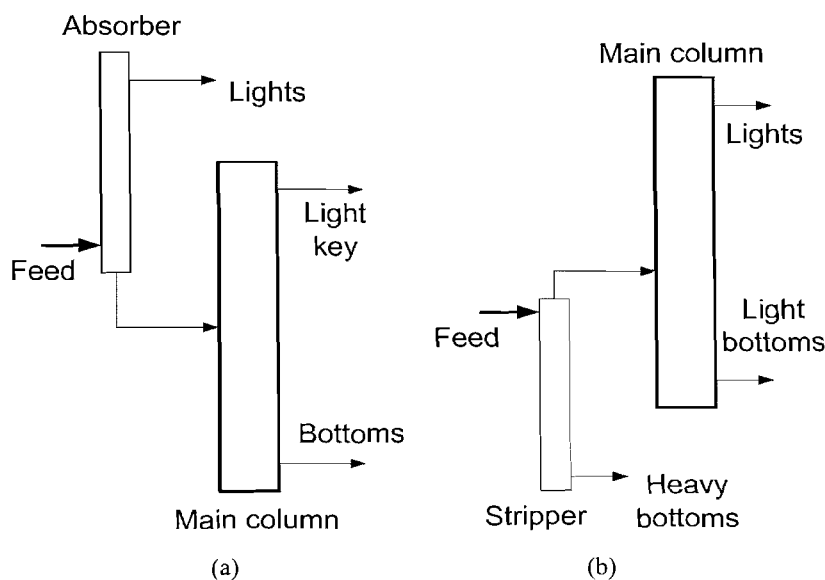


Figure 1. Prefractionation arrangements: (a) removing light keys with absorber, (b) removing heavy keys with stripper.

with respect to their costs of operation.^{16]} Hybrid processes of distillation and vapor permeation can be alternatives to azeotropic and extractive distillation and lead to improved separation systems.^{17]}

Thermally coupled multiple effect distillation columns are well known in energy saving;^{15,8]} the feed is sent into two columns operating at different pressures, and temperatures of the condensing vapors and boiling liquids will be different from each other by a minimum temperature difference ΔT_{\min} . As Fig. 2 shows, the heat from the condensing vapor in the column below is transferred to the reboiler within the column above. Feed split can be adjusted to have equal duties of adjacent boiling and condensing streams. Therefore, the heat duties of boiling and condensation, Q_{eff} , are approximately equal to the heat duty for a single effect, Q , divided by the number of effects ($Q_{\text{eff}} = Q/N_{\text{eff}}$). This saves energy despite an extra operating and capital cost of equipment.^{15]} On the other hand, in a diathermal system with heat exchangers all along the column, or interstage heat exchangers, or internal tray design with heat exchanging coils, it is possible to adjust the flow ratio of the phases to vary the slopes of operating lines. Consequently, the operating lines become closer to equilibrium curves, and, hence, the irreversibility due to mass transfer can be reduced. However this requires

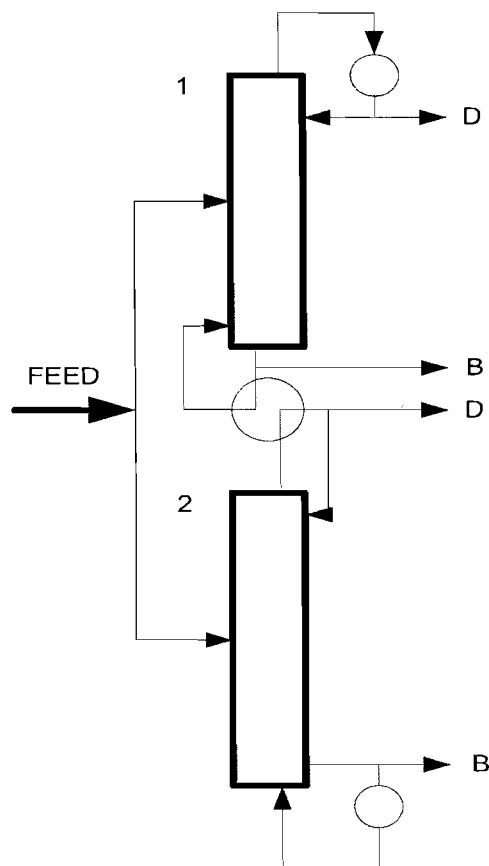


Figure 2. Two-effect distillation column;^[5] B: bottom product, D: distillate.

taller columns, and, hence, an economical analysis to evaluate the gains and losses,^[9] although the side reboilers reduce the consumption of expensive high-pressure steam. Optimum locations of heating and cooling zones could lead to maximum exchangeable energy loads.^[10] Such modifications have been mainly carried out for binary systems, although some work on heat integration for multicomponent distillation systems is also reported.^[11,12]

Column and heat exchanger network integration in refinery operations is highly popular.^[13–22] In the synthesis of a heat exchanger network, the main objective is to determine the maximum energy recovery based on the heating and cooling requirements of the process streams leading to the minimum hot and cold utilities, which can be calculated by a linear programming

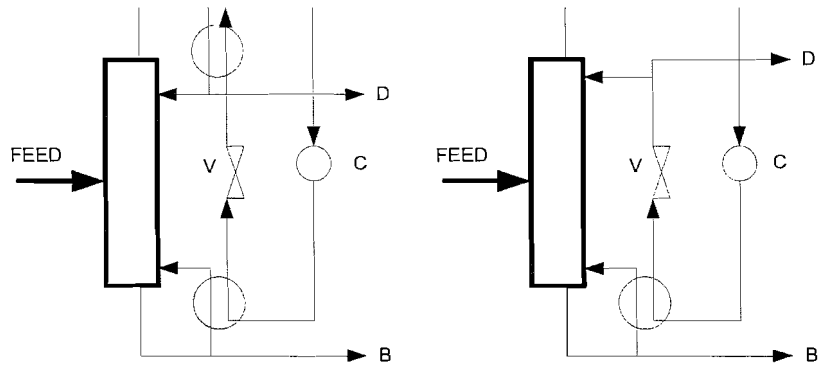
approach.^[5] Column retrofit models and heat exchanger network retrofit models may be optimized based on a successive quadratic programming solver.^[22] Less energy consumption and more free capacity at a minimum capital investment may be possible by installing intermediate reboilers,^[14,17] pumps-around at certain locations, and adjusting the cooling duty for each pump-around,^[15] preflashing units before the crude oil distillation unit,^[16] and reducing the operating pressure and increasing the preflash overhead vapor (Fig. 3).^[5,18] The reboiler flashing is relatively the most economical among these configurations.^[5] For close boiling feeds for which small pressure changes are required, the cost of compression is not too high. In the close boiling system of propylene-propane separation, a heat pump lowers the annual cost by about 37%, and minimizes the flue gas emissions by about 60%.^[23] The optimality criterion may be the payback period for a preliminary economic analysis of heat pump-assisted distillation systems.^[24] However, designers should consider the power consumption and water management aspects of heat pump operations for an economical operation.^[24–26]

Attainable region analysis is a graphical optimization mainly used to find a complete set of all possible outcomes from a specified feed set. It is applied to a binary distillation operation with side condensers and reboilers, and the attainable region of composition, cost, and reflux/boil up ratio space is constructed.^[27] Cost of the heat transfer units is included in the objective function to be minimized; the optimized solution could reduce column size and energy cost up to 15%.^[27,28]

Feed conditioning is another important external modification; it is less expensive compared with the inter heating or inter cooling, and feed precooling or preheating can be useful to unload the top or bottom sections of the column. Cold feed may require a large amount of heat exchange below the feed stage to strip the light components. Using a process simulator, optimum split ratio and feed location can be obtained; feed splitting and preheating with the bottom product can save up to 50% energy (Fig. 4).^[29,30] Of course, one should evaluate thoroughly the economic cost of internal and external modifications, which may be identified and evaluated by incorporating the principles of thermodynamics; for example, it may be possible to reduce the exergy loss or to distribute the driving forces as evenly as possible in the modified system. Thermodynamic analysis is presented in the next sections.

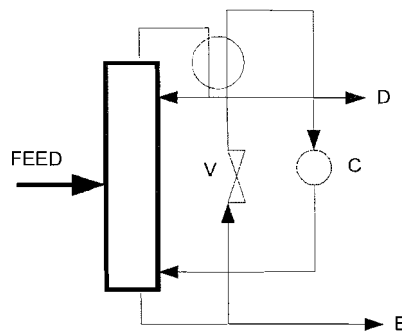
THERMODYNAMIC ANALYSIS

Efficiency in separation systems is often calculated from the first law of thermodynamics. However, since thermal energy cannot be converted into



(a) Heat pumping

(b) Vapor recompression



(c) Reboiler flashing

Figure 3. Various distillation configurations;^[5] B: bottom product, C: compressor, D: distillate, V: valve.

work completely, the quality of thermal energy should be taken into account.^[5,31] As distillation systems consume about 95% of the total thermal energy used in separation systems in the United States,^[31] a considerable part of this energy is dissipated into the environment. Thermodynamic analysis can identify the part of total energy convertible to work, and, hence, the possible ways of reducing the dissipated energy. It calculates the entropy production due to irreversibilities, which is directly proportional to

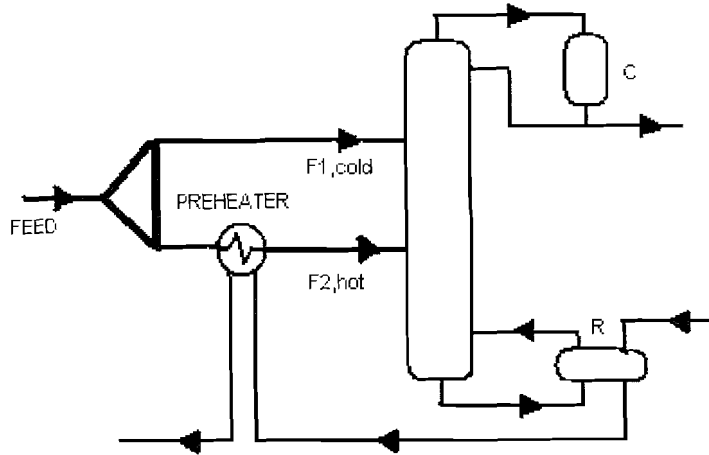


Figure 4. Splitting the feed in such a way that the non-heated fraction keeps the reflux ratio low and the heated one recovers energy from the reboiler.^[30]

the dissipation of available energy. However, how to use the thermodynamic analysis to optimize a separation system has not always been clear.

The rate of entropy production is always positive and calculated as the product of fluxes and thermodynamic forces operating within a system;^[2,32,33] fluxes are expressed as linear functions of all the forces when a system is not far from global equilibrium. The key concepts for thermodynamic analysis are: (i) availability (exergy), (ii) lost work (dissipation), and (iii) environmental cost due to thermodynamic imperfections.

A general energy balance for a control volume with multiple streams is

$$\frac{d(nU)_{\text{sys}}}{dt} + \Delta \left[\dot{n} \left(H + \frac{1}{2} u^2 + zg \right) \right]_{\text{fs}} - \dot{Q}_o - \sum_i \dot{Q}_i + \sum_j \dot{W}_j = 0 \quad (1)$$

where the first term is the change in internal energy, the second is the net change of enthalpy, kinetic, and potential energies of flow streams within the control volume, \dot{Q}_o is the heat input rate from the surroundings at temperature T_o , $\sum_i \dot{Q}_i$ is the heat input rate from a reservoir at temperature T_i , and $\sum_j \dot{W}_j$ shows the work that includes mechanical shaft work, expansion or contraction work, and electrical work. Assuming that the kinetic and potential energy over the control volume are negligible, Eq. (1) becomes

$$\frac{d(nU)_{\text{sys}}}{dt} + \Delta[\dot{n}(H)]_{\text{fs}} - \dot{Q}_o - \sum_i \dot{Q}_i + \sum_j \dot{W}_j = 0 \quad (2)$$

Entropy balance for the same control volume and its surroundings is

$$\frac{d(nS)_{\text{sys}}}{dt} + \Delta[\dot{n}(S)]_{\text{fs}} - \frac{\dot{Q}_o}{T_o} - \sum_i \frac{\dot{Q}_i}{T_i} = \Phi \quad (3)$$

Here the first term is the change of entropy of the system, the second is the net rate of entropy flow, $-\dot{Q}_o/T_o$ is the rate of decrease in entropy of surrounding at T_o , and $-\sum \dot{Q}_i/T_i$ is the sum of the rates of entropy decrease of the heat reservoirs at various temperatures of T_i . The term Φ shows the rate of entropy production due to irreversibility, which is zero when processes and heat flows between the system and its surrounding are reversible. Equation (3) shows that entropy is not conserved. Elimination of \dot{Q}_o in Eqs. (2) and (3) yields

$$\begin{aligned} \frac{d[n(H - T_oS - PV)]_{\text{sys}}}{dt} + \Delta[\dot{n}(H - T_oS)]_{\text{fs}} - \sum_i \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i \\ + \sum_j \dot{W}_j + T_o\Phi = 0 \end{aligned} \quad (4)$$

From the first and second terms we have a quantity called the availability A : $A = H - T_oS$. Change in A represents the minimum work required to achieve a change. Availability is related to the maximum useful work a system can deliver when it is brought to equilibrium with the environmental conditions in reversible mode.

The last term in Eq. (4) $T_o\Phi$ is called the rate of lost work $L\dot{W}$

$$L\dot{W} = T_o\Phi \geq 0 \quad (5)$$

or loss of availability, or exergy destroyed. The lost work is a quantitative measure of the thermodynamic cost or imperfections in a system, and is related to availability through Eq. (4)

$$L\dot{W} = -\frac{d[n(A - PV)]_{\text{sys}}}{dt} - \Delta[\dot{n}(A)]_{\text{fs}} + \sum_i \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i - \sum_j \dot{W}_j \geq 0 \quad (6)$$

Heat and work terms in Eq. (6) show transferred availabilities between a system and its environment. For a steady-state process the lost work can be related to the change in availability, heat, and work terms, and we obtain

$$\begin{aligned} L\dot{W} = \Sigma(\dot{n}A)_{\text{in}} - \Sigma(\dot{n}A)_{\text{out}} + \Sigma \left[\dot{Q} \left(1 - \frac{T_o}{T}\right) \right]_{\text{in}} - \Sigma \left[\dot{Q} \left(1 - \frac{T_o}{T}\right) \right]_{\text{out}} \\ + \Sigma \dot{W}_{\text{in}} - \Sigma \dot{W}_{\text{out}} \geq 0 \end{aligned} \quad (7)$$

The lost work has two important features: (i) it identifies and quantifies the power lost due to various irreversibilities, and (ii) it relates the evolution of a system to the environmental conditions. For a steady state and adiabatic system, Eq. (6) becomes

$$L\dot{W} = -\Delta[\dot{n}(A)]_{fs} - \sum_j \dot{W}_j \geq 0 \quad (8)$$

Equation (8) shows that when availability decreases, and work is transferred from surrounding to system then the lost work will be positive; the maximum work that a system can deliver would be the decrease in availability, while the minimum work would correspond to the increase in availability

$$(\sum_j \dot{W}_j)_{\max} = -\Delta[\dot{n}(A)]_{fs} \quad \Delta A = (-) \quad (9)$$

$$(\sum_j \dot{W}_j)_{\min} = -\Delta[\dot{n}(A)]_{fs} \quad \Delta A = (+) \quad (10)$$

Only, the zero lost work has no impact on the environment.

Reducing the cost in a separation system needs careful elaboration of the concept "cost." The lost work causes the inefficient use of energy (loss of exergy), and environmental cost due to (i) discharging lost exergy into the environment, and (ii) the depletion of natural resources because of inefficient use of fossil fuels. Hence, the lost work may affect the sustainable development adversely. In most of the continuous distillation system, the net availability increases because of the heat input in the reboiler, and the difference between the availability of products and feed streams determines the minimum work required for a reversible separation

$$W_{\min} = \sum_{\text{out}} nA - \sum_{\text{in}} nA \quad (11)$$

The thermodynamic efficiency is expressed by using the lost work

$$\eta = \frac{\dot{W}_{\min}}{L\dot{W} + \dot{W}_{\min}} \quad (12)$$

The thermodynamic efficiency of distillation systems is generally low, and the thermodynamic analysis may lead to innovative systems with increased efficiency by decreasing the thermodynamic imperfections and, hence, the lost work.^[2,5,31,34-37]

Case Study: 1. Distillation of Propylene–Propane Mixture

Propylene–propane mixture is a closed boiling mixture. A reflux ratio of 15.9 (close to minimum) and 200 equilibrium stages are necessary. Table 1 shows the enthalpy and entropies of the saturated feed and saturated products

Table 1. Conventional column operation for the separation of propylene and propane. Thermodynamic properties are estimated by Soave-Redlich-Kwong equation of state.^[5]

Stream	Temperature K	Flow rate kmol/h	Enthalpy kJ/mol	Entropy kJ/mol K
Feed	325	272.2	13,338	-4.1683
Distillate	319.5	189.2	12,243	-13.8068
Bottoms	330.9	113	14,687	-2.3886

from the simulation results with the Redlich-Soave equation of state.^[5] The reboiler and condenser duties are 8274.72 kW and 8280.82 kW, respectively. The reference temperature is 294 K. The lost work is obtained from Eq. (7) as $LW = 1902.58$ kW. Availability analysis yields $W_{\min} = \sum_{\text{out}} nA - \sum_{\text{in}} nA = 140.81$ kW, and the thermodynamic efficiency η is

$$\eta = \frac{W_{\min}}{W_{\min} + LW} = 0.0689 \text{ or } 6.89\%$$

The low exergetic efficiency is typical for distillation systems with close boiling mixtures, and when a large amount of energy is required in the reboiler. An alternative is to use reboiler-liquid flashing as shown in Fig. 3(c), where the feed has the pressure of 108 psia by a power-recovery turbine. A compressor is used to return the reboiled vapor to the bottom of the column. The required reboiler duty is somewhat larger than the required condenser duty, an auxiliary steam-heated reboiler is needed. So the power used in the compressor is traded off with the large reduction in the reboiler steam.^[5] The alternative distillation system has produced the lost work = 501.6 kW, availability $W_{\min} = 38.2$ kW, and the efficiency of $38.2 / (38.2 + 501.6) = 7\%$. The lost work, 501.6 kW, is smaller compared with the conventional column of 1902.58 kW, yet the column efficiency is still very low.

Case Study: 2. Distillation of a Five-Component Mixture

The second column has a feed with five components of ethane, propane, n-butane, n-pentane, and n-hexane. Table 2 shows the configuration of the column and the simulation results obtained from the Aspen Plus with the Peng-Robinson equation of state. The column has the condenser duty of 3395.336 kW and the reboiler duty of 3432.206 kW. The condenser and the

Table 2. Column configuration for a five-component distillation. Simulation results from Aspen Plus (Version-11). Thermodynamic properties are estimated by the Peng-Robinson equation of state. $Q_C = 3395.3367$ kW; $Q_R = 3432.2069$ kW; $N = 14$; $N_F = 7$; $RR = 8.87$.

	Feed	Distillate	Bottom
Flow (kmol/h)	453.59	102.51	351.08
Pressure (Atm)	17.01	16.87	17.14
Temperature (K)	380.37	319.30	400.26
Vapor fraction	0.2830	1.0	0.0
Enthalpy (kJ/kmol)	$1.3457 \cdot 10^5$	$1.0284 \cdot 10^5$	$1.4346 \cdot 10^5$
Entropy (kJ/kmol K)	-403.93	-277.61	-443.76
Compositions			
Ethane	0.0299	0.1326	$4.642 \cdot 10^{-6}$
n-Propane	0.1999	0.8450	0.0116
n-Butane	0.3699	0.0219	0.4716
n-Pentane	0.3499	$1.404 \cdot 10^{-4}$	0.4521
n-Hexane	0.0499	$2.507 \cdot 10^{-8}$	0.0646

reboiler temperatures are 319.3 and 400.2 K, respectively. The reference temperature (dead state temperature), T_o , is assumed to be 300 K. The simulation results show the lost work = 531.37 kW, $W_{\min} = 117.49$ kW, and the efficiency from Eq. (12) as 18.1%.

PINCH ANALYSIS

Pinch analysis optimizes systems with their utilities using the principles of thermodynamics. The second law determines the direction of heat flow, and prevents crossovers of the hot and cold stream temperatures. Temperature-enthalpy diagrams called the composite curves represent the thermal characteristics of hot and cold streams (Fig. 5). Hot and cold streams can only exchange energy up to a minimum allowable temperature difference ΔT_{\min} . The temperature level at which ΔT_{\min} is observed in the system is called the pinch point or pinch condition, which defines the minimum driving force, hence, the minimum entropy production allowed in a network. Pinch is easy to identify by the composite curves, and approaches zero as the area for heat transfer equipment approaches infinity. Above the pinch, only the hot utility is required, while only the cold utility is required below the pinch, and no heat should be transferred across the pinch. For estimating the minimum hot and cold utilities required, Linnhoff and Flower^[38,39] developed the temperature-interval method based on the work of Hohmann.^[40]

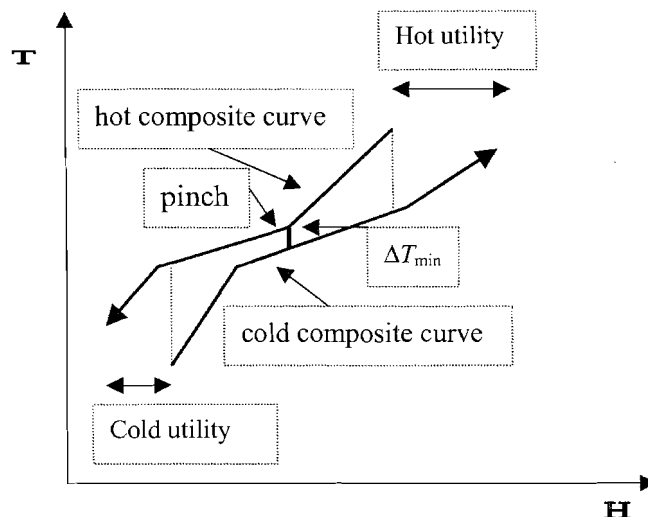


Figure 5. Hot and cold composite curves.

Similarly, grand composite curves show the variation of heat supply and demand in a system. These diagrams enable engineers to identify the suitable utility and target appropriate loads for various utility levels by minimizing the expensive utilities and maximizing the least expensive utilities, network area, and number of heat exchanger units; they also provide insights for optimum integration of distillation columns, evaporators, condensers, furnaces, and heat pumps to reduce the utility requirements of the combined system.

An increase in ΔT_{\min} causes higher energy costs and lower capital costs (less heat exchanger area). For example, an increase of 5°C from a value of $\Delta T_{\min} = 10^{\circ}\text{C}$ decreases heat exchanger area by 11% and increases the required minimum energy by about 9%.^[41] To find the value of optimum ΔT_{\min} , total annual cost is plotted against ΔT_{\min} (Fig. 6). An optimum ΔT_{\min} exists where the total annual cost of energy and capital costs is minimized. Once the ΔT_{\min} is chosen, minimum hot and cold utility requirements can be evaluated from the composite curves. Since heat recovery and utility system constraints are considered systematically, the pinch analysis can estimate the reduced annual cost in networks by comparing the cost of fuel and the capital cost of a network. It is possible to obtain an accurate estimate (within 10%–15%) of overall heat recovery system cost without having to design the system.^[42,43] Pinch analysis has been applied widely in industry leading to

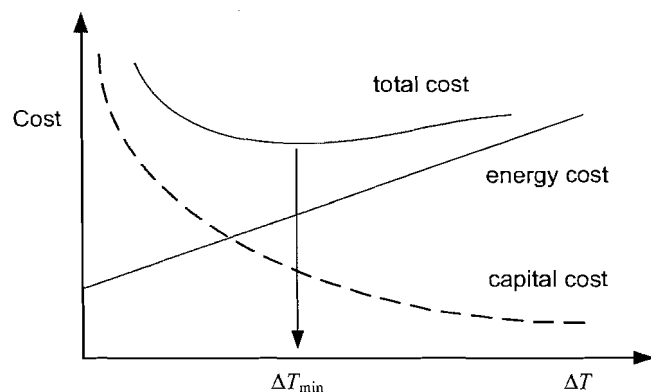


Figure 6. Optimum ΔT_{\min} from energy cost and capital cost changes.

considerable savings,^[44,45] and it can identify energy targets, minimum driving forces, and capital cost targets.^[46] Dhole and Linnhoff^[46] developed the vapor and liquid composite curves for representing combined heat- and mass transfer loss in a column system. Some of the pinch techniques consist of minimizing pressure-drop effects, water and wastewater, and plant emissions.^[47-49]

Pinch analysis can specify the exchanged heat and mass between hot/rich and cold/lean streams based on the first and second laws. According to the second law of thermodynamics:

$$\begin{aligned} & (\text{heat/mass lost by hot/rich streams below the pinch point}) \\ & - (\text{heat/mass gained by cold/lean streams below the pinch point}) \leq 0 \end{aligned} \quad (13)$$

Using the state space approach to process synthesis, heat and mass exchanger network representation of distillation systems can be analyzed and optimized.^[50,51] Pinch analysis has also been extended to the integration of chemical reactor systems with heat exchangers,^[52] optimization of industrial ammonia plant,^[53] and nitric acid plant.^[54] For example, column grand composite curves,^[19-21,46,48] can be used to modify the column and heat exchanger network; a possible modification is the use of heat pumps in columns by identifying the heat sinks and sources, leading to considerable saving and a shorter pay back period.^[47]

Some of the advantages of the pinch analysis over conventional ones are the ability to set energy cost and capital cost targets for a network, update the

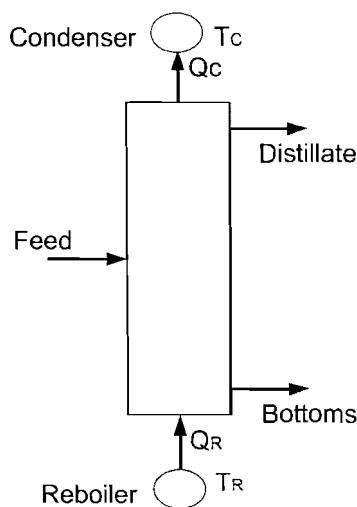


Figure 7. Distillation column as a heat engine between reboiler (R) and condenser (C).^[35]

process flowsheeting, and debottlenecking of distillation columns (Fig. 7). However, some of the modifications imposed by the pinch analysis may require substantial capital investments and changes in internal stage design of distillation columns. Also, pinch analysis may not deliver the desired result, unless it is applied before completion of the process design stage and in consultation with the process specialists. The analysis will be successful if target temperatures and utilities are set on the basis of process objectives rather than on flowsheeting. For example, a flowsheet may mix two streams with different temperatures to prepare a feed for a process. This causes degradation of available energy or thermodynamic driving force. To prevent this, the temperatures of both streams should be increased to the process operating temperature. Also, heat recovery from special streams like two-phase streams should be completed in a single heat exchanger due to phase separation and large pressure drops; also, the destination of process streams should be fully evaluated to avoid adverse effects of streams with hazardous chemicals. However, process integration would be more complete and meaningful if it targets environmental protection, emission control, and depletion of natural resources beside the cost of energy. It is encouraging to note that this issue is addressed in several extensions of the analysis.^[47,48] Moreover, the software developed for process integration should be able to interact with the available simulation software to access a wide range of design models.^[49]

**Case Study: Pinch Analysis: Column Grand Composite
Curves: $T-H$, or Stage- H**

For the column configuration described in Table 2, the column grand composite curves ($T-H$; Stage- H) for a five-component mixture have been obtained using the Aspen Plus column-targeting tool capability for thermal analysis. This analysis is helpful in identifying the targets for appropriate modifications in order to reduce utility and capital costs, improve energy efficiency, and facilitate column debottlenecking. It is based on thermodynamically reversible column operation at minimum reflux with appropriate heat integration. The column grand composite curves (Figs. 8a, 8b) are based on the practical near minimum thermodynamic condition approximation proposed by Dhole and Linnhoff,^[46] and show the theoretical minimum heating and cooling duties within the temperature range. The stage-enthalpy calculations take into account the losses or inefficiencies stemming from the actual column design, such as pressure drops, multiple-side products, etc. Figure 8(a) can be useful for identifying the targets for feed preparation and location, reflux ratio, and heat integration modifications. The column's grand composite curves indicate distortions as significant projections around feed stage location (pinch point), if the current feed stage is inappropriate. Figure 8b shows a distortion at the pinch point (stages 8 and 9). To compensate inappropriate feed stage location, extra local reflux may be needed. Beside that, a feed stage too high up or too low in the column will display sharp enthalpy changes on the condenser and on the reboiler, respectively. The sharp enthalpy changes on the grand composite curves indicate the need for adjustment of feed quality. Figure 8 shows almost equal enthalpy changes on both the reboiler and condenser sides of the curves. However a sharp enthalpy change on the reboiler side suggests that the feed is subcooled, and a preheater should be installed. The horizontal gap between the pinch point and the ordinate in Figure 8a, which is about 200 kW, indicates the possible reduction in heat duties by reducing the reflux ratio with the expense of increasing number of stages to achieve the specified separation. Obviously, the increase in the capital cost for a taller column should be traded off with savings in utility costs. Figure 8a also shows that the reboiler side is relatively close to ideal operation while the condenser side is far from ideal operation. The significant area underneath the pinch suggests the need for a side condenser at an appropriate temperature level. The need for heat integration through side condensing or side reboiling could be quantified from the area between the ideal and actual enthalpy profiles after considering the capital cost increase due to the modification. However, external modification of feed conditioning is usually preferred to internal modification of heat integration. Heat integration by positioning the side reboilers and side condensers in a

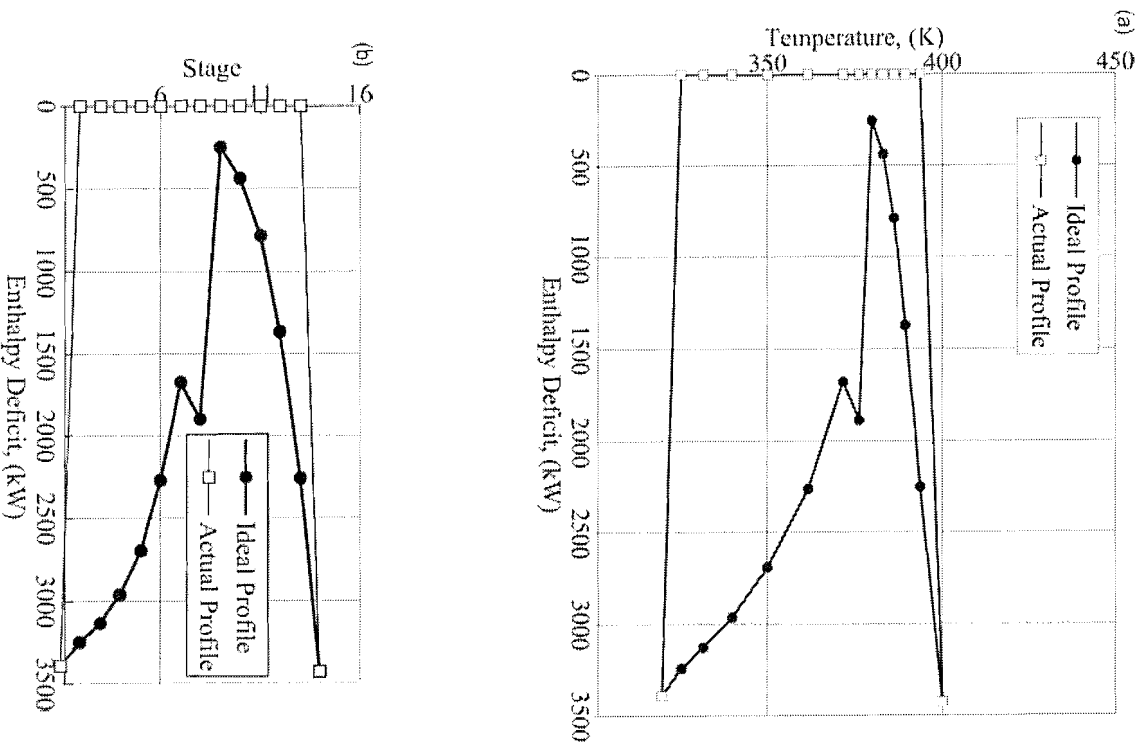


Figure 8. (a) Column grand composite curve of temperature enthalpy obtained from the simulations with the Aspen Plus Radfrac block using the Peng-Robinson equation of state. The column configuration is given in Table 2. (b) Column grand composite curve of temperature enthalpy obtained from the simulations with the Aspen Plus Radfrac block using the Peng-Robinson equation of state. The column configuration is given in Table 2.

column has similarities to use of hot and cold utilities in efficient heat exchanger network.

Pinch analysis is a well-established tool in designing an efficient heat exchanger network. In the context of distillation, the significance of the pinch is that there should be no side reboiling below the pinch and no side condensing above the pinch in a heat integrated column. Still, the pinch analysis is constantly being expanded to optimize a whole plant operation containing not only heat transfer, but also separation and reaction units as well. Some examples of such expansions with case studies are heat integrated crude oil distillation systems,^[20] total process energy integration in retrofitting an ammonia plant with 44 hot and cold streams,^[53] heat exchanger network of a nitric acid plant,^[54] and combination of the chemical reactor network with the heat exchanger network.^[52]

EXERGY ANALYSIS

The quality of energy always degrades in a process. Exergy is the maximum available work when some form of energy is converted reversibly to a reference system, which is in thermodynamic equilibrium with the environment, and has no ability to perform work. Exergy also is a measure of distance of a system from global equilibrium; as the exergy is consumed the state variables of temperature, pressure, and composition of system approach those of the environmental conditions.^[56] Therefore, the reference state is called the dead state.^[55] The total exergy of multicomponent streams is calculated from the three contributions: exergy change due to mixing, chemical exergy, and physical exergy,^[5,55,57-66] and is expressed by

$$X_{\text{total}} = (H - H_o) - T_o(S - S_o) \quad (14)$$

where the subscript *o* indicates the enthalpy, entropy, and temperature of the environment. The exergy of mixing results from the isothermal and isobaric mixing of streams at actual process conditions. The chemical exergy is the difference in chemical potentials between the process components and the reference components in their environmental concentration, temperature, and pressure. The physical exergy is the maximum obtainable amount of shaft work (electrical energy) when a stream is brought from process condition (*T*, *P*) to equilibrium at ambient temperature by a reversible heat exchange. Exergy relates the evolution of a process to the environmental conditions, and consequently to the ecological impact. This brings a distinctive feature to the optimization of systems.

Exergy analysis identifies and quantifies unused parts of available energy and determines the thermodynamic efficiency of distillation systems.

Traditionally, exergy analysis is based on the overall thermodynamic efficiency that is the ratio of the lost work to the ideal work required for separation.^[56–59] The overall exergy efficiency for distillation is the product of external and internal exergy efficiencies. The external efficiency depends on thermal integration among units, coproduction, and recompression of overhead vapor to be used in the reboiler, while the internal exergy depends on the column internal design, feed composition and state, number of stages, and utility requirements. The exergy efficiency for distillation systems is low; many operate with about 20%–25% exergetic efficiency, which could be increased to around 60% with certain modifications.^[5] To separate a component with low composition by distillation is highly inefficient, and integration of several functions into single equipment, such as an exchanger-dephlegmator or reactive distillation and absorption may increase the efficiency and the investments required. Feed conditions and feed plate location affect irreversibility, and, hence, the efficiency of separation systems.^[60]

It is a common approach to assume that the mass transfer (evaporation or condensation) is controlled by the vapor phase. With this assumption, the exergy analysis mainly uses a graphical tool called the exergy loss profiles or the exergy-utilization diagrams.^[61–64] Every process accepts or donates energy in equal amounts: $\Delta H_d + \Delta H_a = 0$, while exergy loss or entropy change is not conserved: $\Delta S_d + \Delta S_a \geq 0$. The exergy changes of energy donor ΔX_d and acceptor ΔX_a based on a reference temperature T_o are expressed by

$$\Delta X_d = \Delta H_d - T_o \Delta S_d = \Delta H_d x_d \quad (15a)$$

$$\Delta X_a = \Delta H_a - T_o \Delta S_a = \Delta H_a x_a \quad (15b)$$

where x_a and x_d are the energy levels, which show the ratio of available energy (exergy) to total energy, and expressed by $x_d = 1 - T_o \Delta S_d / \Delta H_d$ and $x_a = 1 - T_o \Delta S_a / \Delta H_a$. Then, the exergy loss XL between an energy donor and an energy acceptor is expressed by

$$XL = \Delta H_a (x_d - x_a) \geq 0 \quad (16)$$

Therefore, the energy level of the donor process must be greater than or equal to that of the energy level of the acceptor process, and the value of XL is positive as $\Delta H_a > 0$. The abscissa of the exergy-utilization diagram displays the amount of accepted energy, ΔH_a , while the ordinate shows the energy levels of x_d and x_a ; therefore, the area displays the exergy loss.^[64]

Stage-exergy losses occur due to heat exchanged and mixing between the phases on stages causing cooling, heating, condensation, evaporation, and mixing.^[64]

For cooling of the vapor phase, the energy levels at stage i are expressed by

$$x_{d,i} = x_{c,i} = 1 - \frac{T_o \Delta S_{c,i}}{\Delta H_{c,i}} \quad (17)$$

$$x_{a,i} = 1 - \frac{T_o \Delta S_{c,i}}{T_{G,i} \Delta S_{c,i}} = 1 - \frac{T_o}{T_{G,i}} \quad (18)$$

where

$$\Delta H_{c,i} = V_{i+1} \sum y_{i+1,j} (h_{G,i,j} - h_{G,i+1,j}), \text{ and } \Delta S_c = V_{i+1} \sum y_{i+1,j} (s_{G,i,j} - s_{G,i+1,j}).$$

For heating of the liquid phase the energy levels are:

$$x_{a,i} = x_{h,i} = 1 - \frac{T_o \Delta S_{h,i}}{\Delta H_{h,i}} \quad (19)$$

$$x_{d,i} = 1 - \frac{T_o}{T_{L,i}} \quad (20)$$

where

$$\Delta H_{a,i} = \Delta H_{h,i} = L_{i-1} \sum x_{i-1,j} (h_{L,i,j} - h_{L,i-1,j}), \Delta S_{h,i} = L_{i-1} \sum x_{i-1,j} (s_{L,i,j} - s_{L,i-1,j})$$

The exergy loss at stage i is expressed by Eq. (16):

$$XL_i = \Delta H_{d,i} (x_{d,i} - x_{a,i}) \geq 0$$

Exergy losses due to evaporation and condensation are expressed by

$$XL_{\text{evap}} = \sum n_j \Delta H_{\text{evap},j} x_{\text{evap},j} + \Delta H_Q x_Q \quad (21)$$

$$XL_{\text{cond}} = \sum n_j \Delta H_{\text{cond},j} x_{\text{cond},j} - \Delta H_Q x_Q \quad (22)$$

$$x_a = x_{\text{evap}} = \sum \left(1 - \frac{T_o \Delta S_{\text{evap},j}}{\Delta H_{\text{evap},j}} \right) \quad (23)$$

where ΔH_Q shows the heat supplied at the energy level x_Q . Condensation takes place at the liquid phase temperature

$$\Delta H_{a,i} = \Delta H_{h,i} = L_{i-1} \sum x_{i-1,j} (h_{L,i,j} - h_{L,i-1,j}) \quad (24)$$

$$\Delta S_{h,i} = L_{i-1} \sum x_{i-1,j} (s_{L,i,j} - s_{L,i-1,j}) \quad (25)$$

The vapor flow from the stage $i + 1$ mixes with the vapor phase on stage i , and the exergy loss is expressed by

$$XL_{m,G,i} = -RT_o V_{i+1} \sum [y_{i+1,j} (\ln y_{i,j} - \ln y_{i+1,j}) - (y_{i,j} - y_{i+1,j})] \quad (26)$$

The liquid flow from stage $i-1$ mixes with the liquid phase on stage i , and the exergy loss is given by

$$XL_{m,L,i} = -RT_o L_{i-1} \sum [x_{i-1,j} (\ln x_{i,j} - \ln x_{i-1,j}) - (-x_{i,j} - x_{i+1,j})] \quad (27)$$

In distillation columns using side heating and cooling, energy utilization diagrams can describe the relation between exergy loss in the column and separation performance.

Mass transfer in separation systems, such as rectification, absorption, desorption, and membrane separation, is optimum when the conditions on the concentration profiles provide the minimal irreversibility.^[67] Analysis in sieve tray distillation columns reveals that the irreversibility on a tray is mostly due to the bubble-liquid interaction, and the exergy loss could be reduced considerably for the same operating conditions with moderate investments.^[68-70] The optimal concentration and temperature profiles can be derived by minimizing the entropy production rate for specified heat and mass fluxes, which can be expressed by linear flux-force relations if the transport system is not far from global equilibrium.^[2,32,71]

There has been hesitation and delay for the simulation packages to incorporate the exergy analysis in property calculations and process analysis. However, for the last 10 years, exergy analysis in simulation has become popular.^[65,66,71-74] In 1996, Hinderink et al.^[65,66] integrated the subroutines of exergy calculations with the flowsheeting simulator of Aspen Plus and applied the codes to synthesis gas production from natural gas. These subroutines were developed by Exercom licensed by Stork Comprimo, Amsterdam, the Netherlands for applying exergy analysis as a diagnostic tool in process development and design.^[75] Exergy analysis within a flowsheeting can display the process inefficiencies. Such an analysis, performed for a part of a refinery, has revealed that 70% of exergy losses can be prevented, corresponding to 40% reduction of primary fuel consumption for the crude oil distillation column. In the same refinery, splitting the feed stream has reduced the fuel consumption by 10%.^[55] For the optimization of feed conditions and reflux, exergy analysis can be helpful.^[76-78] A complete exergy analysis, however, should include the exergy losses related to economical cost and environmental cost, as well as suggestions of modifications to reduce the costs.^[65] Unless that is accomplished, the analysis is mainly interpreted as theoretical calculations if system engineers are not trained adequately to implement the results. Consequently, this may undermine the effectiveness of the exergy analysis.

The computer tools such as Aspen Plus, Hysys, Mathcad, and Pro II may be useful in analyzing distillation column systems to improve recovery, separation capacity, and decrease the rate of entropy production. A recent simulation

study^[79] suggests that if the positioning of side stream withdrawals and returns is optimized (for example, liquid stream returning as vapor enters at a position where the vapor phase has similar composition), heat integration improves the recovery and the separation capacity and decreases the exergy loss, but it increases the number of stages required for a given separation.

Synthesis strategies of simple and complex distillation systems are based on heuristics and algorithmic analysis.^[6] Also, thermodynamic optimum structure for the synthesis is often considered.^[80-85] Separation trains may result through successive modification of thermodynamically optimum but economically unaffordable flow sheets. The thermodynamic approach can be used for analyzing the structural stability of multicomponent flash and distillation operation.^[85] However, thermodynamic consideration is often a complimentary design support and may not be a final selection tool.^[4]

The design of a subambient system involves distillation, heat exchanger network, and refrigeration, which are interdependent. The thermodynamic analytical strength of exergy analysis with practical targeting capability of pinch analysis can be combined to calculate exergy grand composite curves for subambient processes; for example, ethylene and liquefied natural gas process designs have yielded an average shaft work savings of 15% over the results obtained from normal pinch analysis.^[45] In another industrial application,^[86] the exergy analysis has been applied to cryogenic air distillation plant using Aspen Plus to quantify the exergy loss in various sections; compressors are the source of a large exergy loss that can be reduced by half by using better compressors, while the total exergy loss can be reduced by 25%.^[31,86] Some software tools, such as Super Target of Linnhoff March Ltd. Aspen Pinch, and Sprint use pinch analysis;^[52] obviously, the pinch analysis should be integrated with an economic analyzer for the thermodynamic optimum and the economic optimum.

Exergy analysis for adiabatic and diabatic distillation systems for separating ethanol from water shows that the largest exergy loss occurs on a stage with the largest composition differences, and the total exergy losses are 433.8 kJ/kg in an adiabatic distillation and 248.41 kJ/kg in a diabatic operation corresponding to a 42% decrease.^[56] For a specified number of stages, minimum distance between the operating and equilibrium curve corresponds to optimum exergy usage.^[87] Analysis of a heat-integrated distillation column utilizing the heat pump principle revealed that the exergy loss is considerably lower than that of a conventional column.^[87-90] The exergy loss profiles may lead to successful design modifications, which are outlined for deethanizer column and distillation of ammonia water.^[90,91] For example, through tray design parameters associated with the entropy production, an optimal operation and energy saving in distillation systems could be possible.^[92,93]

Case Study: 1. Exergy Loss Profiles for a Five-Component Distillation Column

The Aspen Plus thermal analysis tool estimates the stage exergy loss profiles consisting of temperature-exergy, stage-exergy, and Carnot factor $(1 - T_o/T_{\text{stage}})$ -exergy profiles. Figure 9 shows the vapor phase composition profiles and the exergy loss profiles for the column configuration given in Table 2. The vapor phase composition profiles (Fig. 9a) can display the levels of maximum and minimum concentrations of the key components, and the sharp concentration changes around the feed stage. The stage-exergy loss profiles (Fig. 9b) show the degradation of available work at each stage due to irreversibility sources of momentum loss, thermal loss, and chemical potential loss. Figure 9b clearly identifies the excessive loss of exergy on and below the feed stage, and suggests heat integration through a side condenser should be considered to reduce the excessive loss of exergy. The combined exergy and pinch analysis would be a rigorous and effective tool to optimize individual process or integrated processes.

Distillation column system optimization starts by identifying the regions with the largest exergy losses using the stage-exergy profiles of a converged simulation. Following this, column modification such as feed condition, feed stage location, and possible heat integration based on the more uniform distribution of exergy loss would be considered.^[79–82,98] The best modifications, which are friendly with the environment and compatible with the rest of operation should be chosen. Obviously, at the same time, entropy production rate minimization should be sought.^[89,92,93] For example, heat integration with the combined advantages of direct vapor recompression and diabatic operation at half of the normal column height may be one of the best modifications for close boiling mixture separation.^[5] Another diabatic option is the use of two heat exchangers integrated in the column replacing the reboiler and condenser where large exergy losses occur frequently.^[91] Also, changing the feed stage or splitting the feed can reduce exergy loss in a column section,^[30,78,98] when the excessive exergy loss due to mixing at the feed stage is identified, the design engineer may use the prefractionator to reduce the losses.

Case Study: 2. Single- and Two-Stage Crude Oil Distillation

Al Muslim et al.^[22] performed the exergy analysis of single- and two-stage crude oil distillation. The single-stage system consists of a crude heating furnace and a 27-tray atmospheric distillation column. The feed is introduced in tray 23. The two-stage system consists of a furnace, a 13-tray atmospheric distillation

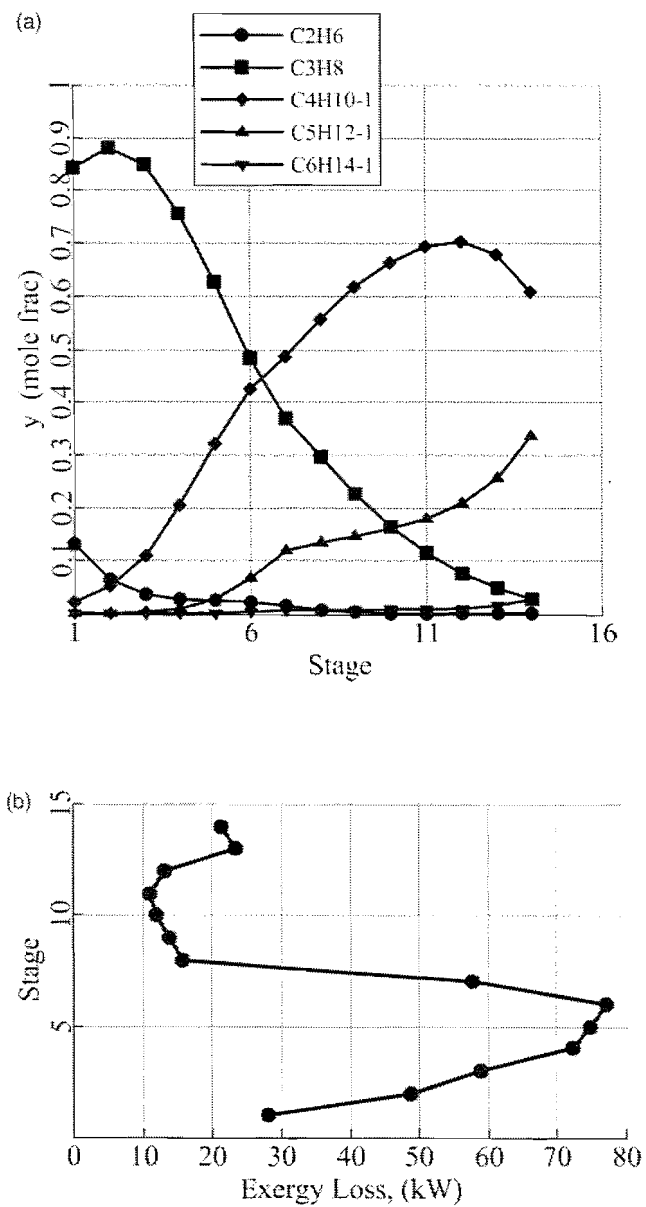


Figure 9. (a) Vapor phase composition profiles obtained from the simulations with the Aspen Plus Radfrac block using the Peng-Robinson equation of state. The column configuration is given in Table 2. (b) Stage exergy loss profiles obtained from the Aspen Plus thermal analysis tool.

Table 3. Exergy analysis for single-stage and two-stage crude oil distillation systems.^[22]

System	Exergy input (MW)	Exergy output (MW)	Overall exergy loss (MW)	Overall exergy efficiency (%)	Column exergy losses (MW)
Single-stage	498.8	69.8	429.0	14.0	137.2
Two-stage	352.0	110.9	241.1	31.5	121.6
% Difference	29.4	58.8	43.8	125	11.4

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column, another furnace to heat the bottom product of the first unit, and a second distillation column with 14 trays. The feed is introduced in tray 12. Table 3 compares the exergy analysis of the systems, and shows considerable reduction in exergy losses. The exergy efficiency is^[22]

$$\eta_x = \frac{\sum_i (X_{out})_i}{\sum_i (X_{in})_i} \quad (28)$$

Case Study: 3. Refinery Operation Optimization by Exergy Analysis

Rivero^[56] reported exergy analysis for an existing refinery operation using the general definition of exergy from Eq. (14). Table 4 shows the considerable economical gains due to the reduction in exergy losses after the optimization studies.

EQUIPARTITION PRINCIPLE

The rate of entropy production described by the linear nonequilibrium thermodynamics approach gives a detailed mathematical formulation of the dissipated power (work) in a system at local thermodynamic equilibrium.^[2,71,94,95] Nonequilibrium molecular dynamics simulations show that the assumption of local equilibrium in a column system is acceptable.^[70] For steady state linear flux-force relations, constant transport coefficients, and local equilibrium, separation systems with uniform driving forces in space and in time will dissipate less of the available energy, and, hence, are thermodynamically optimum.^[36] For example, for a given flux, a column with uniform driving forces is smaller in size, alternatively, it requires less contact time for a given size, and thus a

Table 4. Exergy analysis and loss reduction in a modified refinery.^[56]

Unit	Exergy loss before optimization (%)	Exergy loss after optimization (%)	Proposal investments (\$1000)	Payback time (Months)	NPV ^b 10 years of investments
Combined distillation unit	20.4	17.2	2,822.3	17	7.37
Naphtha HDS unit	3.2	2.7	1,101.2	69	1.80
Naphtha reforming unit	10.9	7.9	1,204.8	5	3.98
HDS ^a unit	3.4	2.8	834.0	53	2.04
Catalytic cracking unit	19.5	12.7	7,822.0	3	47.4
Visbreaking unit	2.9	3.7	1,000.0	3	33.27
Utilities plant	39.8	36.7	660.6	4	32.19
Total	100.0	84.3	15,245.0	5	24.48

^aHDS: Hydrodesulphurization.

^bNPV: Net present value (only operating cost is taken into account).

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higher throughput. One way of achieving uniform driving forces in a distillation system may be the heat integration.^[61,62]

The rate of volumetric entropy production due to heat and mass transfer Φ for a binary mixture is expressed by^[70,71,94]

$$\Phi = -J_q \frac{\nabla T}{T^2} - \frac{1}{T} \sum_i J_i \nabla \mu_{i,T} = \sum_i J_i X_i \quad (29)$$

where the J_q is the heat flux, J_i is the mass flux for component i , and X is the thermodynamic force. When the pressure is constant, we have $\nabla \mu_{i,T} = \nabla \mu_i^c$, which is the concentration dependent part of the chemical potential gradient. The linear phenomenological equations that follow from Eq. (29) are

$$J_q = -L_{qq} \frac{\nabla T}{T^2} - L_{ql} y_l \frac{\nabla \mu_l}{T} \quad (30)$$

$$J_d = -L_{lq} \frac{\nabla T}{T^2} - L_{ll} y_l \frac{\nabla \mu_l}{T} \quad (31)$$

where J_d (in $\text{m}^3 \text{m}^{-2} \text{h}^{-1}$) is the relative mass flux between heavy and light components across the interface ($J_d = J_l/y_l - J_h/y_h$), J_h and J_l are the mass fluxes of heavy and light components, respectively, y_h and y_l are the compositions of heavy and light components, respectively, and the constant parameters, L_{ji} , are the local phenomenological transport coefficient, which can be determined from experiments. For isothermal conditions, the phenomenological coefficients for mass transfer are

$$L_{ll} = - \left(\frac{J_d T}{y_l \nabla \mu_l} \right)_{\Delta T=0} \quad (32)$$

Using the chemical force for the mass transfer

$$y_l \frac{\nabla \mu_l}{T} = \frac{J_d}{L_{ll}} - \frac{L_{lq}}{L_{ll}} \frac{\nabla T}{T^2} \quad (33)$$

the heat flow becomes

$$J_q = - \left(L_{qq} - L_{ql} \frac{L_{lq}}{L_{ll}} \right) \frac{\nabla T}{T^2} + \frac{L_{lq}}{L_{ll}} J_d \quad (34)$$

On the other hand, Fourier's law of heat conduction without mass transfer is

$$(J_q)_{J_d=0} = -k \nabla T \quad (35)$$

Therefore, the thermal conductivity, k , is defined in terms of the phenomenological coefficients

$$k = \left(L_{qq} - L_{ql} \frac{L_{lq}}{L_{ll}} \right) \frac{1}{T^2} \quad (36)$$

Diffusion of the light component is defined by Fick's law for the gas phase

$$J_l = -D \frac{\Delta c_l}{\Delta z} \quad (37)$$

where D is the diffusion coefficient of the light component and Δc_l is the concentration difference of light component across the distance Δz . The concentration difference in the gas phase in terms of the total pressure P_T is

$$\Delta c_{l,g} = \frac{P_T}{RT} (y_l - y_l^*) \quad (38)$$

where the mole fraction y_l^* is the inlet composition in the liquid. By introducing Eq. (36) into Eq. (34), and with the assumptions of constant driving forces, the average phenomenological coefficient of mass transfer \bar{L}_{ll} is obtained as^[70]

$$\bar{L}_{ll} = \frac{T}{y_l \Delta \mu_l} \left[D \Delta c_l \left(\frac{1}{y_l} + \frac{1}{y_h} \frac{\Delta H_l}{\Delta H_h} \right) \right] = \frac{\int_0^{\Delta z} L_{ll} dz}{(\Delta z)^2} \quad (39)$$

where ΔH_h and ΔH_l are the heat of vaporizations for the heavy and light components, respectively. The phenomenological coefficients may vary considerably from enriching section to stripping section, and this should be taken into account in the optimization criterion. In a recent study, the rate of entropy production was calculated at every stage with the coupling between the heat and the mass transport, and verified with experimental data of ethanol-water distillation.^[92,96]

The thermal efficiency based on the second law of thermodynamics may be defined as in Eq. (12)

$$\eta = \frac{W_{\min}}{W_{\min} + \int_0^V \Phi dV} \quad (40)$$

A maximum in the second law efficiency may be obtained by minimizing the entropy production rate with respect to one of the forces. For example, assuming that the contribution due to the difference in chemical potential is dominant, the change of the entropy production with respect to the chemical force can be studied.

From Eqs. (29)–(31) the amount of separation $J_{d,i}$ and the corresponding rate of entropy generation at stage i Φ_i are obtained as

$$\int_V J_{d,i} dA dz = \int_V L_{ll,i} X_i dA dz \quad (41)$$

$$\Phi_i = \int_V L_{ll,i} X_i^2 dA dz \quad (42)$$

where X_i shows the chemical force at stage i . As the level of separation is fixed, the boundary conditions for the forces are specified, and an increase in the force in one stage must lead to a reduction in another stage. It is desired to have an increase in the flow for a given entropy production rate, and a reduction in the entropy production rate for a specified separation; the yield Y is defined as the benefit-cost ratio in an economic sense, and given by

$$Y = \frac{J_{d,i}}{\Phi_i} = \frac{L_{ll,i} X_i}{L_{ll,i} X_i^2} = \frac{1}{X_i} \quad (43)$$

When the derivative of Y with respect to X_i is higher in one stage than in another, increasing or reducing the driving force adjusts the rate of entropy production. We can maximize the separation output, by redistributing of forces between the stages. The distribution is obtained with the differentiation $d(1/X_1)/dX_1 = d(1/X_2)/dX_2$, which leads to $X_1 = X_2$. The equality of forces is independent of the individual values of the phenomenological coefficients. The reversible operation is a limit case, and is achieved when X_1 and X_2 approach zero and Y increases toward infinity. Therefore, the

practical improvement of the second-law efficiency is to apply the relationship between dX_1 and dX_2 . For example, the following relationship at constant J_d

$$dX_1 = -\frac{\bar{L}_{II,1}}{\bar{L}_{II,2}} dX_2 \quad (44)$$

relates the driving forces at two stages. By knowing L_{II} across the column, we can determine the possible locations for modifications. A uniform entropy production rate corresponds to either minimum energy costs for a required separation and area investment, or minimum investment for a specified energy cost, and leads to thermodynamically optimum design.^[70]

Stage exergy calculations are used to prepare exergy profiles throughout column. Such profiles firstly show the current level of utilization of available energy, and secondly the effects of operating conditions and design parameters on the efficiency of operation. Most of the researchers are focusing on how to use the exergy loss profiles, which are becoming straightforward and part of flowsheeting. For example, Ishida and Ohno^[61] and Ishida and Taprap^[62,63] prepared the exergy utilization diagram to show the transformed energy level, and unit height of the column, and, hence, help to identify the targets for reducing energy and exergy consumptions.^[97] Based on the exergy loss profiles, modifications on the feed stage location, feed condition, and the use of intermediate exchangers can be considered. For example, exergy loss due to the mixing at the feed stage can be identified and reduced using an external modification of the prefractionator.^[98] Beside that, the profiles recently were used to prove that a uniform distribution of driving forces leads to a higher thermodynamic efficiency;^[36,98] locating the heat exchangers in the regions where the largest deviations from isoforce exist, may lead to the uniform driving forces over the internal stages for a binary distillation system. The results of isoforce operation should be proportional to the variation in the primary phenomenological coefficient.^[99] An isoforce operation of a diabatic column is consistent with a minimum exergy loss in a section where large reflux ratios are avoided.^[100]

Assuming that a column is a reversible heat engine (Fig. 7), work available from the thermal energy is expressed by

$$W_{\text{heat}} = Q_R \left(1 - \frac{T_o}{T_R}\right) - Q_C \left(1 - \frac{T_o}{T_C}\right) \quad (45)$$

where T_o is the ambient temperature, and T_R and T_C are the temperatures for reboiler and condenser, respectively. The temperature corrections (Carnot efficiencies) describe the maximum fraction of theoretical work extracted from thermal energy at a particular ambient temperature.^[35,101,102] On the other

hand minimum separation work, W_s , required for a separation is the net change in availability

$$-W_s = \Delta A_s = A_{\text{prod}} - A_{\text{feed}} \quad (46)$$

The change of availability of separation is the difference between the work supplied by the heat and the total work required for separation W_{ts}

$$\Delta A_s = W_{\text{heat}} - W_{\text{ts}} \quad (47)$$

Energy use can be reduced by minimizing the pressure drop; lost work due to high-pressure drop (as high as 10 psi) is considerable at the condenser and reboiler systems, and is relatively less through the trays (0.1 psi or less). Change of pressure affects the distance from equilibrium, causes the large temperature difference, and, hence, utility costs between the condenser and reboiler of distillation column.

Feed tray location may also be adjusted to reduce the lost work. Commonly, the feed location is determined at the minimum utility loads and tray count or simply by taking into account light-key and heavy-key component compositions. The relative cost of the heating and cooling media will also influence the location of the feed stage. The basic trend of improving thermodynamic efficiency leads to taller and more slender columns.

Case Study: Distillation Systems with Isoforce Operation

Adiabatic columns are highly irreversible and often the irreversibility is not evenly distributed. The stage-exergy loss profiles indicate the distribution of stage irreversibility, and hence the distribution of driving forces in a column operation. Figure 9b shows clearly that the operation is far from isoforce operation, especially on and below the feed stage; and a heat integration modification through a side condenser should be considered. Nonequilibrium thermodynamic approach may be used to determine how to position the heat integration in the column.^[99] This will reduce the excessive loss of exergy and bring the distillation column relatively close to isoforce operation. Distillation columns operating with close to uniform thermodynamic forces are analyzed for separating n-pentane from n-heptane^[89,99] (Table 5), and ethanol from water (Table 6).^[100] Equation (31) shows that chemical separation force is $y_i \nabla \mu_i / T$, and should be uniform throughout the column. For the top and bottom parts of the column for ethanol-water separation, a conventional McCabe-Thiele diagram has small distances between the operating lines and equilibrium curve; in the top, azeotrope exist, and in the bottom part compositions are close to pure components. In the middle part of the McCabe-Thiele diagram an operating line may be plotted using $y_{i,n+1} = kx_{i,n}$

Table 5. Reboiler and condenser duties and entropy production change for the adiabatic, heat integrated and operating with isoforce and a near-optimum column for n-pentane and n-heptane.^[99]

Operation	Q_R MW	Q_C MW	Reduction in entropy production (%)
Adiabatic	2.37	0.704	—
Isoforce	1.89	0.732	13.56
Near optimum	1.90	0.797	13.33

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$\exp(-C/Rkx_{i,n})$, where C is a chosen constant driving force, k is Henry's laws' constant, and indices n is the stage number; using this middle operating line, isoforce lines in ethanol-water separation are plotted and used in the column analysis.^[100] This analysis leads to more than one isoforce operating line based on the chosen value of C and may be confusing. Table 5 indicates clearly that a thermodynamically optimum distillation column should operate with a uniform or close to uniform driving force in separation. This is in line with the operation in which exergy loss is distributed evenly within the column. However, in minimizing the exergy loss or the rate of entropy production, one should avoid operation with too small driving forces (pinch in separation) at any stage.

One has to note that the equipartition principle is mainly investigated for binary separations by distillation, and should be extended to multicomponent separations with nonideal mixtures and by accounting for the coupling between driving forces. However, the general principle is not restricted to binary systems only.^[36] For example, Zemp et al.^[98] used the exergy loss profile to determine the distribution of driving forces in a five-component distillation column. Still, one has to keep in mind that the treatment of multicomponent diffusion as opposed to binary diffusion is fundamentally different

Table 6. Comparison of the performance of a diabatic column with a isoforce column operation for separation of ethanol-water mixture.^[100]

Operation	Total exergy losses kJ/h	Distillate flow rate kg/h	Distillate composition (%)
Adiabatic	44.23	0.969	87.53
Isoforce	14.24	0.974	87.13
Diabatic	15.89	0.973	87.22

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and is essentially incompatible with the Fick law, which is not capable of accounting for coupling between diffusive fluxes of various species.^[2,32,71,94,95,103] Multicomponent diffusion is much more appropriately treated by means of the Stefan-Maxwell equations, which involve setting up equations relating the corresponding thermodynamic forces to mass fluxes of all the components.^[95,104,105]

THERMOECONOMICS

The US Department of Energy Web site, "Energy Savers for Industry Plant Managers and Engineers,"^[106] offers a wide variety of energy saving possibilities, such as an energy management action plan. Energy is conserved in all processes. However, the available part of energy that is exergy is not conserved. The process engineer should minimize the input cost of a process by reducing exergy loss due to thermodynamic imperfections. Within this context, thermodynamic analysis simultaneously considers the interrelations among the use of energy, economy, and ecology.^[56] Such considerations may have positive impact on sustainable development. For example, thermodynamic analysis of a solar desalination unit shows that thermoeconomic evaluation of the system is closely related to a complete economic analysis of the possible improvements leading to a less irreversible unit.^[107]

Optimizing a plant is complex, since the whole plant should be cost effective.^[108-110] Separation systems should be optimized considering both capital cost and operating (energy) cost.^[111] The heuristics of using a reflux ratio of 1.03–1.3 times the minimum reflux ratio is in line with both the capital cost and operating cost for binary distillation systems.^[111-119]

The concept of thermodynamics cost relates the thermodynamic limits of separation systems to finite rate processes^[120-122] and considers the environmental impact through the depletion of natural resources within the exergy loss concept.^[2,56] Still, economic analysis and thermodynamic analysis perceptions may not be in parallel. For example, it is estimated that a diabatic column has a lower exergy loss (39%)^[121] than does an adiabatic distillation; however, this may not lead to a gain in an economic sense, yet it is certainly a gain in the thermodynamics sense. That is why the thermodynamic analysis needs careful interpretations and applications of its results. Thermodynamic analysis is also capable of quantification of coupling in transport processes.^[2,32,71,94,122] Especially in diabatic columns, heat and mass transfer coupling may be considerable and should not be neglected.^[121,122] The results of thermodynamic analysis may be in line with those of economic analyses when the thermodynamic cost optimum not the maximum thermodynamic efficiency is considered with process specifications.^[123]

Although this review emphasizes distillation systems, the use of thermodynamic analysis is also becoming popular for other separation systems, like super critical extraction,^[124] desalination processes,^[125] hybrid vapor permeation-distillation,^[7] and cryogenic air separation.^[31,86] For example, energy requirement analysis of common cycles used in supercritical extraction has utilized exergy losses, and an optimum extraction pressure, which produces a minimum in exergy loss for specified temperature and separation pressure.^[124] Thermodynamic analysis also has been used for the economics of desalination technologies by membranes and distillation^[125] five main desalination systems considered are: reverse osmosis, electrodialysis, vapor compression, boiling evaporation, and flash evaporation.

Exergoeconomics is highly popular for analysis and optimization in thermal energy systems, yet it is far from a breakthrough methodology for separation processes mainly due to their characteristics and complexity. The objective of exergoeconomics should be chosen with care; for example, the optimization should target both capacity expansion and exergy loss in separation systems.^[126,127]

The minimization of entropy production is not always an economic criterion; sometimes, existing separation equipment may be modified for an even distribution of forces or even distribution of entropy production. For example, to determine an economic optimum for an extraction we assume that the operating costs are a linear function of the entropy production, and the investment costs are linear function of the space and time of the process. Then the total cost C_T is expressed as^[36]

$$C_T = a\Phi + b + c\tau Vt = \int_t \int_V (aLX^2 + c\tau) dV dt + b \quad (48)$$

where τ is the amortization rate and a , b , and c are the constants related to the costs, V is the volume or size, t is the time, L is the transport coefficient, X is the driving force, and Φ is the rate of entropy production. Integral in Eq. (48) is subject to the constraint of a specified flux given by

$$J = \int \int LX dV dt \quad (49)$$

The variational technique can be used to minimize the total cost, and the Euler equation for the variable X is given by

$$\frac{\partial}{\partial X} (aLX^2 + c\tau + \lambda LX) = 0 \quad (50)$$

where λ is a Lagrange multiplier. Eq. (50) yields

$$2aLX + \lambda L = 0 \quad (51)$$

$$X = -\frac{\lambda}{2a} = \text{constant} \quad (52)$$

Equation (52) shows that the distribution of the thermodynamic force, X , is uniform when the total cost subject to the specified flux, J , is minimum.

Consider a steady-state operation in which the forces are uniformly distributed; the investment cost, C_i , of a transfer unit is assumed to be linearly related to the size, V , and the operating costs, C_o , are linearly related to the exergy consumption

$$C_v = C_i - C_{if} = AV \quad (53)$$

$$C_o = C_{of} + B\Delta X \quad (54)$$

where C_{if} is a fixed investment cost and C_{of} is a fixed operating cost, and A and B are the cost parameters. Exergy loss ΔX_c is expressed as

$$\Delta X_c = \Delta X_m + T_o \Phi_{av} \quad (55)$$

Here T_o is a reference temperature (dead state), and ΔX_m is a thermodynamic minimum value. The total flow $J = LVX_{av}$, can be written by using Eq. (53)

$$J = \frac{LX_{av}C_v}{A} \quad (56)$$

where C_v is the variable part of the investment cost. Eliminating the constant (average) force X_{av} between Eq. (55) and the total entropy production Φ_{av} , = $J\Delta X_{av}$, we obtain^[36]

$$\Phi_{av} = \frac{AJ^2}{LC_v} \quad (57)$$

Substituting Eq. (57) into Eq. (53) and the latter into Eq. (54), a relationship between the operating and investment costs is obtained

$$C_o = \frac{ABT_oJ^2}{LC_v} + C_{of} + B\Delta X_m \quad (58)$$

The optimal size is obtained by minimizing the total cost of operating and investments costs, which is linearly amortized with the amortization

rate τ . $C_T(C_i) = \tau C_i + C_o$. The minimum of C_T is obtained as $dC_T/dC_i = 0$, and we have

$$\frac{B\Phi_{av}}{(C_v)_{opt}} = \frac{B\Phi_{av}}{AV_{opt}} = \frac{\tau}{T_o} \quad (59)$$

According to Eq. (59), the quantities $BT_o\Phi_{av}$, which are related to irreversible dissipation and τV_{opt} , should be equal in any transfer unit. Generally, operating costs are linearly related to dissipation, while investment costs are linearly related to the size of equipment. The optimum size distribution of the transfer units is obtained when amortization cost is equal to the cost of lost energy due to irreversibility. The cost parameters A and B may be different from one transfer unit to another; when $A = B$, then Φ_{av}/V_{opt} is a constant, and the optimal size distribution reduces to equipartition of the local rate of entropy production.^[36] The optimal size of a transfer unit can be obtained from Eq. (53)

$$(C_v)_{opt} = C_{i,opt} - C_{if} = J \left(\frac{ABT_o}{L\tau} \right)^{1/2} \quad (60)$$

$$V_{opt} = J \left(\frac{BT_o}{AL\tau} \right)^{1/2} \quad (61)$$

By distributing the entropy production as evenly as possible along the space and time line, an economical separation process would be designed and operated.^[36] Later it was argued that the equipartition of a driving force rather than equipartition of entropy production rates should be adapted in a binary distillation.^[100] Dissipation equations show that both the driving forces and fluxes play the same role in quantifying the rate of entropy production.^[2,94] Therefore, equipartition of entropy production principle may point out that the uniform distribution of driving forces is identical with the uniform distribution of fluxes.

One major trend that appears is that of pinch analysis, exergy analysis, and equipartition principles being combined to analyze process and energy systems.^[100,126–128] This will enable the scientists to modify existing systems or design new systems with complete objectives and targets including the environmental concerns and the natural resources.

Thermoeconomics is not a new concept; however, it has been formulated in a more systematic way, mainly during the last 20 years. From an exergetic point of view, cost analysis is performed by using (a) cost accounting methods that use average costs as a basis for a rational price assessment and (b) optimization methods that employ marginal costs in order to minimize the costs of the products of a system or a component.^[129–132] To account for the environmental impact in a more systematic way, a resource-based quantifier, called

“extended exergy,” is employed to calculate the resource-based value of a commodity.^[130] Consider a separation process with outputs containing hot streams with various chemicals having the conditions considerably different from those environmental temperatures and concentrations. To achieve a zero environmental impact, these streams must be brought to both thermal and chemical equilibrium with the surroundings: thus, the real (exergetic) cost of the zero-impact would correspond to the extended exergy ideally required to bring the conditions of effluents to equilibrium conditions with the surroundings.^[129,130] If an acceptable level of pollutant or the “tolerable environmental impact limit” for a certain pollutant would be specified, then the environmental cost may be quantified. Despite all the systematic efforts on formulating the thermoeconomics, its use in design and economic evaluations is still limited.

CONCLUSIONS

Energy saving in separation systems, particularly in distillation systems, is a research field that has attracted considerable innovative approaches. A distillation system is an essential separation process yet it is inefficient in using thermal energy, and may operate with adverse environmental impact as it discharges a large amount of thermal energy into the environment. Innovative research incorporating the principles of thermodynamics for energy efficient distillation systems is in an advanced stage through pinch analysis, exergy analysis, and equipartition principle. Thermodynamic analysis simultaneously considers the critical interrelations among energy cost, thermodynamic cost, and ecological cost. The task of a process engineer is to decide the target cost or the costs to be optimized using the thermodynamic analysis. The thermodynamic analysis is still not widely used. However, with the current level of research efforts, engineers and scientists should use the analysis in design, retrofits, economic analysis, and environmental problems.

NOMENCLATURE

<i>a,b,c</i>	cost constant in Eq. (48)
<i>A</i>	availability (J mol^{-1}), area (m^{-2})
<i>B</i>	Bottom product (kmol h^{-1})
<i>A, B</i>	cost parameters
<i>C</i>	concentration (mol L^{-1}), cost
<i>C_{if}</i>	fixed investment
<i>D</i>	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), Distillate, (kmol h^{-1})

g	gravitational acceleration
H	enthalpy
J_q	heat flux
J_d	separation flux ($\text{mol m}^{-2} \text{s}^{-1}$)
J_i	mass flux for component i ($\text{mol m}^{-2} \text{s}^{-1}$)
k	thermal conductivity ($\text{J m}^{-1} \text{s}^{-1} \text{K}$)
L_{ij}	phenomenological coefficient
LW	lost work (J mol^{-1})
n	molar mass (mol)
P	pressure (kPa)
Q	heat flux ($\text{J mol}^{-1} \text{m}^{-2}$)
Q_C	condenser duty (kW)
Q_R	reboiler duty (kW)
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
RR	Reflux ratio
S	entropy ($\text{J mol}^{-1} \text{K}^{-1}$)
t	time (s)
T	temperature (K)
u	average velocity (m s^{-1})
U	internal energy (J)
z	elevation, gas film thickness (m)
x	liquid mole fraction, distance
X	thermodynamic driving force
y	mol fraction
V	volume (m^3)
Y	yield
W	work (J)

Greek Symbols

η	efficiency
λ	Lagrange multiplier
μ	chemical potential (J mol^{-1})
τ	amortization rate
Φ	entropy production rate ($\text{J K}^{-1} \text{s}^{-1}$)

Subscripts

a	acceptor
c, C	cooling, condenser
cw	cooling water

d	donor
evap	evaporation
fs	flow stream
G	gas
h	heating, heavy
l	light
L	liquid
m	mixing
min	minimization
max	maximization
o	environmental
prod	production
R	reboiler
s	separation
sys	system
t	total

REFERENCES

1. Humphrey, J.L.; Siebert, A.F. Separation technologies: An opportunity for energy savings. *Chem. Eng. Prog.* **1992** (March), 92.
2. Demirel, Y. *Nonequilibrium Thermodynamics Transport and Rate Processes in Physical and Biological Processes*; Elsevier: Amsterdam, 2002.
3. Freswater, D.C.; Ziogou, E. Reducing energy requirements in unit operations. *Chem. Thermal Eng.* **1976**, *11*, 215.
4. Koehler, J.; Aguirre, P.; Blass, E. Evolutionary thermodynamic synthesis of zeotropic distillation sequences. *Gas Sep. Purif.* **1992**, *6*, 153.
5. Seider, W.D.; Seader, J.D.; Lewin, D.R. *Product & Process Design Principles*, 2nd Edn.; Wiley: New York, 2004.
6. Porter, K.E.; Momoh, S.O. Finding the optimum sequence of distillation columns—an equation to replace the rules of thumb' (heuristics). *Chem. Eng.* **1991**, *46*, 97.
7. Fahmy, A.; Mewes, D.; Ebert, K. Design methodology for the optimization of membrane separation for hybrid vapor permeation-distillation processes. *Sep. Sci. Technol.* **2001**, *36*, 3287.
8. Liu, X.G.; Qian, J.X. Modeling, control, and optimization of ideal internally coupled distillation columns. *Chem. Eng. Technol.* **2000**, *23*, 235.
9. Jones, V.E.; Vais, A.M.; Wilson, J.A. Getting the maximum benefit from a side-reboiler. *Chem. Eng. Comm.* **1999**, *171*, 195.

10. Christodoulou, P.A. Energy economy optimization in separation processes—Optimizing the separation of sucrose/water and non-sugars. *Int. Sugar J.* **1996**, *98*, 419.
11. Pradubsripetch, D.; Naka, Y.; Fan, Z. Analysis of heat demand and supply in multicomponent distillation systems. *J. Chem. Eng. Japan* **1994**, *27*, 188.
12. Fraga, E.S.; Zlinkas, A. Evaluation of hybrid optimization method for the optimal design of heat integrated distillation sequences. *Adv. Eng. Software* **2003**, *34*, 73.
13. Gadalla, M.; Jobson, M.; Smith, R. Increase capacity and decrease energy in existing refinery distillation columns. *Chem. Eng. Process* **2003** (April), 44.
14. Ito, A.; Asano, K. Thermal effects in non-adiabatic binary distillation effects of partial condensation of mixed vapors on the rates of heat and mass transfer and prediction of H.T.U. *Chem. Eng. Sci.* **1982**, *37*, 1007.
15. Budiman, A.; Ishida, M. Optimal side heating and cooling in a distillation column. *Energy* **1998**, *23*, 365.
16. Harbert, W.D. Preflash saves energy in crude units. *Hydrocarbon Proc.* **1978**, *57*, 23.
17. Rivero, R.; Anaya, A. Exergy analysis of a distillation tower for crude oil fractionation, and computer aided energy systems analysis, Proc. of Winter Annual Meeting of ASME 1, 25 and 55, Dallas, TX, 1990.
18. Frazer, A.C.; Sloley, A.W. Consider modeling tools to revamp existing process units. *Hydrocarbon Proc.* **2000**, *79*, 57.
19. Dhole, V.; Buckingham, P. Refinery column integration for debottlenecking and energy saving, ESCAPE IV Conf, Dublin Ireland IChemE, Rugby, UK, 1994.
20. Gadalla, M. Retrofit design of heat integrated crude oil distillation systems. UMIST: Manchester, UK, 2003; Ph.D. thesis.
21. Bagajewicz, M.J. Energy savings horizons for the retrofit of chemical processes. Application to crude fractionation units. *Comp. Chem. Eng.* **1998**, *23*, 1.
22. Al-Muslim, H.; Dincer, I.; Zubair, S.M. Exergy analysis of single-and two-stage crude oil distillation units. *J. Energy Resource. Tech.* **2003**, *125*, 199.
23. Annakou, O.; Mizsey, P. Rigorous investigation of heat pump assisted distillation. *Heat Recov. Sys. & CHP.* **1995**, *15*, 241.
24. Gopichand, S.; Omideyi, T.O.; Kasprzycki, J.; Devotta, S. The economics of heat pump assisted distillation systems—II. Analysis of ethanol-water mixtures. *J. Heat Recovery Sys.* **1984**, *4*, 271.

25. Fonyo, Z.; Benko, N. Enhancement of process integration by heat pumping. *Comp. Chem. Eng.* **1996**, *20*, S85.
26. Gopichand, S.; Omideyi, T.O.; Kasprzycki, J.; Devotta, S. The economics of heat pump assisted distillation systems—I. A design and economic model. *J. Heat Recover, Sys.* **1984**, *4*, 187.
27. Kauchali, S.; McGregor, C.; Hildebrandt, D. The attainable region for simple binary distillation. The annual AIChE meeting, Dallas, TX, Oct. 31–Nov. 5, 1999.
28. Kauchali, S.; McGregor, C.; Hildebrandt, D. Binary distillation re-visited using the attainable region theory. *Comp. Chem. Eng.* **2000**, *24*, 231.
29. Kohler, J.; Kuen, T.; Blass, E. Minimum energy demand for distillations with distributed components and side-product withdrawals. *Chem. Eng. Sci.* **1994**, *49*, 3325.
30. Soave, G.; Feliu, J.A. Saving energy in distillation towers by feed splitting. *Appl. Thermal Eng.* **2002**, *22*, 889.
31. Cornelissen, R.L.; Hirs, G.G. Exergy analysis of cryogenic air separation. *Energy Convers. Mgmt.* **1998**, 1821.
32. Demirel, Y.; Sandler, S.I. Irreversible thermodynamics in engineering and science. *J. Phys. Chem. B* **2004**, *108*, 31.
33. Moran, M.J.; Shapiro, H.N. *Fundamentals of Engineering Thermodynamics*, 4th Edn.; Wiley: New York, 2000.
34. *Assessment of Potential Energy Savings in Fluid Separation Technologies: Technology Review and Recommended Research Areas*; U.S. Dept. of Energy Office of Industrial Programs: Washington, DC. Document No. DOE/ID [24763-1] (Dec. 1984).
35. Ognisty, T.P. Analyze distillation columns with thermodynamics. *Chem. Eng. Prog.* **1995** (February), 40.
36. Tondeur, D.; Kvaalen, E. Equipartition of entropy production. An optimality criterion for transfer and separation processes. *Ind. Eng. Chem. Res.* **1987**, *26*, 50.
37. Sauar, E.; Rivero, R.; Kjelstrup, S.; Lien, K.M. Diabatic column optimization—compared to isoforce columns. *Energy Convers. Mgmt.* **1997**, *38*, 1777.
38. Linnhoff, B.; Flower, J.R. Synthesis of heat exchanger networks I. Systematic generation of energy optimal networks. *AIChE J.* **1978a**, *24*, 633.
39. Linnhoff, B.; Flower, J.R. Synthesis of heat exchanger networks II. Evolutionary generation of networks with various criteria of optimality. *AIChE J.* **1978b**, *24*, 642.
40. Hohmann, E.C. Optimum networks for heat exchange. Univ. Southern California: Los Angeles, 1971; Ph.D. dissertation.
41. Serna, M.; Jimenez, A. An area-targeting algorithm for the synthesis of heat exchanger networks. *Chem. Eng. Sci.* **2004**, *59*, 2517.

42. Spank, B. The Chemical Engineer's Resource page. <http://www.cheresourcess.com/pinchtech2.shtml>, 2004.
43. The Environmental Technology. http://www.envirotechnet.com/pinchtechnology.com/pinch_home.htm, 2004.
44. Al-Kawari, M.A. Pinch technology: an efficient tool for chemical plant energy and capital-cost saving. *Appl. Energy* **2000**, *65*, 45.
45. Dhole, V.R.; Linnhoff, B. Overall design of low temperature processes. *Comp. Chem. Eng.* **1994**, *13*, S105.
46. Dhole, V.R.; Linnhoff, B. Distillation column targets. *Comp. Chem. Eng.* **1993**, *17*, 549.
47. Ficarella, A.; Laforgia, D. Energy conservation in alcohol distillery with the application of pinch technology. *Energy Convers. Mgmt.* **1999**, *40*, 1495.
48. Briones, V.; Perez, A.L.; Chavez, L.M.; Mancilla, R.; Garfias, M.; Del Rosal, R.; Ramirez, N. Pinch analysis used in retrofit design of distillation units. *Oil & Gas J.* **1999**, *97*, 41.
49. Smith, R. State of the art in process integration. *Appl. Thermal Eng.* **2000**, *20*, 1337.
50. Bagajewicz, M.J.; Pham, R.; Manousiouthakis, V. On the state space approach to mass/heat exchanger network design. *Chem. Eng. Sci.* **1998**, *53*, 2595.
51. Bagajewicz, M.J.; Manousiouthakis, V. Mass heat-exchange network representation of distillation networks. *AIChE J.* **1992**, *38*, 1769.
52. Wang, Y.; Du, J.; Wu, J.; He, G.; Kuang, G.; Fan, X.; Yao, P.; Lu, S.; Li, P.; Tao, J.; Wan, Y.; Kuang, Z.; Tian, Y. Application of total process energy-integration in retrofitting an ammonia plant. *Appl. Energy* **2003**, *76*, 467.
53. Lavric, V.; Bactens, D.; Plesu, V.; De Ruyck, J. Entropy generation reduction through chemical pinch analysis. *Applied Thermal Eng.* **2003**, *23*, 1837.
54. Matijasevia, L.; Othmaeia, H. Energy recovery by pinch technology. *Appl. Thermal Eng.* **2002**, *22*, 477.
55. Doldersum, A. Exergy analysis proves viability of process modifications. *Energy. Convers. Mgmt.* **1998**, *39*, 1781.
56. Rivero, R. Application of the exergy concept in the petroleum refining and petrochemical industry. *Energy Convers. Mgmt.* **2002**, *43*, 1199.
57. Petlyuk, F.B.; Platonov, V.M.; Slavinskii, D.M. Thermodynamically optimum method for separating multicomponent mixtures. *Int. Chem. Eng.* **1965**, *12*, 555.
58. Fonyo, Z. Thermodynamic analysis of rectification: I. Reversible model of rectification. *Chem. Eng.* **1974**, *14*, 18.

59. Petlyuk, F.B. Thermodynamically reversible fractionation process of multicomponent azeotropic mixtures. *Theor. Found. Chem. Eng.* **1978**, *12*, 270.
60. Bandyopadhyay, S. Effect of feed on optimal thermodynamic performance of a distillation column. *Chem. Eng. J.* **2002**, *88*, 175.
61. Ishida, M.; Ohno, T. Application of energy-direction factor diagram for exergy analysis of distillation columns. *J Chem. Eng. Japan* **1983**, *16*, 281.
62. Ishida, M.; Taprap, R. Application of energy-utilization diagram for graphic exergy analysis of multicomponent distillation column. *J. Chem. Eng. Japan* **1992**, *25*, 396.
63. Ishida, M.; Taprap, R. Introduction of individual energy level for exergy analysis of process systems with multiple components. *J. Chem. Eng. Japan* **1993**, *26*, 437.
64. Taprap, R.; Ishida, M. Graphic exergy analysis of processes in distillation column by energy-utilization diagrams. *AIChE J.* **1996**, *42*, 1623.
65. Hinderink, A.P.; Kerkhof, F.P.J.M.; Lie, A.B.K.; De Swaan Aron, J.D.; Van der Koo, H.J. Exergy analysis with a flowsheeting simulator—I. Theory: calculating exergies of material streams. *Chem. Eng. Sci.* **1996**, *51*, 4693.
66. Hinderink, A.P.; Kerkhof, F.P.J.M.; Lie, A.B.K.; De Swaan Aron, J.D.; Van der Koo, H.J. Exergy analysis with a flowsheeting simulator—II. Application; synthesis gas production from natural gas. *Chem. Eng. Sci.* **1996**, *51*, 4701.
67. Tsirlin, A.M.; Kazakov, V.A.; Berry, S. Finite-time thermodynamics: Limiting performance of rectification and minimal entropy production in mass transfer. *J. Phys. Chem.* **1998**, *98*, 3330.
68. Ray, S.; Sengupta, S.P. Irreversibility analysis of a sieve tray in a distillation column. *Int. J. Heat Mass Transfer* **1996**, *39*, 1535.
69. Ray, S.; Panja, A.K.; Sengupta, S.P. Irreversibility analysis of a separation system using sieve tray distillation column. *Chem. Eng. Sci.* **1994**, *49*, 1472.
70. Ratkje, S.K.; Sauar, E.; Hansen, E.M.; Lien, K.M. Analysis of entropy production rates for design of distillation columns. *Ind. Eng. Chem. Res.* **1995**, *34*, 3001.
71. Demirel, Y.; Sandler, S.I. Linear nonequilibrium thermodynamics theory for coupled heat and mass transport. *Int. J. Heat Mass Transfer* **2001**, *44*, 2439.
72. Rosen, M.A.; Barry, G.F. The enhancement of the SALT-simulation and analysis code for first and second law analysis. In *Thermodynamic Analysis and Improvement of Energy Systems (TAIES '89)*, Proceedings

- by the International Symposium, Beijing, (China); Ruixian, C., Moran, M.J., Eds.; Int. Academic Publishers, Pergamon Press: Oxford, 1989, 472–480.
73. Rosen, M.A.; Scott, D.S. The enhancement of a process simulator for complete energy-exergy analysis. In *Analysis of Energy Systems—Design and Operation*; Gaggioli, R.A., Ed.; AES-1, ASME: New York, 1985, 71–80.
 74. Yang, Y.; Yang, J.; Zhu, X.; Ling, W. Enhancement and application of a flowsheeting simulator for second law analysis, ECOS '92, International Symposium on Efficiency, Cost, Optimization and Simulation, Zaragoza, (Spain), ASME: New York, 1992; 85–91.
 75. Lie, A.B.K.; Eigeman, P.M. ExerCom: calculating exergies in Aspen Plus (PC-version) user manual, Stork Comprino report 61285-0037-303-01. 1994.
 76. Maia, M.L.O.; Zemp, R.J. Thermodynamic analysis of multicomponent distillation column: Identifying optimal feed conditions. *Brazilian J. Chem. Eng.* **2000**, *17*, 751.
 77. Yong, P.S.; Moon, H.M.; Yi, S.C. Exergy analysis of cryogenic air separation process for generating nitrogen. *J. Ind. Eng. Chem.* **2002**, *8*, 499.
 78. Fonyo, Z.; Rev, E.; Szitkai, Z.; Emtir, M.; Mizsey, P. Energy savings of integrated and coupled distillation systems. *Comput. Chem. Eng.* **1999**, *23*, 241.
 79. Bjorn, I.N.; Gren, U.; Svenson, F. Simulation and experimental study of intermediate heat exchange in a sieve tray distillation column. *Comp. Chem. Eng.*, **2002**, *26*, 499.
 80. Andersen, T.R.; Siragusa, G.; Andresen, B.; Salamon, P.; Joergensen, S.B. Energy efficient distillation by optimal distribution of heating and cooling requirements. *ESCAPE* **1999**, *10*, 709.
 81. Lynd, L.R.; Grethlein, H.E. Distillation with intermediate heat pumps and optimal sidestream return. *AIChE J.* **1986**, *32*, 1347.
 82. Mullins, O.C.; Berry, R.S. Minimization of entropy production in distillation. *J. Phys. Chem.* **1984**, *88*, 723.
 83. Ratkje, S.; Kjelstrup, S.; De Swaan, A.J. Denbigh revisited: reducing lost work in chemical processes. *Chem. Eng. Sci.* **1995**, *50*, 151.
 84. Rivero, R.; Cachot, T.; Ramadane, A.; LeGoff, P.L. Diabatic or quasi reversible rectification. *Int. Chem. Eng.* **1994**, *43*, 240.
 85. Hangos, K.M.; Alonso, A.A.; Perkins, J.D.; Ydstie, B.E. Thermodynamic approach to the structural stability of process plants. *AIChE J.* **1999**, *45*, 802.
 86. Yong, P.S.; Moon, H.M.; Yi, S.C. Exergy and cryogenic air separation process for generating nitrogen. *J. Ind. Eng. Chem.* **2002**, *8*, 499.

87. Rivero, R. Exergy simulation and optimization of adiabatic and diabatic binary distillation. *Energy* **2001**, *26*, 561.
88. Nakaiwa, M.; Huang, C.; Owa, M.; Akiya, T.; Nakam, T.; Sato, M.; Takamatsu, T.; Yashitome, H. Potential energy savings in ideal heat-integrated distillation column. *Appl. Thermal Eng.* **1998**, *18*, 1077.
89. De Koeijer, G.M.; Kjelstrup, S.; Salamon, P.; Siragusa, G.; Schaller, M.; Hoffmann, K.H. Comparison of entropy production rate minimization methods for binary diabatic distillation. *Ind. & Eng. Chem. Res.* **2003**, *41*, 5826.
90. Chang, H.S.; Chuang, S.C. The intrinsic and extrinsic exergy losses of distillation columns. *J. Chinese Inst. Chem. Eng.* **2001**, *32*, 469.
91. LeGoff, P.; Cachot, T.; Rivero, R. Exergy analysis of distillation processes. *Chem. Eng. Technol.* **1996**, *19*, 478.
92. Liu, Q.L.; Li, P.; Zhang, Z.B. Energy-saving nonequilibrium thermodynamic analysis for distillation-mathematical model development. *Chem. J. Chinese Univ.* **2001**, *22*, 1209.
93. Kjelstrup, S.; Hafskjold, B. Nonequilibrium molecular dynamics simulation of steady-state heat and mass transport in distillation. *Ind. & Eng. Chem. Res.* **1996**, *35*, 4203.
94. De Groot, S.R.; Mazur, P. *Nonequilibrium Thermodynamics*; North Holland: Amsterdam, 1962.
95. Kuiken, G.D.C. *Thermodynamics of Irreversible Processes: Applications to Diffusion and Rheology*; Wiley: Chichester, 1994.
96. Kjelstrup, S.; de Koeijer, G.M. Transport equations for distillation of ethanol and water from the entropy production rate. *Chem. Eng. Sci.* **2003**, *58*, 1147.
97. Budiman, A.; Ishida, M. Three-dimensional graphical exergy analysis of a distillation column. *J. Chem. Eng. Japan* **1996**, *29*, 662.
98. Zemp, R.J.; deFaria, S.H.B.; Maria, MDLO. Driving force distribution and exergy loss in the thermodynamic analysis of distillation column. *Comp. Chem. Eng.* **1997**, *21*, S523.
99. De Koeijer, G.M.; Kjelstrup, S.; van der Kooi, H.J.; Groß, B.; Knocke, K.F.; Andersen, T.R. Positioning heat exchangers in binary tray distillation using isoforce operation. *Energy Convers. Mgmt.* **2002**, *43*, 1571.
100. Sauar, E.; Rivero, R.; Kjelstrup, S.; Lien, K.M. Diabatic column optimization compared to isoforce columns. *Energy Convers. Mgmt.* **1997**, *38*, 1777.
101. Naka, Y.; Terashita, M.; Hayashiguchi, S.; Takamatsu, T. An intermediate heating and cooling method for a distillation column. *J. Chem. Eng. Japan* **1980**, *13*, 123.

102. Rivero, R.; Cachot, T.; Ramadane, A.; Le Goff, P. Diabatic or quasi-reversible distillation: exergy analysis-industrial application, analysis of thermal and energy systems, Proc. of Int. Conf., Athens, Greece, 1991.
103. Kolev, S.D. Coupled diffusion of multiple ionic species in ion-exchange membranes with fixed ionic groups. *Sep. Sci. Technol.* **2003**, *38*, 237.
104. Demirel, Y. On the multicomponent diffusion calculations by means of the Maxwell-Stefan equations, *Chim. Acta Turc.* **1986**, *14*, 114.
105. Krishna, R.; Wesseling, J.A. The Maxwell-Stefan approach to mass transfer. *Chem. Eng. Sci.*, **1997**, *52*, 861.
106. The U.S. Department of Energy. Energy Savers for Industry Plant Managers and Engineers, www.energysavers.gov/industry 2003.
107. Arcia-Rodriguez, L.; Gomez-Camacho, C. Exergy analysis of the SOL-14 plant. *Desalination*, **2001**, *137*, 251.
108. Kokossis, A.C.; Floudas, C.A. Synthesis of isothermal reactor separator-recycle systems. *Chem. Eng. Sci.* **1991**, *46*, 1361.
109. Linhoff, B.; Dondorf, H.; Smith, R. Heat integration of distillation column into overall processes. *Chem. Eng. Sci.* **1983**, *38*, 1175.
110. Andrecovich, M.J.; Westerberg, A.W. A MILP formulation for heat-integrated distillation sequence synthesis. *AIChE J.* **1985**, *31*, 1461.
111. Jobson, M.; Hildebrandt, D.; Glasser, D. Variables indicating the cost of vapor-liquid equilibrium separation processes. *Chem. Eng. Sci.* **1996**, *51*, 4749.
112. Koehler, J.; Aguirre, P.; Biass, E. Minimum reflux calculations for non-ideal mixtures using the reversible distillation model. *Chem. Eng. Sci.* **1991**, *46*, 3007.
113. Shultz, M.A.; Stewart, D.G.; Harris, J.M.; Rosenblum, S.P.; Shakur, M.S.; O'Brien, D.C. reduce cost with dividing-wall columns. *Chem. Eng. Progress* **2002** (May), 64.
114. Rev, E.; Emtir, M.; Szitkai, Z.; Mizsey, P.; Fonyo, Z. Energy savings of integrated and coupled distillation systems. *Comp. Chem. Eng.* **2001**, *25*, 119.
115. Ricterova, V. Application of heat pump in rectification decreases energy consumption in the chemical industry. *Energy Convers. Mgmt.* **1991**, *32*, 519.
116. Olujic, Z.; Fakhri, F.; de Rijke, A.; de Graauw, J.; Jansen, P.J. Internal heat integration—the key to an energy-conserving distillation column. *J. Chem. Technol. Biotechnol.* **2003**, *78*, 241.
117. Finn, A.J. Rapid assessment of thermally coupled side columns. *Gas Sep. Purif.* **1996**, *10*, 169.

118. Schuller, M.; Hoffmann, K.H.; Siragusa, G.; Salamon, P.; Andresen, B. Numerically optimized performance of diabatic distillation columns. *Comp. Chem. Eng.* **2001**, *25*, 1537.
119. Nilsson, K.; Sunden, B. Optimizing a refinery using the pinch technology and the mind method. *Heat Recovery. Sys. & CHP.* **1994**, *14*, 211.
120. Kaibel, G.; Biass, E.; Kohler, J. Thermodynamics—Guideline for the development of distillation column arrangements. *Gas. Sep. Purif.* **1990**, *4*, 109.
121. De Kojer, G.; Rivero, R. Entropy production and exergy loss in experimental distillation columns. *Chem. Eng. Sci.* **2003**, *58*, 1587.
122. Demirel, Y.; Sandler, S.I. Effects of concentration and temperature on the coupled heat and mass transport in liquid mixtures. *Int. J. of Heat Mass Transfer* **2002**, *45*, 75.
123. Sieniutycz, S.; Shiner, J.S. Thermodynamics of irreversible-processes and its relation to chemical-Engineering—2nd law analysis and finite-time thermodynamics. *J. Non-Equilib. Thermodyn.* **1994**, *19*, 303.
124. Smith, R.L.; Inomata, H.; Kanno, M.; Arai, K. Exergy analysis of supercritical carbon dioxide extraction processes. *J. Supercrit. Fluids* **1999**, *15*, 145.
125. Spiegler, K.S.; El-Sayed, Y.M. The energetics of desalination processes. *Desalination* **2001**, *134*, 109.
126. Zhang, G.; Hua, B.; Chen, Q. Exergoeconomic methodology for analysis and optimization of process systems. *Comp. Chem. Eng.* **2000**, *24*, 613.
127. Chen, Q.L.; Yin, Q.H.; Hua, B. An exergoeconomic approach for retrofit of fractionating. *Energy* **2002**, *27*, 65.
128. Sorin, M.; Paris, J. Combined exergy and pinch approach to process analysis. *Comp. Chem Eng.* **1997**, *21*, S23.
129. Bejan, A.; Tsatsaronis, G.; Moran, M.J. *Thermal Design and Optimization*; Wiley: New York, 1996.
130. Sciubba, E. Cost analysis of energy conservation systems via a novel resource-based quantifier. *Energy* **2003**, *28*, 457.
131. Erlach, B.; Serra, L.; Valero, A. Structural theory as standard for thermo-economics. *Energy Convers. Mgmt.* **1999**, *40*, 1627.
132. Ayres, R.U. Eco-thermodynamics: economics and the second law. *Ecol. Economics* **1998**, *26*, 180.