

Conceptual design for synthesis of benzaldehyde from natural cinnamomum cassia oil: experiments and simulation

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Abstract. The results of the synthesis of benzaldehyde from trans-cinnamaldehyde in natural cinnamon essential oil are presented in this study. The synthetic experiments were carried out to get the primary input parameters for design and simulation, including reaction and extraction steps. The highest conversion of trans-cinnamaldehyde to benzaldehyde of 33.5 % and the required amount of ethyl acetate solvent (3825 kg/h) were used as the initial parameters for designing and simulation by using the Aspen Plus® software. The optimal stage of extraction was six, and the optimal quantity of ethyl acetate solvent was 3695 kg/h. In the distillation stage, a two-column design was proposed. The first column was for ethyl acetate solvent removal, whereas the second one was used for purifying the target product (benzaldehyde). The operating conditions of the columns were optimized not only based on the vapor feed but also on the equipment cost to minimize the investment budget. The optimal parameters for the first column (D-1) and the second column (D-2) were the theoretical plate numbers of 7 (D-1) and 11 (D-2); the feed position of 3 (D-1) and 5 (D-2); the real reflux ratio of 0.11 (D-1) and 2.59 (D-2); and the distillate for feed fraction of 0.9536 (D-1) and 0.2171 (D-2), respectively.

Keywords: design and simulation, separation and purification, benzaldehyde, trans-cinnamaldehyde, cinnamomum cassia oil.

Classification numbers: 1.1.2, 1.4.6

1. INTRODUCTION

Benzaldehyde (BA) is the second-largest perfume globally that is widely used in the dyestuff, perfumery, and pharmaceutical industries. The demand for natural benzaldehyde is

increasing as consumers tend to pay attention to and use high quality products of natural origin, [1, 2]. Nowadays, it is widely known that benzaldehyde can be produced from several natural products such as: cinnamon cassia oil, apricots, peaches, prunes, etc. [3]. Among the compounds mentioned above, cinnamon cassia oil (containing > 80 wt.% of trans-cinnamaldehyde (CA)) or pure cinnamaldehyde (> 99 wt.% of trans-cinnamaldehyde, that is purified from cinnamon cassia oil in vacuum distillation) are often used as precursors in the synthesis of benzaldehyde [4].

Many different methods are possible to produce natural benzaldehyde from trans-cinnamaldehyde. Buck *et al.* [3] studied a synthetic reaction that used aqueous hydroxide ions as the catalyst (pH range of 11 to 13). The results showed that conversion yields of at least 75 % from cinnamaldehyde to benzaldehyde could be achieved. Philip Wright *et al.* [5] investigated the conversion of trans-cinnamaldehyde in the presence of hydrogen peroxide and water. In their work, the oxidation of cinnamaldehyde by alkaline peroxide resulted in the epoxidation of the double bond to form cinnamaldehyde epoxide. It was followed by a further reaction of a ring-opening and side-chain cleavage to yield benzaldehyde and acidic fragments. In other studies, Hong-Bing Ji *et al.* [6, 7] presented the synthesis of natural benzaldehyde from cinnamaldehyde using sodium hypochlorite as an oxidant and modified β -cyclodextrin as a phase-transfer catalyst (β -CDP). The paper mainly discussed the dependence of the reaction yield on different parameters such as the stirring speed, the amount of catalyst, the reaction temperature, and the molar ratio of NaClO to cinnamaldehyde. The optimal conditions were 400 rpm stirring speed, 70 °C reaction temperature, and the NaClO to cinnamaldehyde ratio of 4:1. In these conditions, the cinnamaldehyde conversion reached 92 % in 2 hours, but the selectivity to benzaldehyde was only 57 %. They also reported the oxidation of cinnamaldehyde using catalyst as cellulose-cross-linked 2-hydroxypropyl- β -cyclodextrin. Accordingly, the conversion of cinnamaldehyde could reach 97 % with the benzaldehyde selectivity of 81 %. The work reported by Yadav, G.D *et al.* [8] showed the cinnamaldehyde conversion of 70 % in 4 hours with a selectivity of 100 % when a novel Al-Mg hydrotalcite catalyst was used. Xin Gao *et al.* [9] reported that the synthesis of natural benzaldehyde was carried out in a novel reactive distillation using β -cyclodextrin as a phase transfer catalyst. The results indicated that higher cinnamaldehyde conversion and yield of benzaldehyde could be obtained with shorter residence time and lower reactants ratio comparing to the conventional process. Chen H. *et al.* reported that the formation of by-products (e.g., 1-naphthalenemethanol, etc.) could be inhibited by using a strongly alkaline environment and high temperature when synthesizing benzaldehyde from cinnamaldehyde [10]. However, according to our best knowledge, the conceptual design and simulation to obtain optimal operating conditions for the three-stage production of natural benzaldehyde have not been reported yet.

In this study, the initial parameters of the system were derived from experiments in which the optimal conditions were obtained by studying the effect of key parameters on the reaction conversion and yields. Based on these data, the Aspen Plus® software (Ver. 10) [11-13] was used to estimate the structural parameters of the equipment and to simulate and optimize the process synthesis of natural benzaldehyde from trans-cinnamaldehyde.

2. MATERIALS AND METHODS

2.1. Materials

Trans-cinnamaldehyde 99 wt.% was purified by a vacuum packing distillation column (at a pressure of 1 - 3 mmHg) from cinnamomum cassia oil at the Arenex Co., Viet Nam. Before each

experiment, the purity of cinnamaldehyde was determined using gas chromatography, indicating that the content of the *trans* isomer was more than 99 wt.%.

Other chemicals, including surfactants (Sodium dodecyl sulfate – SDS), sodium hydroxide (analytical grade), and ethyl acetate solvent (analytical grade), were purchased from Sigma Aldrich. Deionized water (with the conductivity less than 0.5 $\mu\text{S}/\text{cm}$) was used in all experiments.

2.2. Analytical methods

The components of the oil-phase samples were analyzed using a gas chromatography instrument with a flame ionization detector GC-FID (Thermo Scientific™ TRACE™ 1310 Gas Chromatograph) and a BPX-5 column (30 m \times 0.25 mm \times thickness 0.25 μm). The temperature of the injector was 255 $^{\circ}\text{C}$, and the detection temperature was 250 $^{\circ}\text{C}$. A temperature program has been set up to recognize ethyl acetate as the solvent, naphthalene as the internal standard, benzaldehyde as the desired product, *trans*-cinnamaldehyde as the reactant, and *cis*-cinnamaldehyde as the by-product. The brief description of the program is as follows: the starting temperature was kept at 80 $^{\circ}\text{C}$ for 1 min, followed by increasing to 140 $^{\circ}\text{C}$ and 190 $^{\circ}\text{C}$ with the heating rate of 20 $^{\circ}\text{C}\cdot\text{min}^{-1}$ and 3 $^{\circ}\text{C}\cdot\text{min}^{-1}$, respectively. This temperature was remained constant for 1 min.

2.3. Synthesis of benzaldehyde from *trans*-cinnamaldehyde

The synthesis of benzaldehyde from *trans*-cinnamaldehyde was reported by Buck *et al.* [3]. Briefly, the procedure can be described by two reactions (Figure 1): (1) The hydrolysis of cinnamaldehyde in an alkaline medium and (2) the side reaction yielding 1-naphthalenemethanol.

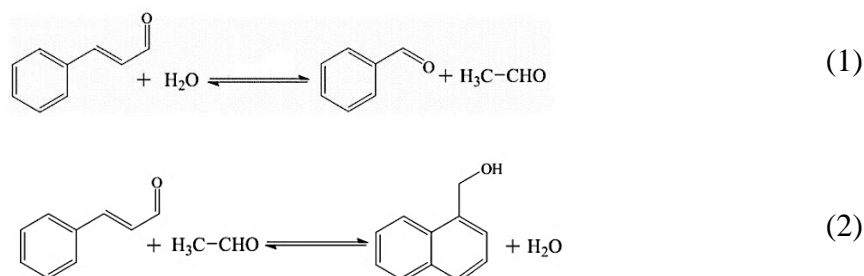


Figure 1. Reaction scheme for the conversion of cinnamaldehyde to benzaldehyde.

The reaction catalyzed by hydroxide ion at the optimal condition was following the procedures: (1) The reactor was a 250 mL three-necked round-bottom flask equipped with a reflux condenser, (2) An amount of *trans*-cinnamaldehyde (99 wt.%) and water were poured into the reactor; (3) The mixture containing sodium hydroxide, SDS, and water was added to the reactor; (4) The mixture was stirred by a magnetic stirrer, then heated to 105 $^{\circ}\text{C}$ using an oil bath, and kept at this temperature for one hour [14].

When the reaction finished, a certain amount of NaCl (solid) was added to the reactor to support the sedimentation of the water phase. After that, the liquid-liquid extraction process was carried out three times using ethyl acetate (30 mL each) to get the organic layer at the bottom of the separatory funnel. The water trace in this organic layer was then removed by magnesium sulfate, followed by a filtration process to get the dry organic phase. Next, it was moved to a

rotatory evaporator at 40 °C to remove ethyl acetate from the mixture. A mixture of benzaldehyde, trans-cinnamaldehyde, and other organic compounds (trace) could be obtained after extraction. In the final step, pure benzaldehyde was collected by using a distillation column.

The conversion of trans-cinnamaldehyde (CA), the yield of benzaldehyde (BA), and the selectivity (S) of the reaction are defined as follows:

$$C_{CA,tot} = \frac{n_{CA,ini} - n_{CA,final}}{n_{CA,ini}} \times 100 \% \quad (1)$$

$$Y_{BA,tot} = \frac{n_{BA,tot}}{n_{CA,ini}} \times 100 \% \quad (2)$$

$$S = \frac{Y_{BA,tot}}{C_{CA,tot}} \times 100 \% \quad (3)$$

where: $C_{CA,tot}$: conversion of trans-cinnamaldehyde (%); $Y_{BA,tot}$: yield of benzaldehyde (%); S : selectivity of reaction; $n_{BA,tot}$, $n_{CA,ini}$, and $n_{CA,final}$: total moles of benzaldehyde at the end of the reaction, and of cinnamaldehyde at the beginning and the end of the reaction, respectively.

2.4. Simulation and optimization

In this study, Aspen Plus[®] software (Ver. 10) was used for the conceptual design of technological processes based on the experimental data. Following each performance, the structural and operational parameters were adjusted and optimized to archive the maximum yield.

3. RESULTS AND DISCUSSION

3.1. Experimental results

In order to identify suitable input parameters for the design and simulation step, various factors influenced on the efficiency of the reaction were studied, including the molar ratio between the catalyst and trans-cinnamaldehyde (CA), the pH of the reaction mixture, and the reaction time. The detailed specifications and results were presented in Table 1.

Table 1. The effect of different reaction parameters on the trans-cinnamaldehyde (CA) conversion yield and benzaldehyde (BA) production yield.

| Parameters/ Outcomes | Experiment number (Exp. No.) | | | | | | |
|-----------------------------|------------------------------|------------|------------|------------|------------|-------------------|------------------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 ^(*) |
| Trans-cinnamaldehyde (mmol) | 65.52 | 65.35 | 65.236 | 65.253 | 65.235 | 65.228 | 65.355 |
| Catalyst/CA molar ratio | 0.024 | 0.073 | 0.153 | 0.024 | 0.073 | 0.5 | 0.5 |
| Stirring rate (rpm) | 400 | 400 | 400 | 600 | 600 | 600 | 600 |
| Conversion of CA (%) | 22.1 ± 2.0 | 46.4 ± 4.6 | 61.1 ± 7.1 | 19.1 ± 1.7 | 65.9 ± 6.1 | 78.2 ± 8.3 | 88.5 ± 12 |
| Yield of BA (%) | 15.7 ± 2.3 | 18.2 ± 2.3 | 23.0 ± 2.6 | 15.2 ± 2.3 | 21.8 ± 2.9 | 33.5 ± 2.0 | 30.5 ± 1.9 |

Other conditions: the mass of SDS is 0.0362 g, and the mass of H₂O is 145 g; the reaction temperature: 105 °C, reaction pressure: 50 mmHg, pH of reaction mixtures: ~ 12.0 - 12.5; the reaction time: 1 hour.
^(*) Experimental validation: pH = 13.5, reaction time: 3 hours.

It can be observed that the RISE of the catalyst/CA mole ratio increased both the conversion of CA and the yield of BA due to the growth in the reaction rate. The reason is that a strong base can accelerate the hydrolysis of cinnamaldehyde. However, in a too-strongly

alkaline environment, the yield of BA would decrease due to the rise of other side reactions, such as the polymerization of benzaldehyde and an Aldol condensation between acetaldehyde (a by-product) and cinnamaldehyde [10].

Another factor that is also crucial to the reaction is the stirring rate, particularly at the high mole ratio of the catalyst over CA. The higher the stirring rate, the more homogenization of the mixture, resulting in a higher interfacial area between the oil and water phases. Therefore, more catalyst ions can take part in the hydrolysis reaction within the oil-water emulsion system.

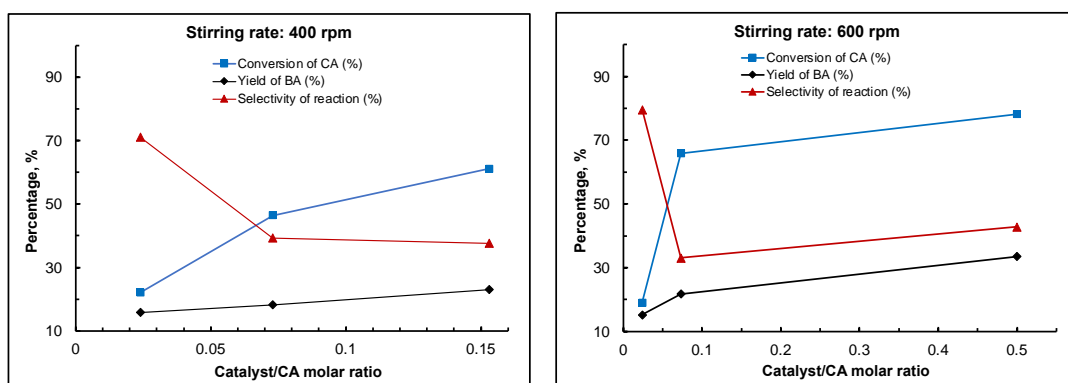


Figure 2. The effect of the catalyst/CA ratio on the conversion of CA, yield of BA, and the selectivity (S) of reaction with the different stirring rates during the reaction process.

At 400 rpm and 600 rpm stirring rates, Figure 2 depicts the relationship between catalyst/CA ratio and CA conversion, BA conversion, and reaction selectivity. The conversion of CA and the yield of BA were the lowest in Exp. No.1 and Exp. No.4, whereas the selectivity (S) of BA was the highest ($> 70\%$). The proposed method can therefore recycle unreacted CA following the distillation process. In contrast, the conversion efficiencies of BA and CA in Exp. No. 3, 6, and 7 were higher (23 and 33.5 %, respectively), but the reaction selectivity was low. It means most of the CA amount was converted to by-products, which could waste the reactant and require a more complex separation.

Based on the experimental results, the design approach was proposed using the reaction conditions in experiment No. 6 with the highest BA conversion efficiency ($Y_{BA,tot} = 33.5\%$, $S = 43\%$). Then, the simulation and design were performed using Aspen Plus® software.

3.2. Conceptual design, simulation, and optimization results

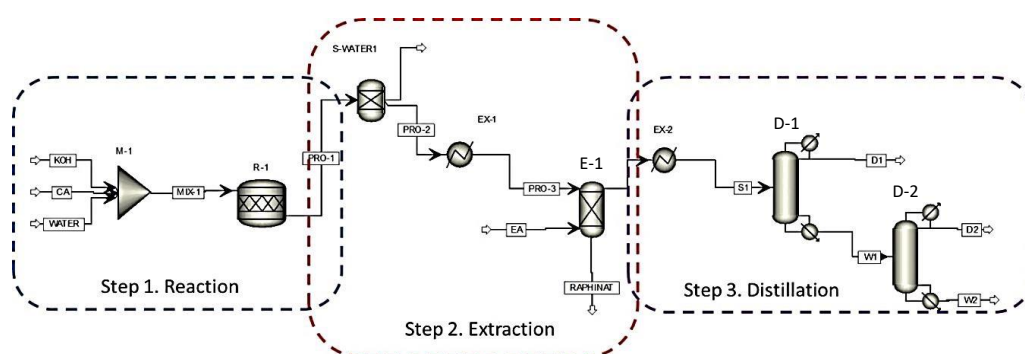


Figure 3. Schematic three-step for producing pure benzaldehyde from trans-cinnamaldehyde in an aqueous hydroxide environment.

The design of a pilot-scale process flow is described in Figure 3, indicating three units: reaction, extraction, and distillation.

In the reaction step, trans-cinnamaldehyde (including fresh and recycled trans-cinnamaldehyde), water, and a NaOH solution are mixed in mixer M-1 and transferred to the reactor (R-1). The reaction temperature and BA yield are set at 105 °C and 33.5 %, respectively. After a certain time, the reaction mixture is cooled down to room temperature. Before performing the distillation step to get the pure target product (*i.e.*, BA), the mixture goes to the extraction step. The S-water unit aims to remove the water phase, to eliminate hydroxide ions in the mixture because these ions may cause the hydrolysis of organic compounds in the distillation unit. Then, the reaction mixture goes to the top of the extraction column (E-1). The recycled ethyl acetate (EA) with a certain amount of fresh EA used as the extracting solvent goes to the bottom of E-1. After the separation, the organic phase is led to pass the heat exchanger (EX-2), and the mixture containing benzaldehyde is fed into the first distillation column (D-1). The distillate (D-1) is sent to a flash separator to recover EA. The bottom product in D-1 is transferred to the second distillation column (D-2) to gain pure benzaldehyde (up to 99 wt.%) in the distillate flow. The bottom product, mainly consisting of trans-cinnamaldehyde, is recycled to the feed flow of the reaction unit.

The following describes in detail each step of the design and simulation to obtain the output parameters of each unit.

3.2.1. CA-BA reactor (R-1)

The yield of BA and the reaction time were used for the conceptual design of the reaction model. A stoichiometric reactor based on known fraction conversion (R-1) in the Aspen Plus[®] software was chosen for the model reactor. This type of reactor only requires the parameters that define the reactions and their extent (e.g., the overall reaction, the yield of products, or selectivity) without any reaction kinetic information.

The reaction can be written:



A benzaldehyde synthesis reactor is designed based on the following experimental data: Reaction time: $t_R = 1$ (hrs); Extra time (assumed): $t_P = 0.5$ (hrs); Reaction efficiency: $u_K = 0.355$; Reaction selectivity: $S_p = 0.43$; Product yield: $\dot{n}_p = 0.76 \left(\frac{\text{kmol}}{\text{hrs}}\right)$.

Suppose the initial cinnamaldehyde concentration is calculated from Exp. No. 6:

$$C_k^o = 0.409 \text{ kmol/m}^3 \quad (4)$$

Then, the volume of the reaction is determined by the formula:

$$V_R = \dot{n}_p \frac{(|v_k|/v_p) t_R + t_P}{C_k^o S_p u_k} = 19.34 \text{ m}^3 \quad (5)$$

The choice of the device diameter (D) is 2.1 m, and the device height (H) is 6.05 m.

Feed materials, including CA, NaOH, and water with the optimal molar ratio CA:NaOH:H₂O of 4.78:1:80 determined from experiment, were mixed evenly in mixing device M-1 before being transferred to reactor R-1. The output product (the product components and their mass flow rate) would be PRO-1, providing information for the next stage. The detailed

input (Feed) and output (PRO-1) and other operating conditions of the reaction stage are summarized in Table 2.

Table 2. Operating conditions and simulation results of the reaction stage.

| Operating conditions and simulation results | | |
|---|-------------|-------------------------------|
| Pressure, atm | 1 | |
| Temperature, °C | 105 | |
| Fraction conversion of CA | 0.335 | |
| Mass flow rate, kg/h | Feed | Output Product (PRO-1) |
| Trans-cinnamaldehyde (CA) | 300 | 199.5 |
| Water | 5016 | 5092.3 |
| Benzaldehyde (BA) | 0 | 80.7 |
| NaOH | 62.76 | 62.76 |
| Acetaldehyde | 0 | 33.5 |

3.2.2. The oil-water separator and the oil extractor

Separator S-water aims to remove the water phase (the upper stream or the light phase) from PRO-1. The lower stream, or the heavy phase, goes to separator E-1. This simulation has the following assumptions: the ratio of the water phase (containing NaOH) to the lower stream (the product) is 9:1 in mass; the amount of ethyl acetate (Aceta-01) generated due to the evaporation is eliminated with an efficiency of 100 %; the content of either CA or BA that goes into the light-phase solvent is less than 1 %. Therefore, a component separator is chosen based on specified flow or split fractions. Trans-cinnamaldehyde and benzaldehyde are the main components of the heavy phase that would come to PRO-2, whose parameters are the input for designing and simulating the next step. The outcomes of the first separator step simulation are listed in Table 3.

Table 3. The simulation results of the separation step.

| Component | Split fraction in light phase (S-Water) | Mass flow rate in PRO-2, kg/h | Mass fraction in PRO-2 |
|----------------------|---|-------------------------------|------------------------|
| Trans-cinnamaldehyde | 0.01 | 197.5 | 0.249 |
| Water | 0.90 | 509.23 | 0.642 |
| Benzaldehyde | 0.01 | 79.89 | 0.100 |
| Acetaldehyde | 1.00 | 0 | 0 |
| NaOH | 0.90 | 6.276 | 0.0079 |
| Ethyl acetate | 0.00 | 0 | 0 |

The aim of the extraction unit is to remove water in the oil phase deeply. In designing the extraction step (E-1), it is of great importance to determine the number of extraction stages and the solvent-to-feed ratio because they closely relate to the extraction efficiency.

Figure 4 indicates the change in the optimal quantity of solvent EA and the fraction of water split concerning the extraction stage number. Observably, as the number of stages rises from 2 to 9, the optimal quantity of EA solvent and the water content in the extract phase decrease. Typically, the extraction efficiency also increases with the increase of the solvent-to-feed ratio. However, if the solvent-to-feed ratio is too high, it would cause excessive solvent extraction and require a long time for the separation in a distillation column system. Besides, a low number of extractive stages corresponds to a higher amount of extraction solvent, higher energy consumption, and larger distillation equipment. The solvent-to-feed ratios are almost unchanged when the number of stages is more than 6. Hence, the number of extraction stages was chosen to be 6 for further calculation with the optimal solvent-to-feed ratio corresponding to this stage is 3825 kg.h^{-1} .

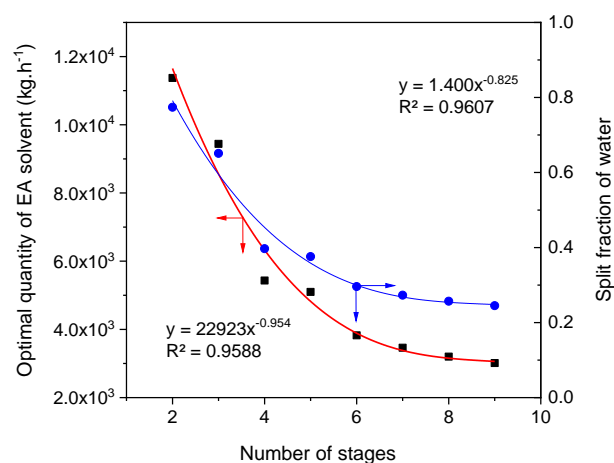


Figure 4. The effect of the number of extraction stages on the optimal quantity of solvent and the amount of ability to deeply separate H_2O from the oil phase (BA-CA).

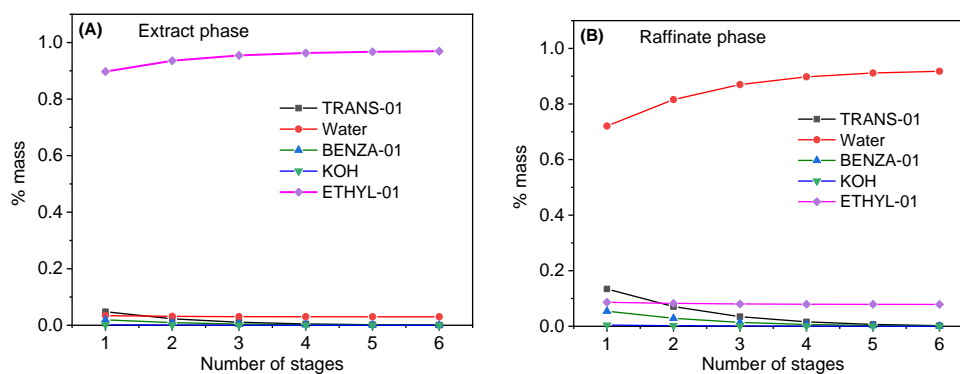


Figure 5. Simulation results: The composition profile of the components in the extract/raffinate phases at each stage of the extraction unit.

The key components were chosen as follows: in the first liquid phase (the extract phase), BA and CA were the key components, and in the second liquid phase (the raffinate phase), water was the key component. The assumed conditions for the extraction included the operation pressure of 1 atm, the operation temperature of $25 \text{ }^\circ\text{C}$, and the initial EA solvent flow rate of 3825 kg.h^{-1} . The simulation results are presented in Figure 5.

The simulation results in Figure 5 show the increase in the extraction yield after each stage, which is almost insignificant from stage 5. After six extraction stages, water is almost removed from the extract phase. The efficiency of the extraction for each component is given in Table 4. The next distillation process was designed and simulated based on the obtained results.

Table 4. Mass split fraction of components in extraction units.

| Component | The 1 st phase (Extract phase) | The 2 nd phase (Raffinate phase) |
|---------------------------------|--|--|
| Trans-cinnamaldehyde (TRANS-01) | 0.995 | 0.005 |
| Water | 0.276 | 0.723 |
| Benzaldehyde (BENZA-01) | 0.995 | 0.005 |
| NaOH | 0.005 | 0.995 |
| Ethyl acetate (ETHYL-01) | 0.995 | 0.005 |

3.3. The distillation column (D-1) and (D-2) analysis

The distillation units were shown in Figure 6, in which the column D-1 was designed to remove solvent EA and trace water from the extraction product. The outlet stream of D-1 containing only BA and CA components, labeled as W1, was fed to column D-2 to separate, and collect the final products.

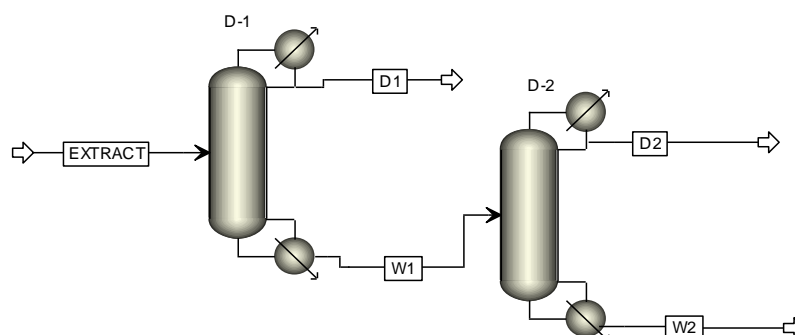


Figure 6. The design of the distillation units for removing the solvent, trace water in the extraction product, and separating BA from CA in the mixture.

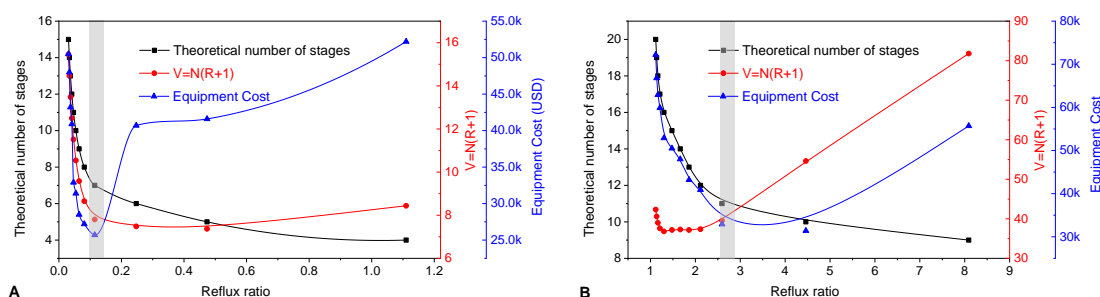


Figure 7. The reflux ratios and the vapor flow (V) depending on the theoretical stages of (A) column D-1 and (B) column D-2.

Parameters chosen for the distillation unit D-1 consist of the recovery of a light key component: ETHYL-01 = 0.9999 and a heavy key component: TRANS-01 = 0.0001. In the design of distillation D-2, these parameters are the recovery of the light key component: BENZA-01 = 0.999 and the recovery of the heavy key component: TRANS-01 = 0.001. The calculation of these distillation columns was performed by using the Winn-Underwood-Gilliland method and the simulation results were presented in Figure 7.

The choice of the theoretical number of stages for the distillation column depends mainly on the vapor flow (V) value. The reflux ratio would be chosen so that the vapor flow can reach the minimum value ($V_{\min} = 7.37$ for D-1 and 37 for D-2). However, if the economic parameters are considered as well, the most suitable value of the theoretical number of stages for D-1 and D-2 should be 7 and 11, respectively. These values are in accordance with the lowest cost, and V values are very close to V_{\min} . Consequently, the corresponding reflux ratio values are 0.126 for D-1 and 2.57 for D-2.

The simulation results for the distillation units are listed in Table 5 and Figure 8.

Table 5. Operating conditions and simulation results for the distillation units.

| Input parameters of the distillation units | | | | | | |
|---|----------------------|---------|--------|----------------------|-------|--------|
| Parameters | D-1 | | | D-2 | | |
| Number of stages | 7 | | | 11 | | |
| Feed position N_F | 6 | | | 7 | | |
| Minimum reflux ratio | 0.012 | | | 0.673 | | |
| Real reflux ratio | 0.126 | | | 2.57 | | |
| Top flow rate (distillate product), $\text{kg}\cdot\text{h}^{-1}$ | 3840 (ethyl acetate) | | | 74.52 (benzaldehyde) | | |
| Operating pressure, (mmHg) | 50 | | | 50 | | |
| Reboiler heat required ($\text{kcal}\cdot\text{sec}^{-1}$) | 15.42 | | | 11.50 | | |
| Mass flow rate ($\text{kg}\cdot\text{h}^{-1}$) | Feed | D1 | W1 | Feed | D2 | W2 |
| Total | 4118.22 | 3840.84 | 277.38 | 277.38 | 74.52 | 202.85 |
| CA | 196.57 | 0.002 | 196.55 | 196.55 | 0.019 | 196.53 |
| Water | 140.69 | 140.67 | 0.021 | 0.021 | 0.021 | 0 |
| BA | 79.51 | 5.328 | 74.18 | 74.18 | 74.11 | 0.074 |
| NaOH | 6.24 | 0 | 6.24 | 6.24 | 0 | 6.24 |
| Acetaldehyde | 3695.19 | 3694.82 | 0.369 | 0.369 | 0.369 | 0 |

Table 5 indicates that the EA composition has reached 96 wt.% in the distillate of column D-1. This might imply that the solvent is being recirculated into the extraction process. On the other hand, the distillate of column D-2 contains 99.8 % of benzaldehyde, meeting the requirement of product purity.

Figure 8 displays the profiles of the composition and temperature at different stages of column D-2. The high concentration of BA (99.8 %) is achieved at the top of the column (stage 1) and remains very low at the bottom of D-2 (stage 10th). In the case of the CA component, the concentration varies in the opposite trend, compared to that of BA (*i.e.*, the highest CA

concentration is at stage 10 and the lowest is at stage 1. Simultaneously, the distillation temperature increases from the top (stage 1) to the bottom of the column.

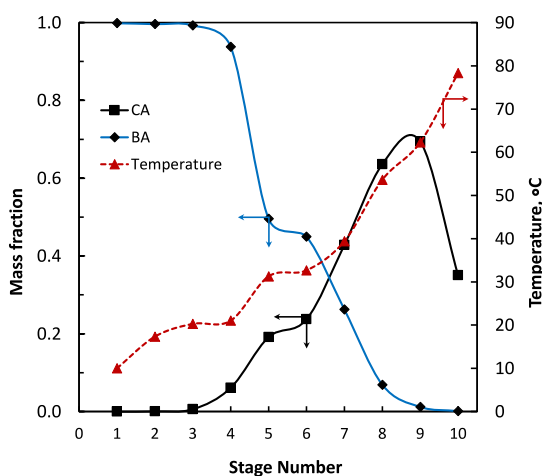


Figure 8. Simulation results: The temperature and composition (% mass) profiles at different stages of the column D-2.

The results confirm that the calculated values of the stage number and the reflux ratio are suitable parameters for designing distillation column and controlling BA purification with high concentration.

Experiment 7 (Table 1) was carried out to confirm the simulation's results. The extraction procedure was used to remove the reaction mixture from the water. Then, this mixture was carried out the BA separating and refining process in a ten-stage batch distillation column. Table 6 compares the result of the simulation and experiment.

Table 6. Comparison of the result of the simulation and experiment.

| Parameters | Simulated results | Experimental data | Error (%) |
|--|-------------------|-------------------|-----------|
| Reaction unit | | | |
| - Conversion of BA | 0.335 | 0.305 | + 8.95 |
| Extraction unit | | | |
| - Split fraction of water | 0.723 | 0.71 | + 1.8 |
| Distillation unit (in vacuum condition) | | | |
| - Purity of BA | 0.998 | 0.993 | + 0.5 |

Figure 9 shows the analytical results of the reaction mixtures in absolute ethanol (by gas chromatography (GC)) after carrying out the vacuum distillation by the batch distillation pilot. Figure 9 (a) shows the GC analysis of the reaction mixture in this diagram. There are two peaks at retention times of 10.118 minutes and 17.023 minutes, corresponding to the signals of benzaldehyde and trans-cinnamaldehyde. Figure 9 (b) exhibits the result of GC analysis of the top product of the distillation unit after carrying out the refining process of BA in the vacuum distillation process. In this diagram, there appears only the benzaldehyde peak. Thus, the results

in Table 6 and Figure 8 demonstrate that the simulation results are comparable to the experimental results.

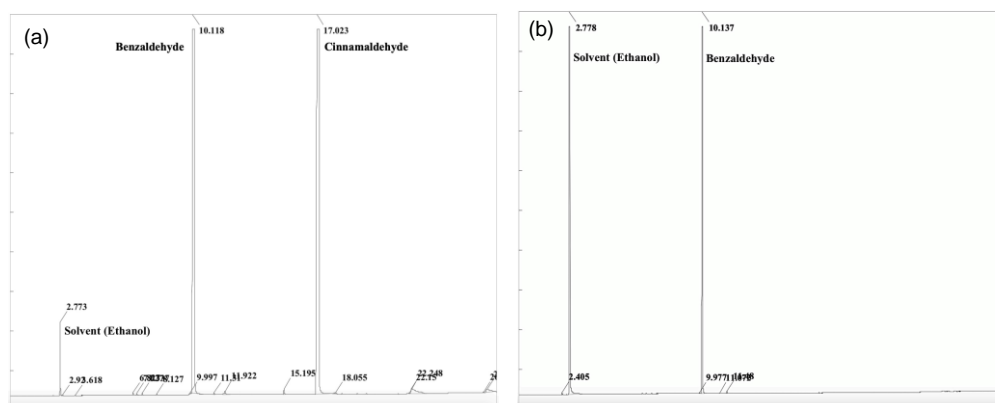


Figure 9. The GC diagrams of the reaction mixture after separating water (a) and top product (b) of the distillation unit.

4. CONCLUSION

The synthesis of natural benzaldehyde processes from trans-cinnamaldehyde is performed, which provides input parameters for the design and simulation of the process. The optimal condition of the reaction is as follows: the mole ratio of catalyst/CA of 0.5, pH of 12.5, and reaction time of 1 hour, then the corresponding yield of BA is 0.335. The design and simulation for the industrial up-scale resulted in a reaction model accompanied with a stoichiometric reactor; the optimal stage of the extract is 6 for the extraction module, and the extraction efficiency can reach up to 99.5 wt.%. In the distillation stage, the two-tower distillation process consists of solvent EA removal and separation of CA from BA. The simulation results allow the specific design of each unit of the process and the equipment, as well as the calculation of the preliminary cost of the stages. The production process is then improved based on system-operating features and cost, providing optimal investment efficiency estimations on the industrial scale.

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CRedit authorship contribution statement. Nguyen Trung Dung and Pham Ngoc Quang: Conceptualized and wrote the manuscript based on experimental data provided by Pham Ngoc Quang, Nguyen Van Anh, and Cao Hong Ha. Ta Hong Duc: Reviewed the language and verified the simulation results. Xuan-Mi Meyer, Jean Francois Blanco, Patrick Cognet, and Michel Meyer: Supported the licensing of Aspen Plus® software and provided methods for simulation. Nguyen Ngoc Quang and Cao Hong Ha: Conducted the experiments. Nguyen Trung Dung: Analyzed the data. Cao Hong Ha: Took overall responsibility for the manuscript.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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