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SEPARATION OF MULTICOMPONENT MIXTURES

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Rectification is the main separation technology used for purifying the products in the chemical and petroleum industry. Development of distillation equipments and processes is important because of their vast energy needs and their incidence. Recently, systematic synthesis of separation sequences is developed significantly. This paper presents a case study of the separation of a multicomponent cracked gas. A separation system created by heuristic rules and an "optimal" structure characterized by minimal costs were compared. Rules that can be generalized based on the actual example of the separation sequence synthesis are emphasized. The separation structure developed by applying these generalized rules unambiguously depend on the thermodynamics properties of the multicomponent mixture and the specification of the products.

Keywords: separation of multicomponent, separation system synthesis, boiling point order (BPO), difference of boiling points (DBP), cracked gas.

Introduction

In the chemical industry separation systems are used to cover the purity of the products. Distillation is the most often used fluid separation technology which based on differences the volatility of components. It is common that the separation systems have more than two product. The separation tasks can be carried out with number of columns depending on the components and products number. Conventional distillation columns separate the feed stream into two products (head product, bottom product). The complex column configurations (side product, side stripper, etc.) can be decomposed into a sequence of conventional columns. Therefore the separation of a multicomponent mixture can be realized as a sequence or sequences of separation steps with two products.

The separation system synthesis is a complex problem because the number of possible system structure rises exponentially by increasing the number of products.

Several methods are known for the determination of the best separation sequence [1, 2], for example:

- algorithmic approaches involving established optimization principles (algorithmic methods),
- heuristic methods based on rules of thumb,
- evolutionary strategies wherein improvements are systematically made to an initially created separation sequence, and
- thermodynamic methods involving applications of heat cascade principles.

In some cases two or more methods are often combined in the process synthesis of distillation systems. Disadvantages of the evolutionary and algorithmic methods are that their applications requires special mathematical background and computational skills from the user. Although heuristic rules can be applied easily to narrow down the number of possible separation sequences, several heuristic rules unfortunately contradict each other, [3]. *Table 1* shows the most often used heuristic rules [4, 5, 6].

Table 1: Historical overview of the development of main heuristic rules

Heuristic rules	**Author, year**
Perform the easiest separation first	Harbert, 1957; Douglas, 1988
Perform equimolar splits (50/50)	Harbert, 1957; Heaven, 1969; King, 1971; Douglas, 1988
The heaviest separation last	Rudd, 1973; Douglas, 1988
First remove the most plentiful component	Nishimura in Hiraizumi, 1971; King, 1971; Rudd, 1971; Douglas, 1988
The cheapest separation first	Harbert, 1957; Rudd, 1973; Douglas, 1988
Perform separation with the lowest CDS [2, 7]	Nath in Mothard, 1981
Perform separation with the highest CES [2, 7]	Nadgir in Liu, 1983
Perform separation with the lowest energy index	Lien, 1983
Perform direct sequence	King, 1971
Perform sequence without non-key components	King, 1971;Gomez in Seader, 1976

Although the individual heuristic rules often contradict each other still the heuristic rules decrease the number of solutions of a multi-solution problem. Accordingly the final decision can only be made based on the detailed technical and economical analysis of the individual structures. Such planning can identify the optimal structure only from a narrower set of solutions. If the heuristic rules are appropriate, the number of possible solutions is reduced while the optimal solution still being in the set of possible solutions.

The essence of algorithmic methods is that the best separation system is selected from all the possible separation systems with the help of an objective function. Applying this method, the optimal system according to the given objective function can always be determined.

In this paper, separation structures determined by "heuristic method" and "algorithmic method" are compared. The separation system developed by heuristic method was published in our earlier work [8].

Determination of separation task

A cracked gas from an olefin plant was separated in this case study. The cleaned and cooled cracked gas consists of 36 components; the main compounds of which are methane (No. 3) ethylene (No. 4) propylene (No. 6) and n-octane (No. 12) [9].

Table 2: Products

Mark of products	Components of products	Name of products
A	1-3	Light gas fraction
B	4	Ethylene
C	5	Ethane
D	6	Propylene
E	6-8	Light C3 fraction
F	7-9	Heavy C3 fraction
G	10-16	C4 fraction
H	17-29	C5 fraction
I	30-36	Aromatic fraction

Nine products of the separation system were defined primarily based on market considerations, also taking thermodynamic possibilities into consideration. The products of the separation task are presented in *Table 2*. A product might consist of a single component, or it can be a group of components with close boiling point.

Separation system synthesis by heuristic method

So far in our research we have determined systems capable to solve the separation task [8]. Heuristic rules were applied during the determination of the separation system, emphasizing those rules that can be generalized over the given example. In order to determine the structure of the separation system, the components of the multicomponent mixture was ordered according to their boiling points at the operational pressure in the first step. This sequence is called the boiling point order (BPO). In this case, the BPO is defined at 1 bar pressure in all steps. In the following, the components are signed with their number in the BPO, the most volatile component being the first one. The "concentration and difference of boiling point (DBP)" curve of the cracked gas was also plotted *(Fig. 1)*. The DBP is the difference in the boiling points of two "neighbouring" components in the BPO. The "concentration and DBP" curve is used to determinate the thermodynamic limitations of the separation.

In the next steps, the structure of the separation system was determined by recreating the "concentration and DBP" diagram for the feed of the given separation step. The place of the separation and the key components were defined with the help of these figures. The separations were carried out with the short cut method, prescribing a 99% yield for the key components. The separation system developed with this method is presented in *Fig. 2*.

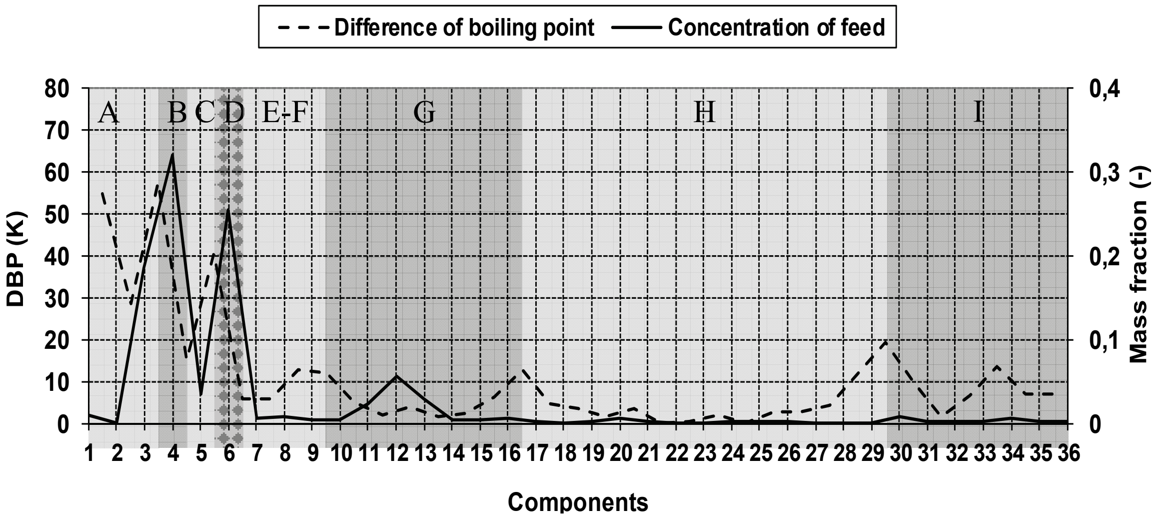

Figure 1: Concentration and DBP diagram

Experience gained during the case study is summarized by the following general rules [8]:

- Beside the application of different indicators measuring the difficulty of the separation, it is expedient to order the components of the mixture to be separated according to their boiling point and plotting concentration and DBP of the components (before all separation steps).
- The "concentration and DBP" diagram helps to define the exact definition of N pieces of product class.
- The "concentration and DBP" diagram helps to define the place of separation and the key components.
- The cut of separation should be placed at the boundary of two neighbouring products.
- The key components should be close to each other in BPO and their concentrations should be relatively high.

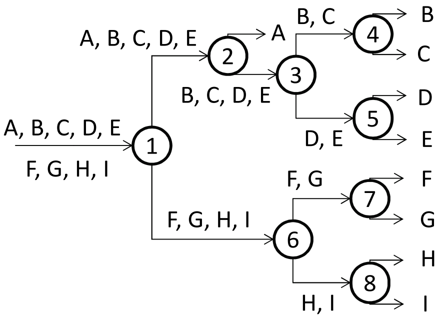

Figure 2: Structure of the separation system by heuristic rules (A3,B3)

Synthesis of the separation system by algorithmic method

In this paper, the separation system generated by the application of above heuristic rules and the optimal separation system were compared. In order to determine the structure of the optimal separation system, all possible structures were implemented and evaluated from an economical point of view.

In the case study, the separation system was created by sequencing two-product single-feed columns. The number of possible connections rises radically by increasing the number of products. For a separation with C products, the number of possible connections is given by Eq. 1, while *Table 3* illustrates the radical growth. The separation can be realized with C-1 columns. 9 products were determined in the case study, which makes the number of possible separation systems 1430.

The implementation of such an extensive simulation is time-consuming, that forced us to narrow down the number of possible connections. Therefore the first separation was taken out and considered as the first step of all the created separation systems. These are high purity separations since the key components are neighbours except in the first column.

This way the separation of the products of the first column is considered as a unique separation task. In processing the head products, one has to examine the possible variations of a 5-product separation system (products: A, B, C, D, E), while the number of bottom products is 4 (F, G, H and I). *Fig. 3* and *4* summarize these structures. The different column configurations are marked with numbers, the configurations for the head product separation are tagged with the letter "A", and the configurations for the bottom product separation are tagged with the letter "B".

The necessary calculations were performed with the AspenPlus^{TM} simulation software. The short cut method was used for the examinations, defining 99% recovery for the key components. A Microsoft Excel application was developed. It implements all the possible separation systems with the help of the Aspen Simulation Workbook, after defining the mixture to be separated, and the products. The investigations were conducted by using this application.

$$N_C = \frac{[2\cdot(C-1)]!}{C!\cdot(C-1)!} \tag{1}$$

Table 3: Number of possible connections

Number of products	2	3	4	5	6	7	8	9
Number of connections	1	2	5	14	42	132	429	1430

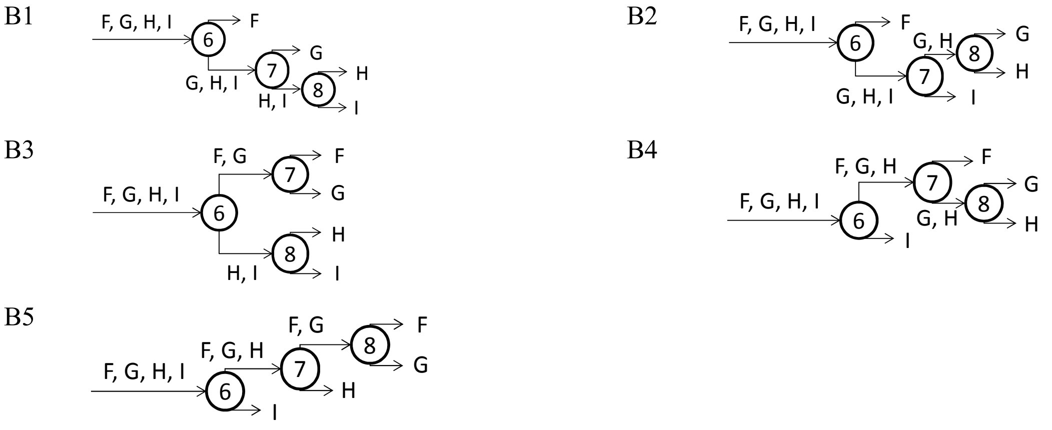

Figure 4: Possible variations of a 4-product separation system

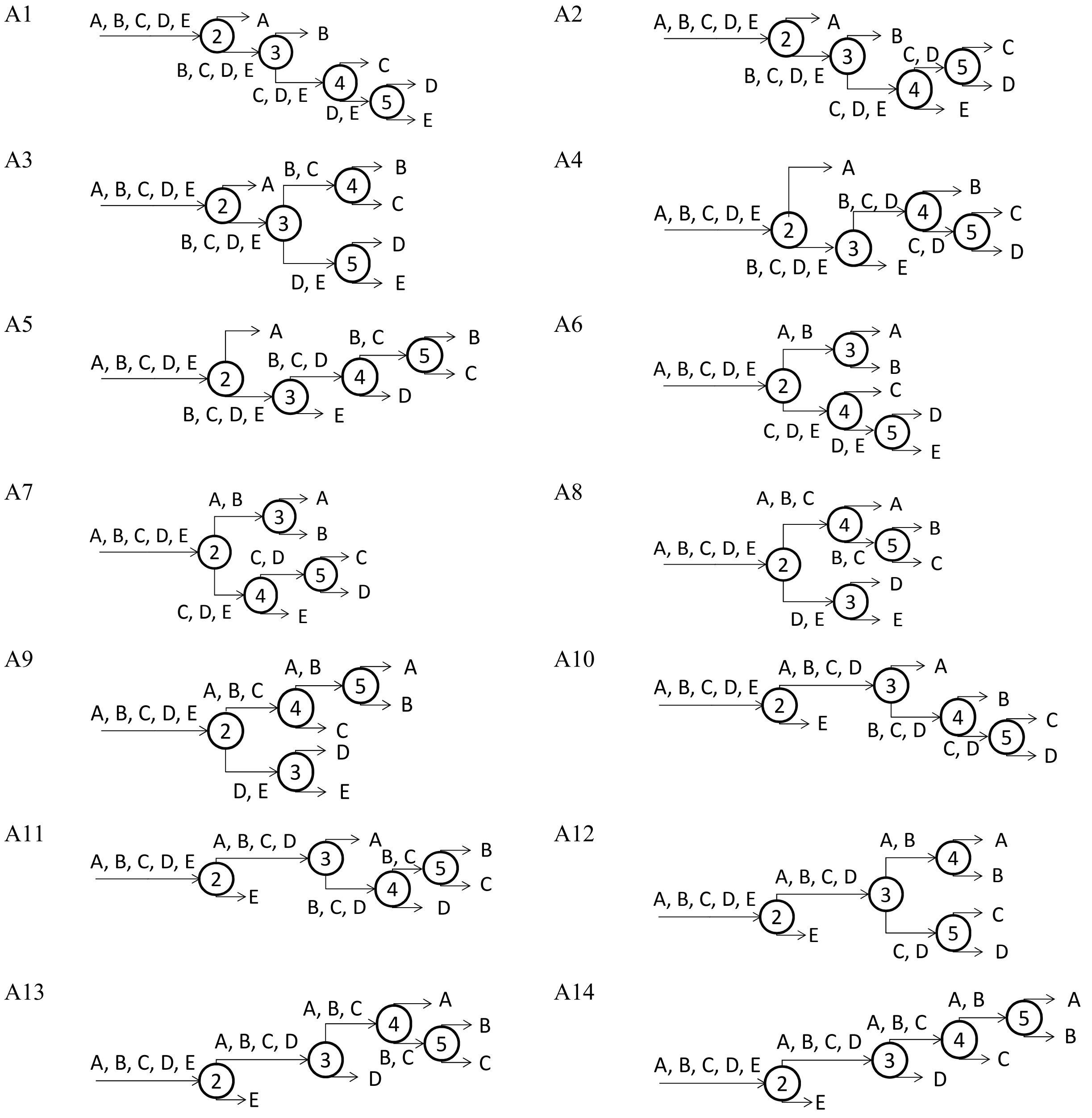

Figure 3: Possible variations of a 5-product separation system

In the case study, the different separation systems were compared with an economical objective function. The cost of the separation system was estimated by Eq. 2. The amortization time was defined over 10 years. Eq. 3 describes the investment cost [5], while Eq. 4 describes the operational cost. *Figs. 5* and *6* contain the auxiliary energy costs.

Two different cases are defined in this case study: in the first case the pressure of the separations are constant 1 bar, in second case the pressure of the separations is varies. In the second case pressure of the separation is the optimal pressure (pressure with minimal cost).

$$Csum = \frac{\sum_{i=1}^{C-1} i\ Cinv}{\tau} + \sum_{i=1}^{C-1} i\ Cop \tag{2}$$

$$\begin{aligned} Cinv^i = {} & \frac{M\&S}{323} \cdot f_1^i + C_b^i + N^i \cdot f_2^i \cdot f_3^i \cdot f_4^i + C_{p1}^i + \\ & + \frac{M\&S}{280} \cdot 328 \cdot \left(\frac{\Delta H^i{}_{reb}}{11250} \right)^{0,65} \cdot V_i^{0,65} + \\ & + \frac{M\&S}{280} \cdot 328 \cdot \left(\frac{\Delta H^i{}_{cond}}{5000} \right)^{0,65} \cdot V_i^{0,65} \end{aligned} \tag{3}$$

$$Cop^i = \Delta H^i{}_{reb} \cdot P(T)_{reb} + \Delta H^i{}_{cond} \cdot P(T)_{cond} \tag{4}$$

where C is number of products; Csum is cost of separation system; $Cinv^i$ is investment cost of column number i; Cop^i is operation cost of column number i; τ is amortization time; M&S is Marshall and Swift index; ΔH^i_{reb} is reboiler duty of column number i; ΔH^i_{cond} is condenser duty of column number i; V_i is vapor rate in the column number i; $P(T)_{reb}$ is cost of the hot utility (depend on temperature); $P(T)_{cond}$ is cost of the cold utility (depends on temperature); f^i_{1-4} factor of column number i [10]; $C_{b,\,t,\,p1}{}^i$ variable of column number i [10]; N^i number of stages of column number i.

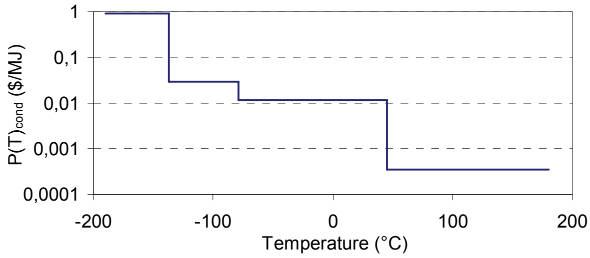

Figure 5: Cost of cold utility

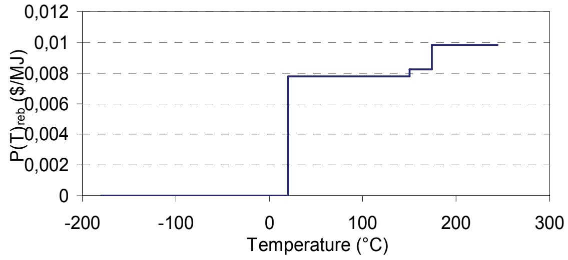

Figure 6: Cost of hot utility

Results

The given cost functions can be rendered to each structure, that makes the configurations comparable and allows determining the structure of the optimal separation system. The results show that, the costs of the separation systems in the first case are significantly higher than in the second case. *Tables 4-7* show the results. The cost order of the structures changed significantly in both cases, however the optimal structure in the process of the head product remained the same.

In the first case the results show that, in processing the bottom product, the separation system created by heuristic rules and the optimal structure are the same (B3). However, in processing the head product, the cost of the separation system created by heuristic rules (A3) is more than the cost of the optimal separation system and takes only the 12th place in the cost sequence.

In the second case the results show that, in processing the head product, the cost of the separation system created by heuristic rules takes last place in the cost sequence. In processing the bottom product, the separation system created by heuristic rules takes 2nd place in the cost sequence.

Table 4: 1st case processing the head product

Number of structure	Cost ($/h)
A14	33959
A7	33976
A12	34001
A9	34666
A6	34748
A13	35584
A8	36298
A10	50481
A11	50723
A2	65675
A1	66447
A3	**66647**
A4	67097
A5	67340

Table 5: 1st case processing the bottom product

Number of structure	Cost ($/h)
B3	**1370**
B1	1373
B2	1554
B4	1557
B5	1570

Table 6: 1st case processing the head product

Number of structure	Cost ($/h)	Pressure of splits (bar)			
		2nd	3rd	4th	5th
A14	1534	1	1	5	13
A13	1770	1	1	17	5
A12	1862	1	1	13	3
A10	1898	1	28	5	3
A11	1960	1	28	5	5
A9	2097	1	1	5	13
A2	2214	24	5	1	3
A7	2249	1	13	1	3
A4	2325	24	3	5	3
A8	2333	1	1	17	5
A5	2387	24	3	5	5
A1	2401	24	5	5	1
A6	2432	1	13	3	1
A3	**2453**	**24**	**5**	**5**	**1**

Table 7: 1st case processing the bottom product

Number of structure	Cost ($/h)	Pressure of splits (bar)		
		6th	7th	8th
B1	282	13	5	3
B3	**290**	**7**	**1**	**3**
B2	299	1	1	5
B4	303	1	1	5
B5	320	1	7	1

Conclusion

The results of the investigations can be summarized as follows:

- The results of the heuristic methods and the algorithmic methods might be the same (“bottom product”) or substantially different (“head product”). The significant difference between the results is caused by the cost of the coldest utility. The effect of the cost of the coldest utility is not taken into account any heuristic rule.
- If the cost of the hottest or the coldest utility is significantly higher, the product with maximum or minimum boiling should be recovered in the last separation step.
- The cost orders of the structures basically change if the pressure of the separations varies.
- The algorithmic methods based on economic information require many calculations but the results are reliable.
- The cost of pressure change is not considered in the case study: taking into account this cost the cost order is supposed to change.

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