CHEMICAL ENGINEERING TRANSACTIONS

VOL. 29, 2012

Guest Editors: Petar Sabev Varbanov, Hon Loong Lam, Jiří Jaromír Klemeš

ISBN 978-88-95608-20-4; **ISSN** 1974-9791

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1229058

Exergy Analysis of Multicomponent Distillation Systems for Efficiency Ranking

Máté Haragovics*[a], Péter Mizsey[a,b]

Budapest University of Technology and Economics, Dept. of Chemical and Environmental Process Engineering, Budapest H-1521, Hungary
[b]Research Institute of Chemical and Process Engineering, University of Pannonia, Veszprém, H-8200, Hungary
harmat@kkft.bme.hu

In this paper a complex methodology is tested and verified to select the most adequate energy integrated distillation structure for a specific separation task. Exergy, economic and environmental analyses are applied to select the most efficient rectification structures for separation of quaternary hydrocarbon mixtures. Distillation structures based on direct sequence and single column configurations are examined.
The ranking depends on the product purification prescription. The direct sequence backwards with heat integration performs best in all cases. This shows that heat integration of distillation columns is a beneficial from both exergetical, economical end environmental points of view in a wide product purity range, and it has a great potential of savings. The overheated vapour feed solution has less attractive properties, therefore it should be avoided if the separation technology allows it.

1. Introduction

Distillation is a versatile separation tool. Apart from crude distillation and hydrocarbon separation other uses are known, such as regenerating solvents or processing wastewater, e.g.,Koczka and Mizsey, 2010 and Tóth et al., 2011. Constantly rising energy prices make energetic efficiency more and more important, thus many scientific works today still investigate energetic aspects of distillation. Most of them is investigating different new improvements on thermally coupled distillation systems (Gadalla et al., 2007; Kencse et al., 2007; Huang et al., 2008; Wang et al., 2008a; Zhu et al., 2009; Kencse and Mizsey, 2010; Liu et al., 2011; Wei et al., 2011; Kiran et al., 2012). These topics show the importance and actuality of saving energy, especially in such energy consuming processes like distillation. It is important both from economic and environmental viewpoints, as these are closely related.
Complex design is also a famous subject of investigation nowadays, thus the need for fast decisions, simple yet easy evaluations is probably higher than ever. Many articles (Grossmann et al., 2005; Wang et al.; 2008a,b; Adiche and Vogelpohl, 2011) discuss automatic methods to design complex distillation structures. Extending these methods to include economic and energetic considerations would be desirable, in order to include viewpoints that usually effect decisions in economy. Regarding petrol industry, not just new equipment is designed, but the old columns and equipment are usually retrofitted. Kencse and Mizsey (2010) provide a methodology that aids integration of technological, economical or environmental design together, that can help these design steps. They presented a simpler way to aggregate these aspects with the desirability function, and tested it on ternary mixtures. This paper is verifying this methodology and its tools on a quaternary hydrocarbon mixture.

Please cite this article as: Haragovics M. and Mizsey P., (2012), Exergy analysis of multicomponent distillation systems for efficiency ranking, Chemical Engineering Transactions, 29, 343-348

2. Complex methodology

2.1 Exergy analysis: energy and efficiency

Processes have been optimised for energy consumption for decades, but usually the value of the energy is not considered. The difference originates from the conversion of one type of energy into the other. Regarding just heat energy, the same amount of heat energy can be more valuable if it is available on higher temperatures. In many cases, despite the large heat energy content, lower temperature heat energy can only be utilised in a few processes. This shows that the availability temperature of the heat energy is strongly associated with its value of utilisation.

Exergy, however, makes a difference between more and less valuable energies. In the calculation of exergy not only the first but the second law of thermodynamics is also taken into account. By definition, exergy is the maximal possible useful work during a process that brings the system into thermodynamic equilibrium with a heat reservoir. The heat reservoir usually is the environment. Exergy can also be expressed like in Eq. 1 where Q is the heat energy, T is the temperature of the heat and index 0 denotes the properties taken at the temperature of the heat reservoir. Another form of exergy is Eq. 2, where H is the enthalpy, S is the entropy and T is the temperature.

$$Ex = Q \times \left(\frac{T - T_0}{T} \right) = Q \times \left(1 - \frac{T_0}{T} \right) \tag{1}$$

$$Ex = \left(H - H_0 \right) - T_0 \times \left(S - S_0 \right) \tag{2}$$

We can summarize the advantage of using exergy analysis: it takes irreversibilities into consideration and expresses that heat energy and work are not equivalents. It also shows that heat degrades from higher to lower temperatures. A simple enthalpy balance fails to indicate these differences.

The second law of thermodynamic states that the entropy in a closed system can only be increased. In the distillation process the heat is passed through the reboiler, then the column where it makes useful work, and finally it is gained back in the condenser at a lower temperature than it was introduced to the reboiler. Degradation of heat energy makes it possible to lower the entropy of the material, that is, the separation of a liquid mixture. Seader and Henley (2006) describe the method of exergy loss and thermodynamic efficiency calculation. First the irreversible entropy loss needs to be calculated(Eq. 3).

$$\Delta S_{irr} = \sum_{out} \left(n \times S + \frac{Q_{cond}}{T_{cond}} \right) + \sum_{in} \left(n \times S + \frac{Q_{reb}}{T_{reb}} \right) \tag{3}$$

Having the entropy loss calculated and knowing the temperature of the heat reservoir, it is possible to calculate the exergy loss (Eq. 4).

$$Ex_{loss} = T_0 \times \Delta S_{irr} \tag{4}$$

The work of separation is also needed, that is, the difference of the exergy flowing in and out (Eq. 5).

$$W_{sep} = \sum_{out} \left(n \times Ex \right) + \sum_{in} \left(n \times Ex \right) \tag{5}$$

Finally the efficiency is calculated by dividing the useful work by the energy we cannot recover, i.e., the useful work plus the exergy loss (Eq. 6).

$$\eta = \frac{W_{sep}}{W_{sep} + Ex_{loss}} \tag{6}$$

The ideal distillation column would be the reversible distillation column (Figure 1) introduced by Fonyó (1974). No irreversible change occurs in it, thus there is no entropy loss. To achieve this, equilibrium is needed in every point of the column which implies an infinite number of plates, negligible pressure drop and infinitesimally small heat transfers along the height of the column at each tray. This implies that the material flow also changes along the height, resulting in an unusual column shape.

The very strict criteria of the reversible column make it an infeasible solution. However, many of its features can be implemented during design of distillation. .Multiple feed inlets, multiple side-draws, internal heat transfer and even distribution of heat energy inputs and outputs are all tools to improve thermodynamic efficiency.

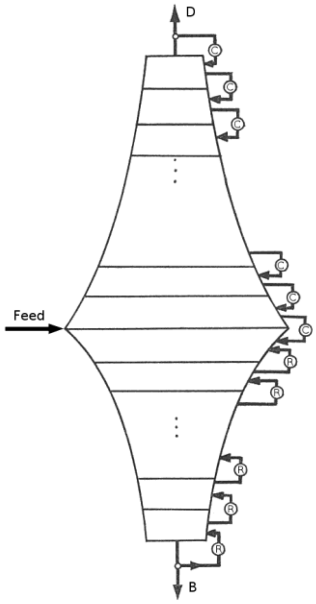

Figure 1: Reversible distillation column

2.2 Estimation of greenhouse gas (GHG) emission

In the past decades efforts were made to regulate the emission of greenhouse gases. CO_2 is emitted in the largest quantity, but other GHG gases also have effect on global warming. This multiplicity is simplified with the calculation of CO_2 equivalent emission (CO_2e) with the help of the global warming potential (GWP). Emissions of gases are multiplied by their GWP and summarized (Eq. 7). Due to the aforementioned importance of GHG emission it is recommended not to leave this viewpoint out of any design process.

$$CO_2e = \sum(\mathrm{GWP} \times \mathrm{GHG\,emission}) \tag{7}$$

In our work, during the comparison of different distillation structures the annual CO_2e emission is taken into account as an indicator.

2.3 Estimation of total annual cost

At the very beginning before choosing the appropriate system cost estimation is done for all systems. The capital cost is estimated with the appropriate equations proposed by Douglas (1988). The operating parameters are the same as during the exergy analysis and GHG emission analysis. The total annual cost (TAC) is calculated as in Eq. 8. The annual capital cost is the capital cost of the system distributed evenly during the designed plant lifetime (Eq. 9).

TAC = Annual capital cost + Annual operating cost (8)

Annual capital cost = Capital cost / Plant lifetime (9)

2.4 Aggregation of properties with desirability function

The final step of the complex evaluation is the aggregation of different indices. This step uses the desirability function proposed by Harrington (1965) The indicators are transformed into an individual desirability value *d* for the desirability function model. Individual desirability functions, *d*–s 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. 10). The D_{fct} is defined as the geometric average of the *k* individual desirability functions, *d*-functions are constructed to reflect the importance of each parameter instead of using the weighing factor. High value of D_{fct} shows that all d_k are toward the target value that indicates the most adequate process alternative.

$$D_{fct} = \left(\prod_{i=1}^{k} d_i^{m_j}\right)^{\frac{1}{\sum m_j}} = \left(d_1^{m_1} \times d_2^{m_2} \times \cdots \times d_k^{m_j}\right)^{\frac{1}{\sum m_j}} \tag{10}$$

3. Case study

To determine the influence of design alternatives on the thermodynamic and the aggregated efficiencies of distillation, different distillation schemes are studied completing the same separation task. Simulations of the separation of a quaternary mixture are made and the exergy loss and efficiency of five distillation structures are examined as well as the CO_2e emission and annual cost of building and operating the given structure. The designed lifetime of the system is 10 years with 8000 operating hours annually.

A quaternary hydrocarbon mixture is separated, it is an equimolar mixture of n-pentane, n-hexane, n-heptane and n-octane. We examine two cases of product purity: a) sloppy separation with lower purities and b) sharp separation with relatively high purities (Table 1).

Table 1: Mole fractions in different product streams

Major comp.	Lightest frac. n-pentane	Middle frac. 1 n-hexane	Middle frac 2 n-heptane	Heaviest frac. n-octane
Sloppy	0.82	0.68	0.64	0.76
Sharp	0.96	0.93	0.90	0.94

The base case of distillation structures is the conventional direct sequence (DS, Figure 2). A backwards heat integrated alternative of the direct sequence is also included in the structures (DQB, Figure 3). This configuration may look odd, but such solution exists in the separation industry. Forward integration proved to be uneconomical according to a previous study by Emtir et al.(1999), therefore it is not investigated.

Another version of the direct sequence (DS-HP, Figure 2) is also examined: the pressures in Col. 2 and Col.3 are higher, equivalent to those needed for backwards heat integration. Parameters are identical to those of the DQB structure (Figure 3). Apart from the conventional direct sequence structures columns with side products are also examined. One is a single column with four products (SC, Figure 4), the other one is the same single column but with a furnace and vapour feed (SC-OHV, Figure 5).

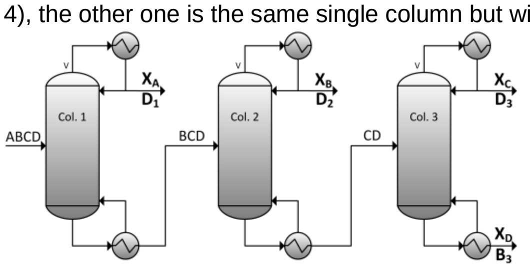

Figure 2: Conventional direct sequence (DS, DS-HP)

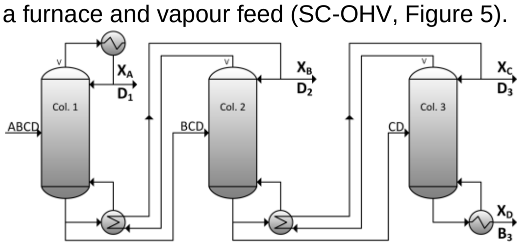

Figure 3: Direct sequence with backwards heat integration (DQB)

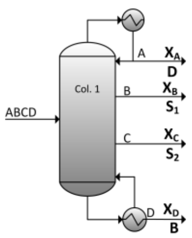

Figure 4: Single column with side products (SC)

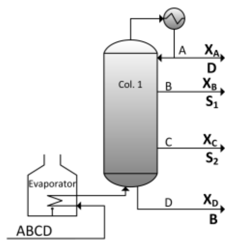

Figure 5: Single column with side products and overheated vapour inlet (SC-OHV)

For the simulations the Aspen Plus software is used. The chosen thermodynamic property is Peng-Robinson.

4. Results

In the case of the sloppy separation the results are shown in Table 2. The single column with side products (SC) and DQB have lower costs and GHG emission while have higher efficiencies than the others. SC-OHV configuration has very low efficiency, making it the most expensive solution.

In Figure 6 the same situation can be observed. DQB and SC configurations outperform the others, DQB has somewhat higher desirability. The base case (DS) has mediocre desirability. The very low desirability of SC-OHV indicates that configurations with overheated vapour should be avoided. The large difference between the desirability of DQB and DS-HP shows the advantages of heat integration in every consideration investigated in this case study.

Table 2: *Thermodynamic efficiencies, CO_2e emissions and total annual costs (sloppy case)*

	SC	SC-OHV	DS	DS-HP	DQB
Efficiency (%)	22.90	5.89	17.39	10.57	19.40
CO_2e (t/y)	539	643	725	861	495
TAC (US$/y)	1115	2184	1687	2062	1036

Table 3: Thermodynamic efficiencies, CO_2e emissions and total annual costs (sharp case)

	SC	SC-OHV	DS	DS-HP	DQB
Efficiency (%)	9.62	1.56	13.38	5.81	17.74
CO_2e (t/y)	1705	2030	1353	2161	631
TAC (US$/y)	4026	7508	3292	5489	1257

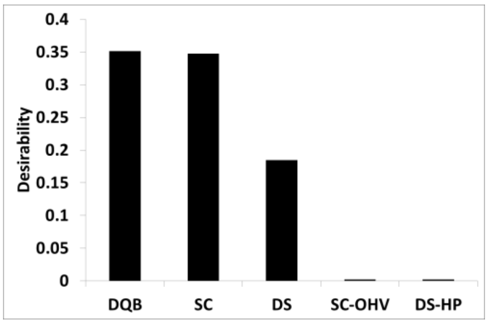

Figure 6: Desirability of distillation systems - sloppy separation

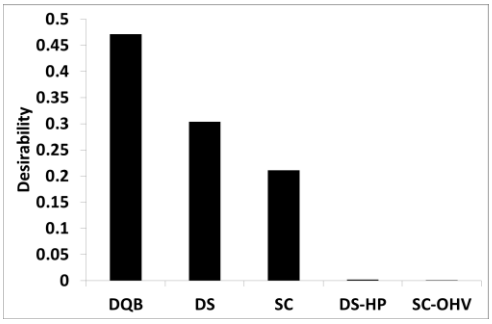

Figure 7: Desirability of distillation systems - sharp separation

In the case of sharp separation the results in Table 3 show some changes compared to the sloppy case. The performance of the single column solution declines in all considerations and shows worse properties than the DS configuration has. Figure 7 shows the desirability values of the sharp separation case. Desirability values reflect the same changes as the different properties: DQB configuration is still the most desirable system. The rising reflux ratios cause SC to be much less desirable than DQB or even DS.

5. Conclusion

In both cases DQB configuration is the most desirable configuration, which indicates that this configuration is widely applicable. Good performance of the DQB structure is in correspondence with previous studies (Emtir et al., 1999; Rév et al., 2001; Kencse and Mizsey, 2009; Kencse and Mizsey, 2010). DQB is a simple and reliable structure with good properties, its usage is recommended, especially for retrofitting, where the application of newer, complicated structures would be impossible.
Performance and desirability of SC configuration is dependent on product purity. This is caused by the difference in reflux ratios. The same additional purity improvement requires more additional reflux rate change. At lower reflux rates, however, SC can be as good choice as DQB.
Overheated vapour feed proves to be very inefficient: thermodynamic efficiency in these cases is extremely low, and costs and GHG emissions are also very high compared to alternatives. Evaporating and overheating the whole feed stream to a temperature much higher than otherwise needed consumes a lot of energy and destroys exergy immediately.
Finally, usage of exergy analysis provides useful information on configurations and is an efficient tool in the design process. Desirability function also proves to be a useful tool during the decision process,

simplifying the distinction between alternatives by providing one simple indicator. This is in correspondence with studies with ternary systems (Kencse and Mizsey, 2010). This approach can be very effective when fast, algorithmic decisions should be made.

Reference

Adiche C. Vogelpohl A. 2011. Short-cut methods for the optimal design of simple and complex distillation columns. Chemical Engineering Research and Design, 89, 1321-1332.

Douglas J. M. 1988. Conceptual Design of Chemical Processes, McGraw-Hill New York, US..

Emtir M., Rév, E., Mizsey, P. & Fonyó, Z. 1999. Comparison of integrated and coupled distillation schemes using different utility prices. Computers & Chemical Engineering, 23, Supplement, S799-S802.

Fonyó Z. 1974. Thermodynamic Analysis of Rectification - 1. Reversible Model of Rectification. International Chemical Engineering, 14, 18-27.

Gadalla, M., Jimenez, L., Olujic, Z. & Jansens, P. J. 2007. A thermo-hydraulic approach to conceptual design of an internally heat-integrated distillation column (i-HIDiC). Computers & Chemical Engineering, 31, 1346-1354.

Grossmann, I. E., Aguirre, P. A. & Barttfeld, M. 2005. Optimal synthesis of complex distillation columns using rigorous models. Computers & Chemical Engineering, 29, 1203-1215.

Harrington, E. C. 1965. The desirability function. Industrial Quality Control, 21, 494-498.

Huang, K., Shan, L., Zhu, Q. & Qian, J. 2008. A totally heat-integrated distillation column (THIDiC) - the effect of feed pre-heating by distillate. Applied Thermal Engineering, 28, 856-864.

Kencse, H., Manczinger, J., Szitkai, Z. & Mizsey, P. 2007. Retrofit design of an energy integrated distillation system. Per. Pol. Chem. Eng., 51, 11-16.

Kencse, H. & Mizsey, P. 2009. Comparative Study of Energy-Integrated Distillation Systems Based on Exergy Analysis and Greenhouse Gas Emissions. Revista De Chimie, 60, 1047-1052.

Kencse, H. & Mizsey, P. 2010. Methodology for the Design and Evaluation of Distillation Systems: Exergy Analysis, Economic Features and GHG Emissions. Aiche Journal, 56, 1776-1786.

Kiran, B., Jana, A. K. & Samanta, A. N. 2012. A novel intensified heat integration in multicomponent distillation. Energy, 41, 443-453.

Koczka, K. & Mizsey, P. 2010. New area for distillation: wastewater treatment. Periodica Polytechnica-Chemical Engineering, 54, 41-45.

Liu, X., Zhou, Y., Cong, L. & Ding, F. 2011. High-purity control of internal thermally coupled distillation columns based on nonlinear wave model. Journal of Process Control, 21, 920-926.

Rév, E., Emtir, M., Szitkai, Z., Mizsey, P. & Fonyó, Z. 2001. Energy savings of integrated and coupled distillation systems. Computers & Chemical Engineering, 25, 119-140.

Seader, J. D. & Henley, E. J. 2006. Separation Process Principles, Wiley.

Tóth, A. J., Gergely, F. & Mizsey, P. 2011. Physicochemical treatment of pharmaceutical process wastewater: distillation and membrane processes. Periodica Polytechnica-Chemical Engineering, 55, 59-67.

Wang, S.-J., Lee, C.-J., Jang, S.-S. & Shieh, S.-S. 2008a. Plant-wide design and control of acetic acid dehydration system via heterogeneous azeotropic distillation and divided wall distillation. Journal of Process Control, 18, 45-60.

Wang, X.-H., Li, Y.-G., Hu, Y.-D. & Wang, Y.-L. 2008b. Synthesis of heat-integrated complex distillation systems via Genetic Programming. Computers & Chemical Engineering, 32, 1908-1917.

Wei, H.-Y., Rokmah, A., Handogo, R. & Chien, I. L. 2011. Design and control of reactive-distillation process for the production of diethyl carbonate via two consecutive trans-esterification reactions. Journal of Process Control, 21, 1193-1207.

Zhu, F., Huang, K., Wang, S., Shan, L. & Zhu, Q. 2009. Towards further internal heat integration in design of reactive distillation columns—Part IV: Application to a high-purity ethylene glycol reactive distillation column. Chemical Engineering Science, 64, 3498-3509.