TECHNOLOGY OF OBTAINING BUTANE AND BUTADIENE FROM BUTENE WITH EXTRACTIVE DISTILLATION METHOD

[1]**Achilov X.T.**, [2]**Musayeva S.A**.
[1]Samarkand State University, Samarkand, Uzbekistan
[2]School 81, Samarkand city, Samarkand, Uzbekistan

Abstract. Nowadays, creation of waste-free technology, rational use of existing raw materials is one of the urgent issues in industrialized countries. Butadiene is used in many fields due to its unique properties. Butane and butene mixtures contained in natural crude oil waste were isolated and butadiene was obtained based on extractive distillation. To solve these problems, this study proposes new improvements: The extractive distillation section is modified with intermediate heating and the classical columns are replaced by a dividing wall column (DWC) using a heat pump. Rigorous simulations were performed in Aspen Plus for a typical ED process. DWC was found to reduce the energy intensity of the classical distillation section of the BASF process by 54.8% and reduce total annual costs by 29.9%. In addition, the intermediate reboiler reduces the energy density of the ED section by 8.3%, while reducing the CAPEX cost of the system due to the need for a smaller recycle compressor.

Keywords: butane, butadiene, extractive distillation, cracking, technological scheme.

I. Introduction

1,3-Butadiene ($1,3\text{-}C_4H_6$) is an important petrochemical raw material for the production of polybutadiene, one of the most important synthetic rubbers [1-2]. The development of production and industry has led to an increase in the demand for $1,3\text{-}C_4H_6$ and its potential in the world market. Typically, the pure $1,3\text{-}C_4H_6$ stream can be separated from the C4 hydrocarbon mixtures produced in steam cracking processes to produce ethylene. $1,3\text{-}C_4H_6$ makes up 30-60% of C_4 compounds, and the rest consists mainly of 1-butene (nC_4H_8), isobutene (iso-C_4H_8) and butane (C_4H_{10}). Close boiling points between $1,3\text{-}C_4H_6$ (268.75 K) and nC_4H_8 in the C_4 mixture. (266.65 K) and their similar molecular structures cause great difficulties in the process of separation using simple distillation. An effective and efficient separation technique is highly required to overcome this challenge [3-4].

It is well known that extractive distillation (ED) process is one of the effective methods for separating high-boiling mixtures. In order to improve the efficiency of the separation, a proper intrainter can be introduced to significantly increase the relative variability of the target component. Thus, it is highly desirable to design an energy-efficient ED process from an economic point of view. In this case, choosing the right coach is always crucial [5].

Solvent class ionic liquids are defined as molten salts with a melting point below 100°C. Due to their unique physicochemical properties, such as excellent solubility, wide liquid range, very low vapor pressure, and flexible design, ILs have received considerable attention for use in a variety of applications. Many studies have been reported for the optimal design of ILs-based ED processes for the separation of azeotropic or near-boiling mixtures such as alcohol/water, alcohol/aliphatic hydrocarbons, aromatic/aliphatic hydrocarbons, etc [6]. Despite the progress

made, the investigation of ILs for the separation of $1,3\text{-}C_4H_6$ and nC_4H_8 is still limited. Existing studies are focused on experimental trial and error approaches (see references. However, due to the large pool of different cation-anion compounds, the experimental procedure is time-consuming and expensive. Importantly, only a small design area can be covered. Therefore, the optimal IL A reliable and effective theoretical method is needed for determination [7].

Reliable prediction of the thermodynamic properties of IL-containing systems is a prerequisite for effective IL screening. To this end, COSMO-RS (conductor-like screening model for real solvents) has been shown to be a promising tool for accurately predicting the thermodynamic properties of IL-containing systems. Relying heavily on experimentally fitted parameters from activity coefficient models (e.g., NRTL, UNIFAC, UNIQAC) and equation of state methods (e.g., SAFT), COSMO-RS is a fully predictive thermodynamic model that combines quantum chemistry with statistical thermodynamics to produce reliable predictions. COSMO-RS is a versatile platform for rapid IL screening with a specific separation task, providing good quality and in most cases acceptable quantitative prediction results. Especially for hydrocarbon systems containing ILs, COSMO-RS has been proven to be robust for characterizing the phase behavior (see refs. i.e. IL screening tool for the regeneration of $1,3\text{-}C_4H_6$ it is recommended to use COSMO-RS as [9].

In this work, high-throughput computational screening of ILs for $1,3\text{-}C_4H_6$ and nC_4H_8 is performed.separation. Two systematic steps are included [10-13]. The first step considers IL screening based on predefined constraints on thermodynamic and physical properties [14]. A thermodynamic evaluation based on COSMO-RS is performed to calculate the infinite dilution capacity and selectivity of the IL candidates. In addition, the physical properties of ILs (i.e., viscosity, toxicity, and melting point) are evaluated using existing property prediction models. After screening, the resulting IL candidates are sent to determine their specific process performance. Process performance evaluation is performed using Aspen Plus simulation (V8.8). As a result, [PMIM][MC] was optimally determined from 36,260 IL, which means a much lower energy consumption compared to the ED process using NMP [15-16].

II.Expremental

Determination of calibration coefficients for calculating the saturation of MAE with C4 hydrocarbons is carried out by analyzing artificial binary mixtures consisting of air (nitrogen) and hydrocarbons (butane, butadiene-1,3) with a purity of at least 97.0%.

To prepare the binary mixture, take a 500 cm3 bottle and measure it to the stopper (using a graduated cylinder). Glass stirring rods are placed in the bottle and closed with a butyl rubber stopper. With a syringe with a capacity of 1 cm3, 0.3-0.5 cm3 of vaporized butadiene-1,3 is injected into the bottle. The gas mixture is mixed. With a clean syringe, 0.5 cm3 of the mixture is taken for analysis. Determine the maximum surface area of butane (butadiene-1,3) in mm2.

III. Discussion of results

The scheme for the preparation of butadiene-1,3 from butane and butene is given below (Scheme 1):

The normal butadiene extraction technology mainly consists of the following parts: extractive distillation, conventional distillation, solvent degassing and solvent recovery. The C4 feed is sent to an extractive distillation unit where it is evaporated and separated using two extractive distillation columns. The top product in the first column consists of butenes and a mixture of butanes and is designated as raffinate-1. The second column is a dividing wall column

consisting of a rectifier and then a washer. It is a crude butadiene product that is sent to a conventional distillation system for further purification. The rich solvent is removed from the bottom of the second column and sent to a solvent degassing system. Crude butadiene is fed to a propyne column, the first of two columns in a conventional distillation unit. Propyne is removed from this column as an overhead and the bottom is sent to the butadiene column. The butadiene product is withdrawn from the top of this column, and C5 s as well as 1,2-butadiene are rejected at the bottom. The rich solvent from the extractive distillation section is fed to the solvent degassing section. The solvent is stripped of C4 s in a degassing column and recycled to the extractive distillation unit. C4 acetylenes are removed as a side stream and can be hydrogenated, used as fuel gas or as cracker feed, or burned in a flare system. The steam from the degassing column is cooled in a separate cooling column, compressed and returned to the extractive distillation unit. An advanced heat recovery system uses most of the solvent's sensible heat, resulting in very low energy consumption. A small solvent stream is continuously fed to the NMP regeneration unit. The solvent is heated with steam under vacuum conditions in a regeneration vessel. The evaporated NMP is condensed and recycled to the extractive distillation unit. The remaining residue is usually incinerated.
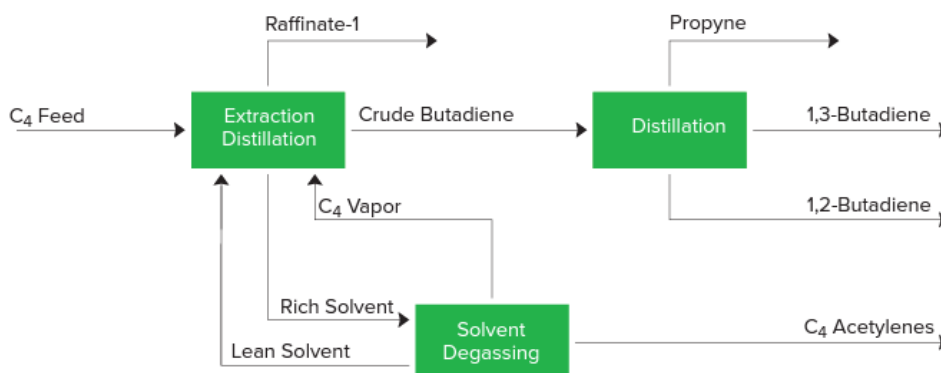

Figure 1. Scheme of the extractive distillation process

The calibration coefficient (K) mg/mm2 is calculated according to the following formula:

$$K_6 = \frac{V_1 * 2,5 * V_2}{S_i V_{6\text{ут}}}$$

where V1 is the volume of butane (butadiene-1,3) taken to prepare the binary mixture, cm3; V2 - the volume of the mixture, cm3; 2.5 - the highest density of butane in the chromatogram, mg/cm3; Si - butane peak area in the chromatogram, mm2; V_but - the volume of the bottle, cm3. After the device is switched on, a cooled sample of 1 mm3 is taken with a microsyringe and sent to the chromatograph. Write the chromatogram according to the above conditions. By adjusting the sensitivity scale to provide optimal peak locations.

Processing the results.

The mass fraction of C4 (X) hydrocarbons is calculated in percent by the following formula:

$$X = \frac{K_6 * S_i * 100}{V * \rho}$$

where Si is the area of the hydrocarbon peak, C4, mm2; Kb - calibration coefficient, mg/mm2; V- sample volume, mm3; r - density of copper-ammonia solution, mg/mm3.
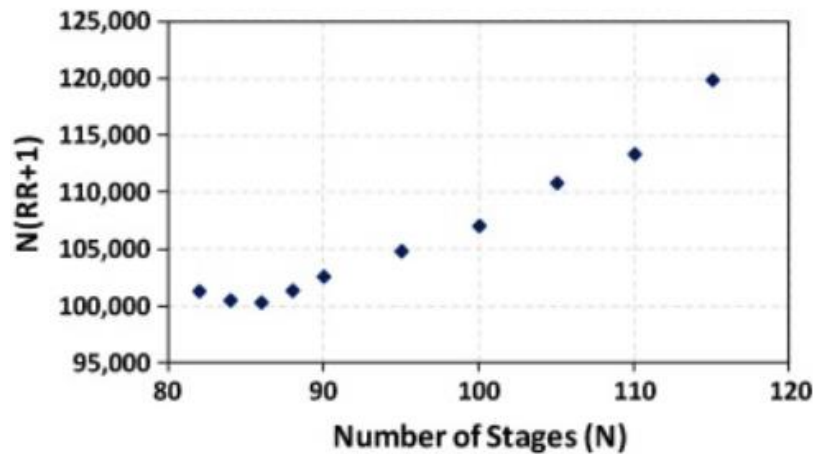
Figure 2. Fraction process on theoretical plates

In the first step, the distillation section of the NMP process is improved by combining two classical distillation columns (shown in Figure 1) into a single unit in the form of a dividing wall column (DWC). DWC reduces energy consumption by minimizing the thermodynamically unfavorable remixing effects that occur in conventional sequencing and lowers investment costs by requiring fewer units.

To simulate the DWC, a two-column sequence model is used, as described in the literature. From the initial simulation, the DWC design is optimized to minimize the objective function $N(RR + 1)$, which is an indirect measure of the total annual cost, combining the column size and energy consumption. For specific stages, the vapor-to-liquid separation ratio, the feed stage, the number of prefractionation stages, and the position of the prefractionator are adjusted sequentially. Each successive adjustment is made only if the separation is improved; if no improvement is observed, no correction is made and the next variable is set. Then, the return ratio is reduced for each adjustment until the same degree of separation is achieved in the conventional sequence. The number of steps is systematically reduced in the execution of this procedure until $N(RR + 1)$ is minimized. Details of this procedure are given in the literature. The result of the number of steps on this objective function is . Note that the number of stages in this plot includes the condenser (stage 1) and the reboiler, so 84 trays are optimal. the final configuration of the optimal DWC block is shown.

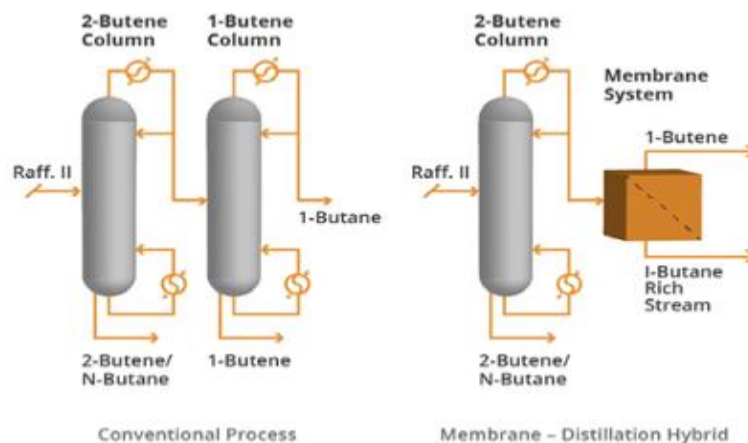The technological scheme of this process is presented in Figure 3.

Figure 3. Technological scheme of butadiene 1,3 production based on the extractive distillation process

The above integration example is a real case study (see also "Integrated Solutions - C4 1-Butene Refining from Raffinate" at www.imtexmembranes.com) where Permilen membrane technology is compared to real C4 system data installed at: operating facility in the Middle East where return costs are known. Here, the membrane system is positioned as a replacement for the 1-butene column separating 1-butene from isobutane. A comparison of the estimated costs of the membrane system with conventional distillation shows that the capital costs, energy consumption and simplicity of deployment are significantly improved, which is shown in part by the significant weight reduction of the membrane system relative to the distillation column and auxiliary equipment. equipment. Modular membrane technology is very easy to move and install, construction work is much simpler. It should be noted that the membrane can also be used to recover purified 2-butene from the bottom of the 2-butene column in this case. The separation of 2-butene / n-butane is almost impossible to achieve by conventional distillation, but due to the facilitated transport mechanism of the membrane, the Permilen membrane system can achieve this separation as easily as any other. The 2-butene produced here would be a suitable material for the metathesis process for the targeted production of propylene.

IV. Conclusion

During extractive distillation, the crude divinyl from the column is washed with solvent. The lighter, less soluble components (butane/butene) are removed from the top of the column - the C_4 raffinate. The bottom stream of the column contains solvent, divinyl and dissolved components. In the recovery column, the solvent recycled to the extraction column is separated from the bottom stream. The divinyl saturated regeneration column distillate is sent for further distillation to remove impurities. Purified divinyl has a concentration of more than 99.5%.

REFERENCES

1. Sattler J. J. H. B. et al. Catalytic dehydrogenation of light alkanes on metals and metal oxides //Chemical reviews. – 2014. – Т. 114. – №. 20. – С. 10613-10653.
2. Jana A. K. Advances in heat pump assisted distillation column: A review //Energy Conversion and Management. – 2014. – Т. 77. – С. 287-297.
3. Mahdi, H. I., & Muraza, O. (2019). An exciting opportunity for zeolite adsorbent design in separation of C4 olefins through adsorptive separation. In Separation and Purification Technology (Vol. 221, pp. 126–151). Elsevier B.V. https://doi.org/ 10.1016/j.seppur.2018.12.004.
4. P.M. Mathias, J.R. Elliott, A. Klamt, Butadiene purification using polar solvents. Analysis of solution nonideality using data and estimation methods, Ind. Eng. Chem. Res. 47 (15) (2008) 4996–5004, https://doi.org/10.1021/ie070774p.
5. Omanov B. S. et al. Optimization of vinyl acetate synthesis process //International Journal of Control and Automation. – 2020. – Т. 13. – №. 1. – С. 231-238.
6. Kindler K., Puhl H. Method for separating a C4-hydrocarbon mixture : пат. 6337429 США. – 2002.
7. Wu Y. C., Hsu P. H. C., Chien I. L. Critical assessment of the energy-saving potential of an extractive dividing-wall column //Industrial & Engineering Chemistry Research. – 2013. – Т. 52. – №. 15. – С. 5384-5399.

8. Uzokov J. R., Mukhamadiev N. K. Sorption characteristics of mesoporous composite $SiO_2 \cdot TiO_2$ //Central Asian Journal of Medical and Natural Science. – 2021. – T. 2. – №. 5. – C. 494-498.

9. Ulugboyeva G. O., Uzokov, J. R., Mukhammadiyev, N. Q., & Mukhamadiyev, A. N. Amorphous silica gel as a surfactant for saponins: support, synthesis, and texture characteristics //Central Asian Journal of Medical and Natural Science. – 2023. – T. 4. – №. 2. – C. 601-607.

10. Wang Y. H., Chien I. L. Unique design considerations for maximum-boiling azeotropic systems via extractive distillation: acetone/chloroform separation //Industrial & Engineering Chemistry Research. – 2018. – T. 57. – №. 38. – C. 12884-12894.

11. Yu J. et al. Improving the performance of extractive dividing-wall columns with intermediate heating //Industrial & Engineering Chemistry Research. – 2015. – T. 54. – №. 10. – C. 2709-2723.

12. Schwarz J., Beloff B., Beaver E. Use sustainability metrics to guide decision-making //Chemical engineering progress. – 2002. – T. 98. – №. 7. – C. 58-63.

13. Mamaziyaeva S. Uzokov, J. R., Mukhammadiyev, N. Q., Synthesis and their texture characteristics of mesoporous silica gel as surfactant supporting rutin //Central Asian Journal of Medical and Natural Science. – 2023. – T. 4. – №. 2. – C. 608-614.

14. Usmonova H. Uzokov, J. R., Mukhamadiev, N. Q.,Study of structural and electronic properties of (ZnO) n (n= 10÷ 30) nanoclusters using quantum chemical methods //central asian journal of medical and natural science. – 2022. – T. 3. – №. 6. – C. 428-434.

15. Mamadoliev I. I., Fayzullaev N. I. Optimization of the activation conditions of high silicon zeolite //International Journal of Advanced Science and Technology. – 2020. – T. 29. – №. 3. – C. 6807-6813.

16. Spivey J. J., Hutchings G. Catalytic aromatization of methane //Chemical Society Reviews. – 2014. – T. 43. – №. 3. – C. 792-803.