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Research Progress on Azeotropic Distillation Technology

Ying Guo[1*], **Lei Wang**[2]

[1]College of Mechanical and Electrical Engineering, Qingdao University of Science and Technology, Qingdao, China
[2]Qingdao Tianhuichen Science and Technology Co., Ltd., Qingdao, China
Email: *976049390@qq.com

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Abstract

Azeotropic distillation is a special distillation method for separating liquid mixtures, which has better distillation effect and obvious advantages of energy saving and consumption reduction compared with traditional distillation. In this paper, the latest research progress of azeotropic distillation technology in separation, synthesis and energy saving at home and abroad is reviewed. The research progress in separation is reflected in product separation and product purification, and the research progress in energy saving is reflected in heat pump distillation and dividing wall column distillation respectively. Existing studies have shown that azeotropic distillation technology can produce higher purity target products than conventional distillation for the separation and purification of azeotropic or near-boiling compounds. Heat pump distillation and dividing wall column distillation are used in azeotropic distillation field, resulting in obvious energy-saving effect for distillation equipment. The follow-up research direction of new separation technology with the goal of reducing energy consumption and exploring new materials as entraining agents should be studied in detail, which provides certain guidance for the development of distillation technology in China's chemical industry.

Keywords

Azeotropic Distillation, Azeotropic Agent, Heat Pump, Dividing Wall Column, Energy Conservation

1. Introduction

With the development and progress of social science technology, the development and application of new technology in China are more and more. Especially, great breakthroughs have been made in the research and development of petrochemical technology, which promotes the sustainable development of petrochemical industry. Although the petrochemical industry has been unprecedented development, there are still some problems in the production of petrochemical industry in China at present, such as high energy consumption and low output [1] [2] [3] [4]. Azeotropic distillation technology can solve the problem that conventional distillation technology is difficult to separate azeotropes or near-boiling substances to obtain high concentration target components [5] [6]. It has been widely concerned and studied by scholars at home and abroad because of its advantages of simple process, high purification rate, large production capacity, recyclable azeotrope, less investment and maintenance costs.

Azeotropic distillation is a method for separating liquid mixtures and is widely used in industries such as chemical industry and oil refining. When the two components to be separated are azeotropic solution system or their volatility is very close, it is difficult to achieve the separation purpose by ordinary distillation method or the number of theoretical plates required is very large, and the reflux ratio is also large, which makes the equipment cost and operation cost too high and uneconomical. At this time, azeotropic distillation can be used. Azeotropic distillation is the addition of a third component to azeotropic solution, which can form azeotrope with one or more components in the original solution, and the volatility of the new azeotrope is significantly higher or lower than that of the original components. The content of each component in the new azeotrope is different from that of the raw material solution, and the common concentrate can be used. According to whether the entrainer can form two liquid phases with one or several components in the system to be separated, azeotropic distillation can be divided into homogeneous azeotropic distillation and heterogeneous azeotropic distillation. The third component (azeotropic agent) is added to the heterogeneous azeotropic distillation to form two liquid phases with the original components, which are layered by a phase separator to azeotrope and target components [7] [8]. The separation is carried out and the recovered azeotrope can be recycled. Homogeneous azeotropic distillation is commonly used for the separation of binary azeotropes by adding an entrainer to alter the properties of the original mixture and then separating the ternary systems. Multi-component azeotropes are refluxed into the column, and the amount and energy consumption of azeotropes are higher for homogeneous azeotropic distillation. The heterogeneous azeotropic distillation has been widely used in industrial production with the advantages of easy separation of the entrainer and the target product, simple operation, low energy consumption, low cost and strong versatility. Liu Wei *et al.* [9] used heterogeneous azeotropic distillation technology to separate furfural-water system. The results showed that the concentration of furfural products obtained by heterogeneous azeotropic distillation was higher, and the equipment investment and energy consumption cost were reduced compared with conventional furfural-water distillation process.

In this paper, the latest research progress of azeotropic distillation technology is reviewed. The research progress of azeotropic distillation technology in separation, synthesis and energy saving are described in detail. Among them, the research on separation application is divided into two aspects of product separation and product purification. The research on energy conservation is divided into heat pump distillation and dividing wall column distillation technology. Finally, the application of azeotropic distillation technology in chemical industry is summarized and prospected, which provides theoretical basis for the research and application of azeotropic distillation technology in chemical industry.

2. Separation Application

2.1. Product Separation

In recent years, most studies have focused on the optimization of distillation separation process. Yan *et al.* [10] studied the separation process of allyl alcohol-water system. It was found that the mass fraction of allyl alcohol obtained by azeotropic distillation was over 99.9%. Fan *et al.* [11] simulated the azeotropic distillation process of tert-butanol-water, and studied the operation parameters which affected the azeotropic distillation effect, obtaining tert-butanol products with high purity. The research on the improvement of conventional rectification by adopting azeotropic rectification technology is numerous, and the development of low energy consumption, low cost and high efficiency is carried out under the premise of ensuring the purity requirements of products.

The selection of azeotropic agent is one of the key steps in the process of azeotropic distillation separation, and the selection of appropriate azeotropic agent has become a focus of attention. Wang *et al.* [12] used heterogeneous azeotropic distillation technology to dehydrate acetic acid, and carried out the screening of azeotropic agents. Comprehensive comparative analysis showed that p-xylene was the best azeotropic agent in the process. Devi *et al.* [13] used n-propyl acetate as an entrainer to separate the n-propanol-water mixture. It was found that the entrainer can destroy the effective azeotropy of n-propanol-water, facilitating the separation of subsequent products and reducing energy consumption.

With the application of azeotropic distillation technology more and more widely, it is particularly important to develop new azeotropic agents. With the characteristics of non-volatility, non-flammability, high chemistry, environmental friendliness and thermal stability, ionic liquids have become the most potential azeotropic agents. Boli *et al.* [14] studied the effect of ionic liquids on the azeotropic mixture of isopropanol and water. It was found that ionic liquids could break the azeotropic state and increase the relative volatility of the isopropanol-water system. The isopropyl alcohol and water were effectively separated, and a high-purity isopropyl alcohol product was obtained. Zhang *et al.* [15] used imidazole-based ionic liquids as azeotropic reagents to separate azeotropic mixture of acetonitrile and methanol. The results showed that the ionic liquids could produce obvious salting-out effect and significantly improve the relative volatility of acetonitrile to methanol.

2.2. Product Purification

Azeotropic distillation is also used in the process of product purification, which has obvious advantages, such as the purification of acetic acid, pyridine and other common substances. In addition, it is also used in the purification of allyl alcohol, butenal and tetrahydrofuran solvents.

For acetic acid purification process, Li *et al.* [16] used azeotropic distillation to purify acetic acid mixture, and finally obtained acetic acid with a mass fraction of 99.5%. Tang *et al.* [17] proposed a "new" acetic acid purification process, in which part of the condensation unit was set between the top of the dehydration tower and the phase separator to avoid excessive accumulation of azeotropes in the dehydration tower. The results showed that the new process could significantly reduced energy consumption and increased the concentration of acetic acid products. Wang [18] simulated the acetic acid-water system with p-xylene as the entrainer, and proposed an optimization scheme based on this, and achieved remarkable results.

For the purification process of pyridine products, Yang *et al.* [19] used homogeneous azeotropic distillation to purify pyridine. Aspen Plus software was used to simulate and verify the simulation results through experiments to obtain pyridine with a mass fraction of 99.85%. Bai *et al.* [20] used n-hexane as azeotrope to purify pyridine products. The effects of tray number, feed position and reflux ratio on the product quality concentration were studied and it was found that the pyridine mass fraction after azeotropic distillation separation could reach 99.98%.

Xiong *et al.* [21] proposed an azeotropic distillation process of allyl alcohol-water. The simulation results showed that the purity of allyl alcohol could reach more than 99.88%, and the product recovery rate could reach 99.99%. Li *et al.* [22] used azeotropic distillation to purify butenal which purity reached 99.0%. Hong *et al.* [23] purified tetrahydrofuran by two-tower pressure swing azeotropic distillation technology. On the premise of meeting the separation requirements of azeotrope, high-quality tetrahydrofuran could be obtained in high-pressure tower kettle.

The application of azeotropic distillation technology in the field of product purification is increasing. It is still a difficult problem in azeotropic distillation technology that how to make the best process plan under the condition of low energy consumption and high efficiency. The optimum technological scheme has been found for some systems. However, for the purification of a large part of other systems, whether the appropriate azeotropic distillation technology can be used and whether the appropriate azeotropic agent can be found to optimize the purity and economy of products still need further study.

3. Application of Synthesis

Although azeotropic distillation has a relatively short history, azeotropic distillation technology can achieve higher demanding target products under low energy consumption and high efficiency compared with conventional rectification. Therefore, the theoretical and experimental research of azeotropic distillation technology in the field of product synthesis has never been interrupted, and has been continuously promoted and applied in the industry.

The key of azeotropic distillation technology lies not only in the selection and amount of azeotropic agent, but also in the distillation time in the field of product synthesis. Yue *et al.* [24] used cyclohexane as an azeotropic agent to prepare anhydrous ethanol by batch azeotropic distillation, and analyzed various parameters affecting the rectification effect. The experimental results showed that when the amount of the entrainer was kept at a certain ratio and the distillation time was constant, the mass concentration of the synthesized water ethanol was 99.88%.

Yang *et al.* [25] synthesized C8 fraction by azeotropic distillation, and investigated the effects of various process conditions on the mass concentration of C8 fraction. The high purity C8 fraction was obtained with optimum operating conditions.

The azeotropic distillation technology not only can obtain high-purity target products, but also has the advantages of improving the utilization rate of raw materials, saving raw materials, speeding up the reaction, and easy control of the process. Wei *et al.* [26] established a new esterification reaction experimental device with azeotropic distillation to synthesize isoamyl acetate products. The results showed that azeotropic distillation could greatly shorten the reaction time and increase the reaction conversion by 2.7% compared with ordinary distillation and water separation esterification unit. Li *et al.* [27] put forward a new process of synthesizing glycerol carbonate by coupling reaction and azeotropic distillation. The bench test of the new process was carried out and high yield glycerol carbonate products were obtained. A new azeotropic distillation device was designed by Tuo *et al.* [28] to synthesize ethyl lactate, and the effects of reaction time and other parameters on the synthesis rate of ethyl lactate were explored. The results showed that the new azeotropic distillation water separator had the advantages of fast reaction speed and high conversion of ethyl lactate.

4. Research on Energy Conservation

Various energy-saving technologies have been proposed due to traditional rectification has the problems of low thermal efficiency and high energy consumption. Studies have shown that the energy-saving effect of applying heat pump distillation technology and dividing wall distillation technology to azeotropic distillation technology is remarkable [29] [30] [31].

4.1. Heat Pump Distillation Technology

The application of split heat pump rectification, steam recompression heat pump rectification and self-entrained heat pump rectification in azeotropic distillation technology is introduced based on the different types of heat pumps.

Li *et al.* [32] and other researches showed that the energy-saving effect of the split heat pump azeotropic distillation was more obvious than that of the conventional rectification. The economic benefit of using the split heat pump azeotropic distillation was better. Chen *et al.* [33] applied the steam recompression heat pump technology to the heterogeneous azeotropic distillation process and calculated and compared it with the traditional heterogeneous azeotropic distillation process. The results showed that the heterogeneous azeotropic distillation process based on steam recompression heat pump technology could greatly reduce energy consumption. Lu *et al.* [34] used heat pump self-entrainment azeotropic distillation process to separate ethanol-toluene-water azeotropic system. The ethanol content obtained by this process was over 99.9%, and energy waste was reduced to a certain extent. Kiss *et al.* [35] focused on the selection of high-efficiency and energy-saving distillation technology for heat pump technology, and proposed that the most promising technologies currently used in azeotropic distillation were steam recompression heat pump distillation and multi-effect distillation.

On the premise of meeting separation requirements, factors such as energy cost and equipment investment cost should be fully considered, and the economic rationality should be evaluated comprehensively when choosing distillation scheme. At the same time, higher requirements are placed on the operation and design of the rectification system. For example, it is necessary to adjust the circulation flow rate of the heat pump and increase the necessary control measures in order to control the rectification process in time and accurately. Heat pump distillation is widely used in chemical industry, but the distillation technology combined with heat pump distillation and azeotropic distillation has not been widely used in chemical industry. How to combine distillation methods to achieve optimal economic performance is the next development direction.

4.2. Dividing Wall Column Distillation Technology

Next-wall tower technology is a distillation technology with remarkable energy saving effect. Its successful application in multi-system separation proves its great potential in reducing energy consumption and equipment investment. In recent years, the application of the dividing wall technology in special rectification systems has increased in order to minimize energy consumption, such as the azeotropic distillation field [36].

For the binary system, Wang *et al.* [37] applied the dividing wall column to the n-propanol dehydration azeotropic distillation process, and obtained high-purity n-propanol products, which reduced the equipment cost by 52.52% and the annual operating cost savings by 70.33%, the total annual cost decreased by 65.02%. Meng *et al.* [38] designed a conventional two-tower process and a dividing wall process for the separation of methyl methacrylate crude monomer. The overall annual cost was used as the target equation for global economic optimization. The results show that the energy consumption of the next-wall column process is 43.5% and the total annual cost of the process is 22.3% less than that of the conventional two-tower process under the same separation conditions. The azeotropic distillation of the next-wall column process has more obvious advantages in energy saving and cost compared with the conventional two-tower process.

For the ternary system, Quang-Khoa *et al.* [39] designed a heterogeneous azeotropic distillation scheme for water, acetic acid and organic components using the Petlyuk dividing wall column, and found that compared with the original scheme, the scheme saves energy consumption. 20%. Ma *et al.* [40] used an adjacent tower to separate toluene-xylene-heavy benzene ternary system, and saved about 41.5% of energy consumption. The above research showed that the application of the next tower to azeotropic distillation technology could greatly reduce energy consumption, and the energy saving effect was very obvious.

For the Quaternary system, Fang *et al.* [41] studied the separation of methanol, ethanol, n-propanol and n-butanol mixture, and established the azeotropic distillation separation process of Kaibel partition distillation column. The results showed that Kaibel neighbouring distillation column could effectively reduce the backmixing degree of intermediate ethanol and n-propanol, and could achieve energy-saving effect of 35.65%.

The application of the dividing wall column in azeotropic distillation technology is becoming more and more extensive. How to combine the dividing wall column with azeotropic distillation technology to obtain greater economic benefits is still one of the important research directions.

5. Conclusions

In this paper, the latest research results of azeotropic distillation technology in separation, synthesis and energy saving are reviewed, especially in product separation and product purification, heat pump distillation technology and wall column distillation technology in energy saving field. Generally speaking, azeotropic distillation technology is developing towards low energy consumption, low cost and clean separation under the premise of meeting production requirements. It has great potential in chemical industry and is one of the main technologies to reduce distillation energy consumption. Although azeotropic distillation technology has made great progress, there are still many problems to be solved urgently. Therefore, azeotropic distillation technology research should focus on the following work in the future.

1) The operation process of azeotropic distillation is relatively high, and the choice of azeotropic agent has a great influence on the azeotropic distillation process, which not only affects the quality purity of the product, but also causes certain environmental pollution if it is improperly handled in the process. For the separation system, the most suitable azeotropic agent should be selected to obtain better distillation effect. At the same time, the most advanced technology and materials in modern science and technology should be constantly explored and found, and applied to azeotropic distillation process, such as the selection of appropriate ionic liquids as azeotropic agent, and ionic liquids as a green ring.

Protecting new materials plays an active and important role in promoting the development of green chemical industry.

2) Azeotropic distillation technology can reduce energy consumption to a certain extent, but the results are still not ideal. It is particularly important to find new separation methods and to reform existing processes so as to improve the economic and environmental benefits of some traditional processes. Therefore, reducing energy consumption is still one of the important directions of azeotropic distillation technology development.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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