Evaluation of Height Equivalent Theoretical Plate of Packing Distillation Column for Benzaldehyde Purification Processing

Nguyen Trung Dung, Phan Ngoc Quang, Pham Duc Anh, Do Nguyen Ha Thu,
Nguyen Van Anh, Ta Hong Duc, Cao Hong Ha*

School of Chemical Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam
*Corresponding author email: ha.caohong@hust.edu.vn

Abstract

This study analyzes the literature review of the techniques for estimating Height Equivalent Theoretical Plate (HETP) values for various packing structure models, ranging from theoretical to semi-empirical to shortcut methods. Packing structures of various meshes and shapes were studied on the purification of benzaldehyde from the mixture of benzaldehyde and cinnamaldehyde. The packing structures M-50, M-80, O-80, and S-80 were estimated using Fenske's approach as 0.052, 0.053, 0.045, and 0.056, respectively. Experiment data and simulation result obtained by commercial software were utilized to validate the packing's HETP value. A pilot of the vacuum batch distillation system was fabricated including a column filled with packing structures. The results indicated that the HETP value between experiment and simulation is within 0.6 percent deviation. On the pilot scale, the results of the benzaldehyde purifying were validated in a batch distillation system with the O-80 packing structure. This system will be developed for the larger scale, and it will practical.

Keywords: Natural benzaldehyde synthesis, HETP evaluation, batch distillation, random packing, simulation

1. Introduction

Among the aldehyde compounds used as aroma compositions for the cosmetic, pharmaceutical, and food industries, benzaldehyde is one of the most important aldehydes used in flavoring additives. Benzaldehyde is known as the almond aroma, this compound is used as a flavor ingredient in biscuits, butter, cheese, etc. In industry, benzaldehyde can be synthesized, extracted from natural fruits (e.g., almond, cherry...) or distilled and converted from cinnamon essential oil.

Many studies have established and suggested various techniques for manufacturing, such as ozonization, near-critical water hydrolysis, toxic phase transfer, and surfactant catalytic processes. To explore and optimize the process of natural benzaldehyde synthesis from cinnamaldehyde, Patrick *et al.* [1] evaluated three methods. The first route is based on Buck's (1987) patent [2], the second route is based on Wright's (1993) research [3], and the third route is based on Yang's (2012, 2013) study [4,5]. The first approach used a high-pH reaction that was simple to set up and observe. This technique, however, may reduce the natural essence of benzaldehyde (high pH condition). Because of the difficult reaction conditions with a powerful oxidant, the second method proved more difficult to manage. The final approach allowed for trans-cinnamaldehyde to be converted to benzaldehyde using a heterogeneous catalytic technique. This technique took a long time to

complete, and the reaction system contained a number of undesired side reactions, resulting in a poor yield of natural benzaldehyde. Purification of benzaldehyde following green synthesis from cinnamaldehyde is also a challenge. The conversion efficiency of cinnamaldehyde to benzaldehyde is around 40-50 percent, according to the results of the study [1]. Purification of benzaldehyde to a purity of 99 wt. % is generally done in a vacuum distillation unit once the reaction is finished.

In the chemical industry, the distillation process is widely employed. It refers to the process of purifying a mixture containing components with various boiling points. The advantages of the packing column are low pressure drop, great mass transfer efficiency, and high capacity. It's especially well-suited to vacuum fractionation applications. The performance of packed columns, for distillation or absorption services, are frequently expressed in terms of Height Equivalent to a Theoretical Plate (HETP) or/and Height of Transfer Unit (HTU). For packed columns, a variety of empirical or semi-theoretical mass-transfer models have been reported in the literature. There are several models in the literature that use equations or graphs to estimate pressure drop and capacity. On the other hand, some models are based on the two-film theory and penetration theory. Bravo *et al.* [6] developed the most commonly used model for calculating the HETP or HTU for structured packing, known as the BRF model. The authors assumed that the liquid-side mass transfer resistance

could be ignored, and that HETP could be approximated to the gas-side mass transfer resistance. Bravo *et al.* [7] proposed a new version of the previous equations called the SRP (Separations Research Program) model. The authors modified the previous assumption about complete wettability of the packing surface area. The SRP model included two corrective factors to predict the effective surface area. The first parameter is the surface enhancement factor (F_{SE}) which accounts for variations of surface packing and the second is a correction factor for total liquid hold-up due to effective wetted area (F_t). By using 31 distinct liquid-gas systems and 67 different types of packings, Billet and Schultes, 1993 [8] investigated the mass transfer process into packed columns for gas absorption and distillation operations (BS model). The authors investigated different height and diameter columns, operating in a counter-current flow with both structured and random packings in this research. The penetration hypothesis was also used to both gas and liquid mass transfer. The mass transfer model in the gas phase is based on the assumption that gas flows in various directions through the packing and that the contact area between phases must be refreshed after a theoretical time (t_G). The packing specific constants, CLBS and CGBS, are dependent on the specific structures and material of the packing.

Short-cut methods, unlike rigorous models, could successfully provide a rapid evaluation of a separation possibility for initial tests and thus have been widely used by chemical engineers. G. Q. Wang *et al.*, 2005 [9] provided a summary of shortcut models available in the recent open literature for predicting the HETP of a packed column. For structured packing with a crimp angle of 45° and troubleshooting purposes, Harrison *et al.*, (1989) suggestion an equation:

$$HETP = \frac{100}{a_p} \qquad (1)$$

where: a_p - packing specific interfacial area [m^{-1}]

For atmospheric distillation, Intalox structured packing, Strigle *et al.*, (1994) [9] proposed equation:

$$HETP = exp(n - 0.187 \ln \sigma_L + 0.213 \ln \mu_L) \qquad (2)$$

where: σ_L - surface tension [N/m] and μ_L - viscosity [Pa.s]

Based on BRF model, good accuracy for estimating the basic HETP of Flexipac packing with organic system, Lockett *et al.*, [9] proposed an equation:

$$HETP = \frac{1.54g^{0.5}(\rho_L - \rho_g)^{0.5}\mu^{0.06}}{a_p\left[1 + 0.78\,exp(0.00058\,a_p)\left(\frac{\rho_g}{\rho_L}\right)^{0.25}\right]^2} \qquad (3)$$

where: g - gravitational constant [m/s^2], ρ - density [kg/m^3].

H. Z. Kister, 1992 [10] corrected of Harrison correlation for conservation by equation:

$$HETP = \frac{100}{a_p} + 0.102 \qquad (4)$$

Carillo *et al.*, (2000) [11] improved and extended Lockett's equation for vacuum or pressure distillation of organic or aqueous systems in columns of sheet packings by:

$$HETP = \frac{5.40g^{0.5}(\rho_L)^{0.5}}{a_p\left[1 + 0.78\,exp(0.00058\,a_p)\left(\frac{\rho_g}{\rho_L}\right)^{0.25}\right]^2} \qquad (5)$$

From the experimental results, the HETP can estimated by equation:

$$HETP = \frac{H}{NTS} \qquad (6)$$

where *NTS* - number of theoretical stages; *H* - packing height

For a binary mixture with constant relative volatility and constant molar overflow, the Fenske equation could be used to compute the number of theoretical stages required to achieve the desired separation.

$$NTS = \frac{ln\frac{x_D/(1 - x_D)}{(1 - x_w)/x_w}}{\ln \alpha_m} \qquad (7)$$

where α_m is the relative volatility of the mixture, and x_d and x_w are the compositions of the top and bottom of the column.

Bessou *et al.*, 2010 [12] modified the Fenske equation for packing distillation by equation:

$$NTS = (n - 1) + \left(\frac{x_{n-1} - x_w}{x_{n-1} - x_n}\right) \qquad (8)$$

where x_n is liquid molar fraction of stage number *n*.

In this paper, the various experimental results were carried out on a batch distillation pilot size to characterize the various packing configurations. The HETP of a packed column must be computed for each packing type. The best packing configuration will be used to purify benzaldehyde from the reaction mixture and the results also will be compared to simulated results using commercial software.

2. Experiments

2.1. Packing Distillation Structures

The material for fabricating difference types of packing was SUS-304 stainless steel mesh (50 and 80 mesh corresponding with packing type: M-50, M-80, S-80, and O-80) with technical parameters shown in Table 1. Packings were cut and shaped by hand. The shapes of the different packings with the average dimensions were shown in Fig.1.

Table 1. Technical data of packaging materials

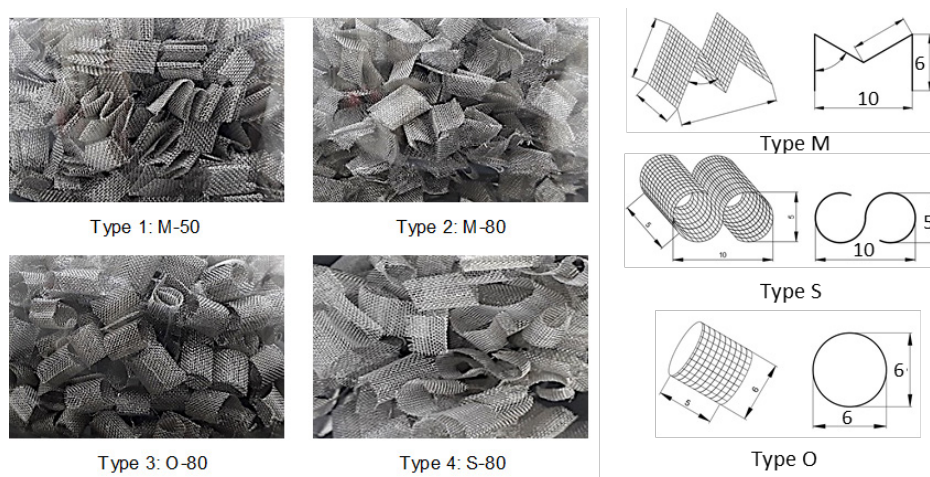|	Stainless steel mesh SUS 304, 50 mesh	Stainless steel mesh SUS 304, 80 mesh
Wire diameter (mm)	0.2286	0.1397
Opening (mm)	0.2794	0.1778
Opening (%)	30	31
Overall thickness (mm)	0.4572	0.2794
Density (g/m^2)	~ 267.99	~ 235.83

Fig. 1. Various geometric parameters of the packings.

2.2. Experimental Setup and Methods

The experiment setup was shown in Fig. 2. The experiment system consists of a still (250 mL round bottom flask) that was heated by a heating mantle for round flasks. Two thermometers were set up at the bottom and the top of the distillation system. A condenser was cooled by water refrigerant. A distillate van and reflux van were designed to control the reflux ratio during the distillation process. The column was isolated by glass wool jacket.

The concentration of n-hexane and cyclohexane were measured by the refractometer Abbe Mark III, Reichert, USA. The cinnamaldehyde distillated from cinnamomum cassia oil (99.0%, purchased from Arenex Co. Ltd. Viet Nam) and benzaldehyde (99.0 wt. %, purchased from Arenex Co. Ltd. Viet Nam) content of the top products and bottom products were determined by Gas Chromatography (GC) method using the SHIMAZU GC-2010 plus (FID detector) system. The chemicals used were as follows: n-hexane 99%, GHTECH, China (CAS 110-54-3) and Cyclohexane 99.7%, GHTECH, China (CAS 110-82-7). The experiments were performed in a laboratory batch distillation column made from a glass tube with 40 mm of inner diameter and 550 mm long. The column was filled with the shaped random packings. This column was designed with a liquid dispenser part

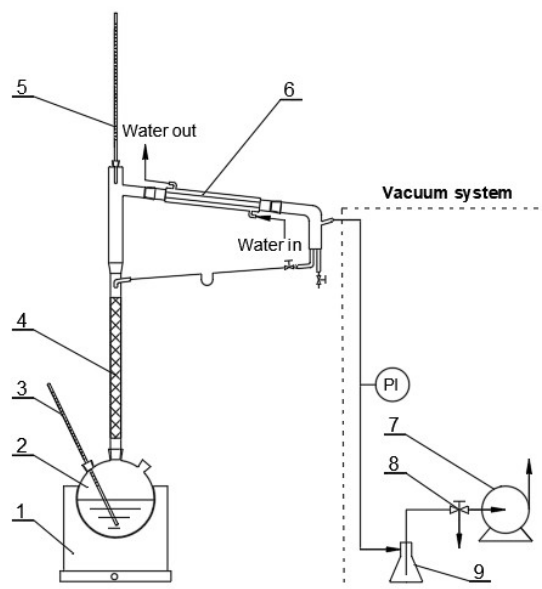that was set right above the top of the packing in the column.

Fig. 2. Experimental setup for HETP evaluation: 1. Heating mantle for round flasks; 2. Still (250 mL round bottom flask); 3 and 5. Thermometer; 4. Column with shaped random packings; 6. Condenser; 7. Vacuum pump; 8. Vale; 9. Liquid separation container.

The bottom mixture was heated by a heating mantle to boiling point, after which the refrigerant fully condenses the vapor at the top of the column. The temperature of the reboiler and the top of the column were measured using thermometers. In this study, the HETP index of the packing was measured based on an n-Hexane/Cyclohexane mixture. This mixture was normally used as an ideal mixture for characterizing the HETP of packing, [12]. One of the major reasons was the high relative volatility of the two components. At atmospheric pressure (101 kPa), the experiments were carried out with a prepared n-Hexane/Cyclohexane mixture. A 100 mL of mixture of the n-Hexane/Cyclohexane with volume ratio ($V_1:V_2$) was prepared for distilling. This mixture was loaded into the reboiler and heated by heating mantle. When the liquid-vapour equilibrium in the system was stable in about 1 hour, the liquid samples at the top and bottom of the column were collected and analyzed by refractometry. The time between the first vapor release and the first sample was almost 60 minutes, and a steady state was considered to be achieved when three successive samples had identical compositions. The mole fraction at both the top and bottom were used to calculate the number of theoretical stages (NTS). The mass transfer was reported in terms of the height equivalent of a theoretical plate (HETP). Three cases researches were performed for each packing type, with the following initial volume compositions: n-hexane (mL): cyclohexane (mL) = V1:V2 = 30:70; 50:50; and 70:30.

2.3. Calibration Curve

In order to analyze the mixture of n-hexane and cyclohexane, a calibration curve of the mole fraction of the n-hexane/cyclohexane mixture and the refractive index was built, Fig. 3. These samples were prepared by mixing and measured by using a refractometer at ambient conditions. Fig. 3 shows that the correlation coefficient between model and experimental values was acceptable with $R^2 = 0.998$. Interpolating from the graph yields the composition of the distillate and bottom products.
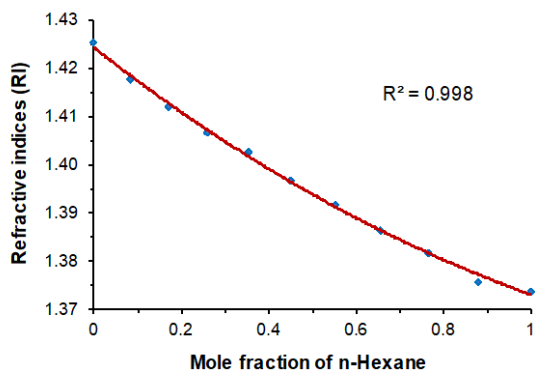
3. Result and Discussion

3.2. HETP Evaluation

Consider the distillation of cyclohexane/n-hexane at 101 kPa at total reflux, Fig. 4 shows the relative volatility (α_{avg}) with composition for this system calculated using NRTL models by AspenPlus® software (Version 10) to estimate constant relative volatilities. This calculation was based on the vapor and liquid mole fraction of n-hexane and cyclohexane. The volatility of the components can be determined by (9):

$$K_i = \frac{y_i}{x_i} \qquad (9)$$

where x_i - liquid mole fraction and y_i - vapor mole fraction; $i = 1$ to n; n - number of simulated data.

Based on the simulated results, we can estimate the average relative volatility of the mixture by (10):

$$\alpha_{avg} = \frac{\sum_1^n \frac{K_{n-hexane}}{K_{cyclohexane}}}{n} = 1.477 \qquad (10)$$

where: α_{avg} - Relative volatility of n-hexane and cyclohexane; $K_{n-hexane}$ - Volatility of n-hexane; $K_{cyclohexane}$ - Volatility of cyclohexane; n - number of simulated data.

Different volume fractions and construction types of packing were used in the laboratory distillation column. The compositions of the top and bottom liquids were determined by calibration curve of the mole fraction of the n-hexane/cyclohexane mixture and the refractive index, Fig 3. The Fenske equation was used to evaluate various HETP values for a part of the column, as shown in Table 2. These results were also the relationship between the input mixture composition and HETP index. The values of relative volatility and geometrics of the packing types effected to HETP values. Therefore, in the process design and the simulation, the average HETP was assumed to be constant in the distillation column.
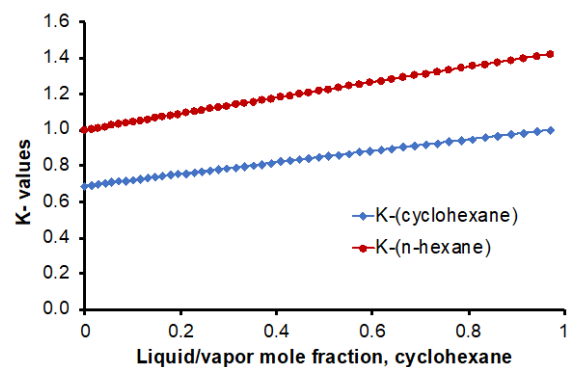

Fig. 3. Calibration curve for mole fraction of n-hexane with RI.

Fig. 4. K-value for cyclohexane/n-hexane

Table 2. $HETP_m$ evaluations

	M-50			M-80			O-80			S-80		
V_1/V_2 (mL/mL)	30/70	50/50	70/30	30/70	50/50	70/30	30/70	50/50	70/30	30/70	50/50	70/30
x_F (% mole)	0.263	0.450	0.660	0.263	0.45	0.660	0.263	0.45	0.660	0.263	0.45	0.660
RI_D	1.390	1.384	1.384	1.391	1.378	1.384	1.383	1.383	1.380	1.379	1.384	1.389
x_D (% mole)	0.572	0.705	0.705	0.566	0.87	0.714	0.731	0.743	0.814	0.811	0.698	0.589
RI_W	1.421	1.415	1.414	1.421	1.408	1.411	1.42	1.421	1.405	1.415	1.409	1.417
x_W (% mole)	0.046	0.137	0.148	0.045	0.25	0.205	0.06	0.045	0.29	0.121	0.219	0.092
NTS	8.987	7.336	7.092	8.984	8.115	6.142	10.15	11.14	6.416	9.305	5.706	7.167
HETP (m^{-1})	0.045	0.055	0.056	0.045	0.049	0.065	0.039	0.036	0.062	0.043	0.070	0.056
$HETP_m$ (m^{-1})	**0.052**			**0.053**			**0.045**			**0.056**		

According to experimental data, the HETP values were not significant changed when the mesh size increases from type M-50 to type M-80. These results could be explained that the opening (%) of the two materials were the same (~ 30 %). However, with various geometrics of the packing, like M, O, and S geometrics, HETP values were changed due to specific packing interfacial area and void fraction as the packing parameters, as they are the most important factors affecting mass transfer for structural packings. Table 2 shows results of the HETP calculation, and the excellent HETP was obtained by the packing with O geometric ($HETP_m$ = 0.045 m^{-1}). By using these results shown in Table 2, the average of the number of theoretical stages of the packing in the experiments could be calculated, NTS = 9.23.

3.2 Validation of the HETP O-80 Geometric Packing

A mixture of benzaldehyde and cinnamaldehyde was used in the batch distillation pilot to validate the HETP result for the O-80 packing structure as shown in the Table 3. The experimental results were then compared to simulated results using Aspen plus software. The still was filled with a mixture was natural benzaldehyde mixing with cinnamaldehyde with the ratio 1:1. The mixture was then raised to a boil. The rising vapor will be condensed and re-circulated completely. During experiments, the working pressure was set to 50 mmHg of vacuum pressure to decrease the decomposition of benzaldehyde and cinnamaldehyde. After the process has stabilized, sampling is performed at the condenser and the temperature of the top column were measured. The distillate composition shown in Table 3 and Fig. 8 including benzaldehyde 99.3 wt. % and cinnamaldehyde 0.7 wt. % In the commercial simulation software, Fig. 5 illustrates a simulation model of the batch distillation process. The number of stages was set at 9 based on the estimated HETP data for the O-80 packing configuration. The simulation pressure was 50 mmHg of vacuum pressure, which was the same as the experimental pressure. The simulation was a total reflux condition. Based on the work of X. Li *et al*., (2014) [13], the thermodynamic model was chosen as the NRTL model.
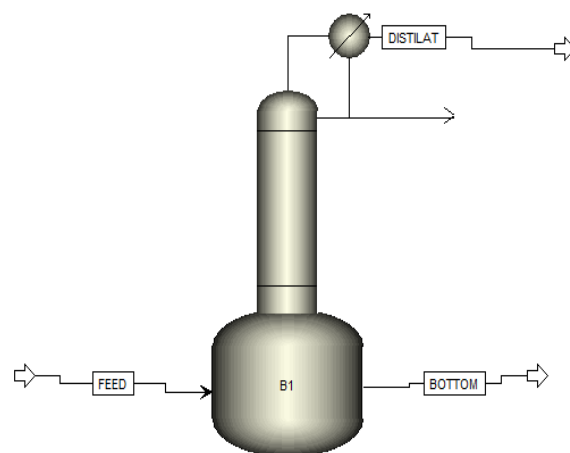

Fig. 5. Batch distillation model in Aspen Plus® software.

Table 3. Comparison between experimental data and simulation results

	Experimental data	Simulate results	Error, %
Initial data:			
- Benzaldehyde (g)	25.0	25.0	
- Cinnamaldehyde (g)	25.0	25.0	
- Operation pressure (mmHg)	50.0	50.0	
- Heigh of column (mm)	550.0	-	
- Number of stage (NTS)	9.23[(*)]	9	
Result:			
- Top temperature (°C)	91.5	94.3	3.06
Distillate composition			
- Benzaldehyde (wt. %)	99.3	99.9	0.60
- Cinnamaldehyde (wt. %)	0.7	0.1	

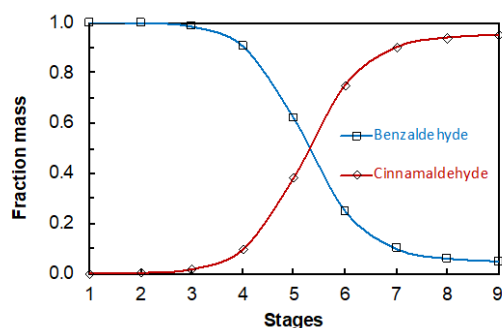[(*)] *calculated by the heigh of column (mm)/HETP*

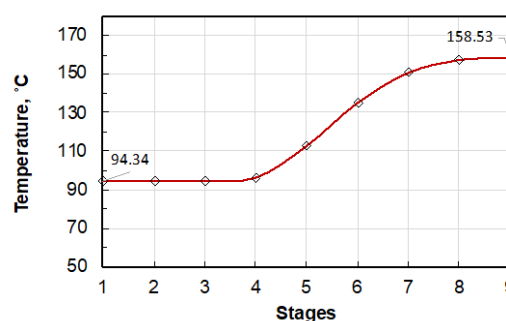Fig. 6. Liquid fraction mass profile in batch distillation.

Fig. 7. Temperature profile in batch distillation.

Fig. 6 and 7 show the mass fraction composition and the temperature profiles in the batch distillation. As shown in Fig. 6, the simulation results showed that the composition of benzaldehyde increases from the 9th stage (bottom stage) to the 1st stage (condenser stage), and the composition of cinnamaldehyde decreases. It means that the cinnamaldehyde component was located mainly at the bottom and the benzaldehyde component was located mainly at the top of the column.

The temperature change of the mixture from the top of to the bottom of the column was shown in the Fig. 7. The temperature was 94.34 °C at the top and 158.53 °C at the bottom of column. These temperatures were the boiling temperature of the two components benzaldehyde and cinnamaldehyde at a vacuum pressure of 50 mmHg [14].

Table 3 shows that the temperature difference between experiment and simulation at the top of the column was 3.06 %. This can be explained by the fact that there was a loss of heat during the experiment. The simulation approach, on the other hand, implies that heat loss was neglected. Furthermore, based on experimental data, the composition of benzaldehyde in the top product was 99.3 wt.%. This value achieved a benzaldehyde concentration of 99.9 wt.% in simulation results. The difference between experimental data and simulation findings was 0.6 %. This study demonstrates that it was feasible to purify benzaldehyde from the reaction mixture after the packing distillation with a very high content (99.3 wt.%). This finding further demonstrates that the HETP data produced for the O-80 type packing structure was suitable with experiments and simulation. After distilling the mixture of cinnamaldehyde/benzaldehyde in the experimental batch distillation, the top products of the each feeding mixture with difference volume compositions: n-hexane (mL): cyclohexane (mL) = *V1:V2* = 30:70; 50:50; and 70:30 were analyzed by GC method to verify the ability separation of the packing type O-80.

Fig. 8 shows the GC analysis results of the premixture composition (mixture of cinnamaldehyde/benzaldehyde), Fig. 8 (a), and the top products, Fig. 8 (b-d). The data indicated that benzaldehyde results in 99.3 wt. % of the total mass. This result also proved the very good separation ability of the packing structure O-80 type.
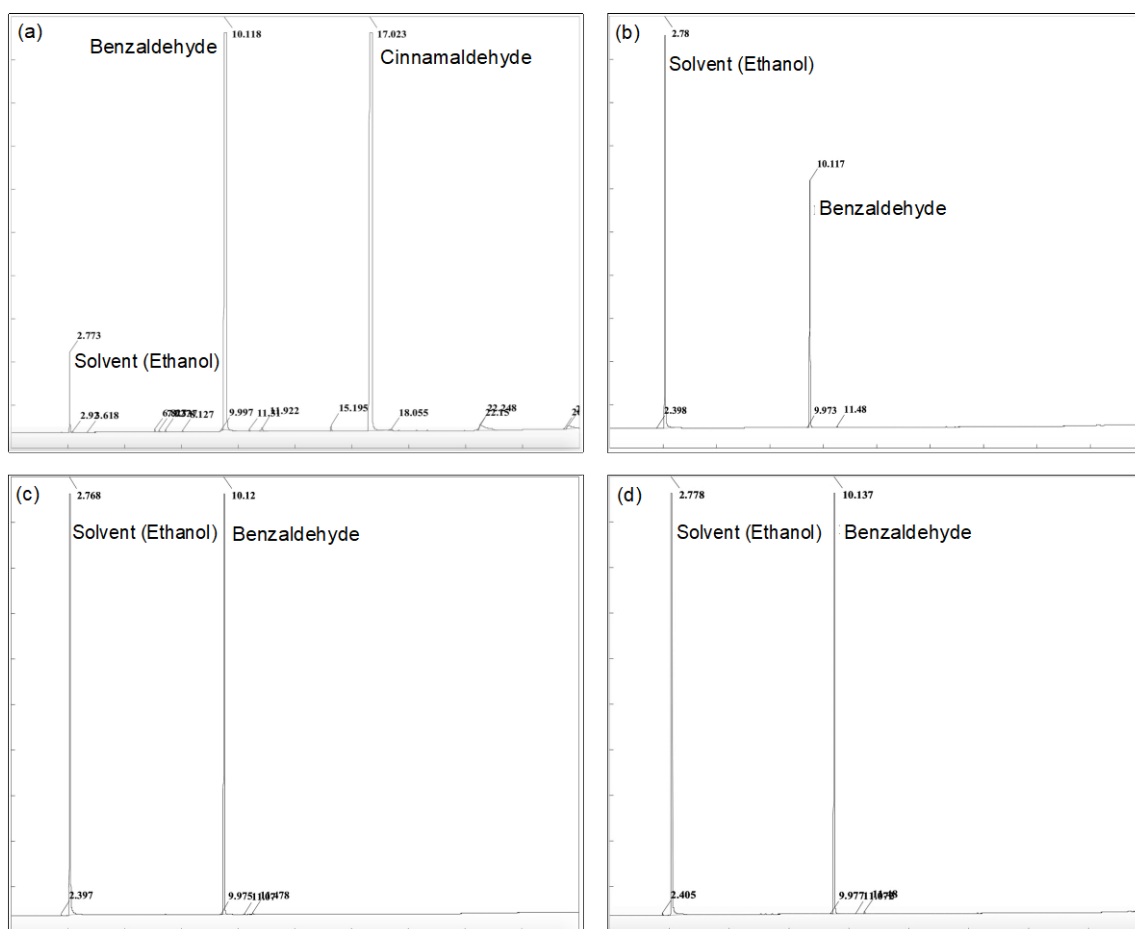
Fig. 8. The GC diagrams of the mixtures in absolute ethanol before and after carrying out the distillation by the batch distillation pilot. (a) The initial mixture of cinnamaldehyde and benzaldehyde; (b - d) Top products of the feeding mixture with different volume compositions: Benzaldehyde (mL): Cinnamaldehyde (mL) = $V1$:$V2$ = 30:70, 50:50, and 70:30 of the distillation process.

4. Conclusion

This study describes a shortcut technique for calculating the HETP value for batch distillation columns. It is employed in the purification of natural benzaldehyde following green synthesis. The experiments indicated that the HETP values for the packing configurations M-50, M-80, O-80, and S-80 are 0.052, 0.053, 0.045, and 0.056, respectively. The comparison of experimental data and simulation results with an error of -0.6 percent illustrates that the short method of estimating HETP is highly reliable, and that this O-80 structure packing can be used on a larger scale. Furthermore, the top product concentration of benzaldehyde is high, up to 99.3 wt.% The purification of the benzaldehyde process by vacuum distillation with O-80 packing is very feasible.

Acknowledgments

References

[1] Nguyen Trung Dung, Cao Hong Ha, Xuan-Mi Meyer, Michel Meyer, Jean-Francois Blanco, and Patrick Cognet, Comparing sustainable methods for synthesis of natural benzaldehyde from trans-cinnamaldehyde: Experimental analysis, Vietnam J. Chem., 2020, 58(4), 471-476.

[2] Buck, Keith T., Anthony J. Boeing, and Joseph E. Dolfini, Method of producing benzaldehyde, U.S. Patent No. 4,673,766, 16 Jun, 1987.

[3] P. Wright, J. Abbot, The oxidation of cinnamaldehyde with alkaline hydrogen peroxide, Int. J. Chem. Kinet., 1993, 25(1), 901-911.
https://doi.org/10.1002/kin.550251104

[4] Z. J. Yang, H.G. Jiang, X. T. Zhou, Y. X. Fang, H. B. Ji, β-Cyclodextrin polymer promoted green synthesis of cinnamaldehyde to natural benzaldehyde in aqueous solution, Supramol. Chem., 2012, 24(6), 379-384.
https://doi.org/10.1080/10610278.2012.688119

[5] Z. Yang, H. Ji. 2-Hydroxypropyl-β-cyclodextrin polymer as a mimetic enzyme for mediated synthesis of

benzaldehyde in water, ACS Sustain. Chem. Eng., 2013, 1(9), 1172-1179.
https://doi.org/10.1021/sc4001059

[6] Bravo, J. L., Rocha, J. A., Fair, J. R., Mass transfer in Gauze Packings, Hydrocarbon Process, 1985, 64, 91-95

[7] Bravo, J. L., Rocha, J. A., Fair, J. R., A comprehensive model for the performance of columns containing structured packings, Inst. Chem. Eng. Symp. Ser. 1992, 128, A489-A507.

[8] Billet, R., Schultes, M., Predicting mass transfer in packed columns, Chem. Eng. Technol. 1993, 16, 1-9.
https://doi.org/10.1002/ceat.270160102

[9] Wang, G. Q., Yuan, X. G., Tang, Z. L., Chen, J. B., & Yu, K. T., A shortcut method for estimating the HETP of structured packed distillation columns at elevated pressure, Chemical Engineering & Technology, 28(7), 767-772. 2005.
https://doi.org/10.1002/ceat.200500065

[10] Henry Z. Kister, Distillation Design, McGraw-Hill, 1992, pp. 523 - 536.

[11] Francisco Carrillo, Ana Martin, and Antonio Rosello, A shortcut method for the estimation of structured packings HETP in distillation, Chemical Engineering & Technology, 23, 2000, pp. 425 - 428.
https://doi.org/10.1002/(SICI)1521-4125(200005)23:5<425::AID-CEAT425>3.0.CO;2-8

[12] V. Bessou, D. Rouzineau, M. Prévost, F. Abbé, C. Dumont, J.-P. Maumus, M. Meyer, Performance characteristics of a new structured packing. Chemical Engineering Science, 2010. **65**(16): p. 4855-4865.
https://doi.org/10.1016/j.ces.2010.05.029

[13] H. Li, M. Han, X. Gao, X. Li, Isobaric vapor-liquid equilibrium for binary system of cinnamaldehyde+benzaldehyde at 10, 20 and 30kPa, Fluid Phase Equilibria, 364 (2014) 62-66.
https://doi.org/10.1016/j.fluid.2013.12.002

[14] C. L. Yaws, M. A. Satyro, Chapter 1 - Vapor Pressure - Organic Compounds, in: C. L. Yaws (Ed.) The Yaws Handbook of Vapor Pressure (Second Edition), Gulf Professional Publishing, 2015, pp. 1-314.
https://doi.org/10.1016/B978-0-12-802999-2.00001-5