

EXTRACTIVE DISTILLATION IN THERMALLY COUPLED COMPLEX COLUMNS: CURRENT STATE AND PERSPECTIVES

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Abstract

The current state and perspectives of extractive distillation in thermally coupled complex columns are discussed. Examples are described the separation of various azeotropic mixtures by extractive distillation in such installations. The energy efficiency is analyzed of complex extractive distillation columns. Examples of industrial application of the process are considered.

Key words: complex column, extractive distillation, energy efficiency

Distillation is the most widely used method to separate different industrial mixtures into pure components. It is a thermodynamically irreversible process, and its energy consumption and entropy production depend on the path of the process, i.e. on the order of the fraction separations. This method has unfortunately been very energy intensive and requires a lot of heat. The problem of distillation energy consumption reduction may be solved by the use of contemporary mass-exchange devices and by using a thermodynamically reversible process (Olujic et al., 2009). These principles have been widely used for the distillation of nonazeotropic mixtures in industrial dividing wall columns (DWC) arranged as Petlyuk (Petlyuk et. al., 1965) or Kaibel (Kaibel et al., 1987, 2004; Kolbe and Wenzel S., 2004) complex columns. Another way to increase the thermodynamic efficiency of distillation is to use partially thermally coupled distillation systems (PTCDS). Common approaches to the synthesis of technological schemes of this class have been proposed by Timoshenko et al. (2001). Several authors have developed other approaches to the synthesis of distillation flowsheets with partially thermally coupled flows (Rong et al. 2003, 2004; Errico et al., 2009; Caballero and Grossman I.E., 2014). PTCDS may also be designed as dividing wall columns.

Extractive distillation (ED) is the method for azeotropic and similar boiling mixture separations. It is an example of the realization of a fundamental principle of the concentration field redistributions between distillation regions (Serafimov and Frolkova, 1997). ED is occurred by introducing an additional component, the so-called entrainer, as an independent additional feed into the column to facilitate a separation. An entrainer should desirable alter the relative volatility of the initial mixture azeotropic components. Extractive distillation is used in the industry for the separation of hydrocarbons with similar boiling points (Liao et al., 2001; Lei et al., 2002; Wentink et al., 2007), the recovery of aromas or fragrances (Berg, 1983; Pollien et al., 1998; Chaintreau, 2001; Chen et al., 2003; Ghaee et al., 2008), the separation of aqueous alcohol solutions (Meirelles et al., 1992; Pinto et al., 2000; Zhigang et al., 2002; Arifin and Chien, 2008; Li and Bai, 2012), the separation of ether and alcohol mixtures (Muñoz et al., 2006; Wang et al., 2010) and the separation of methylal and methanol mixtures (Wang et al., 2012).

The conventional extractive distillation (CED) flowsheet for the separation of binary mixture (Figure 1a) includes extractive column (EC) and entrainer recovery column (RC). The mixture A–B and entrainer E are fed into extractive column. The presence of entrainer alters the relative volatility between A and B components, causing A to move to the top and B toward the bottom of the EC. The extractive column bottom's stream is fed into recovery column to produce almost pure B component as the distillate and almost pure entrainer as the bottom product. Despite the fact that extractive distillation is considered one of the most efficient methods of azeotropic mixtures separation it is characterized as well as conventional distillation by high specific energy consumption. Thus power consumption reduction of ED is the urgent task of the chemical technology.

The traditional ways for energy saving in the ED (Anokhina, 2013) are the search for high-selective entrainers (Xu and Wang, 2006; Kossack et al., 2008), the determination of the unit's optimal

operating parameters (Arifin and Chien, 2008; Muñoz et al., 2006; Wang et al., 2010, 2012; Luyben, 2005, 2008; Xu and Wang, 2006; Kossack et al., 2008; You et al., 2015). Since the distillation is a thermodynamically irreversible process, its effectiveness depends on the way. This way fully corresponds to the residue curve, which is a one-dimensional set of compositions. On the other hand, the flowsheet graph is also one-dimensional set, which corresponds to the residue curve. Thus, the distillation flowsheet is the reflection of the distillation way on the distillation sequence manifold, and another way to decrease an energy consumption is the definition of the optimal distillation sequence (Li and Bai, 2012; Manan and Banares-Alcantara, 2001; Ivanova et al., 2005, 2006; Hernández, 2008; Benyounes and Frolkova, 2010; Errico et al., 2013a).

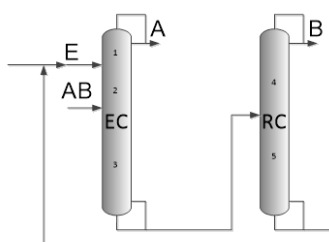


Figure 1. Conventional ED flowsheet, A, B – components of initial feed, E– entrainer, EC – extractive distillation column, RC – entrainer recovery column, 1–5 – column's sections

Recently, the systems with partially thermally coupled distillation columns (PTCDS) have been applied to reduce the energy consumption of extractive distillation. We have developed the algorithm of the extractive distillation flowsheet generation, including PTCDS (Timoshenko et al., 2005, 2007). It is based on the graph algorithm synthesis of the flowsheet which include PTCDC subsystems for zeotropic mixtures distillation (Timoshenko and Serafimov, 2001; Timoshenko et al., 2001). This algorithm can be also applied to the generation of ED sequences with PTCDC for the separation of binary and multicomponent azeotropic mixtures (Timoshenko et al., 2005; Timoshenko et al., 2007). The flowsheet in Figure 1 can be represented in accordance with this algorithm as a graph of Figure 2a. Vertices in the graph correspond to the intersections separating sections of the columns and edges to the flows of vapor and liquid within the column and the streams linking the columns. The merger of the two vertices connected by orienting edge BE of the graph (Figure 2a) gives a graph (Figure 2b) that corresponds to a complex column with a side rectifier (Figure 1b). The algorithm can be applied to the synthesis of ED sequences with PTCDS of multicomponent azeotropic mixture separation.

The first publications began in the early 2000s about the ED sequences with PTCDS application. Somewhat earlier extractive distillation of ethanol-water with ethylene glycol (EG) was examined in a one complex column with side selection, where the ethanol was isolated as a distillate, EG as a bottom stream, and water was removed as a side stream in the vapor phase (Brito et al., 1997) (Fig. 1d).

It has been shown that the energy consumption of such column is 9% lower compared to the classical two-column ED flowsheet, but the quality of the products decreases (ethanol - from 99.94 to 99.71 mol%, water - from 99.7 to 99.27 mol%.) (Brito et al., 1997). It is clear, because it is almost impossible to remove completely EG from the side stream. This problem can be solved by applying a side section. Such arrangement of ethanol-water mixture ED has been proposed in (Anokhina et al. 2012). It gave an ability to obtain the product streams of the same quality as in the two-column scheme considered in (Brito et al., 1997). The power consumption of the ED sequence with PTCDS (PTCED) is 20.1% less than in the reboiler of the complex column with a side stream which has been discussed by Brito et al. (1997) under the same amounts and compositions of the initial feed, the products and the specific consumption of EG (Anokhina et al. 2012). Such arrangement of the distillation sequence can be applied to separate the other mixtures. For example, the PTCED of

acetone-chloroform mixture with dimethylformamide decrease energy consumption in comparing with conventional ED on 28.8% (Timoshenko et al., 2003).

The complex column with the side section have been proposed to use for 1,3-butadiene isolation from the products of the C4 hydrocarbon fraction dehydration, which consists of butanes, butane-1, 1,3-butadiene, and vinylacetylene (Lei, Z. et al., 2002). The tradition two-stage separation sequence is presented in the Figure 3a.

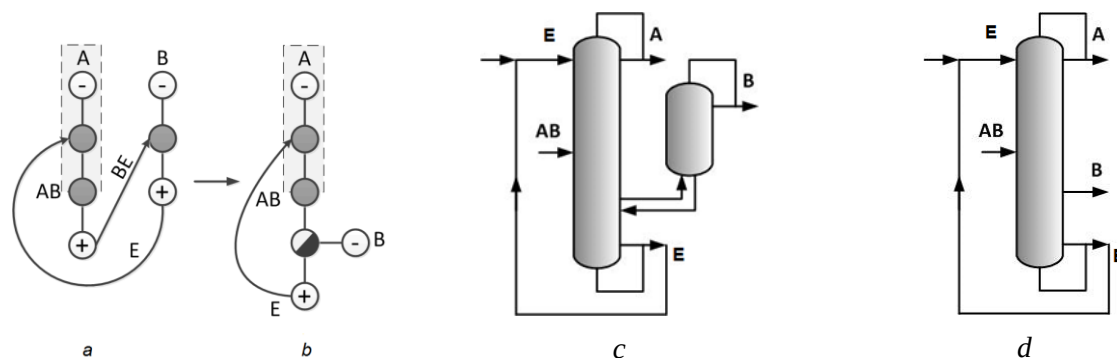


Figure 2. Graphs of flowsheet (see Figure 1) preimage (a), images (b) of the ED with heavy boiling entrainer; ●— feed (input), ⊖— output (exit) with removing heat, ⊕— output (exit) with heat input, ⊙— vertex without properties of input or output, ED system with the partially coupled heat and material flows (c), ED system with side flow of component B, A,B – components of initial feed, E – entrainer.

It has been proposed to eliminate the recovery column (2), because the entrainer is used in the second stage of the process in the column (3). Thus, Lei et al., (2002) consider that it is not useful to separate it from the bottom product of the first extractive column and to expend energy on the evaporation and condensation of 1,3-butadiene. In the scheme in Figure 3b, butane-butylene fraction is isolated in the distillate of the extractive column (1), 1,3-butadiene in the distillate of the extractive column (2), which is "thermally" coupled by SL_1 and SL_2 flows with the side section (3), where the top product is vinylacetylene. Acetonitrile is separated as the bottom product of the column (2) and then it is used after cooling as the entrainer in the (1) and (2) columns (Figure 3b). However, it leads to a considerable increasing of the liquid flow at the bottom of the column (2), the mass transfer devices performance degradation, and lowers the productivity of 1,3-butadiene. To solve this problem, the authors proposed not to return liquid flow from the side section to the main column and send it to recycle, because this flow mainly consists of acetonitrile (Figure 3c). There is no thermally coupled apparatus in the flowsheet (Figure 3c) and it leads to the simplification of the set control. The energy consumption of the schemes 3b and 3c is approximately 17% less than 3a. Another 1,3-butadiene purification process was developed by BASF SE according to information given by Omer et al., (2012), Jobson, (2005), Heida et al. (2002).

Another well-known example of the extractive distillation industrial application is the separation of aromatics from fractions of steam or fluid catalytic cracking. Traditional scheme is shown in Figure 1. Uhde has offered to carry out this process in PTCED which is arranged as DWC (Figure 4). Aromatic hydrocarbons are extracted from the initial feed in the second layer of the packing, where N-methylmorpholine is used as entrainer. It is important, that the right side of the column is divided by a horizontal baffle plate which isolates the section 4 from the top liquid stream. Regenerated entrainer transmits the heat previously in the circulation heat exchanger and then it is cooled additionally and directed to the top of column.

This DWC technology named Morphylane process can be used for the recovery of benzene, toluene or xylenes from various feed stocks (Diehl et al., 2005, Kolbe and Wenzel, 2004). The integrated column

solution (Fig. 4) was applied in 2004 at the Arsol Aromatics GmbH (formerly Aral Aromatics) in Gelsenkirchen, with a feed capacity of 28000 mt/year (Uhde, 2011).

DWC arrangement for PTCED can be used for the separation of different type of azeotropic mixtures. The most attractive currently is the process of bioethanol dehydration. Kiss and Suszwalak (2012) and Kiss and Ignat (2012) propose to save energy by implementation of the DWC arrangement of PTCED for bioethanol dehydration by ED with ethylene glycol. Kiss and Suszwalak (2012) compared conventional two-column ED flowsheet (Fig. 1) and extractive DWC (Fig. 5a, ethanol denotes as A, water denotes as B, ethylene glycol denotes as E) in term of energy consumption in the boilers. Ethanol concentration in the feed stream is near to azeotropic composition (93.5 % mass). Calculated energy consumption decreasing by DWC in ED implementation is about 10 %.

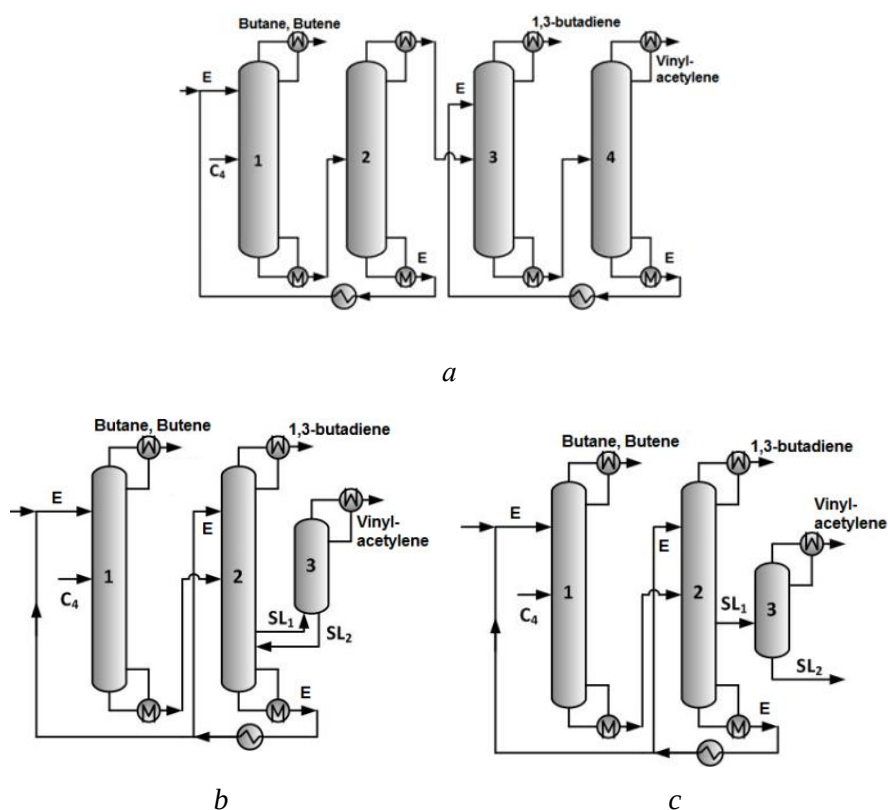


Figure 3. Different schemes for 1,3-butadiene isolation from the products of the C₄ hydrocarbon fraction dehydration by ED with acetonitrile (Lei et al., 2002)

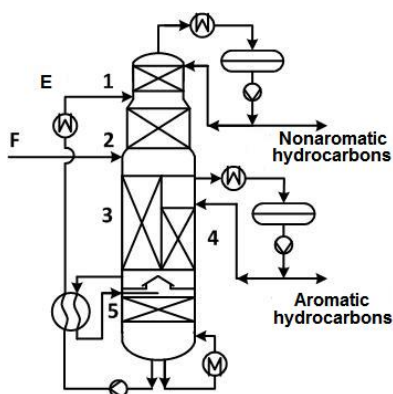


Figure 4. Process Morphylane of Uhde company (Uhde, 2011)

Kiss and Ignat (2012) compared separation sequences consist of three distillation columns: pre-concentrator of ethanol, ED column and entrainer recovery column, and DWC that combines these distillation units into just one column (Fig. 5b). Feed stream with ethanol concentration (10 % mass) was obtained by fermentation. The calculation shows that the application of DWC leads to significant overall energy savings up to 17%, and a similar reduction of the total investment and the total annual costs.

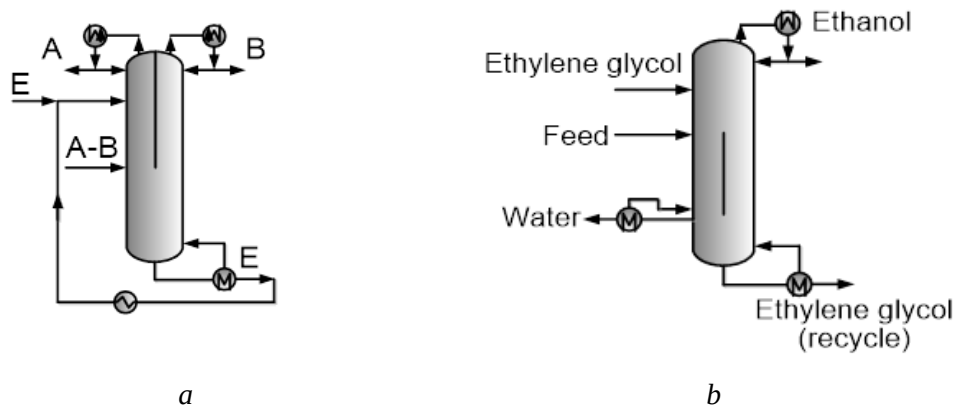


Figure 5. Extractive dividing-wall column obtained by combining of two columns (a) and obtained by combining of three columns (b) into just one distillation unit

Xia et al. (2012) compared conventional two-column ED flowsheet (Fig. 1) and extractive DWC (Fig. 5a) on the example of ED of methylal-methanol mixture with dimethyl formamide. In Fig. 5a methylal denotes as A, methanol denotes as B, dimethyl formamide denotes as E. It was calculated that about 8.3% savings in energy consumption in the boilers, about 17.7% reduction in capital investment cost and 5.8% savings in total annual cost could be obtained by using DWC compared with the two-column ED flowsheet.

In some cases, PTCED decreases the energy consumption in the column boilers up to 20–30% compared to the conventional ED flowsheets (Timoshenko et al., 2003; Anokhina et al., 2008, 2009; Gutiérrez-Guerra et al., 2009). From the other hand, there are examples where there is no significant decreasing of the energy consumption, for instance, the applying of PTCED instead of the traditional sequence leads to the decreasing of energy consumption only about 2.7-2.4%. This problem was investigated in (Anokhina and Timoshenko, 2015) and it was found that that PTCED effectiveness depends on the value of the reflux ratio in entrainer recovery column of the conventional ED flowsheet. If the reflux ratio in that apparatus will have small value, then energy consumption decreases due to using PTCED will be insignificant. It is evident that reduction of energy consumption is not directly proportional to reducing of the reflux ratio in entrainer recovery column. However, if to estimate as a significant reduction in energy consumption at a level equal to or greater than 10%, it can be stated that it is observed at this parameter value close or equal to 1. Thus the criterion for evaluation of PTCED energy efficiency for binary mixture separations can be formulated as follows: PTCED is useful if the reflux ratio of the entrainer recovery column has value equal to or greater than 1.

Thus, the process of extractive distillation in thermally coupled complex columns has gone from a purely theoretical concept to a practical application in industry. Now we have two well-established industrial process for the isolation of aromatic and purification 1,3-butadiene. Due to environmental concerns and the need to reduce greenhouse gas emissions, the researchers directed their attention to the processes of dehydration of ethanol obtained from vegetable raw materials. However, it is quite difficult to obtain significant savings in energy consumption in that process. The explanation of this fact is shown by Anokhina and Timoshenko (2015). It is associated with a high volatility of water relative to entrainer and correspondingly low reflux ratio in the regeneration column. This suggests,

that by very hard boiling entrainer using, such as sulfolane, good power consumption reducing should not be expected due to the use of thermally coupled columns.

Another trend is developing in the scope of PTCED is the controllability analysis of such systems. To date, there are no specific recommendations. Research in this area should continue to develop criteria that allow evaluating the efficiency of the initial design of technological solutions. The further development of these processes lies in the direction the DWC application, a detailed study of controllability, and identification of the objects (mixtures and entrainers) for which they will bring significant economic effect.

Also, the questions are practically not studied using complex columns with the coupled heat and material flows, especially DWC, for the extractive distillation of multicomponent azeotropic mixtures.

In general, actively developing direction on the use of heat integration in the process of extractive distillation, allowed creating fundamentally new technological solutions for the industry of organic compounds and petrochemicals just in 15-20 years. The stereotype has been overcome of the bad controllability of the distillation systems with the coupled heat and material flows. Industrial systems with high capacity have been created.

Work was carried out according to the state task of the Russian Ministry of Education and Science # 10.99.2014/K.

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