Methodology for the Design and Evaluation of Distillation Systems: Exergy Analysis, Economic Features and GHG Emissions

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This work presents a process design methodology that evaluates the distillation systems based on exergetic, economic, and greenhouse gas (GHG) emission aspects. The aim of the methodology is to determine how these three features should be applied in process design to obtain information about the accuracy of the design alternatives. The methodology is tested and demonstrated on three different energy-integrated distillation systems: the direct sequence with backward heat-integration (DQB), fully thermally coupled distillation column (FTCDC), and sloppy distillation system with forward heat-integration (SQF). The average relative emission saving is the highest for the DQB scheme and this sequence shows the most flexible range of use. The case studies prove the accuracy of our evaluation methodology. On the other hand, it highlights and demonstrates that the exergy analysis can predict the results of the economic study and the environmental evaluation to make the decisions, associated with process design, much simpler. © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 1776–1786, 2010

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Introduction

The early stage of process design was practically based on engineering design and the alternatives were evaluated merely according to their economic features.[1] The methodology of process design requires, however, reconsideration and it should be completed with new steps. Nowadays, because of increasing energy prices and strict environmental regulations the investigation of the energy efficiency and the emissions of the process must take place simultaneously at the early stage of process design.

The demand for energy has been continuously increasing for years and operation units with large energy demand have become more difficult to be supplied. The energy efficiency of a system becomes an important criterion during retrofitting and design of industrial processes.

On the other hand, the emission regulations constrain engineers to consider the concept of environmentally consciousness in their work.

Even today, the most frequently studied energy consuming process in the chemical industry is the separation systems based on distillation. The large energy requirement of these processes can be reduced by using energy integration like heat integration, thermocoupling, or heat pumping. Energy integration is an important method for conserving energy in the case of distillation systems, demonstrated by different authors.[2–8] Annakou and Mizsey[2] have studied heat-integrated schemes and fully thermally coupled distillation columns (FTCDC) by rigorous modeling and compared them to conventional schemes. They have found that FTCDC can be competitive with the heat-integrated schemes only in those cases when the concentration of the middle

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component is high and the A/B split is harder than B/C split otherwise FTCDC is less economic than the heat-integrated scheme.

Regarding to the energy demand of the thermally coupled distillation columns Hernandez et al.[7] have studied the Petlyuk column and six alternative arrangements for ternary hydrocarbon mixture separation. They have found that the alternative distillation systems have very similar values of energy demands and thermodynamic efficiencies.

The large energy demand of the distillation urges to study the process and to identify the energy losses. Certainly the low thermodynamic efficiency of distillation is caused not by the separation process but mainly by the work necessary to introduce and remove the heat from the column.[9] To investigate the energy wastes a useful tool is the exergy analysis, which gives an overall view about the location and scale of energy losses in the process. Some published works in literature focus on development of exergy analysis methods and expressive parameters in order to quantify and represent the lost energy and the thermodynamic efficiency of the distillation columns.[10–14] Other research works similarly to this one, apply the basic equations of the second law of thermodynamics and calculate the thermodynamic efficiency for different distillation systems.[15,16]

Suphanit et al. use successfully the exergy loss profile combined with the real column *T-H* profile in order to locate the heat transfer across the wall of the dividing-wall distillation column. The exergy analysis can be applied also for the study of complex distillation plants to identify the process sections with the highest exergy losses and to locate process sections with exergy improvement potential.[16,17]

The use of energy efficient distillation is beneficial also from the point of view of GHG emission because it is limited in most of the countries. The CO_2 emission of distillation systems is investigated by Gadalla et al.[18,19] The authors quantify the CO_2 emission for a propylene-propane splitting process and propose a model for the estimation of CO_2. The model calculates the emissions flow rates from furnaces, boilers, and integrated gas turbines. According to the authors, the CO_2 emission can be decreased by 83%, using internally heat-integrated distillation column compared to conventional alternatives in the case of a state of art propylene-propane split. In our article, the CO_2 emission calculations are verified using the model proposed by Gadalla et al.[19]

These studies, however, do not make a complex investigation of the different energy consuming systems and their environmental effects, that is, how the results of the exergy analysis can be applied to evaluate economic and environmental features in advance making the process design step simpler. Therefore, the goal of this study is to elaborate and propose such an evaluation methodology of process design alternatives that helps to accomplish more energy efficient, economic, and environmental friendly processes. The proposed methodology is evaluated and demonstrated on energy-integrated distillation systems. It helps to decide among the different kinds of energy integration solution for ternary mixture separation.

The final aim is to classify the different process design alternatives to make the evaluation of the synthesis step simpler at the early stage of process design.

The Proposed Methodology

In the course of process design, there are several steps on different design layers of the process synthesis activity.[20] These general steps of a process design project are: conceptual design, detailed engineering design, project execution, start up and trial runs, and finally the production. In the conceptual design step, also known as early stage of the process design, complex evaluation can be carried out since in the last decades the process design became computer aided and does not require as much time and effort as in the past. There are also several attempts to make the process synthesis activity simpler so that the design engineer can find the best process alternative. In this early phase of design, the conception of elaboration methodology has a great importance. Our work proposes an evaluation methodology of distillation systems that consists of three levels and takes in account exergy, economic, and emission criteria in order to find the most adequate process structure.

These three levels of the methodology are the following:

(1) definition of the problem and selection of the competitive process alternatives,

(2) multicriteria evaluation of the process alternatives including exergy analysis, economic study, and GHG emission estimation,

(3) ranking of the process alternatives based on the summarized indicator and the choice of the most adequate one.

The proposed methodology is demonstrated on distillation systems as one of the highest energy utilizing system in the separation industry. The steps of the methodology are shown in Figure 1 and are described as follows.

(1) The first level of the methodology named as the problem definition includes the elaboration of process alternatives, the definition of system boundaries, and the selection of the input/output parameters.

The elaboration of the process alternatives in the case of the distillation processes consists of the preliminary shortcut design defining the number of trays, feed location according to the separation task. The set of the process alternatives increases with the consideration of the available energy integration, which can have different types and they can be used at different locations. This step also includes the selection of the competitive design alternatives from the wide range of solutions.

The second step of the methodology defines the system boundaries of the competitive alternatives. The well-defined process segments include the distillation columns and the process utilities in this work and they are subject to the comparative study.

The selection of identical input/output parameters makes possible the comparative study of the distillation design alternatives. The basic assumption is the fixation of the input and output data in order to study the process itself, thus the different distillation design alternatives can be compared between each other or to a reference process.

(2) The second level of the methodology carries out the multicriteria evaluation of the design alternatives.

The starting step is the collection of data necessary for the different analyses. The summary of the data is presented in Table 1.

The multicriteria evaluation of distillation system alternatives focuses on (i) exergy analysis, (ii) economic study,

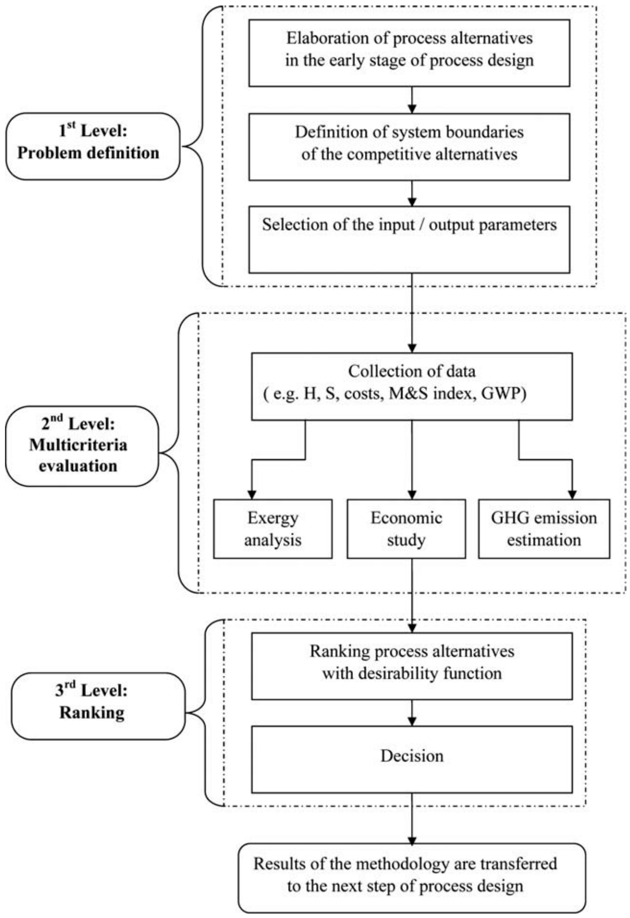

Figure 1. Flow diagram of the evaluation methodology of distillation systems.

(iii) GHG emission estimation. Each of the analysis calculates an indicator that can be summarized at the next level of the evaluation methodology. These indicators are the following: thermodynamic efficiency, total annual cost, and the carbon dioxide equivalent emission. The following section describes the applied analyses in detail.

Exergy analysis

Energy efficiency of the studied process alternatives can be calculated based on the first law of thermodynamics, which conducts to an energy analysis. As not all the heat energy can be converted to useful work, stated by the second law of thermodynamics, exergy analysis proves to be more adequate to determine the thermodynamic efficiency of the process alternatives. By definition, exergy is the maximum capacity of the system to perform useful work as it proceeds to a specific final state in equilibrium with its surroundings.

In the case of distillation systems, the columns can be seen as heat engines and their exergy demand is the minimum isothermal work of separation. Instead of mechanical work, separation work is produced. The aim of the exergy analysis is the comparison of the evaluated distillation systems based on their thermodynamic efficiency. This indicator gives information about the efficiency of the supplied heat conversion into separation work in the distillation systems. The exergy loss calculated in the exergy analysis shows the energy wastes. The distillation design alternatives have good potential for improvement regarding energy saving when it has considerable exergy losses and low thermodynamic efficiencies.[14] The thermodynamic efficiency is selected as indicator in the evaluation methodology and it can be calculated[21] with the following Eq. 1:

$$\eta = \frac{W_{\mathrm{SEP}}}{Ex_{\mathrm{loss}} + W_{\mathrm{SEP}}} \tag{1}$$

where W_{SEP} (kW) is the work of separation, Ex_{loss} (kW) is the exergy loss of the system.

Gouy-Stodola theorem states that the lost available work is directly proportional to the entropy production. The proportionality factor is simply the ambient temperature T_0 (Eq. 2).

$$Ex_{\mathrm{loss}} = T_0 \Delta S_{\mathrm{irr}} \tag{2}$$

where the ΔS_{irr} is the entropy production.

However, the exergy analysis also calculates the exergy loss, only the thermodynamic efficiency is selected as indicator in the evaluation methodology. The reason behind of this selection is that the exergy loss profile can provide information about the location of the energy wastes within the distillation system while the thermodynamic efficiency characterizes the complete process segment. The exergy loss and thermodynamic efficiency together provide useful information e.g., in the case of retrofit design because they indicate the possibility of further energy savings for a specific distillation system.

Economic study

Economic features should be estimated throughout every stage of the process design. The purpose of the economic study is the determination of the economic efficiency in function of their capital and utility costs. The correlation between economic study and exergy analysis is important as well, because e.g., exergy analysis may give hints about economic properties of the system. To compare these results with that of the exergy analysis the same operating conditions are used. Thus, the separation tasks and the inlet and

Table 1. Summary of the Data Required for the Application of the Evaluation Methodology

Analysis	Data
Exergy	Ambient pressure
	Ambient temperature
	Molar enthalpy of component *i*
	Molar entropy of component *i*
	Relative volatility of components *ij*
Economic	Cost of the utilities
	Heat capacity
	Latent evaporation heat
	Marshall & Swift index
	Material costs
Greenhouse gas Emission estimation	Global warming potential of component *i*
	Efficiency of the firing equipment

Table 2. Global Warming Potentials of Different Greenhouse Gases

Greenhouse Gases	GWP Value/100 Years
Nitrous oxide (N_2O)	296
Methane (CH_4)	23
Trifluoromethane (HFC-23)	12,000
1,1,1,2-Tetrafluoroethane (HFC-134a)	1300
Sulfur hexafluoride (SF_6)	22,200

outlet stream properties are identical to the parameters used during the exergy analysis. The objective function is the Total Annual Cost (TAC) that includes capital and utility costs and it is calculated according to the Eqs. 3 and 4.

$$\text{TAC} = \text{Annual capital cost} + \text{Annual operating cost} \quad (3)$$

$$\text{Annual capital cost} = \text{Capital cost}/\text{Plant life time} \quad (4)$$

The operating cost includes the utility costs and it is calculated per year in function of the operating hours. The economic study provides the TAC as indicator that characterizes the different distillation design alternatives.

Greenhouse gas emission estimation

As the environmental emission regulations have become strict in the last decades, the GHG emission estimation has especial importance and should be included in the early stage of process design. This article considers only the GHG emission since this form the significant part of the pollution caused by the studied distillation processes. The emission inventory and quantification motivates the designer to realize environmental friendly processes. These emissions have special impact also on the profitability of industrial processes since the Kyoto Protocol was ratified by many countries and established in 2005, a scheme for GHG emission trading. Some countries have introduced taxes based on the carbon content of the energy products and this tax is called ‘carbon tax’. A ‘carbon tax’ is a charge to be paid on each fossil fuel, proportional to the quantity of carbon emitted when it is burned. Concerning the present demands, carbon dioxide equivalent emissions need to be quantified.

Estimation of Carbon Dioxide Equivalent Emission. Beside of CO_2 emission other greenhouse gases are also estimated like nitrous oxide (N_2O), methane (CH_4), hydrofluorocarbons, and sulfur hexafluoride (SF_6; Table 2).

The carbon dioxide equivalent (CO_2e) is calculated by summing up the GHG emissions multiplied by their GWP value (Eq. 5).

$$CO_2 \text{ equivalent emission} = \sum (\text{GWP} \times \text{Greenhouse gas emission}) \quad (5)$$

The GHG emission estimation calculates the CO_2e emission of the distillation design alternatives per year that can be used as indicator in the evaluation methodology.

(3) The third level of the methodology includes the ranking of the process alternatives and the decision which system is the most adequate for the specific task.

The ranking is based on the desirability function, where the input data are the indicators calculated on the previous level. The indicators provide important information about process performances and allow the comparison of process alternatives with respect to specific aspects. However, they are not suitable for a direct comparison among the different analyses, therefore the desirability function is used to summarize the different indicators.

The desirability function (D_{fct}) approach is a useful statistical method to optimize the multiple characteristics problems. This method proposed by Harrington[22] converts the multiple quality characteristics into a single characteristic problem by maximizing the total desirability. The indicators are transformed into an individual desirability value d for the desirability function model. If the response exceeds the acceptable value, the value of d becomes zero; if the response is at the target value, the desirability value d becomes one. The individual desirability functions, d are continuous functions and they are chosen from among a family of linear or exponential functions. Based on these individual functions the overall desirability function, D_{fct}, is constructed (Eq. 6), and this makes possible the ranking of the process alternatives. The D_{fct} is defined as the geometric average of the k individual desirability functions and desirability includes the designer priorities and desires using the m weight factor[23]. High value of D_{fct} shows that all d_{k} are toward the target value that indicates the most adequate process alternative.

$$D_{\text{fct}} = \left(\prod_{i=1}^{k} d_i^{m_j} \right)^{\frac{1}{\sum m_j}} = \left(d_1^{m_1} \times d_2^{m_2} \times \cdots \times d_k^{m_j} \right)^{\frac{1}{\sum m_j}} \quad (6)$$

where k is the number of indicators and m is the weight factor.

The value of the m weight factor can be chosen equally one for each indictor if all deciding criteria are equally important for the designer. If the design task specifies the rank of the deciding criteria, this can be expressed in the values of the m weigh factor. The result of the ranking is affected by the value of the weight factor, mainly when the different individual indicators would have shown different ranking of the process alternatives. The use of high weight factor value for an indicator presses the result of the global ranking with the D_{fct} toward the ranking of the specific individual indicator.

The last step of the methodology is the decision making based on the D_{fct}. The process alternative with the highest D_{fct} value is the most favorable solution for the specific separation task based on the criteria mentioned in the second level of the evaluation methodology. The selected process alternative can be subject to the detailed engineering design as the next step of the process design project.

However, the evaluation methodology is elaborated for distillation systems it could be used also for other energy-utilizing processes since these processes can be generally characterized with the evaluation criteria applied in the proposed methodology. The use of the D_{fct} makes possible the extension of the deciding criteria with different process specific indicators.

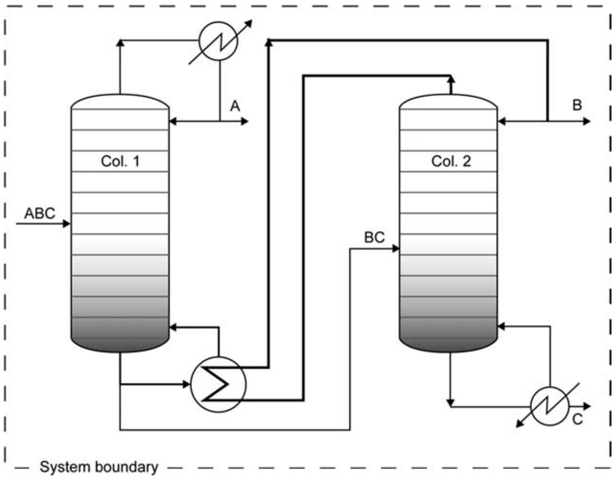

Figure 2. Direct distillation sequence with backward heat integration (DQB).

Distillation System Selected for the Elaboration of the Methodology

The selected case studies are three types of energy-integrated distillation systems. They are subjects of the design methodology. Using the three criteria of the methodology, the energy-integrated distillation systems are compared between each other and to the conventional scheme in the case of ternary mixture separation.

The studied distillation schemes are:

(1) direct sequence with backward heat-integration (DQB);

(2) fully thermally coupled distillation column, also known as Petlyuk column (FTCDC);

(3) sloppy distillation system with forward heat integration (SQF);

(4) conventional direct separation sequence without energy integration which is the base case of the comparison.

The studied distillation systems are selected from different types of conventional and energy-integrated distillation groups and the best connection is chosen from this groups referring to the column coupling and to the direction of energy integration. This selection is in accordance with several authors like[3,24] The first distillation system is a direct sequence with backward heat integration instead of forward because of its better economic and control features highlighted by Rév et al.[3] The same reason is behind of the choice of the forward heat integration in case of sloppy distillation structures. The base case of the comparative study is the direct sequence without energy integration.

The distillation systems selected for study are the following in detail.

Direct sequence with backward heat integration (DQB)

(a) The basis idea of this distillation system is to use the overhead vapor from the second column of increased pressure to provide heat to the first low, usually atmospheric pressure column. The reboiler of the first column is combined with the condenser of the second (Figure 2).

Fully thermally coupled distillation column (FTCDC)

(b) Fully thermally coupled distillation column is also called Petlyuk column consists of a prefractionator and a main column. The required heat amount for the separation is provided through direct contact of the material flows (Figure 3).

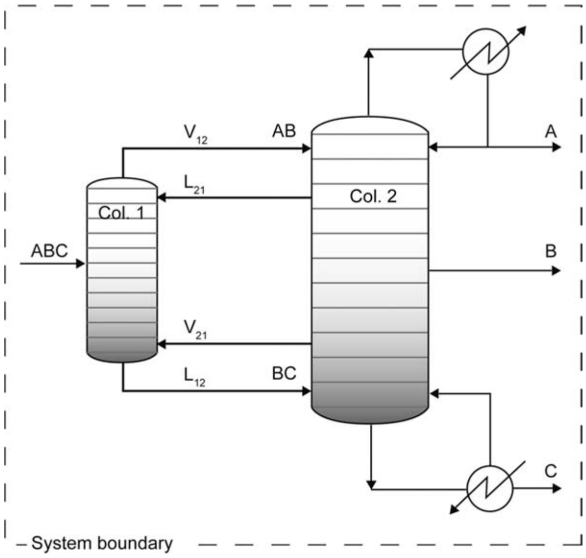

Figure 3. Fully thermally coupled distillation column (FTCDC).

Sloppy distillation system with forward heat integration (SQF)

(c) This distillation system basically is a heat-integrated sequence, but in the prefractionator sloppy separation takes place. The first column is a high-pressure prefractionator, its distillate and bottom product are fed to the second, low-pressure column. The forward heat integration between the two columns is carried out by an integrated heat exchanger, where the overhead vapor from the high-pressure prefractionator is used to boil up the low-pressure column (Figure 4). The forward scheme is selected in this work because previous studies by Emtir et al.[24] have shown that it is better controllable than the backward integration and the forward and backward alternatives have practically the same economic features.

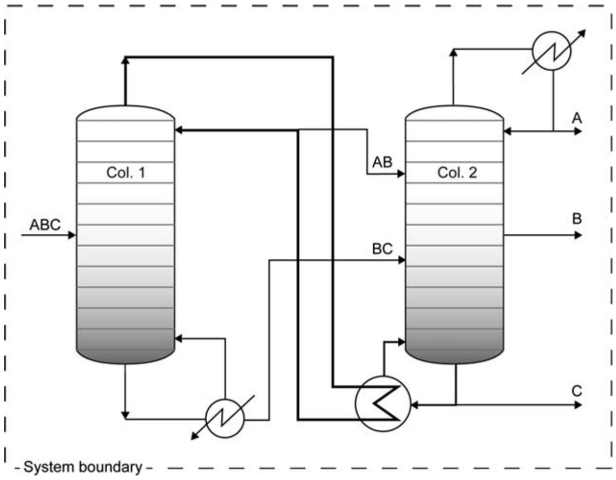

Figure 4. Sloppy distillation system with forward heat-integration (SQF).

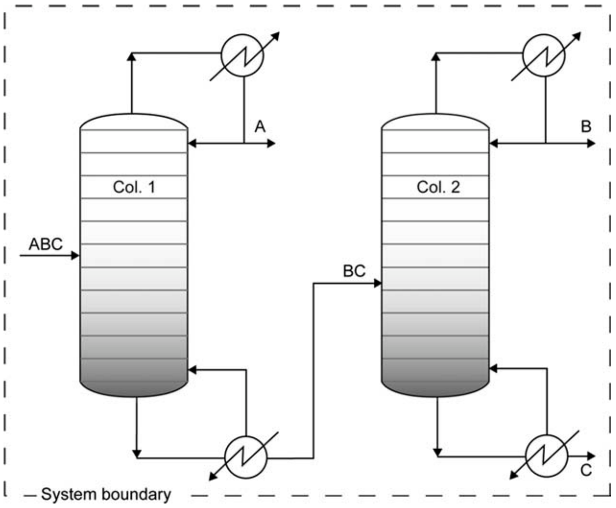

Figure 5. Conventional direct distillation scheme (Conv. Dir.).

Conventional direct distillation scheme (Conv. Dir.)

(d) This separation structure is used as base case for comparison. As it proves to be better than the indirect one in the case studies selected it consists of two simple distillation columns connected in such a way that bottom product of the first column is the feed of the second column. In literature, they are considered to be conventional arrangements for ternary distillation. Direct separation sequence is shown in Figure 5.

Application of the Proposed Evaluation Methodology on the Studied Distillation Systems

Optimal parameters of the aforementioned separation systems are determined. Rigorous tools calculate adequate reflux ratios, number of trays, and optimal feed tray. In the case studies selected, the total number of the theoretical trays of the separation schemes ranges between 70 and 95 and the column diameters range between 0.9 and 1.5 m. The reflux ratios vary according to the ease of separation in a wide range. The simulation models of the studied distillation systems are implemented in the ASPEN PLUS process simulator. Moreover, the applied studies in this work e.g., exergy analysis, economic study require the use of MS-Excel connected to the process simulator where the different exergy calculating equations or the cost functions are introduced.

Definition of the boundaries

The methodology is applied on the process segment that contains the distillation columns and the heat exchangers, including the condensers and reboilers.

Selection of the identical input/output parameters

For the investigation of the distillation systems, three different ternary mixtures are selected (Table 3). Mixtures of more than three components are not considered at the stage of this study so that the complexity of the several designs, that is typical for the more than three component mixtures, do not disturb the overview of our proposed methodology. Because of the same reason, only zeotropic mixtures are considered.

Three product purities are supposed in the economic study: 90%, 95%, and 99%. In the case of the exergy analysis and GHG emission estimation one product purity (95%) is selected.

Feed flow rate is 100 kmol/h and its composition is always equimolar. The chosen ternary mixtures have different ease of separation that can be characterized by the separation index (SI):

$$\mathrm{SI} = \frac{\alpha_{AB}}{\alpha_{BC}} \tag{7}$$

where α_{ij} is the relative volatility. The results of this work are often presented in function of SI which gives indication about the location of the more difficult separation task.

The Soave-Redlich-Kwong model is used to calculate vapor–liquid equilibrium. This model is widely used in the refinery and gas processing industries for the prediction of vapor–liquid equilibria for systems containing non-polar components.

The ambient pressure and temperature is taken 101 kPa and 298 K, respectively.

Results of the exergy analysis

Exergy analysis is applied to the studied energy-integrated distillation systems and to the conventional direct distillation scheme.

To perform the exergy analysis the balance regions has to be fixed. Figures 2–5 shows the system boundaries where the exergy analysis is applied. The analysis takes in to account the inlet and outlet material streams and the heat duty of the reboilers and of the condensers. To compare the thermodynamic efficiency of the studied distillation systems the entering and leaving stream physical properties must be identical. In this study the temperature, pressure, and composition of the inlet and outlet streams are equal for each case study and the product purity of the outlet streams is selected to be 95%. Therefore, the inlet and outlet stream exergies are identical for the studied distillation systems separating one specific ternary mixture. Thus, the separation work does not vary in function of the used distillation system only in function of the separated mixture. The cooling water temperature is taken 283 K and the temperature of the steam used

Table 3. Ternary Mixtures Studied

Case	Mixture	α_A	α_B	α_{AB}	β	SI
1	Isopentane-pentane-hexane	3.62	2.78	1.3	0.68	0.47
2	Pentane-hexane-heptane	7.38	2.67	2.76	0.26	1.03
3	Butane-isopentane-pentane	2.95	1.3	2.26	0.154	1.74

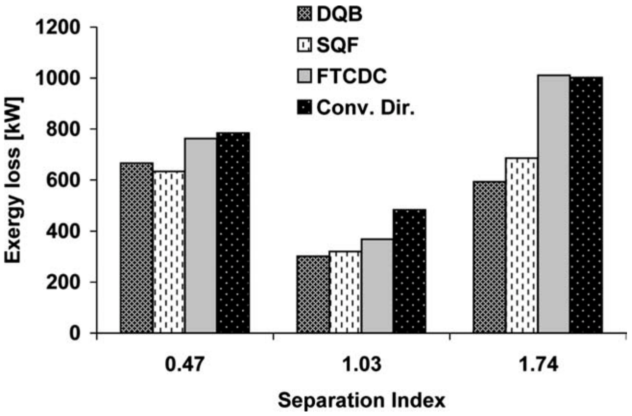

Figure 6. Exergy loss in function of the separation index.

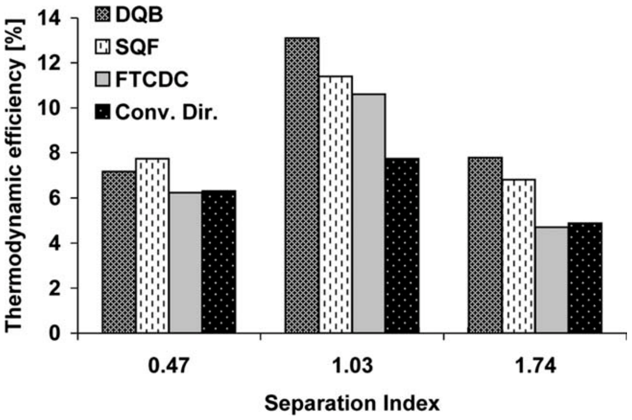

Figure 7. Thermodynamic efficiency in function of the separation index.

in the reboilers is 433 K. The calculated thermodynamic efficiency (Eq. 1) is linear dependent on the taken temperature grades[25] thus one can obtain different efficiency values if the temperature of the used cooling and heating media is different or the ambient temperature is fixed differently.

Each distillation system is studied for three different ternary mixtures (Table 3) in order to investigate also the effect of SI on the energy saving properties of the distillation systems. The distillation systems are ranked according to their exergy loss and thermodynamic efficiency.

In Figure 6, the exergy loss is presented in function of SI for each distillation system. The three SI value represents the three ternary mixtures with different ease of separation. As the figure shows the exergy loss is the lowest when the ease of separation of the mixture is balanced so the SI value is close to 1. If the ease of separation becomes unbalanced thus the SI of the mixture differs from 1 the exergy loss increases. The exergy loss of the distillation systems generally is the highest in the case of the third mixture separation with SI = 1.74. It has to be noted that SI value of the third mixture deviates the most from 1 which means that this mixture is the furthest from the symmetric ease of separation.

The comparison of the different distillation systems shows that the DQB has the least exergy loss followed by SQF. Entirely these two heat-integrated distillation systems show the best energy saving and consequently the thermodynamic efficiency of these systems is the highest (Figure 7).

The thermodynamic efficiency of the FTCDC is better compared to the conventional direct scheme in the case of the mixtures with SI = 1.03 and in the case of the other mixtures there is very slight difference in the thermodynamic efficiency of the FTCDC and conventional direct scheme. Figure 7 shows that the DQB has 5% higher thermodynamic efficiency than that of the conventional direct scheme in the case of mixture 2 with SI = 1.03. These results support the idea that processes with high exergy loss and low thermodynamic efficiency can be energetically improved.[14] The results of the exergy analysis are compared to the energy consumption data of the distillation systems. The calculation of the energy consumption assumes that the distillation systems have only heat requirements neglecting e.g., the electricity usage of the pumps etc. The heat demand of the studied distillation systems is presented in the Figure 8.

One can notice that the tendency of the heat demand is similar to that of the exergy analysis. This can be explained with the identical ambient and utility temperatures for each case study.

The exergy analysis determines the thermodynamic efficiency of the investigated systems which gives information about the supplied heat conversion into separation work and identifies the energy wastes through the exergy loss. This tool reveals the energy saving performance of the system and locates those process units, which need further energetic improvements.

In the case study, the exergy analysis identifies the characteristics of the studied distillation systems regarding to the energy efficiency but it is uncertain how precisely the costs or the CO_2e emission of these systems can be predicted. Therefore, the next steps of this work are an economic study calculating the costs of the studied distillation systems and furthermore the estimation of the CO_2e emission.

Results of economic study

The economic study as a design step is tested on the distillation design alternatives. Based on their economic

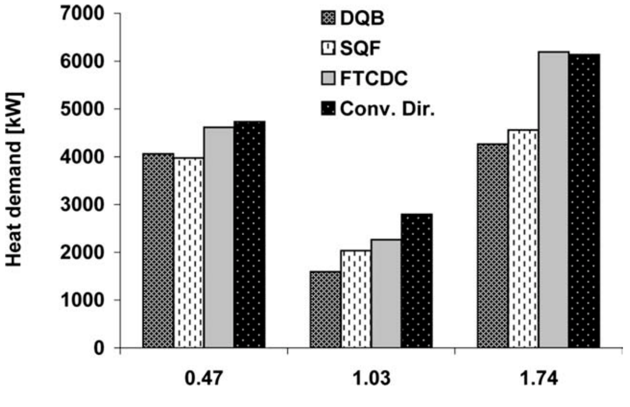

Figure 8. Heat demand of the distillation systems in function of the separation index.

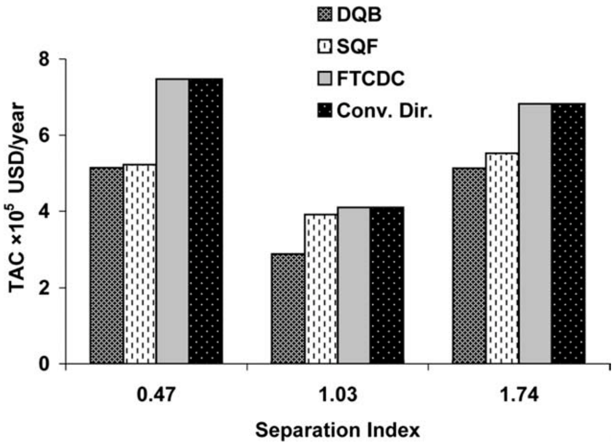

Figure 9. TAC vs. SI when the required product purity is 90%.

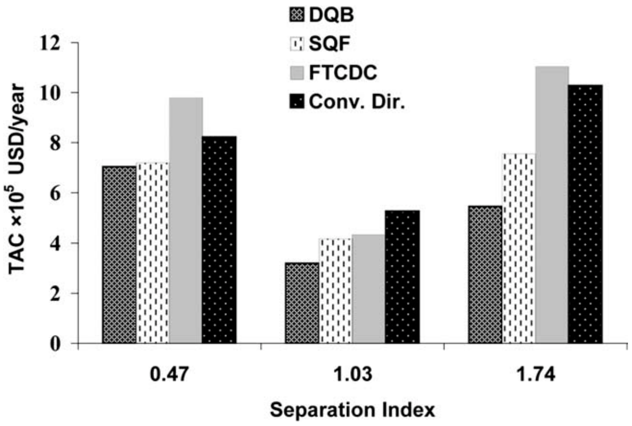

Figure 10. TAC vs. SI when the required product purity is 95%.

efficiency, the investigated distillation schemes are compared between each other and the best energy integration solution can be chosen. The economic study calculates the TAC of the investigated distillation systems. These systems are investigated for the same separation task and within the same system boundaries as in the exergy analysis. The TAC is calculated in the function of the separation index. In the literature, economic feature of energy-integrated distillation schemes have been discussed with increase of product purity.[2,3] However, it has not been investigated in the aspect of separation index, which expresses the ease of separation of the given mixture. The SI allows the generalization of the ternary mixtures based on their relative volatility.

Concerning the TAC (Eqs. 3 and 4) calculation in this case study, the plant lifetime is 10 years with 8000 operating hours per year. The capital cost contains the installed cost of the column shell, tower internals, condenser, and reboiler. These costs are estimated using respective equations proposed by Douglas[20] and updated by the Marshall and Swift index which value is taken from literature.[26] Operating cost contains the cooling water and steam costs. The industrial prices are used to calculate the utility costs.

Results of the comparative economic study for the separation systems and ternary mixtures studied are shown in Figures 9–11. The representation of the results in these three figures differs in the expected product purities. The effect of different product purity requirements is investigated in order to reveal the properties of the investigated distillation system alternatives in detail.

Figure 9 shows the Total Annual Cost (TAC) vs. Separation Index (SI) when the required product purity is 90%. In this case the most economic distillation structure is the direct sequence with backward heat-integration (DQB) followed by the sloppy distillation system with forward heat integration (SQF). Fully thermally coupled distillation columns show savings compared to the conventional direct distillation scheme, which has the highest costs.

In the next case where the required product purity is 95% (Figure 10) total annual cost of each distillation structure increase and the rank between of the heat-integrated distillation systems (DQB, SQF) does not change. The FTCDC has higher costs compared to the conventional direct scheme in the case of the mixtures with unbalanced ease of separation (SI = 0.47, 1.74). The FTCDC proves to be inefficient for these separation tasks.

The results of the economic study in the case of 99% product purity (Figure 11) show that the most economic distillation structure is the DQB and only in the case of mixture with SI = 0.47 it is SQF. Although the SQF is not the most economic structure in every case, but it is not as sensible to the increase of product purity as other structures.

It follows from Figures 9–11 that the TAC has an increasing tendency with the increase of the product purity that correlates with the raised energy usage of high product purity distillations. The studied distillation schemes run with the lowest costs when the ease of separation is balanced (SI = 1.03) and the heat-integrated systems (DQB, SQF) are the most economic arrangements in almost every case and it is always better than FTCDC. The results of the economic study correlate with the results of the exergy analysis.

Results of GHG emission estimation

The GHG emissions of the studied energy-integrated distillation systems are estimated and compared to the emission

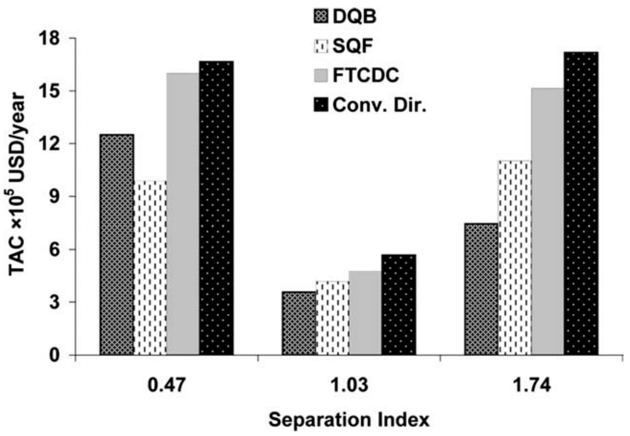

Figure 11. TAC vs. SI when the required product purity is 99%.

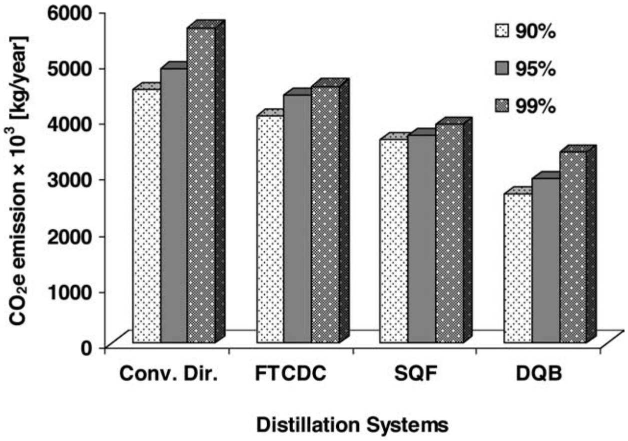

Figure 12. CO$_2$e emission of the studied distillation systems at different product purities in case of mixture with SI = 1.03, with natural gas as fossil fuel.

of conventional distillation scheme. The major emission related to the distillation systems of our case study is the GHG emission caused by the large heat requirement of these systems. Therefore, the energy requirements of the different distillation systems are calculated. Based on the energy consumption data of the distillation schemes, GHG emissions are estimated using SimaPro 6.0 and the results are verified by the model developed by Gadalla et al.[19] for quantifying the emissions associated with distillation systems. Reducing energy requirements of distillation systems leads to lower GHG emission; this is why reconsideration of the design methodology is necessary. Energy integration could be a solution to reach a lower GHG emission through better energy utilization. Carbon dioxide equivalent is used in order to quantify these emitted GHG (Eq. 8). The global warming potential (GWP) values of the GHG are taken for 100 years time horizon (Table 2). These CO$_2$e emissions are estimated assuming four different fossil fuels as heat source: natural gas, oil, coal, and lignite. The emitted greenhouse gases using these fossil fuels are composed mainly by CO$_2$ and by slight amount of N$_2$O and CH$_4$. The amount of emitted halogenous compounds is practically negligible compared to the CO$_2$ emission and therefore it can be neglected.

Appropriate firing equipment is selected for each kind of heat source based on the descriptions found in the literature[27]:

- Natural gas heating atmospheric burner with low NO$_x$ emission with efficiency $\eta = 87\%$.
- Fuel oil (low sulphur) boiler under 100 kW with efficiency $\eta = 87\%$.
- Industrial coal furnace used in range of 1–10 MW with efficiency $\eta = 80\%$.
- Stove lignite briquette 5–15 kW with efficiency $\eta = 70\%$

The results show that the investigated energy-integrated distillation systems have lower CO$_2$e emission compared to the conventional direct distillation scheme. The energy requirement and consequently the associated CO$_2$e emission grow with the increase of the product purity. This tendency is valid for all of the studied distillation systems but the SQF is the least sensitive (Figure 12).

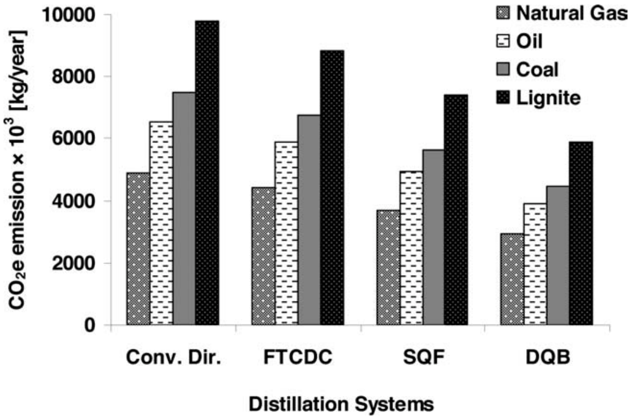

Figure 13. CO$_2$e emission of fossil fired distillation structures, the product purity is 95%, mixture with SI = 1.03.

Energy-integration of the distillation columns can reduce the CO$_2$e emission and further minimization of this emission can be reached by using cleaner fossil energy source.

Figure 13 shows the CO$_2$e emissions of the four studied distillation systems in case of the different fossil fuel used as heat source. CO$_2$e emission is the lowest when natural gas is used as heat source in the case of each studied distillation scheme. This tendency is true for each studied separation problem. The CO$_2$e emission increases if the ease of separation is not symmetric that is when separation index (SI) is far from 1 (Figure 14).

The CO$_2$e emission reduction compared to the base case is also investigated. The CO$_2$e emissions are summarized for all the three product purities into one average CO$_2$e emission saving figure. These figures are shown in one chart (Figure 15) for all the three studied energy-integrated distillation schemes.

Figure 15 shows that the DQB structure has the best figure. This means that the DQB scheme is the most flexible in the CO$_2$e emission issue if product purity changes. The average

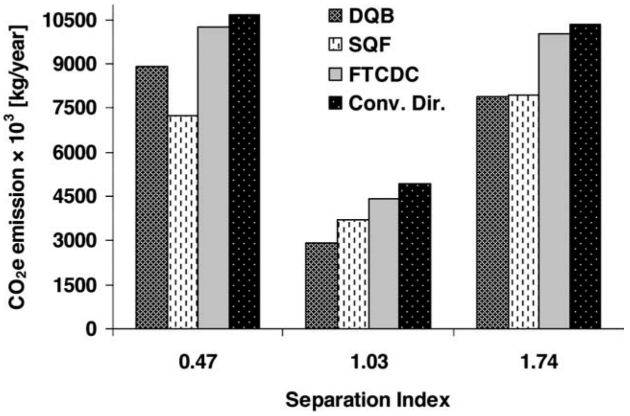

Figure 14. CO$_2$e emission of the distillation systems, in the case of different ternary mixtures.

The required product purity is 95% and with natural gas as fossil fuel.

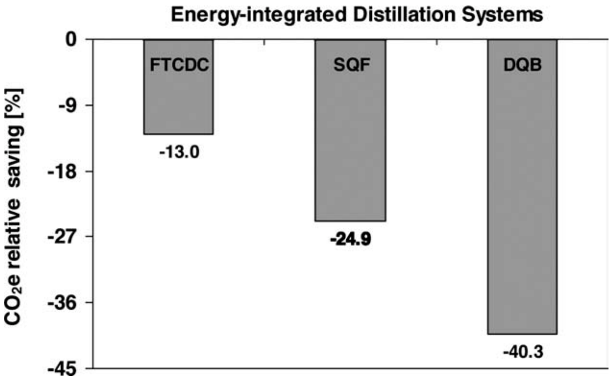

Figure 15. CO_2e relative emission saving correlate to the conventional direct distillation scheme.

emission saving of DQB reaches 40%. The CO_2e emission confirms the results of the previous studies of this work and draws the attention to the consequences of wasted energy.

Ranking the process alternatives

The ranking of process alternatives is based on the different process indicators from the exergy analysis, economic study, and the GHG emission estimation. The indicators are numerically presented in the Figures 7, 10, and 14 and they are transformed into an individual desirability value d from 0 to 1. In the case of thermodynamic efficiency, maximization is desirable, while the TAC and CO_2e emission should be minimized. The weighting factors of the different indicators are taken equally one in this case study; however, the desirability function method allows the use of weighted indicators if the criteria are not equally important. According to the Eq. 6, D_{fct} is calculated and presented in function of the different ternary mixtures and the investigated distillation systems (Figure 16).

Decision

The evaluation methodology reveals that the most adequate distillation system is the SQF in the case of the mixture with SI = 0.47 and the DQB in the case of the mixtures SI = 1.03 and 1.74. The case study investigations prove that the results of the exergy analysis are in linear correlation with the economic features as well as with the emissions. The methodology for the simple estimation of the different process design alternatives can become quite simple. We can conclude that the results of the exergy analysis are in strict correlations with the results of the economic and environmental analysis. Therefore, it can be concluded that it is satisfactory for the evaluation of the different design alternatives to pay special attention to the thermodynamic efficiency determined on exergy analysis basis. Considering that this methodology can be used in the process design stage, the basic assumption of the process design should be applied also in this methodology. This basic assumption is that the ambient parameters should be identical in each case. It means that the temperature, pressure, and compositions of the input and output streams must be the same for each process design alternative.

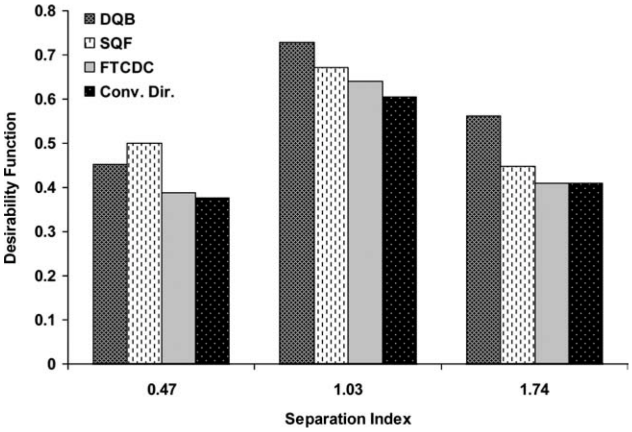

Figure 16. D_{fct} vs. SI for the studied distillation systems.

Conclusions

The proposed process investigation methodology for distillation systems helps to evaluate process alternatives from a complex point of view. Following this methodology, the problem defined on the first level is suitable for the complex comparative study. The second level is the multicriteria evaluation and it forms the hearth of the methodology. In this level, three different kinds of analysis are carried out in order to evaluate the distillation systems based on exergetic, economic, and environmental impact aspects. In the last level of the methodology, the D_{fct} aggregates these three aspects in order to help the selection of the most adequate distillation design alternative giving one general characteristic figure for each process design alternative.

In the case study, three energy-integrated distillation systems are investigated and compared to the conventional direct scheme. The input/output parameters and the system boundaries are defined similarly for these investigated systems. In the case of the exergy analysis, the base of comparison is their thermodynamic efficiency. This analysis shows that the heat-integrated distillation structures (DQB and SQF) are the most energy-efficient among the studied ones. The thermodynamic efficiency of all the studied distillation systems is the highest when the ease of separation is symmetric, that is, the exergy loss is the minimal one in such cases. Economic study supports the results of the exergy analysis and shows that the heat-integrated distillation structures have the best economic features as well. Although the FTCDC is less economic than the other investigated heat-integrated systems but it shows energy savings compared to the conventional sequence. CO_2e emission reduction can be achieved with the use of cleaner fossil energy source, and using heat-integrated distillation schemes. CO_2e emissions of the distillation systems can be decreased by on the average of 40% using DQB arrangements instead of conventional alternative. The CO_2e emission estimation demonstrates that in most of the cases, the DQB has the lowest CO_2e emission but the SQF is less sensitive to the product purity change. Applying the D_{fct} reveals that among the different distillation schemes the heat-integrated DQB alternative proves to be the best applicable since it shows the features in a wide and flexible range.

This work also shows that the thermodynamic efficiency determined during exergy analysis predicts the results of the economic study and provides further information about the system. Based on the results one can conclude that the generally favored economic study can be replaced with exergy analysis in the early stage of process design. Moreover, the exergy analysis can also predict the emissions associated with the utilized energy and this proportionality can simplify the decision-making during the process synthesis step. This emphasizes the improving importance of the exergy analysis also in the process design practice.

Acknowledgments

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Notation

Latin symbols

A = the most volatile component of the ternary mixture
B = middle component of the ternary mixture
C = the heaviest component of the ternary mixture
CO_2e = carbon dioxide equivalent (kg)
d = individual desirability value
D_{fct} = desirability function
DQB = direct distillation sequence with backward heat integration
$\mathrm{Ex}_{\mathrm{loss}}$ = lost exergy rate (kW)
FTCDC = fully thermally coupled distillation column
GWP = global warming potential
L_{12} = liquid flow rate from column 1 to column 2 (kmol/h)
L_{21} = liquid flow rate from column 2 to column 1 (kmol/h)
M&S = Marshall and Swift index
m = weight factor
n = mole flow (kmol/h)
SI = separation Index
SQF = sloppy distillation system with forward heat-integration
T_0 = ambient temperature (K)
TAC = total annual cost ($/year)
V_{12} = vapor flow rate column 1 to column 2, (kmol/h)
V_{21} = vapor flow rate from column 2 to column 1, (kmol/h)
W_{SEP} = work of separation, (kW)

Greek letters

α_i = volatility of component i
α_{ij} = relative volatility of components i, j
β = optimal fractional recovery of the middle component
ΔS_{irr} = entropy production (kJ/h K)
η = thermodynamic efficiency

Literature Cited

1. Peters MS, Timmerhaus KD. *Plant Design and Economics for Chemical Engineers*, 4th ed.; New York: McGraw-Hill, 1991.
2. Annakou O, Mizsey P. Rigorous comparative study of energy-integrated distillation schemes. *Ind Eng Chem Res.* 1996;35:1877–1885.
3. Rév E, Emtir M, Szitkai Z, Mizsey P, Fonyó Z. Energy savings of integrated and coupled distillation systems. *Comput Chem Eng.* 2001;25:119–140.
4. Petlyuk FB, Platonov VM, Slavinskii DM. Thermodynamically optimal method for separation multicomponent mixtures. *Int Chem Eng.* 1965;5:555–561.
5. Olujic Z, Sun L, de Rijke A, Jansens PJ. Conceptual design of an internally heat integrated propylene-propane splitter. *Energy.* 2006; 31:3083–3096.
6. Nakaiwa M, Huang K, Owa M, Akiya T, Nakane T, Sato M, Takamatsu T, Yoshitome H. Potential energy savings in ideal heat-integrated distillation column. *Appl Therm Eng.* 1998;18:077–1087.
7. Hernandez S, Segovia-Hernandez JG, Rico-Ramirez V. Thermodynamically equivalent distillation schemes to the Petlyuk column for ternary mixtures. *Energy.* 2006;31:2176–2183.
8. Kencse H, Manczinger J, Szitkai Z, Mizsey P. Retrofit design of an energy integrated distillation system. *Per Pol Chem Eng.* 2007; 51:11–16.
9. Olujic Z, Fakhri F, de Rijke A, de Graauw J, Jansens PJ. Internal heat integration—The key to an energy-conserving distillation column. *J Chem Technol Biotechnol.* 2003;78:241–248.
10. Fonyo Z. Thermodynamic analysis of rectification. 1. Reversible model of rectification. *Int Chem Eng.* 1974;14:18–27.
11. Fonyo Z. Thermodynamic analysis of rectification. 2. Finite cascade models. *Int Chem Eng.* 1974;14:203–210.
12. LeGoff P, Cachot T, Rivero R. Exergy analysis of distillation processes. *Chem Eng Technol.* 1996;19:478–485.
13. Zhu P. An improved calculation of the thermodynamically based allocation of cumulative exergy consumption in the petroleum distillation process. *Chin J Chem Eng.* 2008;16:104–107.
14. Bandyopadhyay S. Thermal integration of a distillation column through side-exchangers. *Chem Eng Res Des.* 2007;85:155–166.
15. Suphanit B, Bischert A, Narataruksa P. Exergy loss analysis of heat transfer across the wall of the dividing-wall distillation column. *Energy.* 2007;32:2121–2134.
16. Tijani AS, Ramzan N, Witt W. Process and plant improvement using extended exergy analysis, a case study. *Rev De Chim.* 2007; 58:392–396.
17. Rivero R, Rendón C, Gallegos S. Exergy and exergoeconomic analysis of a crude oil combined distillation unit. *Energy.* 2004;29: 1909–1927.
18. Gadalla M, Olujic Z, de Rijke A, Jansens PJ. Reducing CO2 emissions of internally heat-integrated distillation columns for separation of close boiling mixtures. *Energy.* 2006;31:2409–2417.
19. Gadalla M, Olujic Z, Jobson M, Smith R. Estimation and reduction of CO2 emissions from crude oil distillation units. *Energy.* 2006; 31:2398–2408.
20. Douglas JM. *Conceptual Design of Chemical Processes*. New York: McGraw-Hill, 1988.
21. Seader JD, Henley EJ. *Separation Process Principles*. Wiley, 2006.
22. Harrington EC. The desirability function. *Ind Qual Control.* 1965;21:494–498.
23. Derringer G, Suich R. Simultaneous optimization of several response variables. *J Qual Technol.* 1980;12:214–219.
24. Emtir M, Rev E, Fonyo Z. Rigorous simulation of energy integrated and thermally coupled distillation schemes for ternary mixture. *Appl Therm Eng.* 2001;21:1299–1317.
25. Al-Muslim H, Dincer I, Zubair SM. Effect of reference state on exergy efficiencies of one- and two-stage crude oil distillation plants. *Int J Therm Sci.* 2005;44:65–73.
26. *ChemicalEngineering*. New York: Access Intelligence, 2005.
27. Frischknecht RUB, Bosshart S, Ciot M, Ciseri L, Doka G, Hischier R, Martin A, Dones R. Gantner U. Ökoinventare von Energiesystemen, Grundlagen für den Ökologischen Vergleich von Energiesystemen und den Einbezug von Energiesystemen in Ökobilanzen für die Schweiz, 1996.

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