

On the Integration of Reaction and Separation in a Batch Extractive Distillation Column with a Middle Vessel

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In this work, the integration of reaction and separation in a batch extractive distillation column with a middle vessel/reactor is analyzed for azeotrope-forming mixtures. This equipment configuration has the potential to promote the complete conversion of reactants; therefore, the main process characteristics are investigated. A mixture showing several azeotropes and involving an esterification reaction was selected as an academic example. The first part of the paper deals with the phase-equilibrium analysis of the mixture. The nodes (pure components and azeotropes) and the distillation regions of the multicomponent mixture are obtained. The analysis of the topology of the residue-curve map is used to select one of the reagents as entrainer. Feasibility of the combined operation is studied based on the phase-equilibrium analysis and the investigation of the feasible cuts at infinite separation power. The second part of the contribution focuses on the different steps of the process. The influence of operating and process parameters on the operation performance is studied with the aid of a process simulator. Physical explanations are given for the results. Results show the advantages of integrating reaction and separation to enhance both reagents conversion and product separation.

Introduction

A middle vessel batch distillation column consists of a rectifier, a stripper, and a feed vessel in between. The feed mixture is loaded into the middle vessel, and the products are simultaneously obtained from the top and bottom of the apparatus while the middle vessel contents are increasingly purified.¹ An ideal ternary mixture can be separated into a light-component-rich fraction as the distillate, a heavy-component-rich fraction as the bottom, and an intermediate-component-rich fraction that accumulates in the middle vessel. With this equipment configuration, however, minimum-boiling azeotropic mixtures cannot be separated.

Batchwise extractive distillation in a column with a middle vessel has the potential to break minimum-boiling azeotropic mixtures.² A heavy entrainer is fed close to the top of the rectifier in order to overcome the azeotrope. The entrainer absorbs one of the azeotropic components of the mixture from the rising vapor, making the other azeotropic species the distillate product. The entrainer is recovered as the bottom product and recycled into the entrainer vessel once it has been cooled. The main advantage of this configuration is to avoid filling the middle vessel.³

A middle vessel batch column can be also used to improve the performance of reactive batch distillation when the reaction products are the light and heavy component of the mixture.⁴ In the case of an equilibrium reaction taking place in the middle vessel, it is possible to achieve complete conversion of the reagents. In azeotropic mixtures, azeotropes normally consist of both reagents and products; therefore, it may not be possible to reach complete conversion with the middle vessel configuration.

In this work, the integration of reaction and separation in a batch extractive distillation column with a

middle vessel is analyzed for azeotrope-forming mixtures. This equipment configuration has the potential to promote the complete conversion of reactants; therefore, the main process characteristics are investigated. The esterification of ethanol and acetic acid was selected as an academic example because the mixture exhibits highly nonideal phase behavior and it has several azeotropes. Moreover, acetic acid can be used as solvent; hence, it is not necessary to add a new species to the multicomponent mixture. To provide insight for exploring process alternatives and examining the influence of operating and process parameters on the operation performance, CAPE tools are employed. The phase equilibrium is modeled with the Wilson equation, and the reaction is confined to the middle vessel, for convenience.

The first part of the paper deals with the phase-equilibrium analysis of the mixture. The nodes (pure components and azeotropes) and the distillation regions of the multicomponent mixture are obtained.^{5,6} The analysis of the topology of the residue-curve map is used to select one of the reagents (acetic acid) as entrainer. Feasibility of the combined operation is studied based on the phase-equilibrium analysis and the investigation of the feasible cuts at infinite separation power.

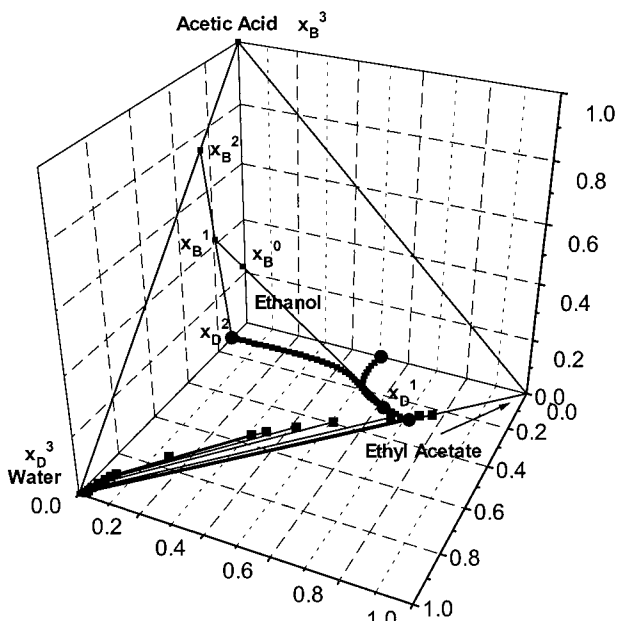
The second part of the contribution focuses on the different steps of the process. The influence of operating and process parameters on the operation performance is studied with the aid of a process simulator. Two different operating regimes are found with their corresponding feasible distillate products. Regimes controlled by a ternary pinch point give rise to distillate products rich in ethyl acetate and water. High purity ethyl acetate distillate products are achieved when the geometry of the internal profile is controlled by a binary pinch.

Results show the advantages of integrating reaction and separation to enhance both reagents conversion and

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Table 1. Node and Kinetic Data for the Reacting Quaternary Mixture

| node identification | composition | T [K] | stability |
|---------------------|---|--------|-----------|
| EtAc–EtOH–W | 0.6317; 0.1111; 0.2572; 0.0000 | 342.92 | unstable |
| EtAc–W | 0.7138; 0.0000; 0.2862; 0.0000 | 343.01 | saddle |
| EtAc–EtOH | 0.5040; 0.4960; 0.0000; 0.0000 | 344.97 | saddle |
| EtAc | 1.0000; 0.0000; 0.0000; 0.0000 | 350.19 | saddle |
| EtOH–W | 0.0000; 0.8928; 0.1072; 0.0000 | 351.11 | saddle |
| EtOH | 0.0000; 1.0000; 0.0000; 0.0000 | 351.32 | saddle |
| W | 0.0000; 0.0000; 1.0000; 0.0000 | 373.14 | saddle |
| AcH | 0.0000; 0.0000; 0.0000; 1.0000 | 390.93 | stable |
| kinetic equation | $r = 7.9 \times 10^{-6} C_{AcH}C_{EtOH} - 2.7 \times 10^{-6} C_{EtAc}C_W$ | | |

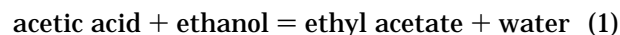
**Figure 1.** Composition tetrahedron and feasible cuts at infinite separation power.

product separation. The thermodynamic analysis at the synthesis step was performed with the CAPE tools AzeoPredictor⁷ and CBD Toolkit⁸ that are able to handle nonidealities in the phase equilibrium. The simulation step was done with the aid of the process simulator Hysys.⁹

Phase Equilibrium Analysis, Reaction Kinetics, and Equipment Configuration

In the reaction mixture, there are three minimum-boiling binary azeotropes (ethyl acetate and water, ethyl acetate and ethanol, and ethanol and water) and one ternary azeotrope (ethyl acetate, and ethanol and water). The azeotrope between ethyl acetate and water is heterogeneous. Figure 1 shows the composition tetrahedron for the quaternary system. The figure presents the eight singular points of the system. The system presents one unstable node (the ternary azeotrope, light component) and one stable node (pure acetic acid, heavy component); therefore, there is only one distillation region although the system presents four azeotropes. All of the binary azeotropes and the remaining pure components are saddle points (intermediate components). The composition, temperature, and stability of each singular point of the quaternary mixture are shown in Table 1. To approach the composition and temperatures of each node, the phase equilibrium was modeled using the Wilson equation. Then, azeotropic compositions, node stabilities, and distillation regions were calculated as explained in Espinosa et al.⁵ and

Salomone and Espinosa⁶ with the aid of CAPE tools (AzeoPredictor, CBD Toolkit).^{7,8} Table 1 also shows the kinetic data for the esterification of ethanol and acetic acid taken from Bogacki et al.¹⁰ These values were taken as representative values of the reaction rate in order to explore the integration possibilities. The reversible reaction scheme is shown in eq 1



It is known that batch reactive distillation can be used for equilibrium-limited reactions where a liquid-phase reaction takes place in the still/reactor and a product is simultaneously removed using a batch rectifier placed above the still. As explained by Venimadhavan et al.,¹¹ this configuration has the potential for essentially complete conversion of the limiting reagent for non-azeotropic mixtures where one of the reaction products is the lightest species in the reaction mixture. However, for azeotropic mixtures, it may be not possible to reach complete conversion due to the presence of low-boiling azeotropes containing one or more reactants. The mentioned authors proposed a novel distillate policy for the case of butyl acetate production.

The lightest node in the quaternary mixture is the ternary azeotrope formed by the two reaction products (ethyl acetate and water) and one of the reagents (ethanol); therefore, complete conversion cannot be achieved by integrating reaction and distillation in the same apparatus. However, conversion enhancement with respect to the reaction followed by separation scheme is even possible with this simple equipment configuration due to the composition of the azeotrope. Figure 1 also shows the feasible cuts at a conventional batch distillation column operated at infinite separation power.^{5,8} The results correspond to a mixture of composition [0.1 EtAc, 0.35 EtOH, 0.2 W, 0.35 AcH]. The number of cuts plus one (the residue) equals the number of components. The ternary azeotrope containing ethyl acetate, water, and ethanol is the unstable node; hence, it will be recovered as distillate during the first cut in a normal batch rectification. The second cut consists of the ethanol–water azeotrope, and pure water will be regained at the top during the third cut. Acetic acid is the stable node, and it will be recovered as a residue at the final step of a batch rectification. All of these cuts and residue will be present when the chemical and distillation steps are combined into an integrated system.

The entire process cycle of batch reactive distillation for the esterification of ethanol and acetic acid consists of three main steps. At the beginning of the first step (start-up period), total reflux operation is maintained until the ternary azeotrope can be drawn-off as distillate. The behavior during the start-up period resembles the operation of the conventional reactor. This step is followed by the production period, where the reaction

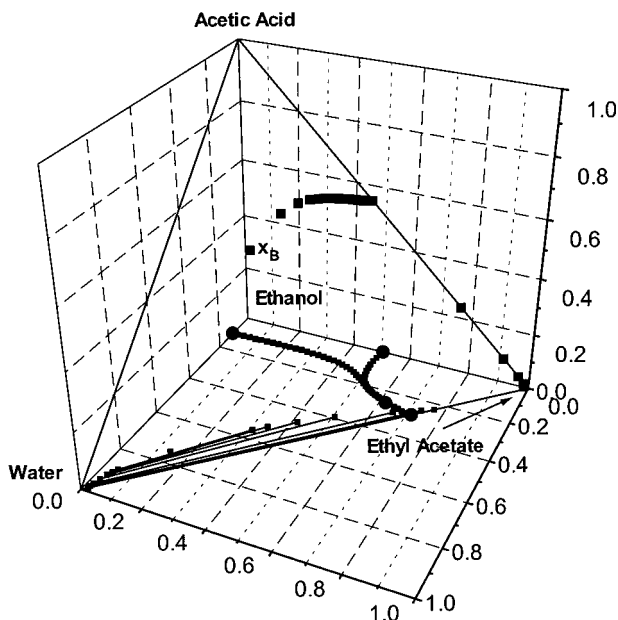


Figure 2. Instantaneous composition profile in a batch rectifier with continuous feeding of entrainer [$V = 55$ kmol/h, $E = 40$ kmol/h, $r = 11.5$].

takes place in the reboiler while the reaction product-rich azeotrope is removed by distillation as overhead product. The elimination of the ternary azeotrope as distillate favors the forward reaction; therefore, a higher conversion of the limiting reactant can be achieved as compared with that of a traditional reactor followed by purification in a batch distillation column. Finally, distillation steps are needed to recover nonreacted ethanol (as the ethanol–water azeotrope) and produce wastewater and leave unreacted acetic acid in the still for recycle to the next batch. A semicontinuous reactive distillation can be also considered. In this case, excess ethanol is fed to the still/reactor during the production step in order to compensate for alcohol losses in the distillate.

Batchwise extractive distillation in a column with a middle vessel has the potential to break minimum-boiling azeotropic mixtures.² A heavy entrainer is fed close to the top of the rectifier in order to overcome the azeotrope. The entrainer absorbs one of the azeotropic components of the mixture from the rising vapor, making the other azeotropic species the distillate product. The entrainer is recovered as the bottom product and recycled into the entrainer vessel once it has been cooled. The main advantage of this configuration is to avoid filling the middle vessel.³ This equipment configuration could be used to overcome the azeotrope and, hence, to achieve near-complete reagents conversion if an appropriate entrainer is available.

An appropriate entrainer, following thermodynamic rules, must be the stable node of the multicomponent mixture where the azeotrope to be broken acts as an unstable node. As we stated previously, acetic acid is the stable node of the multicomponent mixture; hence, the criterion for entrainer selection in processes without distillation boundaries (one distillation region) is obeyed.¹² This statement means that all residue curves must start at the unstable node and terminate at the stable node. As in the case of an ideal mixture, just a single origin and a single terminus of the residue curves must exist. This occurs in the quaternary mixture; hence, acetic acid

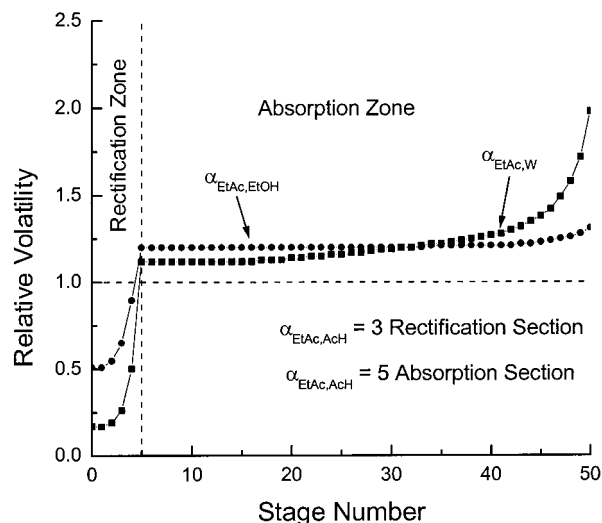


Figure 3. Relative volatilities versus stage number in a rectifier column with an absorption zone [$V = 55$ kmol/h, $E = 40$ kmol/h, $r = 11.5$].

is a feasible entrainer. Figure 2 shows an instantaneous rectifier composition profile in the composition tetrahedron.

The profile was obtained by simulation with Hysys. Acetic acid is used as entrainer to break the ethyl acetate–water–ethanol homogeneous azeotrope; therefore, it is fed near the rectifier top to absorb both water and ethanol leaving high purity ethyl acetate as the distillate. Note that there exists a binary pinch immediately below the feed point and that the internal profile lies far away from the liquid–liquid region due to the high entrainer mole fraction. The feed point divides the column section in an absorption section below the feed point and a rectifier section above the feed stage, where the ester/entrainer separation takes place. The main effect of adding the entrainer near the rectifier top is shown in Figure 3.

The solvent causes a change in the relative volatilities between the azeotrope constituents. Ethyl acetate is the most volatile component in the absorption zone. An inversion in the volatility order occurs in the rectification region, but the vapor feed to this section contains mainly the ester and the entrainer. Without the absorption region, the most volatile component is the ternary azeotrope; therefore, the relative volatility between ethyl acetate and each of the other azeotrope constituents is 1. A discussion about the main conditions that a candidate extractive solvent must satisfy to make the separation feasible can be found in Hilmen et al.³ These rules state that the azeotrope will be replaced as distillate product by one of the saddle nodes of the mixture. For ternary systems, the authors plot the univolatility line in the composition triangle, locus where the relative volatility between the azeotrope constituents is 1. This line extends from the azeotrope to the binary edge between the solvent and the component that will be recovered as the distillate. Although such analysis is beyond the objectives of this work, it can be seen that a feasible distillate product could be the binary azeotrope between ethyl acetate and water (a saddle of the multicomponent mixture). Now, when the analysis is applied for the ternary mixture formed by the binary azeotrope between ethyl acetate and water and the solvent (a face in the composition tetrahedron), it can be concluded that ethyl acetate is a feasible distillate

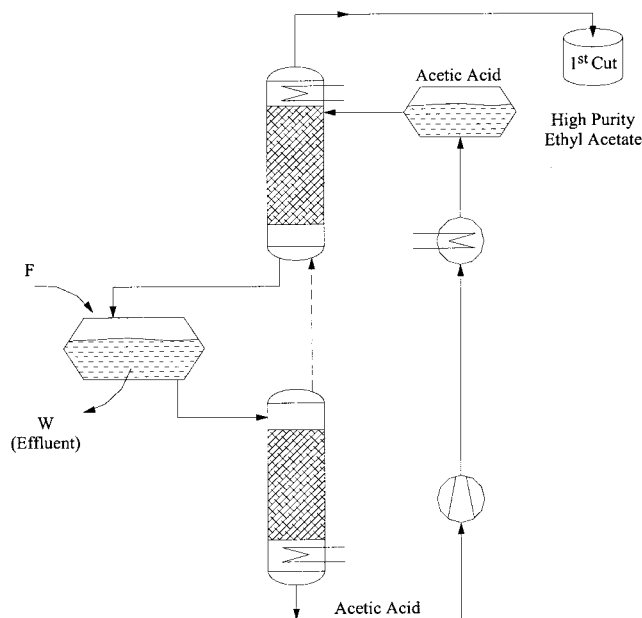


Figure 4. Integration of reaction and separation in a batch-extractive distillation column with a middle vessel/reactor. The feed to the middle vessel contains acetic acid, ethanol, and water.

product, too. Therefore, and depending on both operating and process parameters, high purity ethyl acetate or distillate products rich in ethyl acetate and water can be expected.

With these ideas in mind, the esterification of ethanol and acetic acid could be batchwise performed in a middle vessel column where acetic acid is used as entrainer to break the homogeneous ternary azeotrope. The entrainer is either totally or partially recovered in the stripper section and recycled to the entrainer vessel. At the end of the main production step, the composition of the middle vessel consists of pure water or a mixture of water and acetic acid, and the ethanol conversion approaches unity. As shown in Figure 4, the liquid stream leaving the upper column section is diverted to the middle vessel/reactor while the vapor stream leaving the stripper is passed by to the upper column section. The liquid stream leaving the middle vessel is fed to the stripping section. Although several possible equipment arrangements exist, the configuration where the vapor stream leaving the lower column section is passed by to the upper column section was selected because the practical feasibility of this column configuration was studied for nonreactive mixtures by Barolo et al.¹³

All of the studies in this work are performed for a middle vessel column having 20 stages in the rectifying column, 20 stages in the stripping column, a middle vessel/reactor, a condenser drum, and a reboiler. A simplifying assumption is that the chemical reaction takes place only at the middle vessel. This assumption will be considered here for convenience, because the main objective of this work is to study the main characteristics of the process for azeotropic mixtures. Real implementation of this technology requires removing simplifying assumptions or taking another column arrangements into consideration. Separation of the homogeneous catalyst should be taken into account for homogeneous catalyzed reactions. On the other hand, heterogeneous catalyzed reactions should consider that the reaction takes place in the section of the rectifier immediately above the middle vessel, as implemented

by Schneider et al.¹⁴ for a semibatch process for the production of methyl acetate.

Operating Sequence

Step 1. Startup. Total Reflux and Reboil Ratios Without Solvent Feeding ($r = \infty$, $s = \infty$, $E = 0$). The composition of the reflux drum changes until it achieves the composition corresponding to the ternary azeotrope (unstable node). At the very beginning of this step, however, the ethanol–water azeotrope accumulates in the reflux drum due to the absence of the ester in the middle vessel.

Step 2. Eliminate Off-Spec Product. Total Reflux and Reboil Ratios with Solvent Feeding ($r = \infty$, $s = \infty$, $E > 0$). Because of the absorption effect of the solvent, a product richer in the reaction products than in the ternary azeotrope accumulates in the reflux drum. The level in the middle vessel increases to accommodate the volume of the entrainer added during this period.

Step 3. Production Period. Operation Under Finite Reflux and Reboil Ratios with Solvent Feeding ($r > 0$, $s > 0$, $E > 0$). During this step, a product rich in the reaction products is collected as distillate. The solvent is either totally or partially recovered at the column bottom. The level in the middle vessel decreases from its maximum value at the end of step 2. High limiting-reagent conversion can be achieved depending on operating and process parameters.

Step 4. Eliminate Off-Spec Product. Total Reflux Operation without Solvent Feeding ($r = \infty$, $s > 0$, $E = 0$). At the end of production period (step 3), the middle vessel composition is mainly formed by acetic acid and water. Ethyl acetate and ethanol are only present in small amounts. The solvent feeding is stopped. Total reflux operation is implemented to achieve the composition of the ternary azeotrope in the reflux drum to avoid off-specification product.

Step 5. Recovery of Remaining Ester as Ternary Azeotrope. Operation under Finite Reflux and Reboil Ratios ($r > 0$, $s > 0$, $E = 0$). The azeotropic cut is diverted to the main product tank. The entrainer is removed at the column bottom.

Step 6. Shutdown. The reflux drum content is diverted to the product tank. The middle vessel content, on the other hand, can be processed in a conventional batch rectifier to remove water as distillate product and leave excess solvent in the still for recycle to the next batch. This operation can be also performed in the middle vessel column. Depending on the reflux and reboil ratio policy, either acetic acid or water is collected in the middle vessel at the end of the operation.

Table 2 shows a feasible operating sequence. Results corresponding to a mixture of composition [0 EtAc, 0.45 EtOH, 0.1 W, 0.45 AcH] and an amount of 172.8 kmol are presented in Figure 5a–c.

During the startup period, the composition of the reflux drum changes until it achieves the composition corresponding to the ternary azeotrope (Figure 5a). At the very beginning of this step, however, the ethanol–water azeotrope accumulates in the reflux drum because the feed mixture to the middle vessel does not contain the ester. The middle vessel concentrations of both reaction products increase their values; therefore, a sharp decrease in the reaction rate takes place (Figure 5b,c).

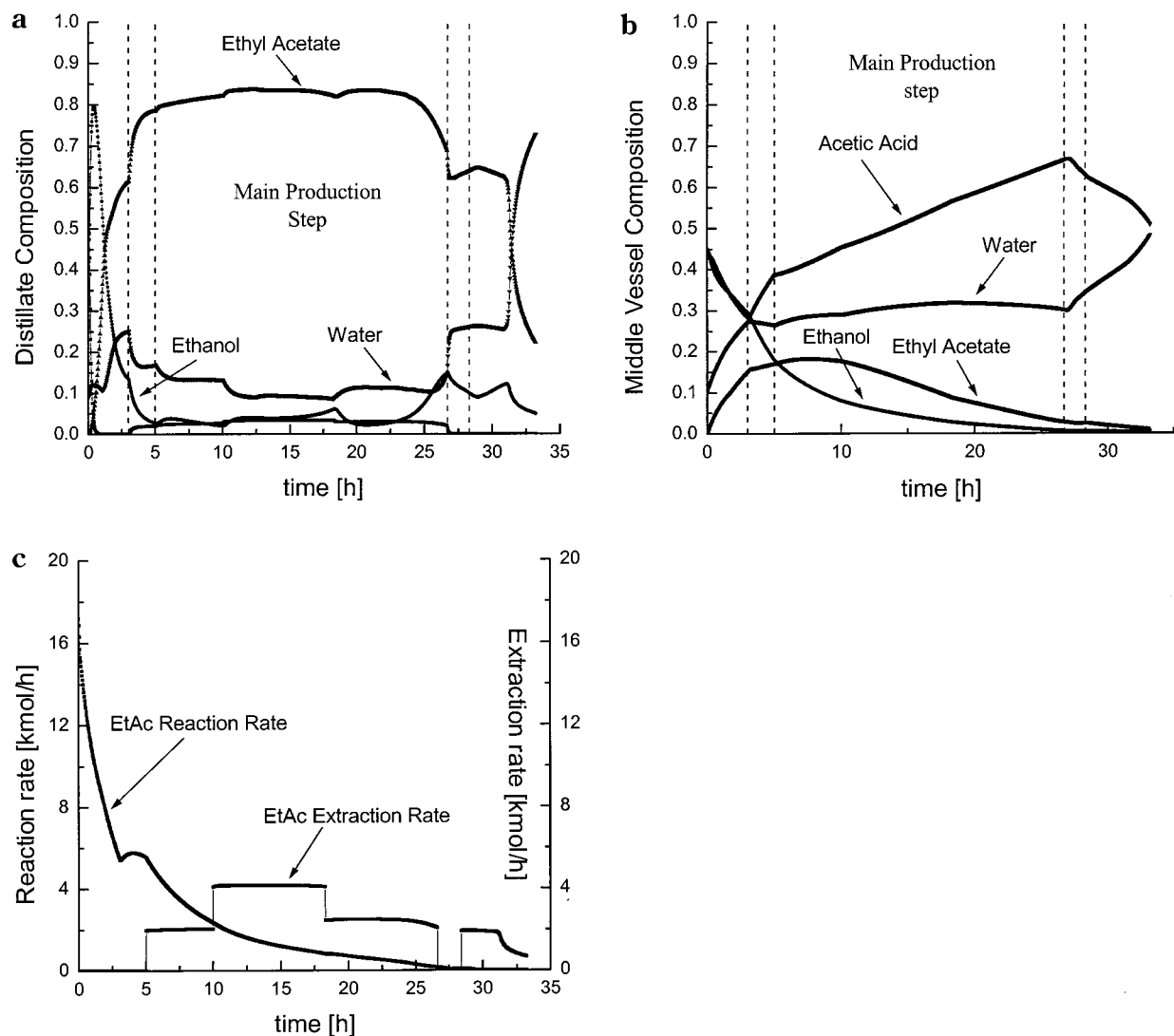


Figure 5. (a) Evolution of the compositions in the reflux drum. (b) Evolution of compositions in the middle vessel. (c) Evolution of ethyl acetate production rate due to reaction and extraction rate by distillation.

Table 2. Feasible Operating Sequence

| time period [min] | operating sequence |
|---|---|
| 0–180, startup (step 1) | $R \rightarrow \infty, S \rightarrow \infty, E = 0$ kmol/h |
| 180–300, eliminate off-spec product (step 2) | $R \rightarrow \infty, S \rightarrow \infty, E = 25$ kmol/h |
| 300–600, main production period (step 3) | $D = 2.5, B = 15, E = 25$ kmol/h |
| 600–1100, main production period (step 3) | $D = 5.0, B = 20, E = 25$ kmol/h |
| 1100–1600, main production period (step 3) | $D = 3.0, B = 20, E = 25$ kmol/h |
| 1600–1700, eliminate off-spec product (step 4) | $D = 0, B = 20, E = 0$ kmol/h |
| 1700–2000, recovery of remaining EtAc as ternary azeotrope (step 5) | $D = 3.0, B = 17, E = 0$ kmol/h |

Two hours are needed in step 2 to achieve an absorption profile in the rectifier and, therefore, to overcome the azeotropic composition. The reflux-drum content increases its ester composition while the concentrations of both water and ethanol decrease, as shown in Figure 5a. The level in the middle vessel increases to accommodate the volume of the entrainer added during this period.

The production period is divided into three steps in the example considered. Because of both the solvent

recovery in the stripper section and distillate removal, the level in the middle vessel slowly decreases from its maximum value at the end of step 2. The distillate composition remains approximately constant during all of the steps, and the ester concentration in the middle vessel starts decreasing only when the instantaneous extraction rate by distillation is greater than the instantaneous production rate by chemical reaction (Figure 5b,c). The distillate rate (reflux ratio) must be decreased (increased) at the end of the period to avoid alcohol build up in the reflux drum. The end of the reaction in the middle vessel corresponds to a sharp decrease in the ester concentration in the distillate at the expense of an increase in the ethanol composition, as shown in Figure 5a. Neither the solvent flow rate nor the distillate flow rate (reflux ratio) is enough to maintain the distillate composition at its constant value because both ethanol and ethyl acetate in the middle vessel are present in small amounts.

During step 4, total reflux operation is re-established and solvent feeding is stopped. As a consequence, the composition of the ternary azeotrope is achieved in the reflux drum.

The ternary azeotrope is collected as distillate in step 5 until a sharp increase in the water concentration in

the distillate occurs (Figure 5a). The ethanol conversion is about 93%. The middle vessel level sharply decreases because solvent recovery is done until operation end. Note however that until the end of step 4 the extraction rate of the solvent is lower than the feeding rate; therefore, a partial recovery of the solvent is accomplished (89%). Although theoretically possible, a complete entrainer recovery depends on the stripper separation power given by the number of stages, reboil ratio, and ease of separation (i.e., relative volatilities). The bottom flow rate was selected in this example to recover pure acetic acid at the stripper bottom. The final mixture in the middle vessel mainly contains acetic acid and water that can be either separated in a conventional rectifier column or in the middle vessel column. Depending on the reflux and reboil ratio policy, either acetic acid or water is collected in the middle vessel at the end of the operation.

The role of steps 1 and 2 was studied in Lelkes et al.¹⁵ for conventional batch extractive distillations. The end of the start-up period is indicated by the steady-state operation of the column (achievement of the ternary azeotrope composition in the reflux drum). Although it is possible to start the solvent feeding before reaching the steady state, the mentioned authors do not recommend this because a significant amount of solvent is consumed without any benefit because the trays are still cold. If step 2 is skipped, on the other hand, the distillate withdrawal begins with a very bad quality product of azeotropic composition. It seems that, in the example considered, an optimal time for each of these periods exists. While the column behavior for large total reflux periods resembles the reactor operation (this is true in the limit of zero condenser and column trays holdup), short total reflux periods lead to a high reflux (or solvent feed rate or both of them) operating policy to achieve products with low limiting-reagent content, as explained in Espinosa and Salomone.¹⁶ For all of the simulations, the time for steps 1 and 2 was fixed to achieve the corresponding steady-state operation.

During step 3, a finite value for the reflux ratio is established; therefore, the ester is recovered at a rate proportional to the distillate flow rate according to its composition. Figure 5c indicates that, most of the time, ethyl acetate was recovered at the column top at a rate greater than its instantaneous production rate by reaction. The average extraction rate by distillation is about 2.1 times the average production rate by chemical reaction. For this reason, the ester composition in the middle vessel decreases as the reaction proceeds. Such a distillate flow rate leads to high limiting-reagent conversion. On the contrary, operation at a very high (low) reflux ratio (distillate flow rate) leads to low ethanol conversions because the ester is recovered at a rate which is lower than its production rate. In this case, the ester composition in the middle vessel increases as the reaction proceeds. Therefore, the distillate rate relative to the reaction rate in the middle vessel plays an important role in the operation performance. This subject was pointed out in Venimadhavan et al.¹¹ and Gadevar et al.¹⁷ by defining the Damkholer number. Similarly, a reaction versus distillation ratio defined as $RD = rV_{MV}/D$ is proposed in Espinosa and Salomone.¹⁶ Constant values of these parameters lead to a decreasing distillate rate policy that intends to keep the rate of product removal proportional to the rate of production.

Table 3. Operation Sequence for Simulations with Different Locations of the Feed Stage

| time period [min] | operating sequence |
|---|---|
| 0–180, startup (step 1) | $R \rightarrow \infty, S \rightarrow \infty, E = 0$ kmol/h |
| 180–300, eliminate off-spec product (step 2) | $R \rightarrow \infty, S \rightarrow \infty, E = 25$ kmol/h |
| 300–600, main production period (step 3) | $D = 2.5, B = 15, E = 25$ kmol/h |
| 600–1100, main production period (step 3) | $D = 5.0, B = 20, E = 25$ kmol/h |
| 1100–1600, main production period (step 3) | $D = 3.0, B = 20, E = 25$ kmol/h |
| 1600–1700, recovery of the remaining EtAc as ternary azeotrope (step 5) | $D = 3.0, B = 17, E = 0$ kmol/h |

Table 4. Influence of the Location of Solvent Feed Stage on Alcohol Conversion, Ester Recovery Rate, and Product Composition^a

| feed stage | χ_{EtOH} σ_{EtAc} | | product composition | | | |
|------------|-------------------------------|--------------|----------------------|--------|---------------|--------|
| | | | AcH | EtOH | EtAc | W |
| 1 | 94.64 | 89.36 | 0.1083 | 0.0329 | 0.7730 | 0.0858 |
| 2 | 93.83 | 93.16 | 0.0276 | 0.0494 | 0.7933 | 0.1297 |
| 4 | 92.97 | 90.29 | 0.0025 | 0.0534 | 0.7671 | 0.1770 |
| 6 | 91.91 | 87.68 | 0.0003 | 0.0607 | 0.7381 | 0.2009 |
| 10 | 90.45 | 83.38 | 2.7×10^{-6} | 0.0700 | 0.6891 | 0.2409 |

^a In all cases, the same operation strategy was employed. The solvent recovery rate is about 76.7%. Maximum in a variable is indicated in boldfaced type.

Influence of Operating and Process Parameters on Operation Performance

In the following, the influence of several operating and process parameters on the operation performance are presented. Physical explanations are given for the results.

Influence of the Feed Stage. Table 3 shows the operation sequence applied for 28 h for different locations of the feed stage of the entrainer. The stage number one is the first stage underneath the condenser. As performance measures the recovery rate of the ester, ethanol conversion and product composition were adopted. The recovery rate of the ester is the ratio of the amount of ethyl acetate in the distillate to the amount of ethyl acetate produced by chemical reaction. The results of several simulations with the variation of the location of the feed stage are shown in Table 4.

The conversion of the limiting reagent decreases from 95% to 90% with the feed stage moving downward in the column. The ester recovery rate and the composition of ethyl acetate in the product, on the other hand, present a maximum when the solvent is fed at the second stage.

In the studied range of feed locations, the solvent mainly absorbs the alcohol. Therefore, the distillate products are rich in ethyl acetate and water. The internal composition profile presents a ternary pinch in the absorption zone.

Both ethanol and water compositions in the distillate increase their values as the absorption zone diminishes because the absorption capacity of the solvent diminishes. Moreover, an inversion in the volatility order between the ester and both the alcohol and water takes place in the rectifying zone above the feed stage. A feeding of the solvent that is too close to the top of the column prevents the necessary removal of acetic acid from the vapor stream in the rectifying section of the column. Two or three stages are required in the rectifying section to get a product with small amounts of

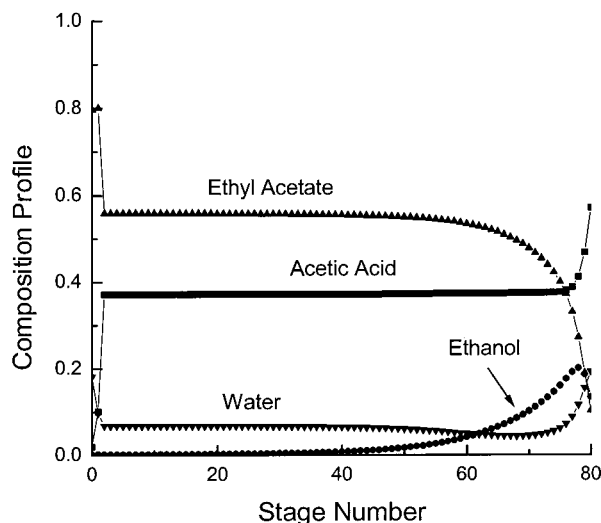


Figure 6. Operation controlled by a ternary pinch point.

solvent. As a consequence, a maximum in the ester concentration is expected.

Because the product amount is the same for all simulations, an increase in the ethanol lost at the column top as the location of the feed stage is increased produces a smaller conversion of the alcohol. The recovery rate of the ester follows the same trend as the composition of ethyl acetate in the distillate.

The optimal location of the feed stage should consider the tradeoff between separation and reaction targets.

Similar results are obtained when the number of stages is increased. In such cases, the alcohol conversion increases for a given feed location because the absorption capacity of the solvent also increases; hence, ethanol is returned to the reaction zone (the middle vessel) in a more effective way. The direct effect of a better conversion is a decrease in the ethanol loss in the distillate product that is balanced through an increment in the ester composition; therefore, the ester recovery is also favored.

Figure 6 shows the instantaneous rectifier profile at the beginning of the main production step for the case of a rectifier having 80 stages. The alcohol is completely returned to the reaction zone, and the absorption zone presents a ternary pinch formed by the ester, acetic acid, and water. Because of the inversion in the volatility order between the ester and water in the section above the feed stage, the product composition will tend, as a limit, to the composition of the azeotrope between both components as the number of stages in the pure rectifying section above the feed stage increases. This behavior agrees with the well-known fact that when a minimum-boiling azeotrope (unstable node) is broken by extractive distillation, the distillate will be formed by one of the intermediate nodes (saddle node) of the multicomponent mixture, as stated by Hilmen et al.³ Distillate products rich in both ethyl acetate and water are obtained when the internal profiles are controlled by ternary pinch points. This behavior can be related to low or moderate absorption capacity in the absorption zone of the rectifier unlike it occurs when the internal profiles are controlled by binary pinch points. Figures 2 and 6 are examples of the two different regimes that can be found for the quaternary mixture being studied here.

Influence of the Solvent Flow Rate. The operation sequence for different entrainer flow rates is shown in Table 5. The increment in the entrainer flow rate

Table 5. Operation Sequence for Simulations with Different Solvent Flow Rates

| time period [min] | operation sequence |
|---|---|
| 0–180, startup (step 1) | $R \rightarrow \infty, S \rightarrow \infty, E = [0,0,0]$ kmol/h |
| 180–300, eliminate off-spec product (step 2) | $R \rightarrow \infty, S \rightarrow \infty, E = [20,25,30]$ kmol/h |
| 300–600, main production period (step 3) | $D = 2.5, B_0 = [20,25,30], E = [20,25,30]$ kmol/h |
| 600–1100, main production period (step 3) | $D = 5.0, E = [20,25,30]$ kmol/h |
| 1100–1500, main production period (step 3) | $D = 3.0, E = [20,25,30]$ kmol/h |
| 1500–1700, recovery of the remaining EtAc as ternary azeotrope (step 5) | $D = 3.0, E = [0,0,0]$ kmol/h |

Table 6. Influence of Entrainer Flow Rate on Alcohol Conversion, Ester Recovery Rate, and Product Composition

| entrainer flow | χ_{EtOH} | σ_{EtAc} | product composition | | | |
|----------------|---------------|-----------------|---------------------|--------|--------|--------|
| | | | AcH | EtOH | EtAc | W |
| 20 | 91.11 | 91.22 | 0.0171 | 0.0543 | 0.7602 | 0.1684 |
| 25 | 92.89 | 93.77 | 0.0264 | 0.0509 | 0.7958 | 0.1269 |
| 30 | 93.94 | 95.33 | 0.0356 | 0.0504 | 0.8186 | 0.0954 |

| entrainer flow | σ_{AcH} | middle $V\%$ level ^{max} | x_{AcH}^{end} | mean reaction rate |
|----------------|----------------|-----------------------------------|-----------------|--------------------|
| | | | | [kmol/h] |
| 20 | 89.21 | 61 | 0.3910 | 2.56 |
| 25 | 87.13 | 69 | 0.4721 | 2.61 |
| 30 | 85.46 | 75 | 0.5466 | 2.64 |

involves increments in the conversion of the limiting reagent, the recovery rate of the ester, and the composition of the ester in the distillate, as can be seen in Table 6.

However, the solvent recovery rate as pure acetic acid at the stripper bottom decreases while the remaining mixture in the middle vessel at the end of step 5 increases both its amount and its acid mole fraction (x_{AcH}^{end}) as the entrainer flow rate increases.

Table 6 also shows the maximum liquid level achieved in the middle vessel during operation. It must be noted that an operating limit to the maximum solvent flow rate given by the flooding condition of the column exists.¹⁸ On the other hand, the limit for the minimum solvent flow rate is related to a poor absorption capacity of the entrainer.¹⁹ It is noteworthy that, in all simulations, the recovery of entrainer at the stripper bottom was performed as fast as possible. To do this, the instantaneous bottom flow rate was changed starting from a flow rate equal to the solvent flow rate in order to maintain the temperature at a certain location of the stripper at the value corresponding to the boiling point of the acetic acid. The improvement in the performance for increased values of the entrainer flow rate is based on two reasons: a better mean reaction rate (Table 6) and a more effective separation between the ester and both water and alcohol in the absorption zone.

The enhancement in the reaction rate is mainly a consequence of the higher concentrations of acetic acid achieved in the middle vessel. To demonstrate the influence of high solvent flow rates in the absorption capacity of the entrainer, a simulation was performed at a high entrainer flow rate. Figure 7 shows the instantaneous rectifier profile at the beginning of the main production step for the case of a very high solvent flow rate. Both ethanol and water are completely returned to the reaction zone; therefore, the ester and acetic acid mainly form the distillate product. The acid

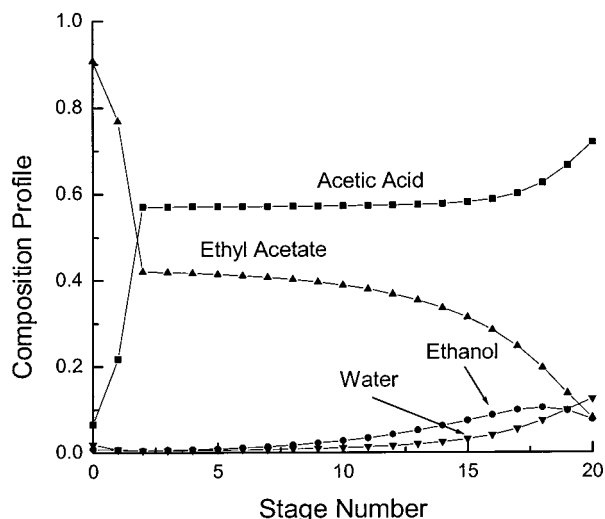


Figure 7. Operation controlled by a binary pinch point.

Table 7. Operation Sequence for Simulations with Different Distillate Flow Rates

| time period [min] | operating sequence |
|---|---|
| 0–180, startup (step 1) | $R \rightarrow \infty, S \rightarrow \infty, E = 0$ kmol/h |
| 180–300, eliminate off-spec product (step 2) | $R \rightarrow \infty, S \rightarrow \infty, E = 25$ kmol/h |
| 300–1100, main production period (step 3) | $D = [2.5, 3.5, 4.5, 6], B_0 = 25, E = 25$ kmol/h |
| 1100–1300, recovery of the remaining EtAc as ternary azeotrope (step 5) | $D = [2.5, 3.5, 4.5, 6], E = 0$ kmol/h |

composition in the distillate can be sharply reduced by increasing the number of stages in the rectifying section above the feed stage, but in this case, a loss of the other components should be expected as explained in the previous section. Note that, for this example, the internal profile is controlled by a binary pinch.

The optimal solvent flow rate should consider the tradeoff between both reaction and separation targets in the first part of the process (until the end of the main production step) and the separation of the mixture acetic acid–water. Also, a constraint on the maximum feasible entrainer flow rate should be taken into account. If the amount of solvent required for a given operation is more than what the column can accommodate without flooding, the middle vessel should be charged to a certain fraction of the maximum capacity, as proposed by Mujtaba.¹⁸

Influence of the Distillate Flow Rate. Table 7 shows the operating sequence followed for different distillate flow rates. As the rising vapor stream is almost constant, an increase in the distillate flow rate means a lower reflux ratio and vice versa. To analyze the operation performance, the following variables were calculated: alcohol conversion, ester recovery rate, product composition, amount of moles remaining in the middle vessel, and throughput. The throughput is defined here as the ratio of the amount of distillate to the operation time.

Table 8 shows that an increment in the distillate flow rate enhances the recovery rate of ethyl acetate and produces a sharp increment in the throughput. Separation water/acetic acid is also facilitated because the remaining amount of moles in the middle vessel sharply decreases. However, there should be an optimum value for the distillate flow rate because both the conversion

Table 8. Influence of Distillate Flow Rate on Alcohol Conversion, Ester Recovery Rate, Product Composition, Middle Vessel Holdup, and Throughput

| distillate flow | χ_{EtOH} | σ_{EtAc} | product composition | | | |
|-----------------|----------------------|------------------------|---------------------|--------|---------------|---------------|
| | | | AcH | EtOH | EtAc | W |
| 2.5 | 86.67 | 50.45 | 0.0202 | 0.0338 | 0.7794 | 0.1666 |
| 3.5 | 88.22 | 68.36 | 0.0224 | 0.0428 | 0.7843 | 0.1505 |
| 4.5 | 89.15 | 85.27 | 0.0240 | 0.0631 | 0.7789 | 0.1340 |
| 6 | 85.02 | 97.18 | 0.0308 | 0.1104 | 0.6216 | 0.2372 |

| distillate flow | MV amount [kmol] | throughput [kmol/h] | mean reaction rate [kmol/h] |
|-----------------|------------------|---------------------|-----------------------------|
| 2.5 | 188.4 | 2.06 | 3.19 |
| 3.5 | 170.1 | 2.83 | 3.25 |
| 4.5 | 151.7 | 3.59 | 3.28 |
| 6 | 101.8 | 4.89 | 3.13 |

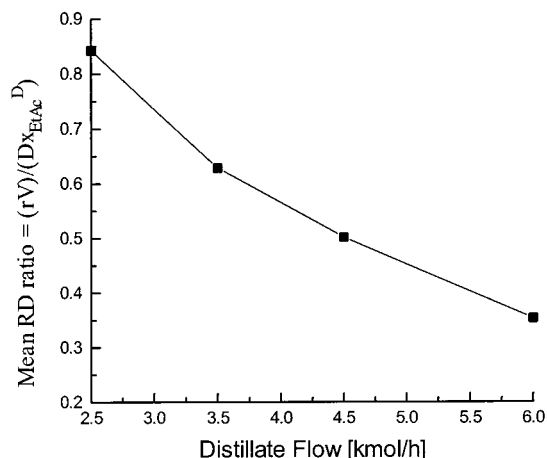


Figure 8. Influence of the distillate flow rate on the mean RD ratio.

of the limiting reagent and the ester composition present a maximum.

A first aspect to be analyzed is the occurrence of a maximum in the mole fraction of ethyl acetate. The internal profile is controlled by a ternary pinch; therefore, the product consists mainly of ethyl acetate and water. The alcohol is almost completely absorbed at total reflux. As the distillate flow rate (reflux ratio) increases (decreases), the absorption capacity of the solvent diminishes from its maximum value at total reflux; therefore, the alcohol increasingly makes the distillate product less pure (Table 8). This behavior corresponds to that observed by Warter et al.,¹⁹ where the difference in the behavior of continuous and batchwise distillation is pointed out. On the other hand, for low-to-moderate distillate flow rates, water follows an inverse trend because of the inversion in the volatility order. At total reflux, the mole fraction of water in the product tends to its maximum value at the azeotropic composition (ethyl acetate–water azeotrope). As a result of these opposite behaviors, there is an optimum distillate flow rate for which the ester composition achieves its maximum value. The minimum in water composition will be explained in the following discussion.

The maximum in the alcohol conversion can be explained with the aid of the mean reaction versus distillation ratio, RD, as defined in Figure 8. This ratio relates the rate of ethyl acetate production by chemical reaction with the rate of removal of the ester by distillation. Figure 8 shows that RD diminishes its value starting from a maximum value below zero as the distillate flow rate increases. This behavior indicates

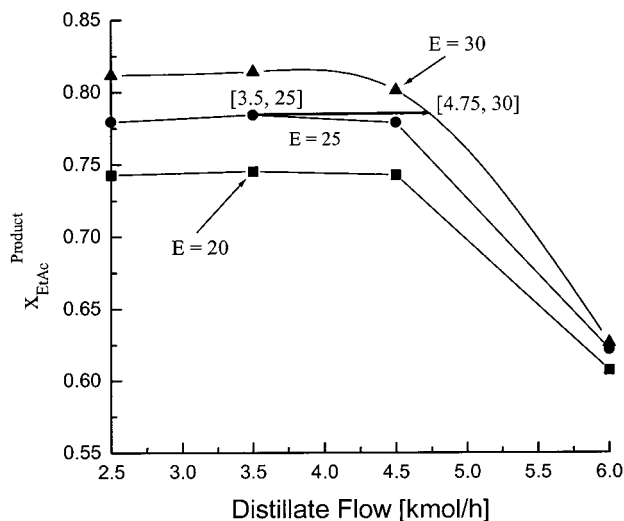


Figure 9. Influence of the distillate flow rate on the ester composition. Each curve corresponds to a given entrainer flow rate.

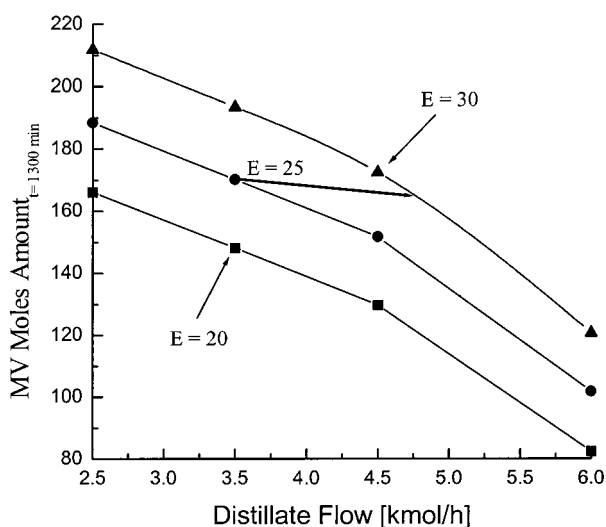


Figure 10. Influence of the distillate flow rate on the amount of material remaining in the middle vessel. Each curve corresponds to a given entrainer flow rate.

that the rate of removal is greater than the rate of production; therefore, both alcohol conversion and reaction rate should also increase because the ester concentration in the middle vessel is maintained as low as possible. However, for high values of the distillate flow rate, both conversion and reaction rate decrease because the low reflux ratio is not enough to maintain the purity of the product; therefore, both reaction products and reagents are carried away together. In the example considered here, this happens at a distillate flow rate of 6 kmol/h, and this is the cause of the sharp increase in water composition.

The same study was done for different entrainer flow rates. The results were qualitatively similar. Figure 9 shows the ester composition in the distillate product. Each curve differs from the others by the entrainer flow rate. Figure 9 indicates that the same ester composition can be obtained either with a low entrainer flow and a low (high) distillate flow (reflux ratio) or with a high entrainer flow and a high (low) distillate flow (reflux ratio). Figure 10 indicates that even if the entrainer flow rate is increased it is possible to diminish the final amount of material in the middle vessel at the operation

Table 9. Comparison between Two Simulations Producing Almost the Same Ester Composition

| <i>E</i> | <i>D</i> | EtOH conversion | EtAc recovery | final MV amount | x_{AcH}^{end} | product amount | x_{EtAc}^P |
|----------|----------|-----------------|---------------|-----------------|-----------------|----------------|---------------|
| 25 | 3.50 | 88.22 | 68.36 | 170.1 | 0.3974 | 61.32 | 0.7843 |
| 30 | 4.75 | 89.90 | 91.32 | 161.5 | 0.5026 | 83.14 | 0.7876 |

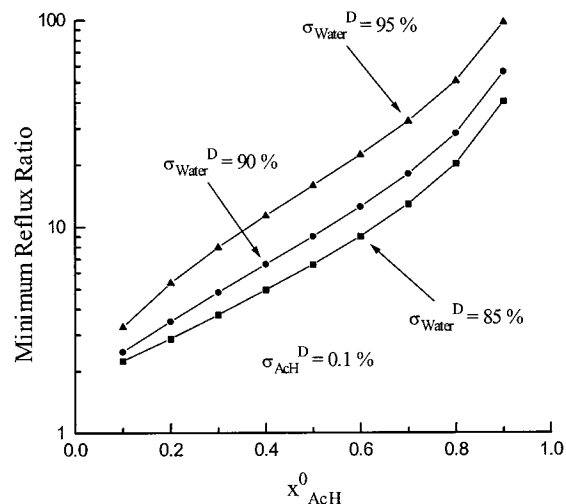


Figure 11. Influence of the solvent composition at the beginning of shutdown period on the minimum reflux for the binary separation water/acetic acid. Each curve corresponds to a given water recovery.

end. Moreover, operation at both high entrainer and distillate flow rate enhances alcohol conversion, ester recovery, and throughput, as shown in Table 9. However, the mole fraction of acid at the end of step 5 (x_{AcH}^{end}) will be larger for the operation at high solvent flow rate.

Binary Separation Water–Acetic Acid. At the end of step 5, the mixture in the middle vessel consists of water and acetic acid; therefore, the remaining solvent must be recovered from the water. As already mentioned, two possibilities to do this exist: conventional operation in a batch rectifier or operation in the middle vessel column.

Meski and Morari²⁰ studied the optimal operation strategy for middle vessel column. For the case of binary separations where the column products are pure components (i.e., pure water as distillate and pure acetic acid as bottom), these authors state that the optimal reflux–reboil ratios policy is to operate the column as in the steady-state operation (i.e., with the middle vessel composition equal to the composition of the initial charge). The column operates at the steady state under constant distillate and bottom flow rates; the only variable that changes is the holdup in the middle vessel. They also conclude that the middle vessel column always requires less time than the batch rectifier.

Figure 11 shows the minimum reflux ratio as a function of the initial composition of acetic acid for the case of a conventional batch rectifier. Note that this composition is the composition in the middle vessel at the end of step 5. Each curve was calculated for a given recovery rate of water in the distillate and for the same solvent loss ($\sigma_{AcH} = 0.1\%$). The simulations were performed with the aid CBD Toolkit that is able to handle nonidealities in the phase equilibrium. For a given water recovery, the minimum energy demand increases with the initial mole fraction of the entrainer in the still. On the other hand, for the same initial amount of

Table 10. Operation Sequence for Simulations with Different Water Concentrations in the Entrainer

| time period [min] | operating sequence, x_W^E |
|---|--|
| 0–180, startup (step 1) | $R \rightarrow \infty, S \rightarrow \infty, E = 0$ kmol/h |
| 180–300, eliminate off-spec product (step 2) | $R \rightarrow \infty, S \rightarrow \infty, E = 25$ kmol/h, $x_W^E = [0.00, 0.05, 0.10]$ |
| 300–1100, main production period (step 3) | $D = 4.5, B_0 = 25, E = 25$ kmol/h |
| 1100–1300, recovery of the remaining EtAc as ternary azeotrope (step 5) | $D = 4.5, E = 0$ kmol/h |

Table 11. Influence of Water Composition in Solvent on Alcohol Conversion, Ester Recovery Rate, and Product Composition

| water composition | χ_{EtOH} | σ_{EtAc} | product composition | | | |
|-------------------|---------------|-----------------|---------------------|--------|--------|--------|
| | | | AcH | EtOH | EtAc | W |
| 0 | 89.15 | 85.27 | 0.0240 | 0.0631 | 0.7789 | 0.134 |
| 0.05 | 88.71 | 81.16 | 0.0150 | 0.0475 | 0.7351 | 0.2024 |
| 0.1 | 87.64 | 80.47 | 0.0115 | 0.0463 | 0.7192 | 0.2230 |

| water composition | MV amount [kmol] |
|-------------------|------------------|
| 0 | 151.72 |
| 0.05 | 174.69 |
| 0.1 | 197.64 |

solvent, the minimum reflux increases with the recovery of water in the distillate.

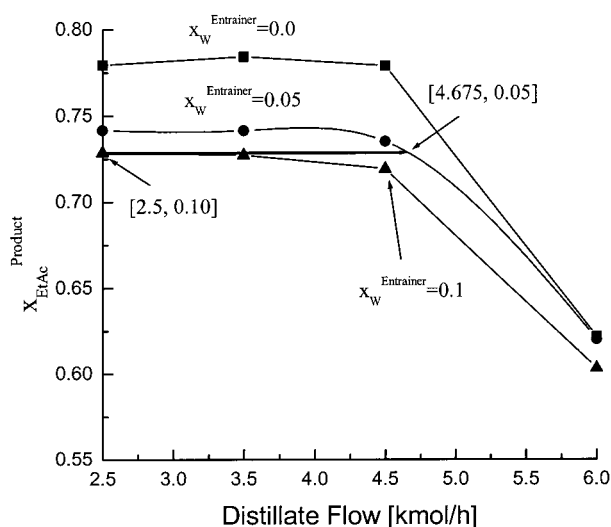
Because the energy demand of the binary separation is determined by the composition and amount of liquid in the middle vessel at the beginning of the last step (shutdown period) and the purity of the entrainer to be recycled depends on this separation, it is clear that both reaction and pure separation steps are very coupled.

The increase in the entrainer flow results, for instance, in an increase of both ethanol conversion and ester recovery rate (see Table 6), but the amount of solvent added increases, and this results in an increasing energy demand of the binary separation. On the other hand, the extent of water recovery as the distillate product in the binary separation determines the solvent purity and therefore influences the absorption capacity of the entrainer during the reaction step.

Influence of the Entrainer Purity. To study the influence of the entrainer purity on the main performance variables, the operation sequence shown in Table 10 was simulated. For all simulations, the entrainer flow rate was fixed at 25 kmol/h while the distillate flow rate of 4.5 kmol/h was selected. The initial bottom flow rate was set at 25 kmol/h, and it was varied in order to maintain a constant temperature at a certain level of the stripper.

Table 11 shows the influence of water concentration in the entrainer on limiting reagent conversion, ester recovery rate, product composition, and amount of moles remaining in the middle vessel at the end of step 5.

Because water is a reaction product, as the water content in the entrainer stream increases, a lowering in both reaction rate and alcohol conversion takes place. Moreover, the ethyl acetate recovery rate suffers a diminution because the water concentration in the pinch region below the feed point increases, giving rise to a

**Figure 12.** Influence of solvent purity and distillate flow rate on ethyl acetate composition.

greater loss (lower recovery rate) of water (ethyl acetate) in the column top. Remember that an inversion in the volatility order occurs in the rectifying section above the feed stage. The ester composition falls from 78% (pure entrainer) to 72% (entrainer containing 10% water). The entrainer recovery policy in the stripper allows for a greater recovery as the water content in the solvent stream decreases.

Figure 12 shows that it is possible to obtain distillate products with the same ester composition, either with a high (low) distillate flow rate (reflux ratio) combined with a pure entrainer, or with a low (high) distillate flow rate (reflux ratio) combined with high water impurity in the entrainer. However, the performance variables indicate the convenience of operating with a pure entrainer, as shown in Table 12.

Conclusions

Integration of reaction and separation in a batch extractive distillation column with a middle vessel for azeotrope-forming mixtures is addressed through an academic example.

This equipment configuration has the potential to promote almost complete conversion of reagents; therefore, there is an incentive to study the main characteristics of the process and the influence of operating and process parameters on its performance.

In the first part of this work, the feasibility of different process configurations is considered with the aid of the phase-equilibrium analysis and the investigation of the feasible cuts at infinite separation power. This task was performed with CAPE tools based on conceptual models. The analysis of the residue-curve map is also used to select the entrainer. The feasibility study is done on the basis of the determination of the topology of the residue-curve map, either directly by calculating a bunch of residue curves or indirectly by determining the stability of each node of the multicomponent mixture. Therefore, this analysis can be extended to other multicomponent mixtures.

Table 12. Performance Comparison between Two Simulations Producing Almost the Same Ester Composition

| $x_W^{\text{Entrainer}}$ | D | EtOH conversion | EtAc recovery | final MV amount | $x_{\text{AcH}}^{\text{end}}$ | product amount | $x_{\text{EtAc}}^{\text{P}}$ |
|--------------------------|--------------|-----------------|---------------|-----------------|-------------------------------|----------------|------------------------------|
| 0.10 | 2.500 | 83.41 | 49.07 | 235.6 | 0.3541 | 44.79 | 0.7287 |
| 0.05 | 4.675 | 88.85 | 84.00 | 171.3 | 0.4048 | 81.26 | 0.7325 |

In the second section, the different steps of the process are stated and the main operation characteristics are analyzed through an example simulated with Hysys. The role of each step and their corresponding operating parameters is highlighted. The reaction versus distillation ratio defined as $RD = rV_{MV}/D$ plays an important role during the main production step because it greatly influences both the limiting-reagent conversion and the product recovery rate.

In the third section, the results of a systematic investigation of the influence of operating and process parameters on limiting-reagent conversion, product recovery rate, and product composition are presented. The main objective of this section is to highlight both the influence of the parameters on the process and the interdependence of the operating parameters. Physical explanations are given to enhance comprehension. Two different operating regimes are found with their corresponding feasible distillate products. Regimes controlled by a ternary pinch point give rise to distillate products rich in ethyl acetate and water. High purity ethyl acetate distillate products are achieved when the geometry of the internal profiles is controlled by a binary pinch.

The strong mutual influence among operating parameters is a consequence of the reaction and separation steps being integrated in the same equipment. Both pure rectification and absorption take place in the rectifier while a chemical reaction occurs in the middle vessel and the solvent is recovered in the stripper section.

Real implementation of this technology requires removing simplifying assumptions or taking another column arrangements into consideration. Separation of the homogeneous catalyst should be taken into account for homogeneous catalyzed reactions. On the other hand, heterogeneous catalyzed reactions should consider that the reaction takes place in the section of the rectifier immediately above the middle vessel as implemented by Schneider et al.¹⁴ for a semibatch process for the production of methyl acetate.

The main conclusion of this work is that the integration of reaction and separation in a batch extractive distillation column with a middle vessel is a promissory technology for multi-azeotropic mixtures; therefore, additional research efforts should be driven in this area.

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Notation

B = bottom flow rate
 C = concentration
 D = distillate flow rate
 E = entrainer flow rate
 MV = middle vessel
 R, r = reflux ratio
 RD = reaction versus distillation ratio
 S, s = reboil ratio
 V = vapor flow rate
 V_{MV} = middle vessel volume
 x = composition

Greek Letters

α_{ij} = relative volatility
 χ_{EtOH} = ethanol conversion
 σ_i = recovery rate of component i

Subscripts

0 = initial
 B = bottom, still
 D = distillate
 MV = middle vessel
 V = vapor

Superscripts

0 = initial
 E, Entrainer, entrainer
 end = final
 max = maximum
 P, product = product

Literature Cited

- (1) Robinson, C. S.; Gilliland, E. R. *Elements of Fractional Distillation*, 4th ed.; McGraw-Hill Book Company, Inc.: New York, 1950.
- (2) Warter, M.; Stichlmair, J. Batchwise Extractive Distillation in a Column with a Middle Vessel; *Comput. Chem. Eng.* **1999**, *S915–S918*.
- (3) Hilmen, E. K.; Skogestad, S.; Doherty, M. F.; Malone, M. F. Integrated Design, Operation and Control of Batch Extractive Distillation with a Middle Vessel. Presented at *AIChE Annual Meeting*, Los Angeles, CA, Nov 1997.
- (4) Mujtaba, I. M.; Macchietto, S. Optimal Operation of Reactive Batch Distillation. Presented at *AIChE Annual Meeting*, Miami Beach, FL, Nov 1992.
- (5) Espinosa, J.; Salomone, E.; Xu, S. Using Conceptual Models for the Synthesis and Design of Batch Distillations. *European Symposium on Computer Aided Process Engineering-10*, 8; Pierucci, S., Ed.; Elsevier: **2000**; pp 1033–1038.
- (6) Salomone, E.; Espinosa, J. Prediction of Homogeneous Azeotropes with Interval Analysis Techniques Exploiting Topological Considerations. *Ind. Eng. Chem. Res.* **2001**, *40* (6), 1580–1588.
- (7) Salomone, E.; Espinosa, J. *AzeoPredictor 1.0*. User manual, Santa Fe, Argentina, 2000.
- (8) Espinosa, J.; Salomone, E. *CBD Toolkit 3.0*. User manual, Santa Fe, Argentina, 2001a.
- (9) Hysys User manual; Hyprotech Ltd.: Calgary, Canada, 1999.
- (10) Bogacki, M. B.; Alejski, K.; Szymanowski, J. The Fast Method of the Solution of a Reacting Distillation Problem. *Comput. Chem. Eng.* **1989**, *13* (9), 1081–1085.
- (11) Venimadhavan, G.; Malone, M. F.; Doherty, M. F. A Novel Distillate Policy for Batch Reactive Distillation with Application to the Production of Butyl Acetate. *Ind. Eng. Chem. Res.* **1999**, *38*, 714–722.
- (12) Stichlmair, J.; Fair, J. *Distillation: Principles and Practice*; Wiley-VCH: New York, 1998.
- (13) Barolo, M.; Guarise, G. B.; Rienzi, S. A.; Trotta, A.; Macchietto, S. Running Batch Distillation in a Column with a Middle Vessel. *Ind. Eng. Chem. Res.* **1996**, *35*, 4612–4618.
- (14) Schneider, R.; Noeres, C.; Kreul, L. U.; Górak, A. Dynamic Modelling and Simulation of Reactive Batch Distillation. *Comput. Chem. Eng.* **1999**, (Suppl.), S423–S426.
- (15) Lelkes, Z.; Lang, P.; Moszkowicz; Benadda, B.; Otterbein, M. Batch Extractive Distillation: the Process and the Operational Policies. *Chem. Eng. Sci.* **1998**, *53* (7), 1331–1348.
- (16) Espinosa, J.; Salomone, E. A Case Study of Conceptual Design applied to Batch Reactive Distillation. *Third MERCOSUR Congress on Process Systems Engineering*, Santa Fe, Argentina, Sept 16–20, 2001b, pp 37–42.

(17) Gadevar, S. B.; Malone, M. F.; Doherty, M. F. Selectivity Targets for Batch Reactive Distillation. *Ind. Eng. Chem. Res.* **2000**, *39*, 1565–1575.

(18) Mujtaba, I. M. Optimization of Batch Extractive Distillation Processes for Separating Close Boiling and Azeotropic Mixtures. *Trans. IChemE* **1999**, *77* (Part A), 588–596.

(19) Warter, M.; Duessel, R.; Stichlmair, J. Separation of Azeotropic Mixtures by Batchwise Extractive Distillation. *Proceedings of Distillation and Absorption '97*, Maastricht, The Netherlands, 1997; paper 57, pp 705–714.

(20) Meski, G. A.; Morari, M. Design and Operation of a Batch Distillation Column with a Middle Vessel. *Comput. Chem. Eng.* **1995**, *19*, S597–S602.

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