Integrated Design, Operation and Control of Batch Extractive Distillation with a Middle Vessel

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Abstract

This paper focuses on the use of batch extractive distillation for separating homogeneous minimum-boiling azeotropic mixtures, where the extractive agent is a high-boiling, miscible zeotropic component. The effect of column design on the operation is evaluated and a control structure for the batch extractive middle vessel distillation is proposed.

In extractive distillation, the non-volatile solvent is fed continuously to the top of the column in order to be present on all the plates during the separation. In a conventional batch column configuration, this semi-continuous operation has two main disadvantages due to accumulation of the extractive agent: (1) filling of the reboiler, and (2) degradation of the composition profile in the column. The first may cause operational problems and the latter decreases the efficiency of the separation.

One way to overcome these problems is to use a middle vessel column. The middle vessel column arrangement consists of two column sections, a batch rectifier and a batch stripper, connected by a middle vessel. The azeotropic mixture to be separated is charged to the middle vessel and the extractive solvent is fed to the head of the rectifying section. This configuration allows for simultaneous removal of product(s) and recovery of the extractive agent. In addition, the volume of the middle vessel can be kept constant or even decreasing with time. Thus, high separation efficiency can be achieved since the sharpness of the column composition profile is maintained during the distillation run. Furthermore, the middle vessel implementation is potentially more energy efficient than conventional distillation due to the combination of a rectifying-extraction section and a stripping section in one column. Batch extractive distillation with a middle vessel is closely related to the well-known continuous extractive distillation except that the separation is performed in one rather than in two columns, which may imply capital savings for the batch implementation.

We propose a novel control configuration for the batch extractive middle vessel distillation where the liquid flow from the middle vessel is manipulated to control the temperature in the stripping section, achieving a desired purity of the extractive agent. This indirectly adjusts

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the vessel holdup and there is no need for level control. The extractive agent feed is used to control the purity of the distillate and the reflux is held constant below its maximum value.

1 Introduction

The work presented in this paper is connected to an industrial project on solvent recovery in pharmaceutical production and fine- and specialty chemical industries. Batch distillation of nonideal liquid mixtures is widely used and the most important separation operation in small-scale production with need for flexibility due to changing product demands. A multicomponent mixture can be separated into a number of product fractions in a single batch column whereas, in continuous distillation several columns are required. A batch distillation column can also handle a wider range of feed compositions, relative volatilities and product specifications. The same column can therefore be used for a number of different separation tasks. However, waste-solvents from the bulk synthesis operations in pharmaceutical- and specialty chemical production often form homogeneous azeotropic (hereafter called homoazeotropic) mixtures which may be impossible to separate into pure components by ordinary batch distillation. The purification of such solvent streams typically involves dehydration of low-boiling organic solvents forming minimum-boiling homoazeotropic mixtures with water. The most common method to separate such mixtures is by means of extractive distillation.

While extractive distillation in continuous columns is extensively described in the literature (see for example Van Winkle (1967), Perry and Chilton (1973), Doherty and Knapp (1993)), the knowledge on operation of extractive distillation in batch columns is limited. Batch extractive distillation is to the authors knowledge not used industrially even though there exist a great need for this technology in the pharmaceutical- and specialty chemical industries that typically benefit from batch operation. This is probably due to its potential complexity of operation, and loss of flexibility which again is one of the main reasons the batch column is chosen. In addition, there is a need for experimental verification and practical implementation of the different operating policies for the process.

This paper focuses on the use of batch extractive distillation for separating homogeneous minimum-boiling azeotropic mixtures, where the extractive agent is a high-boiling, miscible zeotropic component. The effect of two principally different batch column designs on the operation is evaluated and a control structure for the batch extractive middle vessel distillation is proposed. The inherent dynamics of batch distillation operation introduces new aspects to the extractive distillation process as compared to continuous operation.

Other publications on batch extractive distillation

Kogan (1971) describes a laboratory unit of extractive batch distillation and points out the disadvantage of increasing dilution of the still pot by the extractive solvent during the operation. In a series of papers, Yatim and Lang et al. (1993, 1994, 1995) gives experimental as well as simulation results on the operation of extractive distillation in the conventional batch column configuration (i.e. batch rectifier). In the paper by Düssel and Stichlmair (1995), the extractive distillation scheme for a batch rectifier is outlined.

Safrit et al. (1995, 1997) studied the batch extractive middle vessel column for separation of a binary azeotropic mixture using an extractive agent which is continuously removed and recycled.

They compared the separation performance of this column with a conventional continuous extractive distillation column. The middle vessel column showed better performance in regard to energy consumption. The study also showed that the performance of the separation is sensitive to the entrainer flowrate and to the switching times between fractions in the batch operation. They propose a way to 'steer' the middle vessel composition by balancing the two opposite directed effects of product removal to achieve a desired purity in distillate and bottoms product.

Publications on the middle vessel batch distillation configuration

There are two principally different modes, or uses, for the batch distillation with a middle vessel: (1) separation of binary mixtures, and (2) separation of ternary- or multicomponent mixtures. In both cases the mixture is initially fed to the middle vessel (or distributed along the column). In the first mode, the binary separation is performed simultaneously in the batch rectifier and the batch stripper taking out the light component as distillate and the heavy component as bottoms product. The volume of the middle vessel decreases during the operation. In the second mode, separating for example an ideal ternary mixture, intermediate-boiling component of increasing purity can be accumulated in the middle vessel and collected as a pure product at the end of the distillation run.

The idea of using the middle vessel batch distillation column configuration for separating multicomponent mixtures is not new. In the textbook by Robinson and Gilliland (1950), this combined operation of a batch rectifier and a batch stripper is mentioned for accumulating an intermediate component in the middle vessel while removing light- and heavy impurities. Bortolini and Guarise (1970) was to the authors knowledge the first to present an analysis of this column configuration for separating ideal *binary* mixtures. In 1976, Devyatikh and Churbanov described separation of *ternary* mixtures by the middle vessel batch distillation configuration (as quoted by Davydian, Kiva, Meski and Morari (1994)).

Several authors have presented comparative studies between conventional batch distillation columns and the middle vessel configuration for ideal binary and ternary mixtures. Hasebe, Abdul Aziz, Hashimoto and Watanabe (1992) compared the performance of the middle vessel batch distillation column, denoted *complex batch distillation column*, for separating ideal ternary mixtures with conventional batch distillation. The middle vessel batch distillation column was shown to have the best separation performance. The idea of using a middle vessel was later extended to a multi-vessel batch column configuration with total reflux operation for separating more than three components (Hasebe, Kurooka and Hashimoto 1995). They denote this a *multi-effect batch distillation system*. Skogestad, Wittgens, Sørensen and Litto (1995) proposed a generalization of this structure along with novel feedback control strategy for such total reflux multi-vessel batch distillation columns.

In a series papers, Davydian, Kiva and Platonov (1991a, 1991b, 1992a, 1992b, 1993) presented the use of batch distillation columns with a middle vessel for separating binary and ternary mixtures (parallel to the work by Hasebe et al. (1992)). Based on this work, Davydian et al. (1994) present an analytical analysis of the dynamic behavior of the middle vessel batch distillation column for separating multicomponent mixtures. The authors point out several advantages and new opportunities for the middle vessel configuration as compared to conventional batch distillation column designs (Davydian et al. 1994):

- *A binary mixture can be separated into pure components under finite [constant] reboil and reflux ratio and, in some cases, faster than using conventional types*

of batch distillations.

- *For ternary separation one can always choose parameters, like reflux and reboil ratios, such that the composition in the middle vessel tends to either one of the three components [the intermediate-boiling component for ideal mixtures].*
- *A multicomponent mixture can be separated into heavy, intermediate and light fractions simultaneously, so one can remove light and heavy impurities from the mixture.*

Meski and Morari (1995) analyzed the behavior of the middle vessel configuration for binary and ternary mixtures at total reflux and minimum reflux conditions. They confirm the previous results by Hasebe et al. (1992) that the middle vessel batch distillation column always perform better than the conventional design. They also conclude that it is optimal to operate the column under constant reflux- and reboil ratios in the case of binary separation, keeping the composition in the middle vessel constant equal to the initial feed composition with gradual decreasing holdup of the middle vessel. Barolo and Guarise et al. (1996a, 1996b) address issues on design and operation of the batch distillation column with a middle vessel for separating ternary mixtures, partly based on experience from operating a continuous distillation pilot plant in a batch mode.

2 Basic Concepts

Most distillation methods for separating homoazeotropic mixtures rely on the addition of specially chosen chemicals to facilitate separation (Doherty and Knapp 1993). These separation agents, also called entrainers, can be miscible, partly miscible or imiscible, zeotropic or azeotropic (introducing new azeotropes to the system). The distillation techniques to be utilized depends on the resulting vapor- liquid equilibrium behavior of the basic azeotropic mixture with separating agent.

2.1 Extractive Distillation

Benedict and Rubin (1945) gives the following definition of extractive distillation:

> *Distillation in the presence of a substance which is relatively non-volatile compared to the components to be separated and which, therefore, is charged continuously near the top of the distilling column so that an appreciable concentration is maintained on all plates of the column.*

In this paper we focus on extractive distillation for separation of binary minimum-boiling homoazeotropic mixtures. Extractive distillation may be used for separation of multicomponent mixtures as well. Phase equilibrium diagrams like simple distillation residue curve maps (RCMs) and information about the univolatility lines provides a graphical tool to evaluate how the separating agent modifies the volatilities of the azeotrope components in the mixture. Knowing the residue curve map for the resulting ternary system to be separated is sufficient to determine if a given separation objective is feasible, but not whether the objective can be achieved economically (Doherty and Knapp 1993). An overview of the main conditions that a candidate extractive solvent must satisfy in order to make the separation feasible are given in the following[1].

[1]Several authors have outlined solvent selection criteria for extractive distillation (Berg 1969, Doherty and Knapp 1993): 1. Higher boiling temperature than the components to be separated $\Delta T_{S-1,2} > 30^oC$, 2. Sub-

First condition:

The mixture of the binary minimi-boiling azeotrope and solvent should form a VLE diagram of the type shown in figure 1.

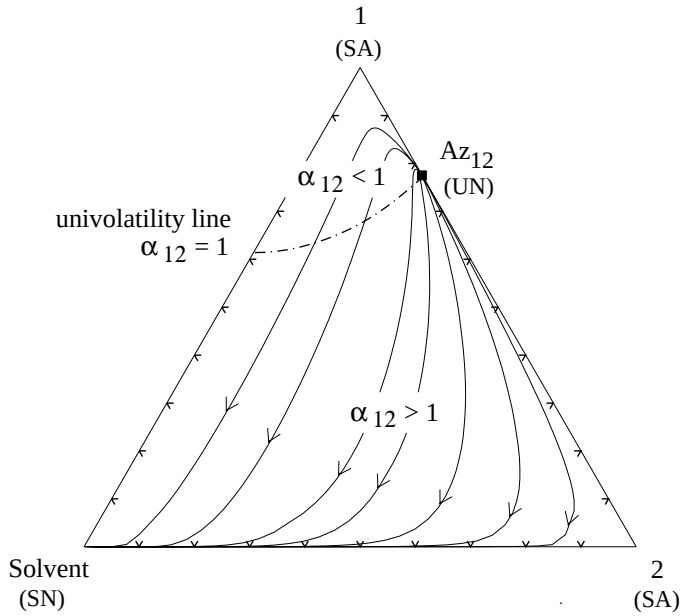

Figure 1: Residue curve map for a ternary azeotropic mixture of components 1, 2 and solvent that is promising for extractive distillation. Az_{12} denotes a binary minimum-boiling azeotrope between 1 and 2. The change in volatility order between 1 and 2 is represented by the univolatility line $\alpha_{12} = 1$.

Second condition:

The solvent must cause a substantial change in the relative volatility between the azeotrope constituents. A measure of the solvent selectivity is the relative volatility between the azeotrope constituents at infinite dilution in the solvent: $\alpha^{\infty}_{12\,(S)} > 2.0$ (typically).

Third condition:

The solvent must have higher boiling-point than the azeotrope constituents, $\Delta T_{S-1,2} > 30^0C$, and preferably large relative volatility between the solvent and the distillate product.

Rule of thumb: The larger boiling-point difference between the agent and distillate, the less number of trays needed in rectifying section (usually $\Delta T_{S-1,2} = 50 - 150^0C$).

The main feature of the diagram shown in figure 1 is the shape of the simple distillation residue curves near the stable node (SN) (the solvent must be a stable node). The presence of an univolatility line deforms the residue curves according to the solvent selectivity (S-shaped residue curves). The minimum-boiling azeotrope is an unstable node (UN) in the whole composition space (triangle). The pure components 1 and 2 are saddle points (SA), but the pure component

stantial change in relative volatility when present at moderate compositions, 3. Low latent heat since part of the agent stream will be vaporized in the reboiler, 4. Thermally stable, 5. Nonreactive with the other components in the mixture, 6. Available and inexpensive, 7. Nontoxic, and 8. Easily separable from the component with it associates.

1 is an unstable node of the binary edge between 1 and solvent. The univolatility line, locus where $\alpha_{12} = 1$ in figure 1, extends from the azeotrope to the binary edge between the solvent and component 1. Thus, component 1 will be recovered in the distillate since it is the most volatile component in the rectifying section (Laroche, Bekiaris, Andersen and Morari 1993).

In continuous extractive distillation columns, component 2 will be taken out as bottoms product together with the solvent. This scheme requires a direct sequence of two columns, one extractive distillation column and one column to separate component 2 from the solvent (for the system given in figure 1).

Composition profile in extractive distillation columns

Extractive distillation obtain a saddle as distillate product and the process works 'against' the simple distillation residue curves. This is the main characteristic of the extractive distillation process. Knapp and Doherty (1994) and Bauer and Stichlmair (1995) presents composition profiles in continuous extractive distillation columns for the acetone-methanol-water mixture and geometric representation of the continuous extractive distillation process is given in a series of papers (Levy and Doherty 1986, Knapp and Doherty 1990, Knapp and Doherty 1994).

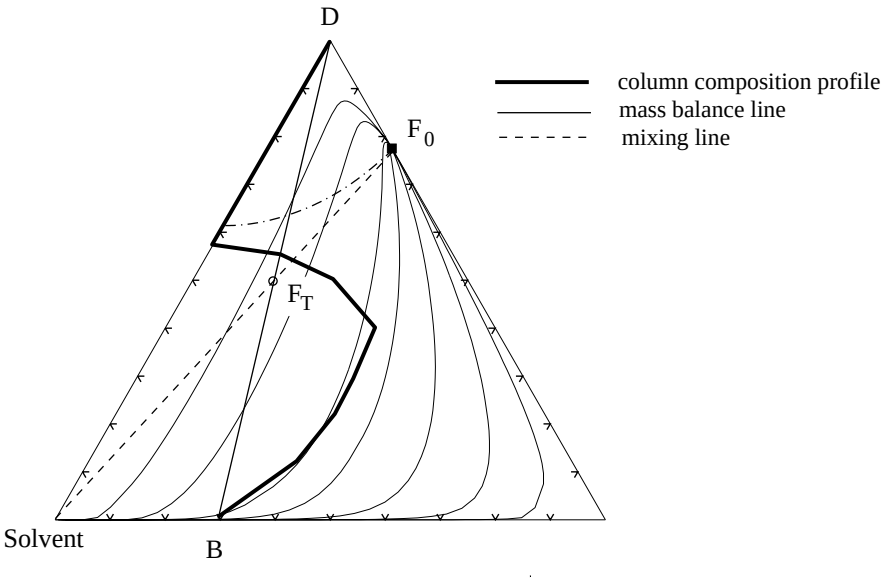

Figure 2: Qualitative form of the composition profile in continuous extractive distillation column. F_0 - azeotropic feed, F_T - total feed in column after solvent mixing, D - distillate, B - bottoms product, M - middle vessel composition, E - solvent feed tray.

In continuous extractive distillation, the steady-state liquid composition profile along the column turns off the binary edge between the distillate product and solvent below the univolatility line of $\alpha_{12} = 1$, see figure 2. The imbalance of mixing due to the extractive solvent feed, causes a shift in the composition profile (i.e. moves across the simple distillation residue curves). The inflexion-point curve is the smooth line through the inflexion-points of the simple distillation residue curves. The sharpness of the inflexion-point curve governs the column composition profile (Bauer and Stichlmair 1995). Extractive solvents with high selectivity makes the inflexion-point curve and the isovolatility line intersect the binary edge far from the extractive agent vertex (Kiva 1997).

Effect of reflux

Previous studies on continuous extractive distillation have shown that there is a maximum as well as a minimum reflux ratio to make the separation scheme feasible (Andersen, Laroche and Morari 1995, Laroche et al. 1993). Increasing reflux leads to achieving the unstable node as top product, i.e. the azeotrope. Too much reflux is harmful in extractive distillation because it weakens the extractive effect of the distillation. As reflux increase, the distillate composition moves from the saddle vertex, pure component 1 for the system given in figure 1, to the azeotrope (unstable node). Increased reflux ratio moves the process from extractive distillation to total reflux distillation (Kiva 1997). Hence, the relative volatility between the distillate product and solvent α_{1S} must be sufficiently large to achieve the desired purity without high reflux for the given number of trays in the rectifying section. Other ways to overcome this problem is to purify the distillate fraction in a second distillation column.

2.2 Example Mixtures

Two systems are studied for the batch extractive distillation in this paper: (a) separation of ethanol and water using ethylene glycol as the solvent, and (b) separation of acetone and methanol using water as the solvent. The separation objective is to fully recover one of the azeotrope constituents as pure component, and to fully recover the solvent for re-use.

The mixture of ethanol and water forms a minimum-boiling azeotrope rich in ethanol. Ethylene glycol is added to the mixture as an extractive solvent. The residue curve map for the resulting ternary system is shown in figure 3.

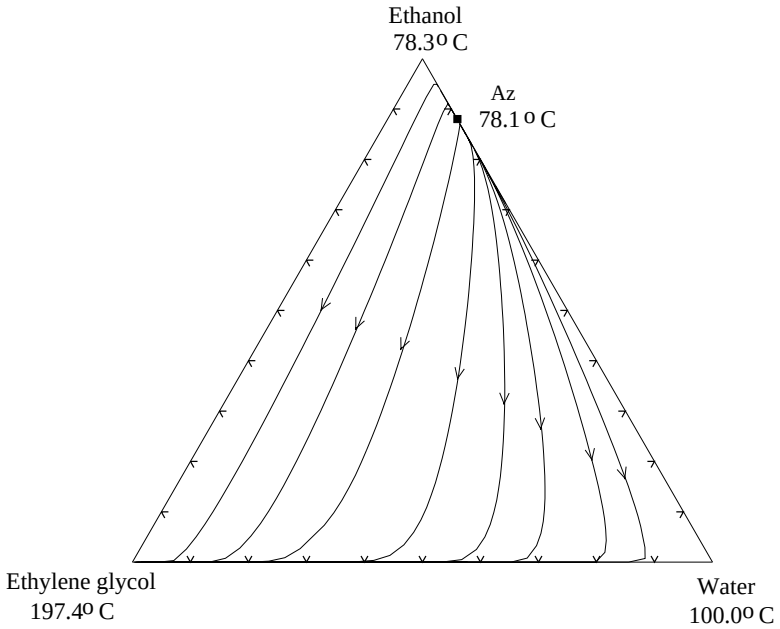

Figure 3: Residue curve map for the ternary azeotropic mixture ethanol (1) - water (2) - ethylene glycol (solvent) at 1 atm (from ASPEN Plus).

This mixture has large boiling-point difference between the solvent ethylene glycol and the azeotrope constituents, $\Delta T_{S-1} = 119.1^oC$ $\Delta T_{S-2} = 97.4^oC$. Thus, only a couple of trays are

needed in rectifying section of the batch extractive distillation column to separate ethylene glycol from the ethanol product. Separating water from ethylene glycol in a second cut or in the stripping section of the middle vessel column is also easy. The separation of ethanol and water by ethylene glycol is classical in continuous extractive distillation and is mainly chosen since it is thoroughly studied in the literature (easy to find comparable examples) and is well-known to most readers. This separation also represents the typical problem in the pharmaceutical- and specialty chemical industries of dehydration of a low-boiling organic solvent forming a minimum-boiling azeotrope with water as mentioned in the introduction.

The mixture of acetone and methanol forms a minimum-boiling azeotrope. Water is added to the mixture as extractive solvent. The residue curve map for the resulting ternary is shown in figure 4.

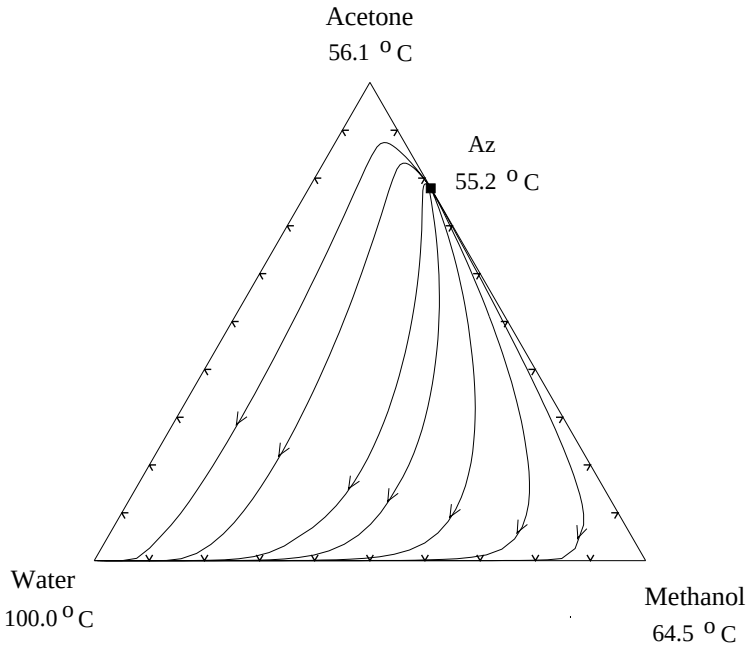

Figure 4: Residue curve map for the ternary azeotropic mixture acetone (1) - methanol (2) - water (solvent) at 1 atm (from ASPEN Plus).

The mixture has relatively large boiling-point difference between the solvent and the azeotrope constituents, $\Delta T_{S-1} = 43.9^oC$ and $\Delta T_{S-2} = 35.5^oC$, and the separation of methanol from water is easy. However, acetone and water forms a tangentially zeotropic mixture as shown in figure 5. This phenomenon is called a *tangent pinch* by Doherty and Knapp (1993). At a high concentration of acetone, the relative volatility between the acetone and water is close to unity. Thus, nearly all the equilibrium stages required in the rectifying section of the batch extractive distillation column will be due to the last purification part of high purity acetone. In extractive distillation reflux is harmful as discussed earlier. Even at high reflux ratios and number of stages the distillate acetone will be contaminated with a small amount of water, and requiring acetone of high purity may cause operational problems. This problem can be avoided by allowing for impurities of water in the acetone distillate product. A distillate fraction of acetone and water can be separated in a second conventional batch distillation column (or in a later step of the batch extractive distillation process). Anyhow, the separation of acetone and methanol by water requires a larger number of trays in the rectifying section as compared to the first example

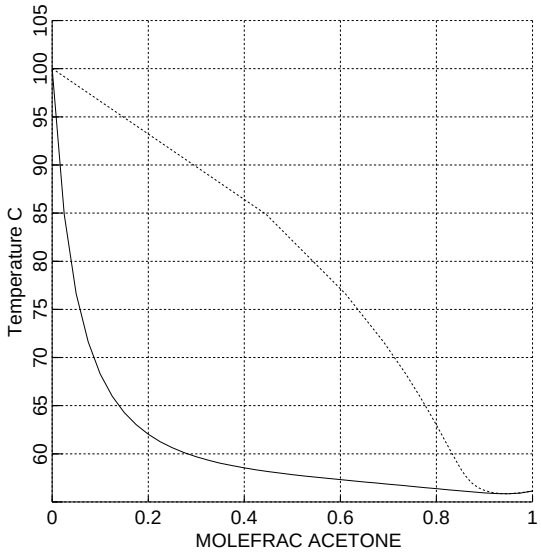

Figure 5: T-xy diagram for the binary tangentially zeotropic acetone and water system (from ASPEN Plus).

mixture due to the specially large relative volatility between ethanol and ethylene glycol. This is the main reason for including the second example mixture of acetone, methanol and water. The importance and effect of the rectifying section in the batch extractive distillation configuration is better illustrated by separation of this mixture.

3 Batch Extractive Distillation

As for continuous extractive distillation, one may feed an extractive solvent to the top of the rectifying section in a batch column. In a batch extractive distillation column, the azeotropic mixture to be separated is initially added to the reboiler or a vessel along the batch distillation column. The component having the greater volatility (not necessarily the component having the lowest pure component boiling point) is taken overhead as the first distillate cut. The solvent can be separated from the remaining component(s) in two ways: (1) by further distillation in the same column and re-used in the next batch, or (2) simultaneously during the distillation in the stripping section of the middle vessel column configuration and re-used in the next batch or re-cycled to the column directly.

Operation of batch extractive distillation can be divided into the same main steps as for conventional batch distillation:

1. Startup period
2. Production period
3. Shut-down period

In this study, only constant reflux- and reboil ratios are considered during the production period. For simplicity, the feed of extractive solvent is held constant.

3.1 Batch Extractive Distillation with Sequential Removal of Products

The first column configuration considered is the batch extractive distillation column with sequential removal of products as illustrated in figure 6.

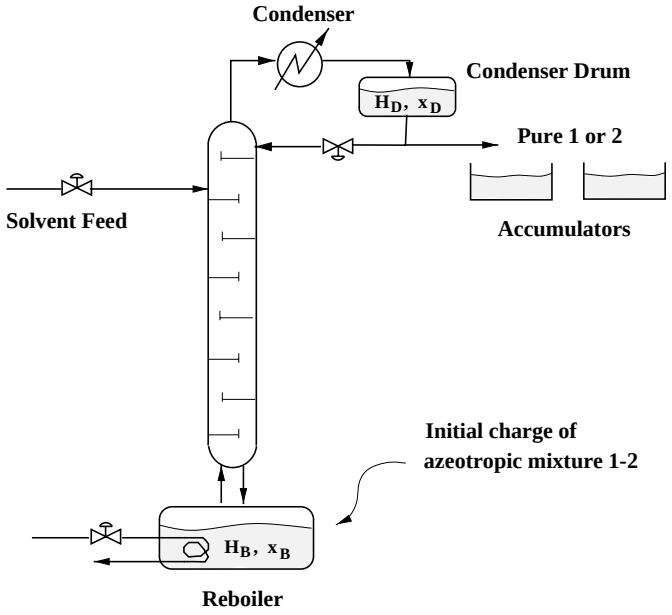

Figure 6: Batch extractive distillation with sequential removal of products.

This conventional batch extractive distillation column consists of the following: a still or reboiler which is heated; a column section with trays (or filled with packing material); a condenser which condenses the vapor leaving the column section; a condenser reflux drum which collects the condensed vapor and one or more accumulator tanks where the distilled products are collected. Some of the distillate is returned to the column section as reflux. The extractive solvent is fed to the upper part of the column section in order to be present on all plates during the separation. Thus, this is a semi–batch distillation operation.

I. Operating sequence

Step 1 Startup.
Total reflux without feed of extractive solvent $(R = \infty, E = 0)$.

Step 2 Eliminate off-spec. product.
Total reflux with solvent feeding $(R = \infty, E > 0)$.

Step 3 Production of first pure product.
Operate under finite reflux with solvent feeding $(0 < R < R_{max}, E > 0)$.

Step 4 Production of second pure product.
Operate under finite reflux without solvent feeding $(0 < R < R_{max}, E = 0)$.

Step 5 Purify solvent by removing an off-cut containing all the residual second product.

Step 6 Remove solvent from the reboiler for re-use.

Step 2 is performed to increase the concentration of the more volatile component in the distillate before taking out product. The step can be omitted and any off-cuts recycled if needed. After step 3, total reflux operation may be implemented to build up the concentration of the second azeotrope component in the condenser to eliminate off-spec. product.

In the extractive middle vessel column configuration, step 4 to 6 are replaced by attaching a stripping section. Removal of products and recovery of extractive solvent is performed simultaneously in the two sections of the distillation column.

3.2 Batch Extractive Middle Vessel Distillation

The second configuration studied is the batch extractive middle vessel distillation column with simultaneous removal of products and recovery of the extractive agent as illustrated in figure 7.

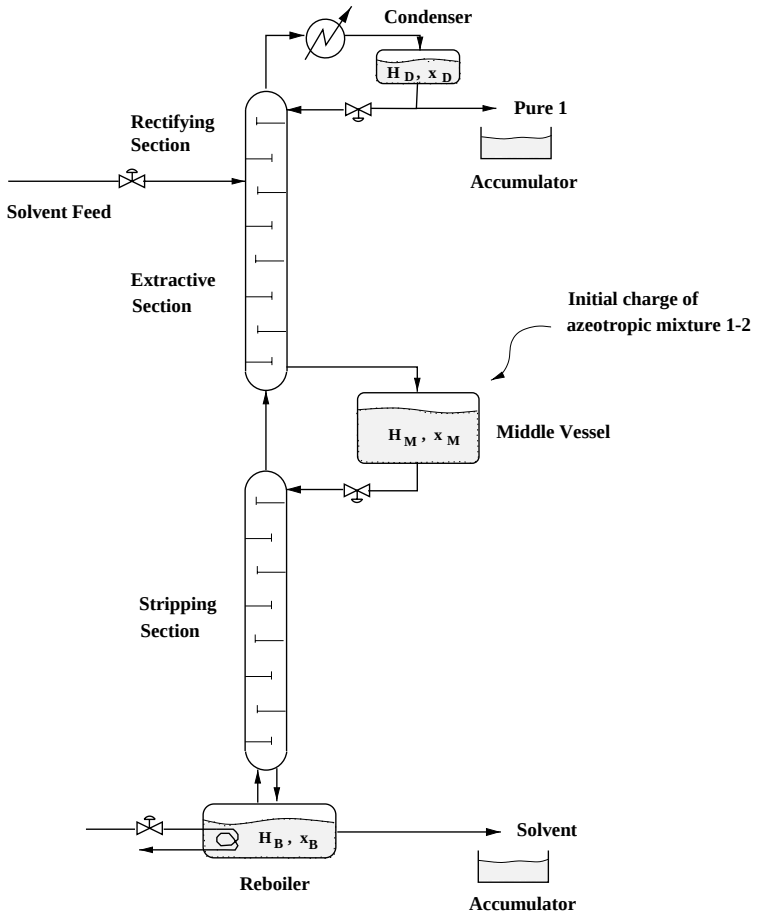

Figure 7: Batch extractive distillation with a middle vessel - simultaneous removal of product(s) and recovery of the solvent.

The extractive middle vessel column arrangement consists of three column sections: a batch rectifying section, an extractive section and a batch stripping section, connected by a middle vessel. The azeotropic mixture to be separated is charged to the middle vessel (or distributed along the column), and the extractive solvent is continuously fed to the head of the rectifying section. This configuration allows for simultaneous removal of product(s) and recovery of the extractive agent. In addition, the volume of the middle vessel can be kept constant or even

decreasing with time. The bottom of the extractive section must have drainage tray to avoid impurities from the liquid holdup in the upper column section contaminate the middle vessel at the end of the operation.

II. Operating sequence

Step 1 Startup.
Total reflux- and reboil without feed of extractive solvent ($R = \infty$, $Q = \infty$, $E = 0$).

Step 2 Eliminate off-spec. product.
Total reflux- and reboil with solvent feeding ($R = \infty$, $Q = \infty$, $E > 0$).

Step 3 Simultaneous production of pure distillate product and recovery of the solvent.
Operate under finite reflux- and reboil with solvent feeding ($0 < R < R_{max}$, $Q > 0$, $E > 0$).

Step 4 Purify the second product in the middle vessel.

Step 2 is performed to increase the concentration of most volatile component in the distillate before taking out the distillate product. The step can be omitted and any off-cuts recycled if needed. Step 4 is performed to purify the second azeotrope component in the middle vessel or to eliminate off-spec. product before taking out the second product (as distillate). The middle vessel column configuration opens up the possibility to directly recycle the recovered extractive solvent from the stripping section. There are two principally different ways of operating the batch extractive middle vessel distillation process for separating ternary mixtures (Davydian et al. 1994): (1) constant composition strategy, and (2) constant reflux- and reboil strategy. The composition of the middel vessel can reach any point in the composition triangle by manipulating the operational parameter D/B as given by Meski and Morari (1995):

$$\frac{dx_M}{d\xi} = x_M - \left(\begin{array}{c} \frac{B}{D+B} \\ \frac{D}{D+B} \end{array} \right) \tag{1}$$

The operating policy proposed by Safrit and Westerberg (1997) for the batch extractive middle vessel distillation column, to 'steer' the composition in the middle vessel by manipulating the reflux- and boilup ratios achieving constant distillate and bottoms product purity, corresponds to the constant composition strategy above.

4 Simulation Results

In all simulations presented in this paper, the column operates under atmospheric pressure, there is no pressure drop in the column and the condenser is total with no sub-cooling. Negligible vapor holdup and constant molar liquid holdup on all trays and in the condenser are assumed. Further it is assumed perfect mixing and vapor- liquid equilibrium on all trays (i.e. 100% tray efficiency). Equal, constant molar vapor flows in the column (i.e. energy balance is neglected) are used in all simulations. The trays are numbered from the top and down with n trays in the rectifying-extractive section and m trays in the stripping section of the middle vessel configuration. The total number of trays in the columns is $N = n + m$ (exclusive the reboiler). Ideal behavior in the vapor phase was assumed and the Antoine equation for the vapor pressure along with the Wilson activity coefficient model were used to describe the liquid phase. The thermodynamic model as well as the Antoine and Wilson coefficients used for the example mixtures are given

in the appendix. In all the simulations, the extractive solvent is fed as pure liquid with a temperature equal to the boiling-point of the more volatile component. The resulting set of nonlinear algebraic and ordinary differential equations (DAE's) is stiff due to widely different time constants of the plates, reboiler and the middle vessel. SpeedUp (1993) was used for the simulations.

4.1 Batch Extractive Distillation with Sequential Removal of Products

In the example of separation of ethanol and water using ethylene glycol as extractive solvent, the initial feed charged to the reboiler contained 65 % ethanol and 35 % water. After total reflux operation to build up the column profile (without feed of solvent), pure ethylene glycol was fed at a constant molar feed flowrate to the upper section of the column (on tray 3). Pure ethanol was taken out as the first distillate cut, pure water as the second cut, followed by an off-cut containing water and ethylene glycol to purify the solvent left in the still for re-use (see figures 8 and 10).

There was a range of extractive solvent feed flowrates (solvent feed to vapor flow ratio) that lead to successful operation. If the feed flowrate of extractive solvent was too low, the azeotrope did not break and was taken out as the first cut. For a solvent feed flowrate much above the needed value, there was obviously no further advantage in terms of separation, and a large amount of the solvent was accumulated in the reboiler.

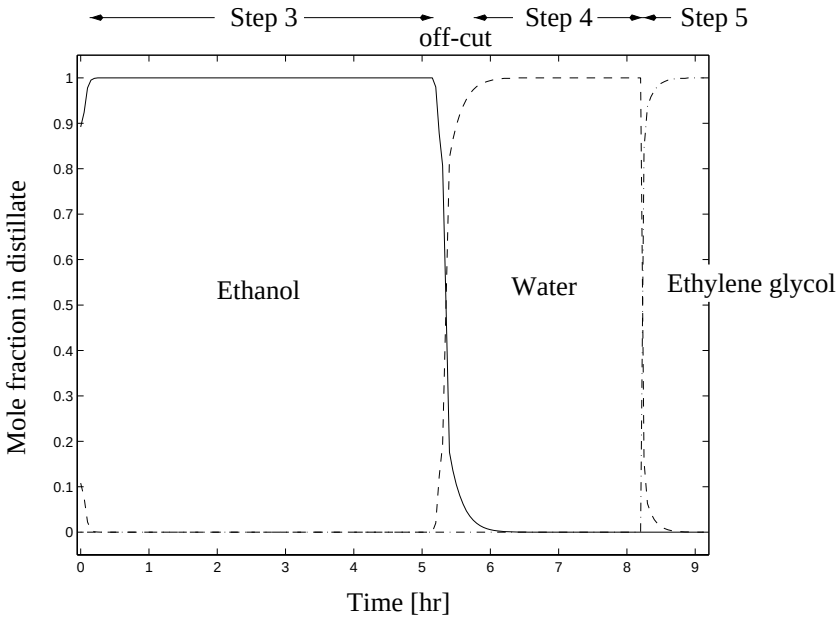

Figure 8: Product sequence in batch extractive distillation of ethanol and water by ethylene glycol producing: 1. pure ethanol (step 3), 2. an off-cut, 3. pure water (step 4), and 4. a second off-cut to purify the ethylene glycol solvent left in the reboiler for re-use (step 5). E=1.0 kmol/hr, R=3, N=30, H(0)=10 kmol, V=5.0 kmol/hr.

Since the relative volatility between ethanol and ethylene glycol is especially large and the separation in the rectifying section only required few trays and low reflux, pure ethanol was

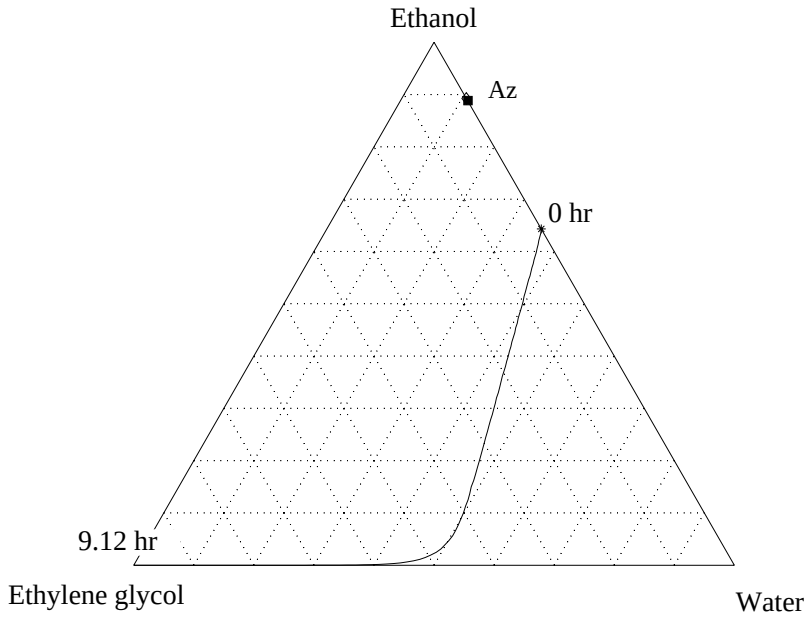

Figure 9: Composition trajectory of the reboiler (from 0 to 9.12 hours) in the batch extractive distillation column separating ethanol and water using ethylene glycol as extractive solvent. E=1.0 kmol/hr, R=3, N=30, H(0)=10 kmol, V=5.0 kmol/hr.

achieved during all the operation. Thus, the specific example of separation of ethanol and water by ethylene glycol is not useful for illustration of the degradation of the column profile and the decreased separation efficiency. In the second example mixture of acetone and methanol by water this was more apparent. The spesifications and operating parameters for the simulations shown in figure 12 to 16 were:

- The initial charge to the reboiler was 5 kmol of 50 mol% acetone and 50 mol% methanol.
- The total number of theoretical trays in the column sections was 40 (20 trays in the rectifying section inclusive the solvent feed tray, and 20 trays in the extractive section).
- The extractive solvent feed was introduced on tray number 20 at a constant feed flowrate.
- The simulation was terminated when the reboiler was empty on the second methanol product (molefraction of methanol $< 1 \cdot 10^{-6}$). The practical extractive distillation process should not be continued to the final times presented in the figures.
- Note that alle the results presented are open loop simulations (no attemt to control the composition of the middel vessel).

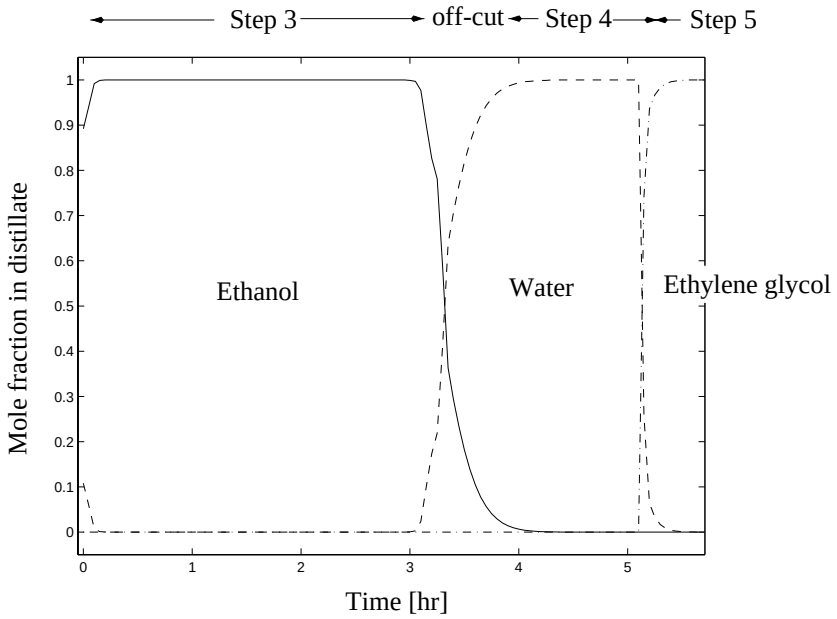

Figure 10: Product sequence in batch extractive distillation of ethanol and water by ethylene glycol producing: 1. pure ethanol (step 3), 2. an off-cut, 3. pure water (step 4), and 4. a second off-cut to purify the ethylene glycol solvent left in the reboiler for re-use (step 5). E=1.0 kmol/hr, R=1.5, N=30, H(0)=10 kmol, V=5.0 kmol/hr.

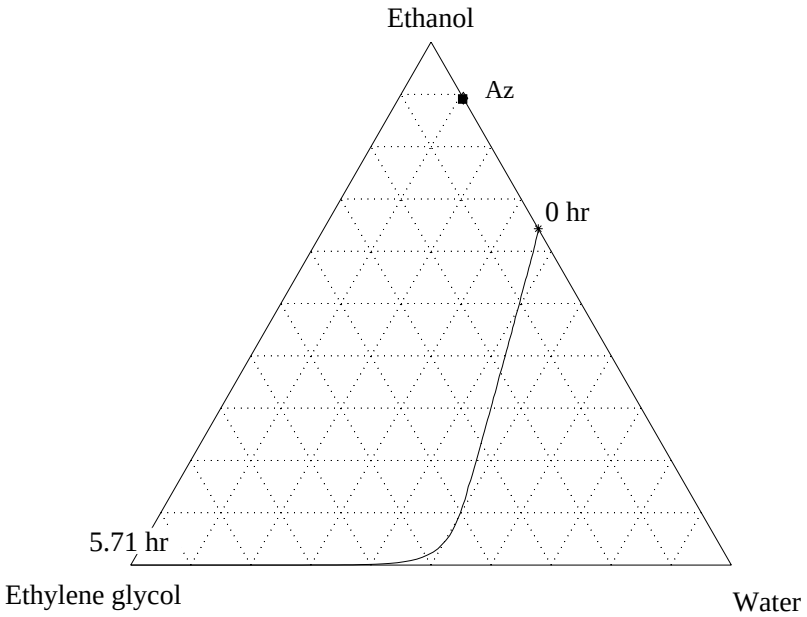

Figure 11: Composition trajectory of the reboiler (from 0 to 5.71 hours) in the batch extractive distillation column separating ethanol and water using ethylene glycol as extractive solvent. E=1.0 kmol/hr, R=1.5, N=30, H(0)=10 kmol, V=5.0 kmol/hr.

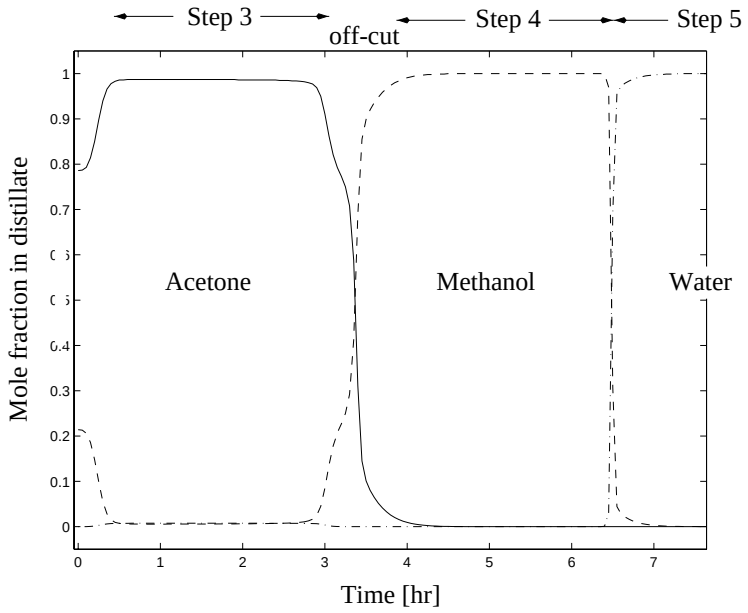

Figure 12: Product sequence in batch extractive distillation of acetone and methanol by water producing: 1. pure acetone (step 3), 2. an off-cut, 3. pure methanol (step 4), and 4. a second off-cut to purify the water solvent left in the reboiler for re-use (step 5). E=2.0 kmol/hr until the distillate purity of acetone is less than the azeotropic composition (< 0.786) (in this case no solvent feed after 3.17 hours), R=5, N=40, H(0)=5 kmol, V=5.0 kmol/hr.

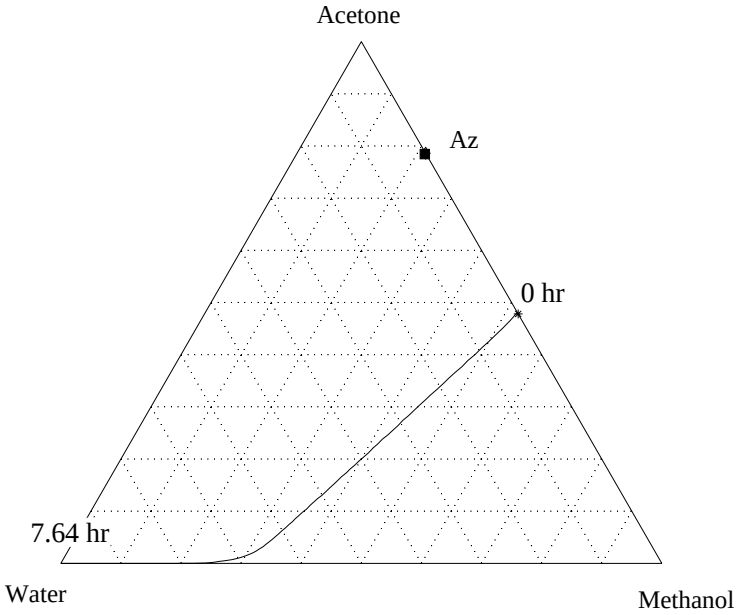

Figure 13: Composition trajectory of the reboiler (from 0 to 6.88 hours) in the batch extractive distillation column separating acetone and methanol using water as extractive solvent. E=2.0 kmol/hr until 3.17 hr, R=5, N=40, H(0)=10 kmol, V=5.0 kmol/hr.

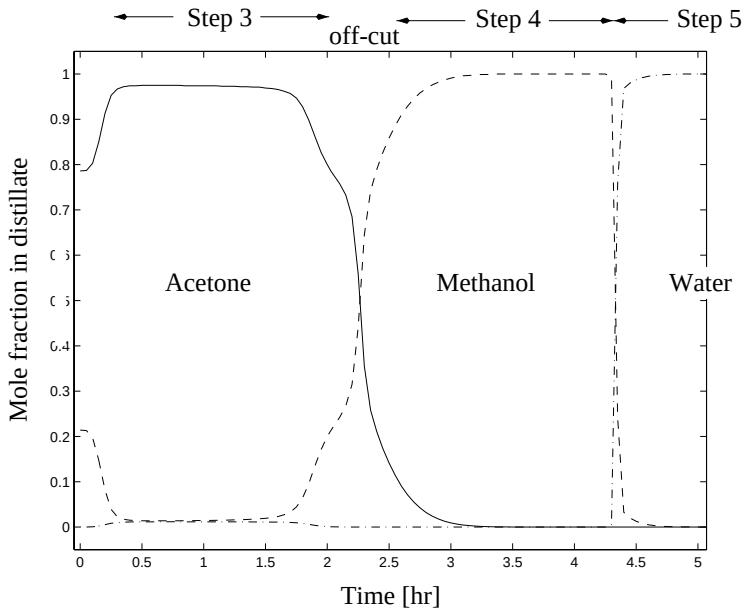

Figure 14: Product sequence in batch extractive distillation of acetone and methanol by water producing: 1. pure acetone (step 3), 2. an off-cut, 3. pure methanol (step 4), and 4. a second off-cut to purify the water solvent left in the reboiler for re-use (step 5). E=2.0 kmol/hr until methanol breakthrough in distillate (impurity of methanol is more than the azeotropic composition (< 0.214) (no solvent feed after 2.0 hours), R=3, N=40, H(0)=5 kmol, V=5.0 kmol/hr.

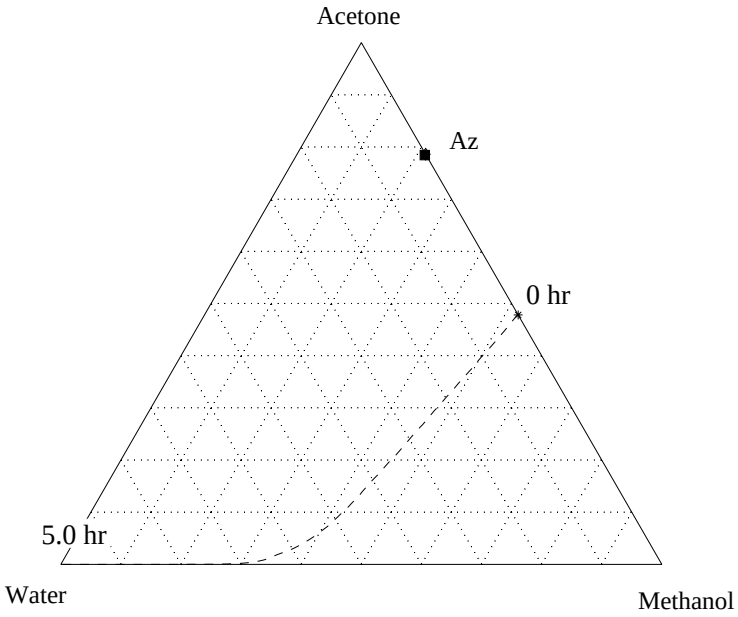

Figure 15: Composition trajectory of the reboiler (from 0 to 5.0 hours) in the batch extractive distillation column separating acetone and methanol using water as extractive solvent.

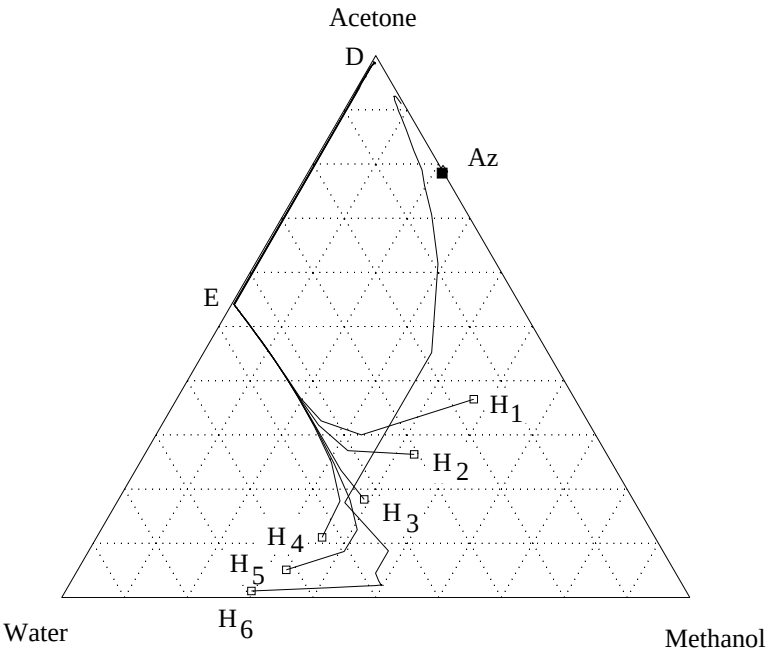

Figure 16: Instantaneous composition profiles in the batch extractive distillation column with sequential removal of products separating acetone (1) and methanol (2) by water (solvent). D - distillate, E - solvent feed tray, H - instantaneous reboiler composition.

In the first instance of the process (after initial feed of solvent), the composition of the reboiler is marked by H_1 in figure 16. For each time step, the composition of the reboiler gets enriched in the water solvent, marked by H_1, H_2, H_3, H_4, H_5, H_6, and it becomes more and more difficult to get pure distillate acetone product. Thus, the separation efficiency decreases with time in the extractive section. When the composition of the reboiler reaches the binary edge, all of the acetone product is taken out as distillate and only the separation of methanol (second product) and the water (solvent) remains, i.e. regeneration of the solvent for re-use.

Thus, for the conventinal batch extractive distillation column configuration, there is a trade-off between two operating schemes: (1) requiring pure distillate product with decreasing separation efficiency during the batch distillation run, or (2) removing a binary distillate fraction of the first product and solvent and purify this fraction in a second column (or in a later batch distillation step). The choice between these two modes depends on the relative volatility between the solvent and the first distillate product and has to be considered in each specific case. For the example mixture of ethanol and water, pure ethanol was achieved during the whole distillation run due to the high relative volatility between ethanol and ethylene glycol and it was sufficient with a few trays in the rectifying column. For the example mixture of acetone and methanol, the separation of acetone from water is more difficult due to the formation of an almost tangent azeotrope as previously described.

Summary: The batch extractive distillation column configuration with sequential removal of products has two main disadvantages due to the gradual accumulation of the high-boiling solvent in the reboiler: (1) filling of the reboiler, and (2) depletion of the azeotrope components in the reboiler which causes a degradation of column profile. The first may cause operational problems and the latter decreases the efficiency of the separation.

4.2 Batch Extractive Distillation with a Middle Vessel

In the second configuration studied, the batch extractive middle vessel column, removal of distillate products and recovery of the extractive agent was performed simultaneously. As previously mentioned, the composition of the middle vessel vary depending on the reflux- and reboil ratios during operation. The best operating policy is probably to hold the composition of the distillate and bottoms product constant by 'steering' the composition of the middle vessel by manipulating the extractive solvent feed flowrate and the reboiler- and reflux ratios (Safrit and Westerberg 1997). In this study, only a simple operating policy was implemented with constant reboiler- and reflux ratios. The specifications and operating parameters for the examples given in the figures were:

- The initial charge to the middle vessel is 5 kmol of 50 mol% acetone and 50 mol% methanol.
- The total number of theoretical trays in the column sections was 60 (20 trays in the rectifying section inclusive the solvent feed tray, 20 trays in the extractive section and 20 trays in the stripping section).
- A constant vapor flow of 5.0 kmol/h (maximum boilup) was set to minimize the time consumption of the batch run as for the previous sequential batch extractive distillation example.
- The extractive solvent feed was introduced on tray number 20 at a constant feed flowrate of 2.0 kmol/h, i.e. $E/V = 0.40$ (see figure 22 for the explanation of the symbols).
- The reflux ratio was held at $R = 3$ constant and the liquid flow out of the middle vessel was held constant at $L_M = L_1 + D + E$ during the two operating regimes of steps 3 and 4. The molar holdup in the reboiler and condenser was set constant to 0.01 kmol. The values given above gives a liquid reflux flowrate from the condenser of $L_1 = 3.75$ kmol/h and a distillate flowrate of $D = 1.25$ kmol/h. Thus, the liquid flowrate out of the middle vessel was set to $L_1 = 7.0$ kmol/h when extractive solvent was fed, and the bottoms flowrate was $B = 2$ kmol/h when extractive solvent was fed and $B = 0$ (total boilup) without extractive solvent feed. The values are by no means ment to be optimal for operation of the middle vessel column.
- The simulation was terminated when the middle vessel was empty on methanol (molefraction of methanol $< 1 \cdot 10^{-6}$).
- Note that alle the results presented are open loop simulations. No attemt was made to control the composition of the middel vessel. The operation of the extractive distillation (with solvent feeding) should not continue on to the final times presented in the figures.

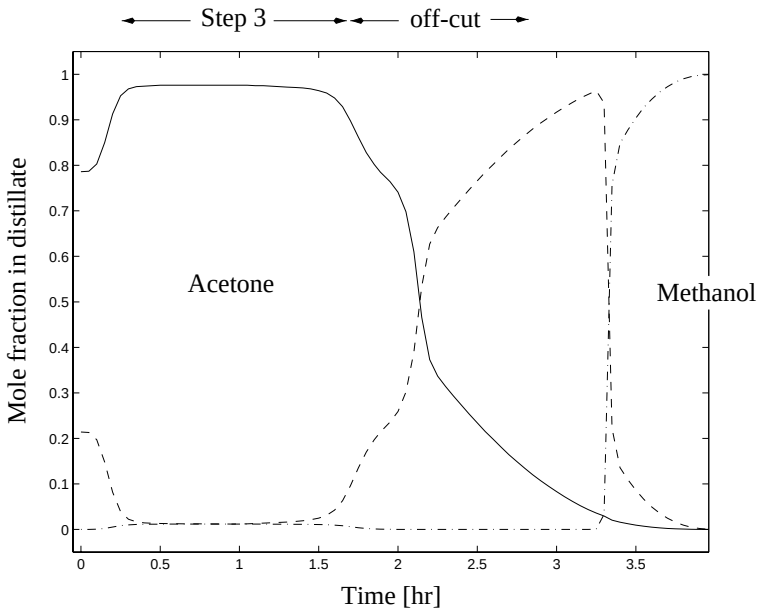

Figure 17: Distillate product sequence in batch extractive middle vessel distillation of acetone and methanol by water producing: 1. pure acetone (step 3) and 2. an off-cut. E=2.0 kmol/hr and Q=2.5 until 1.89 hours and E=0 kmol/hr and total boilup after that, R=3, N=60, $H_M(0)$=5 kmol.

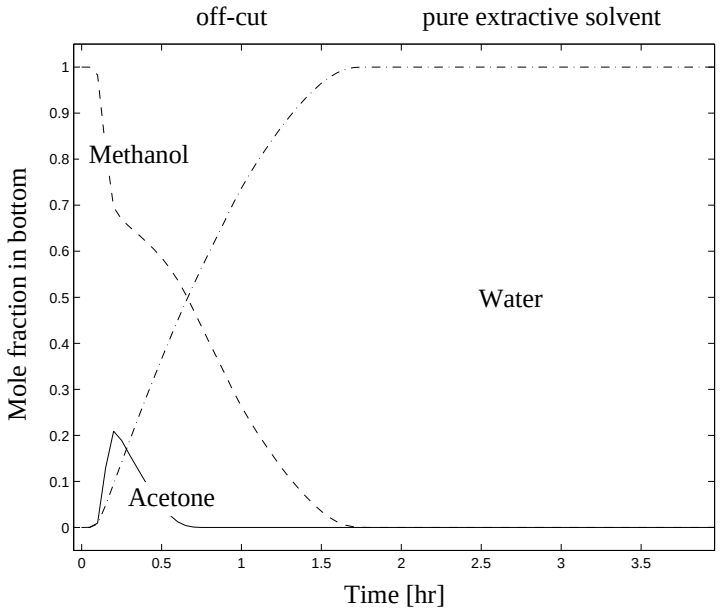

Figure 18: Bottoms product sequence in batch extractive middle vessel distillation of acetone and methanol by water producing: 1. an off-cut and 2. pure extractive solvent (water). E=2.0 kmol/hr and Q=2.5 until 1.89 hours, R=3, N=60, $H_M(0)$=5 kmol.

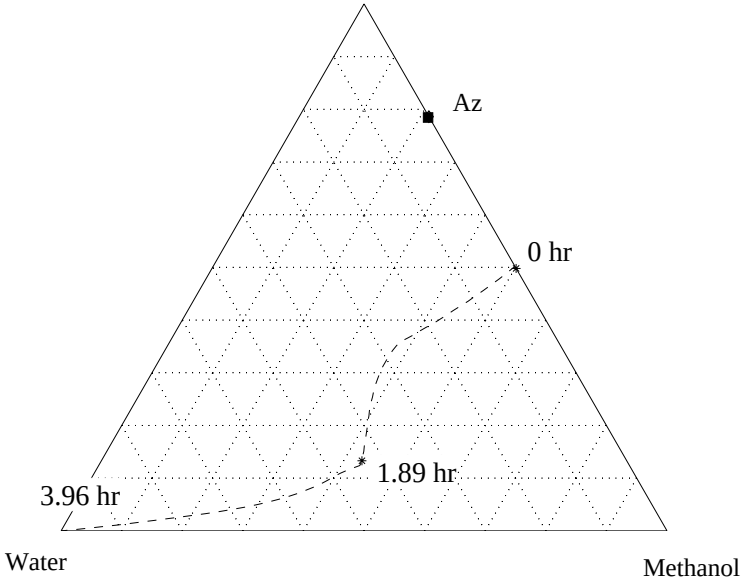

Figure 19: Composition trajectory of the middle vessel (from 0 to 3.96 hours) in the batch extractive distillation column separating acetone and methanol using water as extractive solvent. E=2.0 kmol/hr and Q=2.5 until 1.89 hours, R=3, N=50, $H_M(0)$=5 kmol.

Figure 20, 21 and 20 shows instantaneous composition profiles along the batch extractive middle vessel distillation column separating acetone and methanol using water as extractive solvent.

Summary: The batch extractive middle vessel distillation column configuration solves the previously mentioned problem of solvent accumulation in the reboiler of the conventional batch column configuration. The volume of the middle vessel can be kept constant or even decreasing with time due to the depletion of the high-boiling agent to the stripping section of the column. In addition, the batch extractive middle vessel column is potentially more energy efficient due to the multi-effect nature of combining a rectifying-extraction section and a stripper section in one column (only one condenser and reboiler, and simultaneous removal of products and recovery of the entrainer, i.e. time savings in operation), even when compared to continuous extractive distillation columns (comparable to a direct sequence of two columns). The extractive middle vessel column has a more complex design, but is more flexible and easier to operate. Several aspects of extractive distillation in batch columns remains to be answered such as optimal policy for feed of extractive solvent, required quality (purity, temperature) of the solvent feed, solvent feed tray location, reflux policy and others.

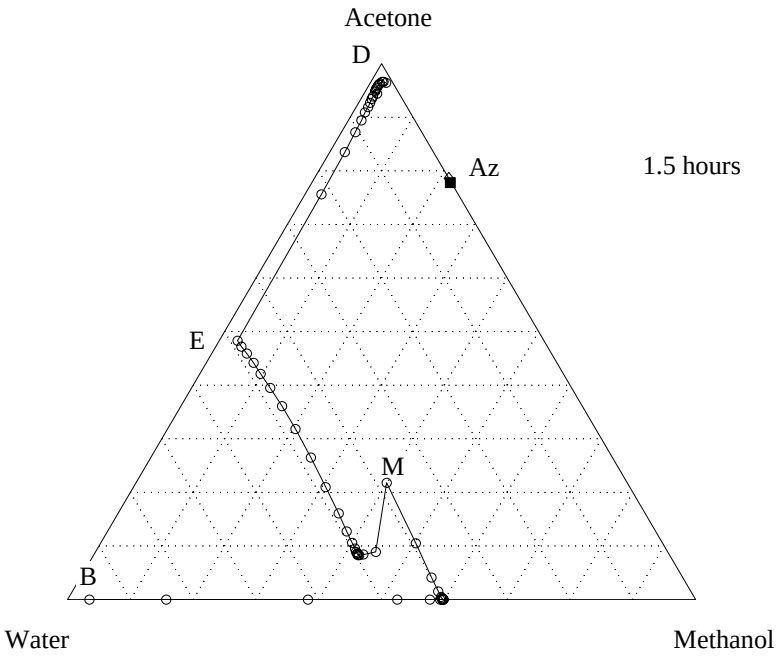

Figure 20: Instantaneous composition profile (snapshot at 1.5 hours) in the batch extractive middle vessel distillation column separating acetone and methanol using water as extractive solvent. D - distillate, B - bottoms product, M - middle vessel composition, E - solvent feed tray.

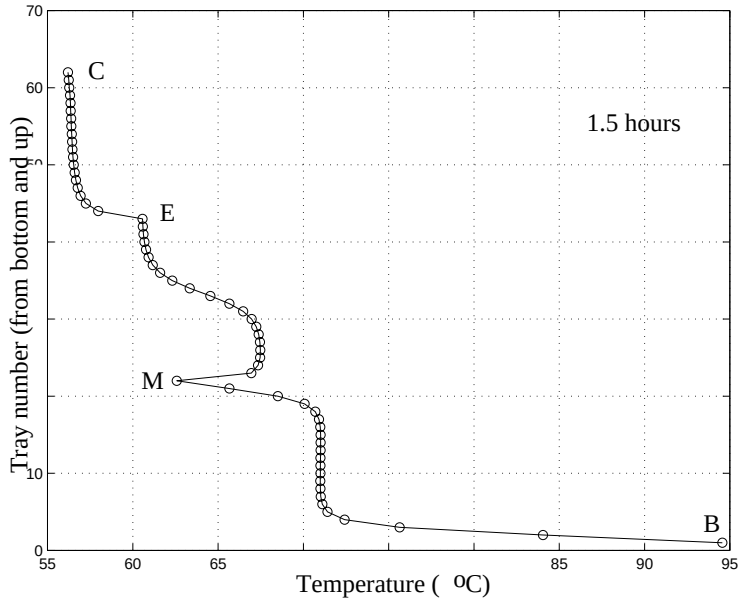

Figure 21: Instantaneous temperature profile (snapshot at at 1.5 hours) in the batch extractive middle vessel distillation column separating acetone and methanol using water as extractive solvent. C - condenser (distillate), B - bottoms product, M - middle vessel composition, E - solvent feed tray.

4.3 Comment on Control

According to Doherty and Knapp (1993), it is widely recognized that azeotropic distillation columns are difficult to operate and control because these columns may exhibit complex dynamic behavior and parametric sensitivity. However, using the proper control configuration, extractive distillations are no more difficult to control than ordinary distillation columns producing high purity products (Jacobsen and Skogestad (1991)).

Farschman and Diwekar (1996) evaluate various control configurations (dual composition control) for the batch distillation middle vessel column configuration for separation of ideal ternary mixtures. They use the ratio of the vapor flow in the rectifying section to the vapor flow in the stripping section as a control parameter (this ratio q was discussed in the paper by Davydian et al. (1994)). In this study, the vapor flow is held constant in both column sections equal to the maximum boilup ($q = 1$). Andersen et al. (1995) studied the effect of design on operation of continuous extractive distillation. The second feed of extractive solvent (called entrainer) to the distillation column introduces an additional design variable which does not exist in conventional distillation. They showed that for continuous systems, this degree of freedom can be conveniently expressed as a relation between the extractive solvent feed flowrate and the internal flows for fixed product specifications, E/V. The effects which govern the trade-off curve are summarized as follows (Andersen et al. 1995):

Entrainer feed flowrate

- **(Ea)** *Increasing the entrainer feed flow increases the relative amount of entrainer in the extractive section and thus improves the relative volatility between the light and the intermediate components.*
- **(Eb)** *Increasing the entrainer feed flow increases the load on the rectifying and stripping sections.*

Internal flows

- **(Ia)** *Increasing the internal flows improves the operating lines in the stripping and rectifying sections.*
- **(Ib)** *Increasing the internal flows reduces the relative amount of entrainer in the extractive section and thus reduces the relative volatility between the light and intermediate components.*

Control structure for the batch extractive middle vessel distillation column

In nonideal systems, the notation *light*, *intermediate* and *heavy* component may be misleading. The relative volatility order between the components may vary in the composition space and is not determined simply from the pure components boiling-points. For continuous extractive distillation of an azeotropic system as given in figure 1, component 1 is more volatile than component 2 in the rectifying section, but opposite in the extractive and stripping sections. The extractive solvent is least volatile component in the whole composition space thus the notion heavy component may be used.

Step 3 (production of acetone): In the rectifying section, separation of the extractive solvent form component 1 (light component) dominates and we propose to control the amount of solvent in the distillate by adjusting the liquid flow from the condenser L_1 as for conventional

distillation columns. In the extractive section, the azeotrope components are separated in the dilution of the extractive solvent. The separation efficiency improves with increased load of the extractive solvent and the solvent feed amount is determinant for the separation. Thus, we propose to control the purity of the light component (component 1) from this section by adjusting the extractive solvent feed flowrate (keeping the fromt of the intermediate component in the extractive section at a certain level).

In the stripping section (during step 3), separation of component 2 (intermediate component) from the solvent dominates and we propose to control the impurity of intermediate component in the bottoms product, or, alternatively the impurity (amount) of solvent in the middle vessel, by adjusting the liquid flow form the middle vessel L_M ('second reflux ratio').

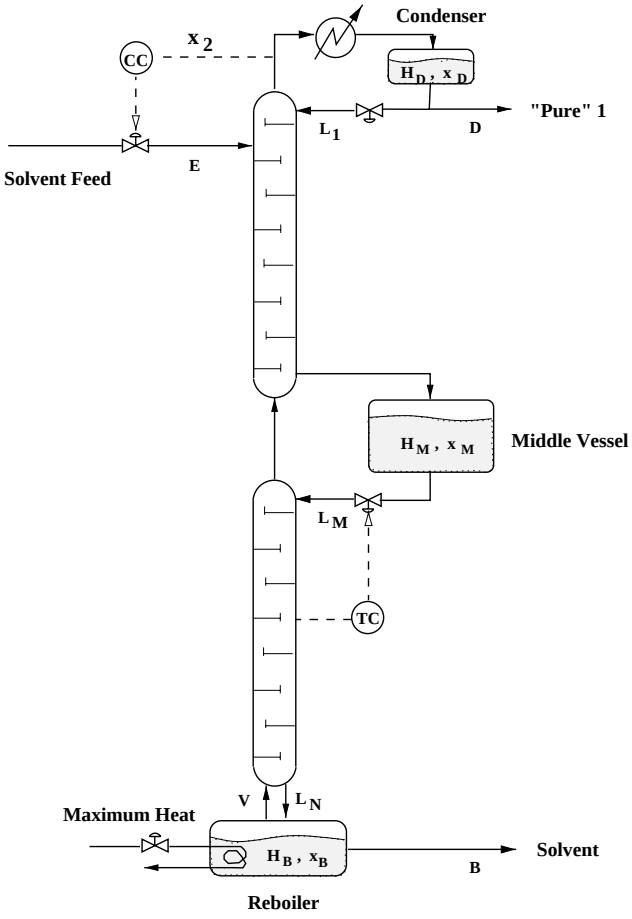

Figure 22: Control configuration of the batch extractive distillation column with a middle vessel

Maximum boilup set to 5.0 kmol/hr was used in all simulations without bottoms product removal (total reboil) in order to minimize the time consumption of the batch run. In the cases with bottoms product removal, the reboil ratio is held constant. The liquid flow out of the middle vessel L_M, was held constant equal 5.0 kmol/hr in simulations without control.

Feedback control on the product compositions

For the separation of ethanol and water using ethylene glycol as extractive solvent, the temperature is (relatively) insensitive to composition changes in the extractive section due to the large amount (dilution) of the solvent on the trays. Since the composition of ethanol and water is not a strong function of temperature in the extractive section we propose to use a measurement or

estimate of the composition of component 2 as input for the control of the extractive solvent feed flowrate (controls the separation of the azeotrope components, which again obviously affects the purity of distillate composition). Specific gravity (density) measurements of the condensed distillate flow may be used, but there will be a time delay between a change in composition in the vapor flow out of the rectifying section is registered in the distillate flow out of the condenser drum. Alternatively, the composition of component 2 in the vapor leaving the rectifying section, or composition of component 2 in the extractive section, can be measure directly by IR or GC analysis (time delay in measurements).

In the stripping section (during step 3), the temperature is more sensitive to composition changes and we propose to adjust the middle vessel holdup indirectly by manipulating the reflux flow out of the vessel to control the temperature at some location in the column section below (scheme of Skogestad et al. (1995)).

5 Conclusion

This paper focuses on the use of batch extractive distillation for separating homogeneous minimum-boiling azeotropic mixtures, where the extractive agent is a high-boiling, miscible zeotropic component. In conventional batch column configuration, the extractive scheme breaks the azeotrope and the components can be recovered as pure products (sequential removal of the products). However, this semi-continuous operation has two main disadvantages due to accumulation of the extractive agent: (1) filling of the reboiler, and (2) degradation of the composition profile in the column. The first may cause operational problems and the latter decreases the efficiency of the separation. The middle vessel column arrangement overcome these problems since it allows for simultaneous removal of pure products and recovery of the extractive agent. The volume of the middle vessel can be kept constant or even decreasing with time. Thus, high separation efficiency can be achieved since the sharpness of the column profile is maintained.

Batch extractive distillation with a middle vessel is closely related to the well-known continuous extractive distillation except that the separation is performed in one rather than in two columns, which may imply capital savings for the batch implementation. Furthermore, the batch implementation is potentially more energy efficient due to the combination of a rectifying-extraction section and a stripper section in one column.

We propose a novel control configuration for the batch extractive middle vessel distillation where the liquid flow from the middle vessel is manipulated to control the temperature in the stripping section, achieving a desired purity of the extractive agent. This indirectly adjusts the vessel holdup so there is no need for level control. The extractive agent feed is used to control the purity of the distillate and the reflux is held constant below its maximum value.

Acknowledgment

We thank Dr. V. N. Kiva for providing valuable insight to the batch extractive distillation process and operation of the middle vessel column configuration, as well as giving references to relevant publications in the Russian literature.

Terms and Concepts

Azeotrope - mixture whose composition corresponds to an extremal point (minimum, maximum or saddle point) on the boiling temperature isobar. In the azeotropic point the vapor and liquid compositions are equal.

Azeotropic - mixtures that form one or several extremal points (minimum, maximum or saddle points) on the boiling temperature isobar at atmospheric or any other pressure, or, equivalently, that form one or several points on the vapor pressure isotherm.

Azeotropic distillation - distillation of an azeotropic mixture and/or distillation with addition of a separating agent forming new azeotropes in the system. Includes single and multiple feed columns.

Distillation (fractional distillation) - sequence of partial vaporization steps where the vapor phase becomes gradually enriched in the most volatile component(s), i.e. a cascade of equilibrium trays.

Extractive distillation - distillation of zeotropic and/or azeotropic mixtures with addition of a relatively non-volatile component (usually called solvent) selective to one of the components in the feed mixture taken out as bottoms product. The solvent is introduced above the mixture feed in a second feed point to the distillation column.

Homoazeotrope - azeotrope where the vapor phase coexists with one liquid phase.

Homoazeotropic distillation - distillation of homoazeotropic mixtures and/or with the addition of a liquid separating agent that is completely miscible.

RCM - (simple distillation) residue curve map. Diagram which shows the locus of the composition of the residue liquid in the still during simple distillation for different initial conditions.

Simple distillation (or open evaporation) - evaporation of a liquid phase where the vapor formed is removed continuously (Rayleigh distillation).

Simple distillation residue curve - the locus of the composition of the residue liquid in the still during simple distillation (open evaporation). Introduced by Schreinemakers in 1901 and termed the *distillation line of the liquid* in the Russian literature.

Zeotropic - (ideal or nonideal) mixtures that do not form azeotropes.

Notation

A_{ij}	binary interaction parameter in the Wilson equation $[cal/mol]$
B	bottom flow for stripping (inverted) column $[kmol/hr]$
D	distillate flow for rectifying (regular) column $[kmol/hr]$
E	extractive agent feed $[kmol/hr]$
F	feed amount $[kmol]$
F_0	basic feed amount (before adding separating agent) $[kmol]$
F_T	total feed amount to column (basic feed + added separating agent) $[kmol]$
$H(0)$	initial liquid molar holdup in reboiler (or still) $[kmol]$
$H(t)$	liquid molar holdup in reboiler (or still) at time t $[kmol]$
H_j	liquid molar holdup on tray j $[kmol]$
L	molar liquid flow rate $[kmol/hr]$
N	total number of trays in the column (excl. reboiler)
n	number of trays in rectifying section
m	number of trays in stripping section
n_c	number of components (in a multicomponent mixture)
P	total pressure $[Pa]$
P_i^{sat}	saturated vapor pressure of pure component i $[Pa = N/m^2]$
Q	boilup ratio, V/B
R	(1) reflux ratio, L/D; (2) universal gas constant, $R = 1.98721$ $[cal/molK]$
T	temperature [K]
t	time $[hr]$
V_i	molar volume of component i $[cm^3/mol]$
V	molar vapor flow rate $[kmol/hr]$
$\underline{x}$	vector of mole fractions in the liquid phase (n_c elements)
$\underline{y}$	vector of mole fractions in the vapor phase (n_c elements)
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase

Greek letters

α	relative volatility
γ	liquid activity coefficient
ξ	dimensionless warped time variable; $\xi = -ln\,\frac{H(t)}{H(0)}$

Subscripts

B	bottom, reboiler (or still)
D	distillate, condenser
M	middle vessel
S	solvent, separating agent, entrainer
0	initial value (at $t = 0$)
$1, 2, 3$	components number

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Appendix: Thermodynamic Data for the Example Mixtures

Constants for the Antoine Equation				
Component	A	B	C	V_i $[\frac{cm^3}{mol}]$
1) Ethanol	23.5807	3673.81	-46.681	58.69
2) Water	23.2256	3835.18	-45.343	18.07
3) Ethylene glycol	25.1431	6022.18	-28.250	55.92

Binary Interaction Parameters for the Wilson Equation			
	$A_{11} = 0$	$A_{21} = 926.263$	$A_{31} = 1539.4142$
	$A_{12} = 393.1971$	$A_{22} = 0$	$A_{32} = -1265.7398$
	$A_{13} = -129.2043$	$A_{23} = 1266.0109$	$A_{33} = 0$

Constants for the Antoine Equation				
Component	A	B	C	V_i $[\frac{cm^3}{mol}]$
1) Acetone	21.3009	2801.53	-42.875	74.04
2) Methanol	23.4999	3643.31	-33.434	40.73
3) Water	23.2256	3835.18	-45.343	18.07

Binary Interaction Parameters for the Wilson Equation			
	$A_{11} = 0$	$A_{21} = 583.1054$	$A_{31} = 1422.849$
	$A_{12} = -161.8813$	$A_{22} = 0$	$A_{32} = 554.0494$
	$A_{13} = 489.3727$	$A_{23} = 19.2547$	$A_{33} = 0$

Form of the Antoine Equation

$$ln\, P_i^{sat} = A - \frac{B}{T + C}, \qquad i = 1, .., n_c$$

where P_i^{sat} $[Pa]$ and T $[K]$

Form of the Wilson Equation

$$ln\, \gamma_i = 1 - ln\left(\sum_{j=1}^{n_c} x_j\, \Lambda_{ij}\right) - \sum_{k=1}^{n_c}\left(\frac{x_k\, \Lambda_{ki}}{\sum_{j=1}^{n_c} x_j\, \Lambda_{kj}}\right),$$

$$\Lambda_{ij} = \frac{V_j}{V_i}\, exp\left(\frac{-A_{ij}}{R\, T}\right)$$

where V_j $[\frac{cm^3}{mol}]$ and A_{ij} $[\frac{cal}{mol}]$

Ideal vapor phase is assumed in all calculations. This gives for the vapor-liquid phase equilibrium $y_i\, P = \gamma_i\, x_i\, P_i^{sat}$. Parameters are collected from DECHEMA series by Ghemeling and Onken et al.