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Applications of Hybrid Process of Distillation-Pervapouration in Chemical Industry

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The hybrid process of distillation-pervapouration as well as its current and forthcoming applications in chemical industry are introduced. Emphasis is given to economic potential analysis through costs comparison between pervapouration-based hybrid processes and traditional separation processes. Finally, the performance in pervapouration techniques is discussed and available solutions together with some optimization processes are summarized, which can be served as a reference for the further development of this technology.

Key Words: Pervapouration, Distillation, Hybrid process, Process optimization.

INTRODUCTION

Pervapouration (PV) is a new kind of membrane separation process in which all components are adsorbed onto the membrane selectively and then desorbed at different rate, in this way, one or more components are removed[1]. Pervapouration has clear advantages over traditional distillation technology: (1) High efficiency and good separation can be reached within one stage. (2) Low energy consumption as compared to azeotropic distillation. (3) Simple and easy to operate together with fewer attached treatment. (4) Without introduction of other/toxic chemicals. (5) Easy to scale-up and couple with other processes[2].

Pervapouration technology has been applied successfully in a great deal of industrial production at present. In most cases, it is not used as a single process but combined with other techniques, for example, a common distillation column or a chemical reactor, in a so-called hybrid process, giving full play to its advantages and improving the process's economy. Up to now, two processes have received most attention and been applied most successfully, namely pervapouration-based hybrid process with distillation and with chemical reaction[3,4], respectively.

In this study, pervapouration-distillation hybrid process as well as its research and applications are mainly introduced and features of different processes are analyzed. Finally, the performance in the pervapouration techniques is discussed then available solutions together with some optimization processes are summarized, which can be served as a reference for the further development of this technology.

Pervapouration and the pervapouration-distillation hybrid process: Pervapouration is a membrane separation process based on the difference of sorption-desorption property among components to the compact and super-polymeric membrane, involving mass and heat transfer simultaneously[5]. It is generally considered that the delivery of permeate through the membrane can be divided into three consequent steps: first, liquid molecules of one or more components in the feed are adsorbed onto the up-side membrane surface. Second, these molecules pass through the membrane. The third step is the desorption of the components on the permeate side as vapour. Therefore, it can be short for adsorption-diffusion-desorption model[6].

Membranes are the most significant part in pervapouration, which are divided into organic (also called polymeric) and inorganic membranes (also called ceramic) according to material. At present, owing to low price, organic membranes are widely used in industry. However, as a newly emerging one, ceramic membranes have a large amount of advantages over organic ones, such as good chemical stability, acid-base and high temperature resistance. Furthermore, these membranes can be operated at much higher temperatures or in a broad pH range or under corrosion environment with high separation performance, good durability and environment-friendly. Nevertheless, their application in practical production is limited not only because the price of ceramic membranes is several times as much as that of organic membranes but also due to their fragility.

Different from distillation, pervapouration depends on the solubility and diffusion coefficient of components in membrane only. Certainly, pervapouration is able to compensate the drawbacks of traditional distillation, especially for the separation of azeotrope. As a result, pervapouration-distillation hybrid processes lead to significant savings in energy and operating costs[7]. At present, there are mainly three models of pervapouration-distillation hybrid process[8]: (1) pervapouration is set precede distillation to break azeotrope or reaches the specified concentration required by consequent distillation; (2) use pervapouration as a post-process for the product from the top or the bottom of the column;(3) couple pervapouration with distillation by adding a side-flow to the column in order to decrease the number of required plates.

Applications of hybrid process of pervapouration-distillation in chemical engineering

Dehydration of isopropyl alcohol (IPA): Isopropyl alcohol-water forms an azeotrope at 87.4 wt % IPA and 12.6 wt % water with a boiling point of 80.3 ºC at atmosphere pressure. Traditionally, the dehydration of IPA on a commercial scale is performed almost exclusively by azeotropic distillation with benzene as entrainer, which is being replaced gradually due to the harmfulness of benzene to human body.

Veerle Van Hoff *et al.*[9] compared traditional azeotropic distillation with a hybrid distillation-pervapouration process and a hybrid distillation-pervapouration-distillation process. In the hybrid processes pervapouration with both polymeric and ceramic membranes were investigated. Aspen Plus and pervapouration design calculation program (RWTH Aachen) were used to simulate the distillation and pervapouration respectively. Taking energy consumption, separation efficiency and economic data into account, it can be concluded that the hybrid distillation-pervapouration process with ceramic membrane is the most economical system that leads to a reduction in total costs by *ca.* 49 % and to a significant saving in energy costs up to 48 %.

In practice the hybrid azeotropic distillation-pervapouration process can be used to separate IPA-water mixture as well. Texaco firm[10] optimized the azeotropic distillation by adding a pervapouration procedure enriching IPA in the distillate of common distillation column from 85 upto 95 wt %, which then flows into azeotropic distillation column. Because in this case water in the feed to the azeotropic distillation column is little, thus the entrainer more suitable than benzene can be used. Similar to Texaco firm, Adams[11] produced super pure IPA with water less than 0.01 wt % through a pervapouration step followed by double-column distillation. In the pervapouration step water is reduced below 0.2 wt %, then distillation is operated to eliminate trace water and any other organic impurity further. This method suits for the production of high-purity IPA in semiconductor manufacture with low equipment investment and simple procedure.

Recovery of THF: Tetrahydrofuran (THF) is widely used in chemical industry. At atmosphere pressure THF-water forms an azeotrope at 94.3 wt % THF with a boiling point of 63.9 ºC. Koczka *et al.*[12] studied hybrid distillation-pervapouration process for the recovery of THF from two different highly non-ideal mixtures THF-water and THF-methanol-water on a industrial scale. First, pervapouration takes place breaking the THF-water azeotrope. THF contained in permeate is recovered with subsequently continuous distillation at nearly azeotrope composition. Water is drawn out from the bottom of the column.

The separation of THF-methanol-water mixture is performed by hybrid process combining extractive distillation (ED) with pervapouration and distillation. Given that methanol in the mixture is easy to penetrate through membrane, a pre-treatment of extractive distillation with water as extractant is necessary to eliminate methanol before the recovery of THF.

In these two cases mentioned above the hybrid processes reduce the utility costs by 84 and 60 %, the total annual costs by 83 and 94 %, respectively in combination with a notable decrease in THF loss.

Separation of dimethyl carbonate (DMC)-methanol: In the production of DMC target product is almost obtained by separating DMC-methanol azeotrope. Shah[13] put forward the hybrid process based on pervapouration to separate this mixture. Firstly, the azeotrope (methanol 70 wt %) is fed into a pervapouration unit. The pervapouration unit uses organophilic (methanolophilic) membrane which contains a PVA supporting layer and a PVA selective layer cross-linked with aliphatic dialdehyde. The permeate (methanol 95 wt %) is recycled to a reactor. The retentate (DMC 45 wt %) is purified further in distillation column producing DMC at 99 wt % from the bottom while the top product is recycled to the pervapouration unit to eliminate the azeotrope. Comparison of economical efficiency indicates that investment costs of the hybrid process is reduced by 33 % and the utility costs include membrane substituting cost is reduced by at least 60 % compared with traditional high pressure distillation. The process of breaking DMC-methanol azeotrope described by Vier *et al.*[14] is similar to the above, so is the separation efficiency. Organophilic PERVAP113F membrane (Sulzer Chemtech) is used. Due to high permeation flux of the pervapouration unit, top product is far away from azeotrope composition, thus the number of theoretical plates and reflux ratio can be decreased appropriately. It can be seen from the comparison of economical efficiency between the hybrid process and traditional double distillation that the utility costs of the hybrid one is saved by 10 to 40 %, although the investment costs of both are almost equal.

Separation of ethanol-ether-C4: At present, there are 20 suits or more equipment for the production of methyl tertiary butyl ether (MTBE) in China with maximum annual output 5×10^5 t. Air products firm[15] in America applied for a patent of hybrid process of distillation and pervapouration to separate MTBE-methanol-C4 mixture previously. Huanlin Chen *et al.*[16] studied on a MTBE process with annual output 2×10^4 t. Through designing calculation of hybrid distillation-pervapouration process with three different connection locations for the separation of MTBE-methanol-C4, we can get the conclusion that with different location pervapouration connected different component can be obtained after separation. These three conditions are described as follows: (1) pervapouration is connected into stripping section. So the separated mixture is MTBE-methanol actually, thus the requirement of membrane performance becomes strict; (2) pervapouration is connected into the top of the column. In this case the process loading of the membrane is four times as much as the output of rectifying section, leading to a significant increase in burden of the pervapouration unit; (3) pervapouration is connected into rectifying section. C4 and MTBE are expected to be obtained in distillate and at bottom, respectively, thus washing step can be removed. Obviously, the hybrid process combining pervapouration into rectifying section is the most reasonable. Lu *et al*.[17] optimized the above mentioned process maximizing pervapouration capability in combination with permeate flux up to 33.8 kmol/h and reflux ratio up to 2.0.

Separation of ethyl *tert*-butyl ether-ethanol mixture[18-20]: In industrial production, ETBE is always obtained by the separation of ETBE-ethanol azeotrope. TsingHua University[20] researched the hybrid distillation-pervapouration process in detail including the performance of polymeric membrane derived by cellulose. The results show that membrane with cellulose acetate butyrate (CAB) 30 wt % and cellulose acetate propionate (CAP) 70 wt % is the best, resulting in a significant increase in effective separation area and permeate flux and a notable reduction in temperature polarization. Applying the derived membrane into the separation of two kinds of ETBE-ethanol mixture with ethanol 10 and 30 wt % respectively, separation performance shows that the hybrid distillation-pervapouration process is the best, not only increasing the recovery ratio of ETBE but also saving energy.

Problems in the hybrid distillation- pervapouration process: The hybrid process of distillation-pervapouration has been widely used in recent decades because it is practical, energy and costs saved as well as environmental friendly compared with traditional processes. Furthermore, the simulation of this process has been also reported[21]. However, concentration and temperature polarizations are the bottleneck for the dramatic development of pervapouration as well as the hybrid distillation-pervapouration process[22]. During pervapouration, all solvents are transferred onto the surface of membrane where not all of them pass by, resulting in the concentration of solute there higher than that of the bulk, which is called concentration polarization. It leads to a increase in pressure drop between feed and permeate side but a reduction in effective pressure drop, thus performance efficiency is declined because of significant decrease in flux rates. In the mean time, vapourization of volatile component takes in heat making the temperature of the hydrophobic membrane surface higher than that of the feed bulk whereas desorption on permeate side absorbs the heat that volatile component releases resulting in temperature of membrane surface is higher than that of the desorption bulk, which is temperature polarization. It reduces the driving force of pervapouration and leads to a decline in permeate rates, thus preventing the process proceeding smoothly.

A large effort has been made to overcome the difficulty[23-25]. Reformations from both process operation and equipment two aspects have been done. On the one hand, improvement on operation style intensifies the turbulence of feed thus reduce concentration polarization and is also helpful to heat transfer. On the other hand, improvement on equipment such as adding a member like heat-exchanger into membrane module can minimize the impact of temperature polarization. Gomez *et al*.[25] researched on these two improvement solutions and added a heat-exchanger into membrane module. Vapour in distillates flows into heat exchange tubes, in which heat is transferred from the vapour to liquid on feed side. Heat exchange not only saves energy but also decreases temperature polariza-tion and increases permeate flux, improving the pervaopration. Furthermore, turbulence of feed is intensified because the space in retentate side becomes smaller after adding the heat-exchanger, so concentration polarization is reduced and it is easier for mass transfer. Researchers also tried to change smooth surface of the membrane into striated one, for example, wave mode membrane. Rough surface can intensify turbulence of the feed leading to a reduction in concentration polarization but a rise in permeate flux to some degree.

Conclusion

With the rapid progress of the world's industrialization and the increase of environmental consciousness, solvent recovery and azeotropic separation process are demanded increasingly. The hybrid process of distillation-pervapouration is replacing traditional separation techniques gradually because it is economic and environmentally friendly. Furthermore, as the development of membrane technology, new ceramic membrane will make up for the drawbacks of polemic membrane with merits such as resistance to high temperature as well as resistance to acid-alkali and difficult to react with solvent and so forth, which will improve the development of the hybrid process. Therefore, this technology will become widely used in the near future.

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