

Design and Control of Dimethyl Carbonate–Methanol Separation via Extractive Distillation in the Dimethyl Carbonate Reactive-Distillation Process

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Dimethyl carbonate is an environmentally benign and biodegradable chemical. It can be produced by a transesterification reaction of methanol with ethylene carbonate, coproducing another useful product, ethylene glycol. A reactive distillation column can be utilized for the complete conversion of ethylene carbonate with methanol in excess. The coproduct, ethylene glycol, is the bottom product while the top product of this reactive distillation column is a mixture of dimethyl carbonate and methanol close to the azeotropic composition. In this paper, an economical separation process via extractive distillation is proposed to obtain pure dimethyl carbonate product and also pure methanol to be recycled to the reactive distillation column. A very simple procedure is proposed in this paper for the quick comparison of alternative entrainer candidates before rigorous process simulation is conducted. Aniline is found to be a very effective entrainer to enhance the relative volatility between methanol and dimethyl carbonate. A problem with small heavy-boiler impurities in the feed stream of the extractive distillation process is also pointed out, with a practical solution given for this problem. Simple overall control strategy of this process is also proposed to maintain product purity despite various feed disturbances. Only one tray temperature control loop is required for each of the columns.

1. Introduction

Dimethyl carbonate (DMC) is an environmentally benign and biodegradable chemical. It is a nontoxic substitute for dimethyl sulfate or methyl halide as a methylating agent or a substitute for phosgene as a carbonylating agent.¹ This useful chemical can be produced by a transesterification reaction of methanol with ethylene carbonate (EC), coproducing another useful product, ethylene glycol (EG).² In the experimental study by Fang and Xiao,² this reaction is reversible with an EC equilibrium conversion of about 80%. A reactive distillation column can be utilized for the complete conversion of EC with methanol in excess. However, the top product of the reactive distillation column is the azeotrope of methanol and DMC because the azeotropic temperature is the lowest of the system. Further separation of this azeotropic mixture is needed to complete the design flow sheet of the overall process to coproduce DMC and EG.

Conventional methods for the separation of azeotrope without adding a third component are two-fold. One method is for the cases where the azeotrope is heterogeneous, which means after cool down it can naturally be separated into two liquid phases. With this unique characteristic, a simple two-strippers/decanter configuration can be used to separate the azeotrope.^{3–5} Methanol–DMC azeotrope does not exhibit this behavior; thus, this separation method cannot be utilized for this system.

Another method is called pressure-swing distillation. This is used for some azeotropic systems that exhibit the desirable property of operating pressure having a strong effect on the composition of the azeotrope. When this occurs, a two-column system can be used to achieve the desired separation.^{6,7} Wang et al.⁸ studied pressure-swing distillation for the methanol–DMC azeotrope and found out that this separation method is not more economical than extractive distillation.

Extractive distillation is another way to separate an azeotrope. In this method, a third component (heavy entrainer) is added

into the system. The entrainer acts to enhance the relative volatility of the original two components so that one original component can go overhead in the extractive distillation column and the other component will go with the heavy entrainer to the bottom of the column. A second entrainer recovery column is used to purify entrainer, which is recycled back to the extractive distillation column.

Entrainer screening is an important step in extractive distillation before the distillation sequence is designed. Several rules have been proposed to obtain a feasible entrainer candidate for the azeotropic mixtures.^{9–12} A comprehensive paper by Gmehling and Mollmann¹³ used several examples to show their procedure for the entrainer selection. A recent nice paper by Kossack et al.¹⁴ used acetone–methanol separation as an example to show a systematic synthesis framework for extractive distillation processes. The effect of solvent on controllability in acetone–methanol separation was further studied by Luyben.¹⁵

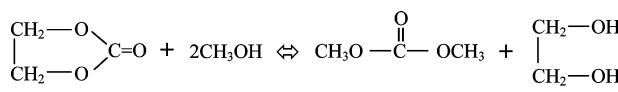
In this paper, design and control of the overall process for the coproduction of DMC and EG is studied. Particular focus will be on the separation of methanol–DMC mixture via extractive distillation. In Wang et al.,⁸ no comparisons of candidate entrainers have been made; only phenol is shown as a feasible entrainer. In this paper, a simple procedure is proposed for quick comparison of candidate entrainers. Aniline is found to be a much more effective entrainer for the methanol–DMC separation. A problem with heavy impurities in the feed stream of the extractive distillation system will also be pointed out, with a proposed practical solution of this problem. The design flow sheet with two recycled streams and the overall control strategy of the process will be developed to meet product specifications.

2. Design of Reactive Distillation Column

The reactive distillation column for this system will be designed first. The reversible reaction is as follows:

The kinetics equation of this reaction is from Fang and Xiao² and can be expressed as follows:

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$$r_{\text{EC}} = k_+ C_{\text{EC}} C_{\text{MeOH}} - k_- \frac{C_{\text{EG}} C_{\text{DMC}}}{C_{\text{MeOH}}} \quad (2-1)$$

$$k_+ = 1.3246 \exp\left(\frac{-13\ 060}{RT}\right) \quad (2-2)$$

$$k_- = 15\ 022 \exp\left(\frac{-28\ 600}{RT}\right) \quad (2-3)$$

where r_{EC} is the reaction rate of EC in moles per liter per minute and C_i is the concentration of the i th component in moles per liter. The above kinetic expression was obtained experimentally with homogeneous catalyst of sodium methylate with its concentration between 0.2 and 0.3 wt %. In the following design study, because of very low concentration, this catalyst component was ignored in the simulation for simplification purpose.

The system to be simulated has four components. The vapor–liquid equilibrium is described by use of a UNIQUAC model for the liquid phase and an RK model for the vapor phase. The experimental data for the MeOH–EG pair are obtained from Gmehling and Onken.¹⁶ The VLE data of the four pairs MeOH–EC, DMC–EC, DMC–EG, and EG–EC are from a paper by Fang and Qian.¹⁷ The VLE data for the remaining pair (MeOH–DMC) are from a paper by Rodriguez et al.¹⁸ Regression has been performed to obtain suitable UNIQUAC parameters for the latter five pairs, and the built-in parameters from Aspen have been used for the MeOH–EG pair. The resulting parameter set can be found in Table 1. Figure 1a displays the prediction of the $y-x$ and $T-xy$ plots of all six pairs by the thermodynamic model. The figure also contains the experimental data for comparison. It is found that the thermodynamic model is excellent in predicting the VLE behavior and the two azeotropes¹⁹ of the system.

The reactive distillation design concept is to feed excess methanol into the system, thus consuming EC to nearly complete conversion. From the residue curve map (RCM) in Figure 2, EG product (nbp 197.08 °C) can be withdrawn from the bottom of the column, while the column top composition approaches the azeotrope of MeOH–DMC (63.73 °C). The design flow sheet of this reactive distillation column is developed by minimizing the total annual cost (TAC) of the system. The TAC includes the utility cost and the annualized capital cost. The utility cost includes steam for the reboiler, cooling water for the condenser, and catalyst cost. The capital cost includes the column shell, internal trays, reboiler, and condenser. A capital charge factor of 3 years is assumed in the calculation. The cost calculation can be seen from appendix E of Douglas.²⁰

The EC feed flow was assumed to be 10 kmol/h, and atmospheric column operation was also assumed. In order to enhance the contact of the two reactants, EC (a heavier boiler) and MeOH (a lower boiler) are fed from the top portion and the bottom portion of the RD column, respectively. The

homogeneous catalyst was assumed to feed into the column with EC feed, thus the column stages below the EC feed location are all reactive stages. The design variables of this system include MeOH/EC feed ratio, total number of stages, number of reactive stages, and MeOH feed location. Iterative optimization procedure was followed to obtain the best values of the above four design variables. For each simulation run, the reactive tray holdup has to be iteratively obtained to agree with the column sizing calculation. The two degrees of freedom of this RD column are fixed to obtain EG product at high purity of 99.5 mol % and EC conversion at 99.95%.

Because the optimization of this RD column is not the focus of this paper, we show only a resulting flow sheet of this RD column but not the details of search procedure. From Figure 3, it is found that the two specifications are met and the distillate product is mainly a mixture of MeOH and DMC. The design of the downstream flow sheet to separate these two components and recycle MeOH to the RD column will be shown in the next section.

A final comment worth mentioning is that experimental verification of reactive distillation in a pilot plant is important to concretely confirm the findings in the simulation study. A recent paper by Schmitt et al.²¹ demonstrated that the reaction kinetics measured in the laboratory cannot always directly be used in the simulation to successfully describe the reactive distillation in real plant. A simple “transfer factor” concept is proposed in that paper to close the gap between reactive distillation simulation and real experimental results.

3. Design of Extractive Distillation System

As can be seen in the second row of Figure 1a, a mixture of MeOH and DMC contains a minimum-boiling azeotrope at 86.47 mol % MeOH and azeotropic temperature at 63.73 °C; thus a single distillation column cannot produce two pure products. The azeotropic composition changes with operating pressure, for example, at 10 atm the azeotropic composition is predicted to be 92.15 mol % MeOH; however, the shift in the azeotropic composition is not significant. The paper by Wang et al.⁸ confirmed that pressure-swing distillation is not an attractive way to separate this azeotrope.

An alternative method for the separation of this mixture is to use extractive distillation by adding a heavy-boiling entrainer into this system. The purpose of the entrainer in this extractive distillation column is to enhance the relative volatility between MeOH and DMC, so that one component (e.g., MeOH) goes to the top of the column and the other component (e.g., DMC) goes to the bottom of the column with the entrainer. The upper section of the column (above the entrainer feed location) is called the rectifying section, and its purpose is to separate MeOH and the entrainer. The middle section of the column (between the entrainer feed stage and the fresh feed stage) is called the extractive section. The purpose of this section is to suppress DMC from going up the column. The bottom section of the column (below the fresh feed location) is called the stripping section, and its purpose is to keep MeOH from going down the

Table 1. UNIQUAC Model Parameters of EC/MeOH/DMC/EG System for Reactive Distillation Study

$i = \text{DMC}, j = \text{EC}$	$i = \text{MeOH}, j = \text{EC}$	$i = \text{DMC}, j = \text{EG}$	$i = \text{EG}, j = \text{EC}$	$i = \text{MeOH}, j = \text{DMC}$	$i = \text{MeOH}, j = \text{EG}$
a_{ij}	2.5273	-0.540 94	0	0	-32.587
a_{ji}	-6.7598	15.892	0	0	2.2712
$b_{ij}(K)$	167.34	4589.3	-236.13	-275.66	-18.065
$b_{ji}(K)$	442.34	-1278.9	-146.88	-27.961	-263.58
c_{ij}	-0.732 11	-2.2771	0	0	0
c_{ji}	1.0398	-2.0488	0	0	0

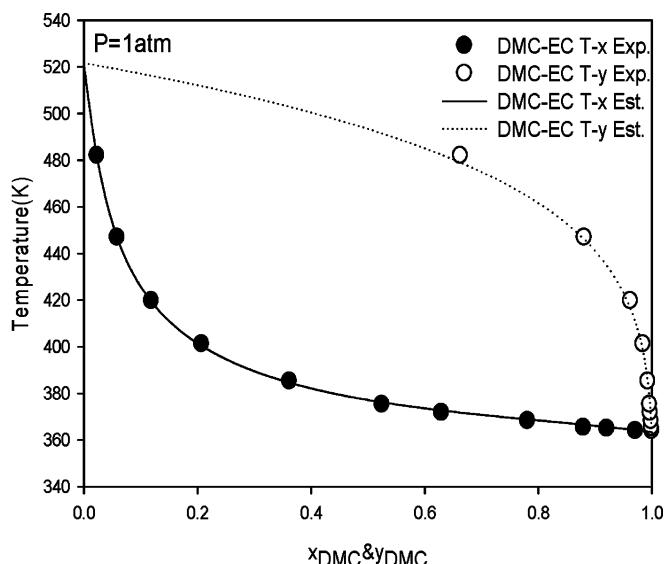
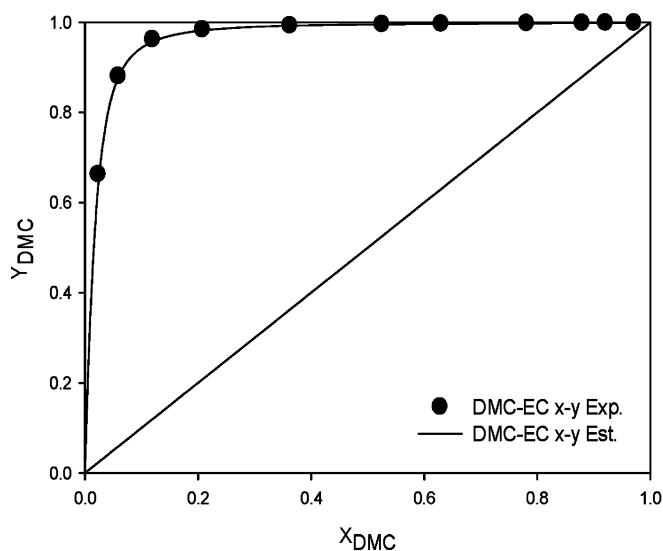
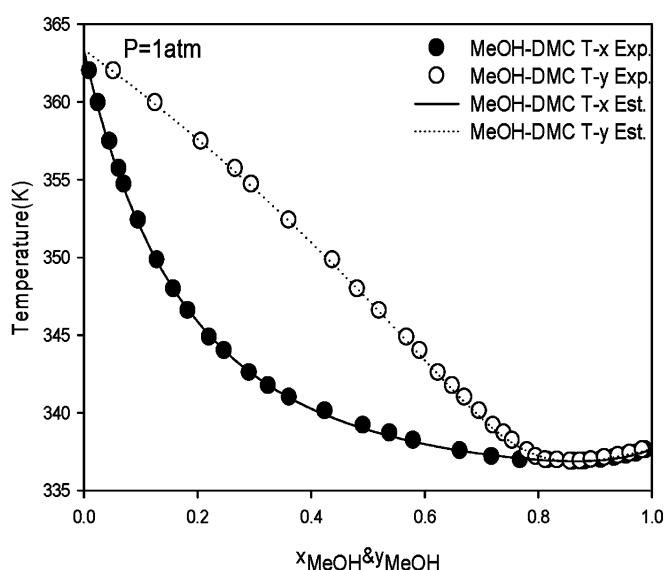
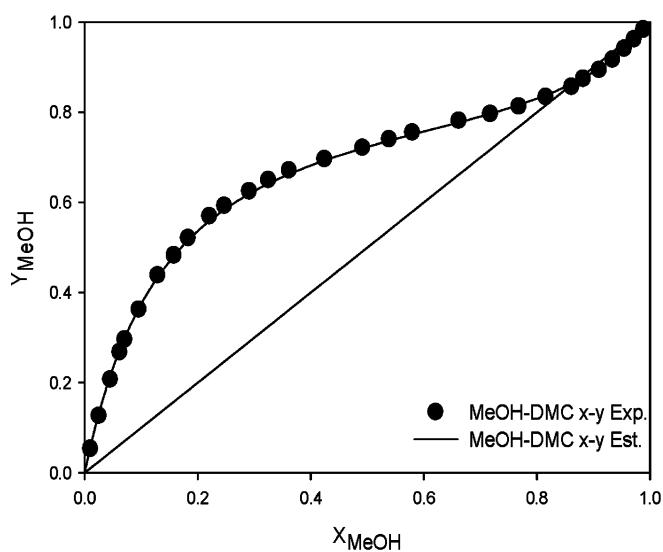
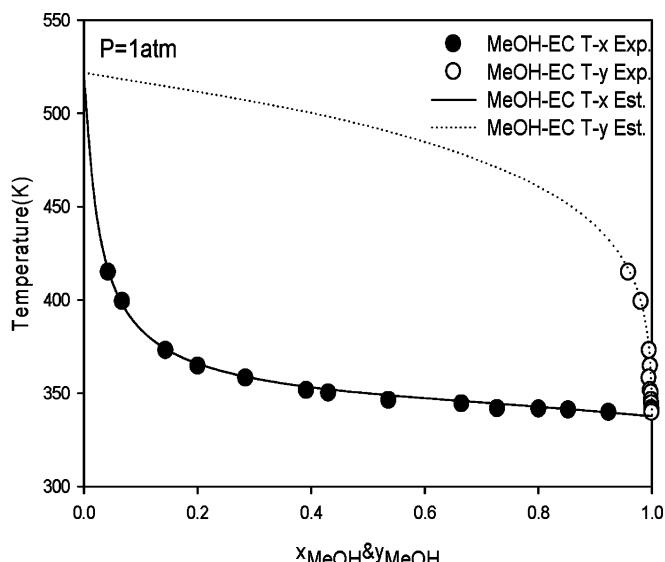
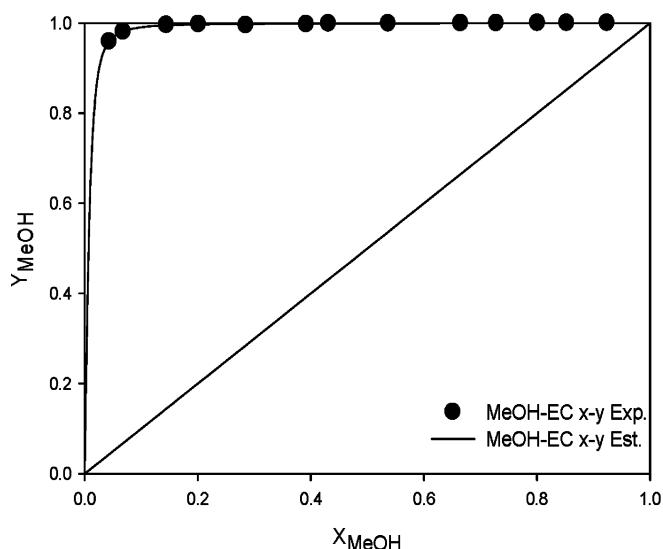
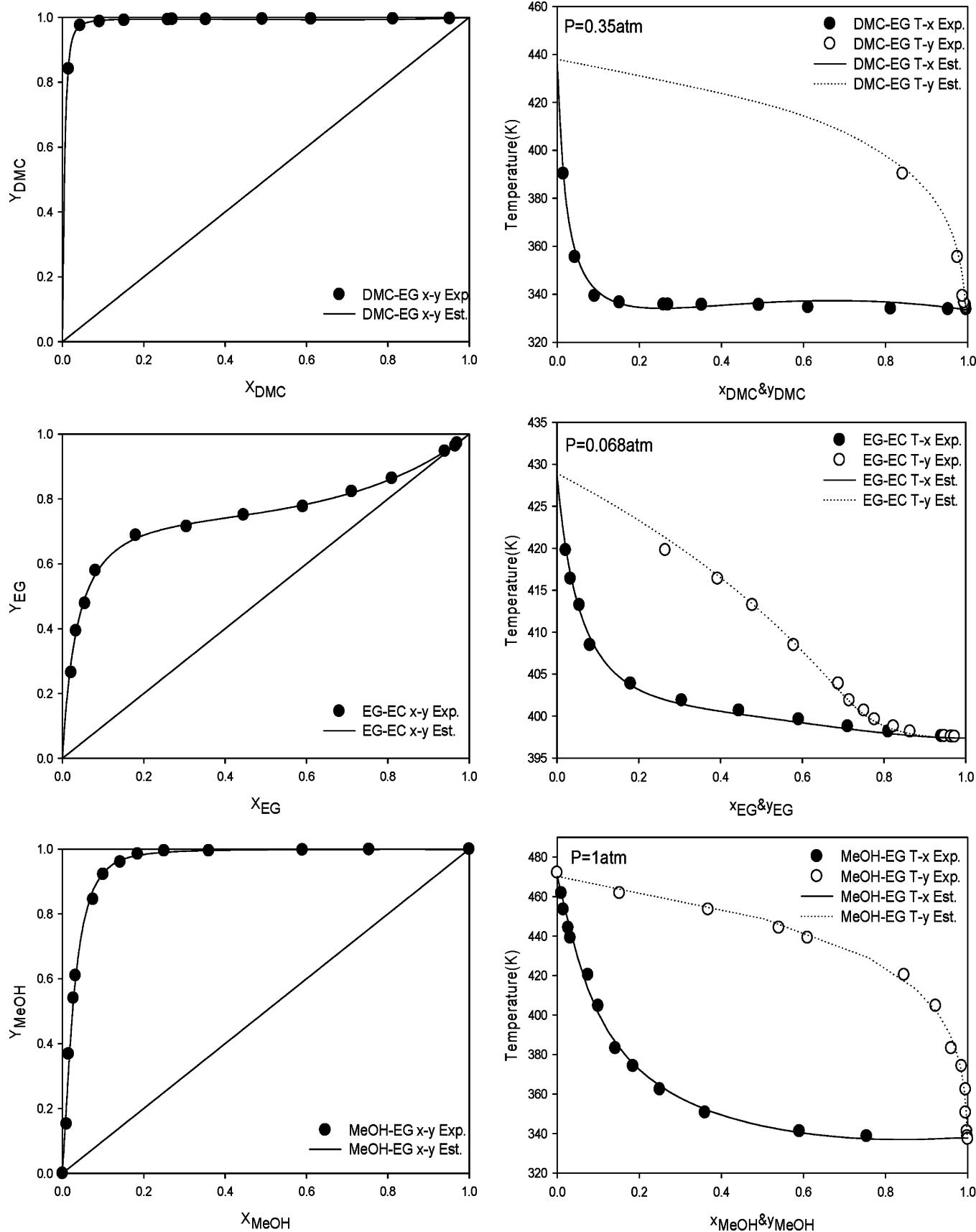


Figure 1a. Continued.

**Figure 1.** $y-x$ and $T-xy$ plots of the RD system.

column. The bottom product of the column is the mixture of DMC and the entrainer, and it is fed to another entrainer recovery column to separate these two components, so entrainer

can be recycled back to the extractive column. The conceptual design of the two-column system via extractive distillation is shown in Figure 4.

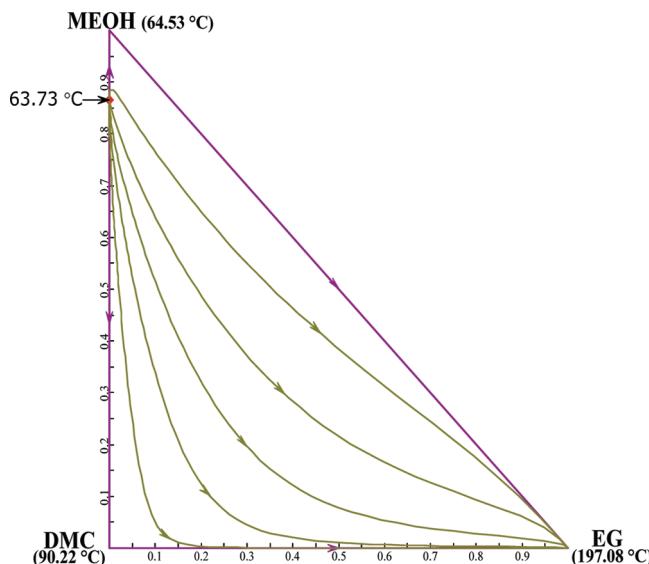


Figure 2. Residue curve map for the ternary system of DMC-EG-MeOH at 1 atm.

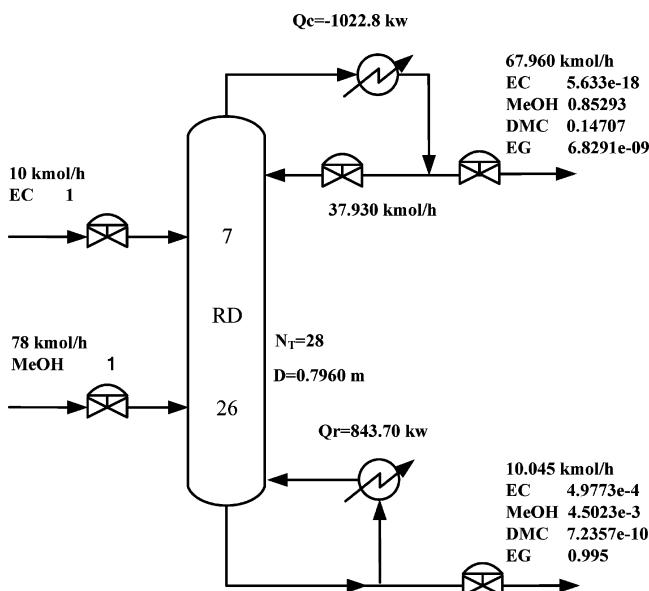


Figure 3. RD design flow sheet.

The entrainer selection is extremely important to make this design flow sheet more attractive. The concept is to find an entrainer that will enhance most of the relative volatility of the original two components but is also easy to separate from either of the two components. As mentioned in the Introduction, good screening procedures through computer-aided molecular design such as UNIFAC were suggested to find a set of feasible entrainers for a particular separation system.^{13,14} After some feasible entrainers have been found, in the following, we will use DMC-MeOH system as an example to illustrate further a simple procedure to quickly compare the performance of candidate entrainers by use of a commercial process simulator.

3.1. Comparison of Candidate Entrainers. In Wang et al.,⁸ phenol was used as the entrainer in the extractive distillation system. Figure 5 displays the isovolatility curve for the MeOH-DMC system at 1 atm with phenol as entrainer. Notice that the volatility between MeOH and DMC is unity in the binary system when it is at the azeotrope (shown on the ordinate in Figure 5 with a temperature of 63.73 °C). As phenol is added, the isovolatility curve moves toward the hypotenuse of the

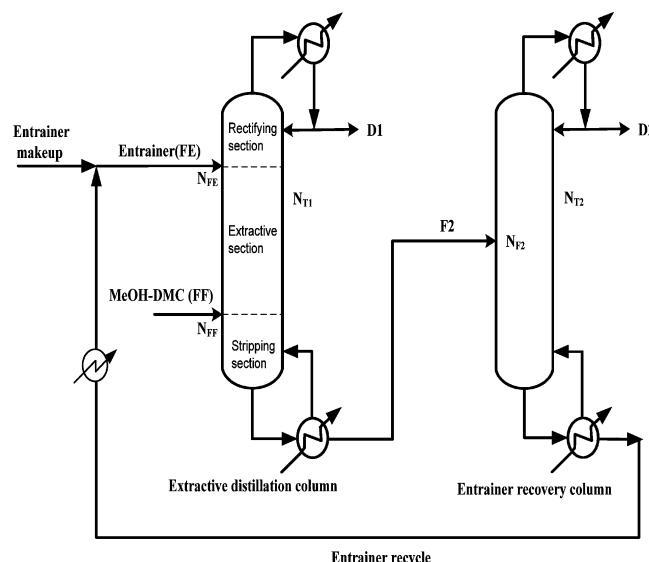


Figure 4. Conceptual design flow sheet of the extractive distillation system.

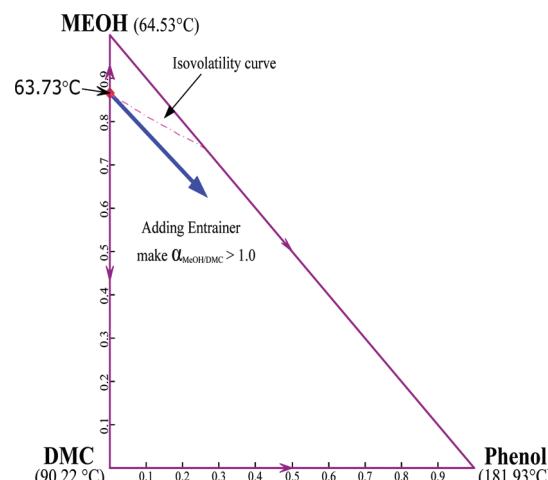


Figure 5. Isovolutility curve at 1 atm with phenol as entrainer.

triangle where the concentration of DMC goes to zero. This observation determines that the overhead product of the extractive distillation column should be MeOH and not DMC. The reasoning is that by adding phenol into the system, the relative volatility between MeOH and DMC will become greater than unity and result in MeOH going up the column. Note that the relative volatility between MeOH and DMC is greater than unity in the region below the isovolatility curve. This can be explained by a binary feed composition of MeOH and DMC mixture in this region. A simple distillation would result in azeotropic composition going to overhead and DMC going to the bottom; thus the relative volatility between MeOH and DMC is greater than unity in this region. On the contrary, a binary feed composition in the opposite region would result in azeotropic composition going to overhead and MeOH going to the bottom; thus the relative volatility in this region is less than unity.

It is worth mentioning that, in an extractive distillation system, the lighter of the original two components cannot automatically be assumed to be the distillate product of this column. A good example is the acetone-methanol separation with chlorobenzene as entrainer.^{14,15} For that extractive distillation system, the methanol is the distillate product although its normal boiling point is higher than that of acetone. The decision of the desirable

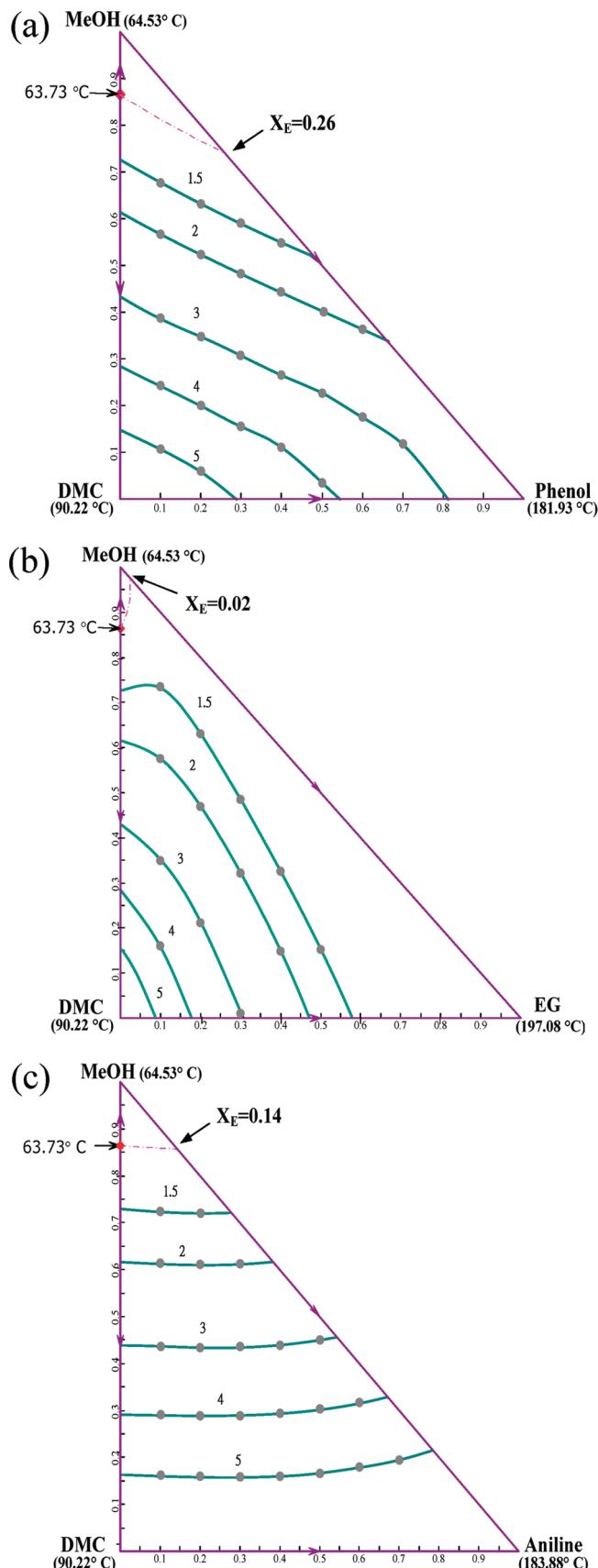


Figure 6. Iso- and equivolatility curves at 1 atm with (a) phenol, (b) EG, or (c) aniline as entrainer.

distillate product can easily be answered by drawing the isovolatility curve.

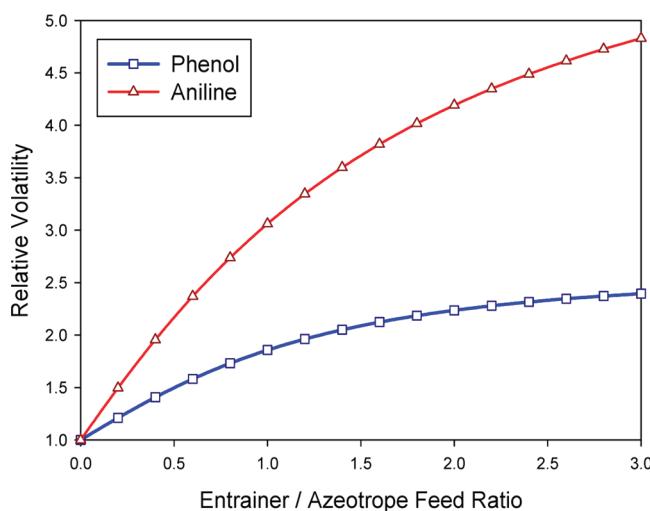


Figure 7. Relative volatility at various feed ratios.

Although phenol is a feasible entrainer for this extractive distillation system, the important question is whether this entrainer is effective enough in enhancing the relative volatility upon addition into the system. This question can be answered by plotting not only the isovolatility curve but also the equivolatility curves (curves with relative volatilities other than unity) of the ternary system.¹⁰

Figure 6 displays the iso- and equivolatility curves at 1 atm for three alternative entrainers. The other two entrainers are ethylene glycol and aniline. These two are picked in a list of commonly used solvent in Gmehling and Mollmann.¹³ From Figure 6, it is easily concluded that aniline is a more effective entrainer for this system that enhancing more of the relative volatility between MeOH and DMC.

Another comment for showing the result of using ethylene glycol as entrainer is elucidated below. Although true in many cases (e.g., comparing the results for phenol and aniline as entrainer), we should not solely rely on the location where the isovolatility curve intercepts the MeOH–entrainer edge of the triangle to determine which one is the more effective entrainer. Figure 6 shows that although the x_E for using EG as entrainer ($x_E = 0.02$) is much smaller than that for using aniline ($x_E = 0.14$), the enhancement of relative volatility between DMC and methanol is much poorer with EG as entrainer. Thus EG is not a good entrainer for this separation.

Another way to demonstrate the effectiveness of the entrainer is using a plot as in Figure 7. In this plot, the starting composition is right at the azeotrope of MeOH and DMC. By gradually adding entrainer into the system, we can calculate the enhancement of relative volatility at various feed ratios. This figure demonstrates again that aniline is a much more effective entrainer than phenol for this separation system.

Generating the above analysis plots is very easy by use of a commercial process simulator such as the one from Aspen Technologies, Inc. The isovolatility curve is readily available in Aspen Plus. The way to generate equivolatility curves in Aspen Plus is to use the Flash2 module in the unit operation library. With any arbitrary feed composition in the ternary diagram, under adiabatic flash operating at 1 atm and with negligible vapor flow, the vapor and liquid composition in equilibrium can be calculated by Aspen Plus. Information is excerpted about MeOH and DMC, and the relative volatility between these two components can be calculated for addition

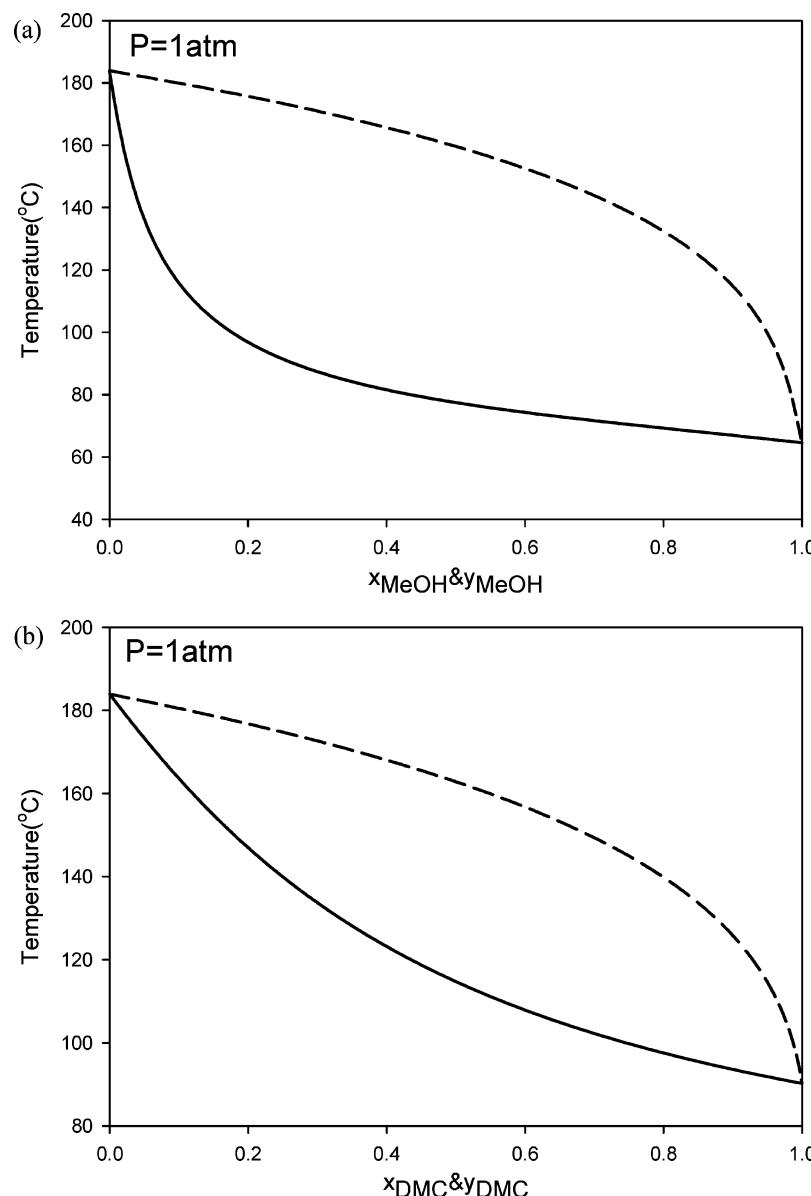


Figure 8. T - xy plots of (a) MeOH–aniline and (b) DMC–aniline.

Table 2. UNIQUAC Model Parameters of the MeOH/DMC System with either Aniline, Phenol, or Ethylene Glycol as Entrainer

$i = \text{aniline}, j = \text{MeOH}$	$i = \text{aniline}, j = \text{DMC}$	$i = \text{phenol}, j = \text{MeOH}$	$i = \text{phenol}, j = \text{DMC}$	$i = \text{EG}, j = \text{MeOH}$	$i = \text{EG}, j = \text{DMC}$
a_{ij}	0	0	0	0.767 07	2.2712
a_{ji}	0	0	0	-1.5058	0
$b_{ij}(K)$	-288.28	-32.733	-420.31	-273.39	-599.11
$b_{ji}(K)$	85.941	101.44	350.24	691.93	10 000
c_{ij}	0	0	0	0	0
c_{ji}	0	0	0	0	0

of any amount of the entrainer component. By collection of the feed compositions resulting in the same relative volatility, a curve can be drawn with equal relative volatility.

Other factors that affect the total annual cost of the design flow sheet are the y - x or T - xy plots for the MeOH–entrainer and DMC–entrainer pairs. For the MeOH–entrainer pair, these plots can be used to determine the ease of separation in the rectifying section of the extractive distillation column. For the DMC–entrainer pair, the plots can be used to determine whether the separation in the entrainer recovery column is easy or not.

Figure 8a shows T - xy plots of the MeOH–aniline pair. From this plot, it is concluded that there is no problem with the

separation of MeOH and aniline. Figure 8b shows the T - xy plot of the DMC–aniline pair. From this plot, it is also concluded that aniline is a good entrainer when we focus on the separation in the entrainer recovery column.

For completeness of information for generating the above plots, the UNIQUAC model parameters for calculating the vapor–liquid equilibrium are listed in Table 2.

From the above analysis, looking into iso- and equivolatility curves and binary VLE diagrams for the MeOH–entrainer and DMC–entrainer pairs, it is concluded that aniline is a better entrainer for this system. In the following, the optimal design flow sheet of this MeOH–DMC separation process with aniline

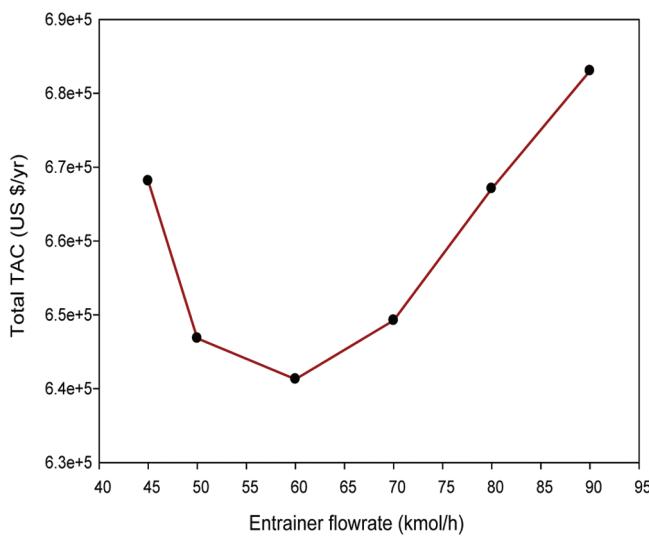


Figure 9. Summary total TAC plot at various entrainer feed rates.

as entrainer will be established to minimize the total annual cost of the overall process.

It is worth mentioning that, apart from the important factors above relating to the phase equilibrium behavior, other factors such as thermal stability, nontoxicity, low price, and other physical properties should also be considered in the entrainer selection.

3.2. Optimal Design Flow Sheet. The proposed design flow sheet with aniline as entrainer can be seen in Figure 4. The product specifications are set to be 99.99 mol % MeOH in the distillate of the extractive distillation column and 99.5 mol % DMC in the distillate of the entrainer recovery column. The feed condition is set to be the same as the distillate of the RD column. Reflux drums of both columns are operated at atmospheric pressure. Column pressure drops are automatically calculated in the Aspen simulation.

The design variables to be determined in the flow sheet include the entrainer feed flow rate with fixed feed rate of 67.96 kmol/h from RD distillate, total stages of the extractive distillation column (N_{T1}), entrainer and fresh feed tray locations (N_{FE} and N_{FF}), total stages of the entrainer recovery column

Table 3. Design Variables and TAC of Extractive Distillation Flow Sheet

extractive distillation column	
FE/FF feed ratio	0.883
total stages (N_1)	32
entrainer feed stage (N_{FE})	5
fresh feed stage (N_{FF})	27
reboiler cost	59 406
condenser cost	55 998
column cost	158 418
tray cost	14 901
steam cost	168 839
cooling water cost in condenser	2965
entrainer recovery column	
total stages (N_2)	18
feed stage (N_{F2})	6
reboiler cost	24 148
condenser cost	15 184
column cost	52 267
tray cost	3301
steam cost	43 752
cooling water cost in condenser	858
entrainer cost	17
cooler cost	39 630
cooling water cost in cooler	1608
total utility cost	218 039
annualized total capital cost	423 253
total TAC	641 292

(N_{T2}), and feed tray location of entrainer recovery column (N_{F2}). Following the suggestion in Knight and Doherty²² and also summarized in Chapter 5 of the book by Doherty and Malone,³ entrainer feed temperature is set to be about 10 °C less than the top temperature of the extractive distillation column, so a cooler is included in the conceptual design flow sheet.

There are many design variables to be determined, so to simplify the optimization procedure the more important and complex extractive distillation column is optimized first. There are three design variables to be determined (N_{T1} , N_{FE} , and N_{FF}) at each entrainer feed rate. The two design specifications for all the Aspen simulations are setting the top composition at 99.99 mol % MeOH and the ratio of MeOH to the sum of DMC and MeOH in the bottom stream to be 0.004. The reason for this bottom specification is to set the MeOH loss through the column bottom. The above two design specifications can be met by

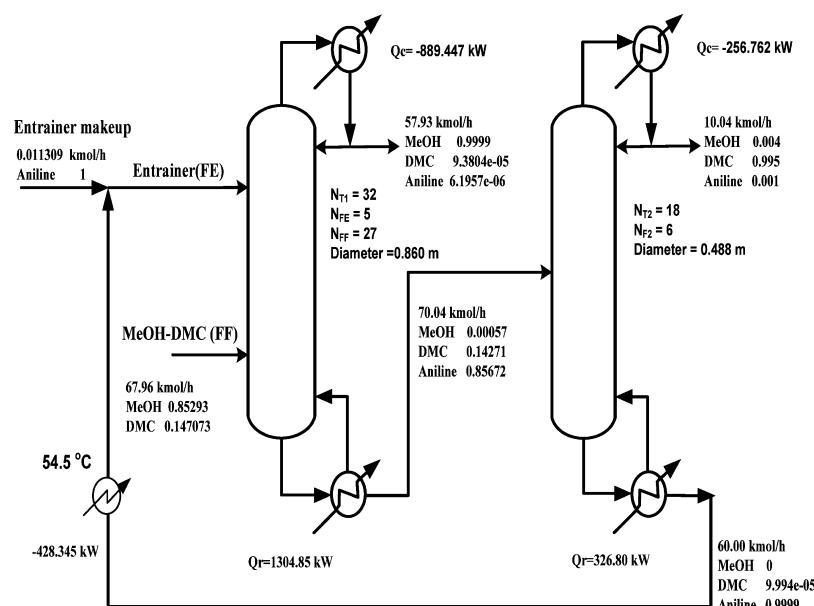


Figure 10. Design flow sheet of the extractive distillation system.

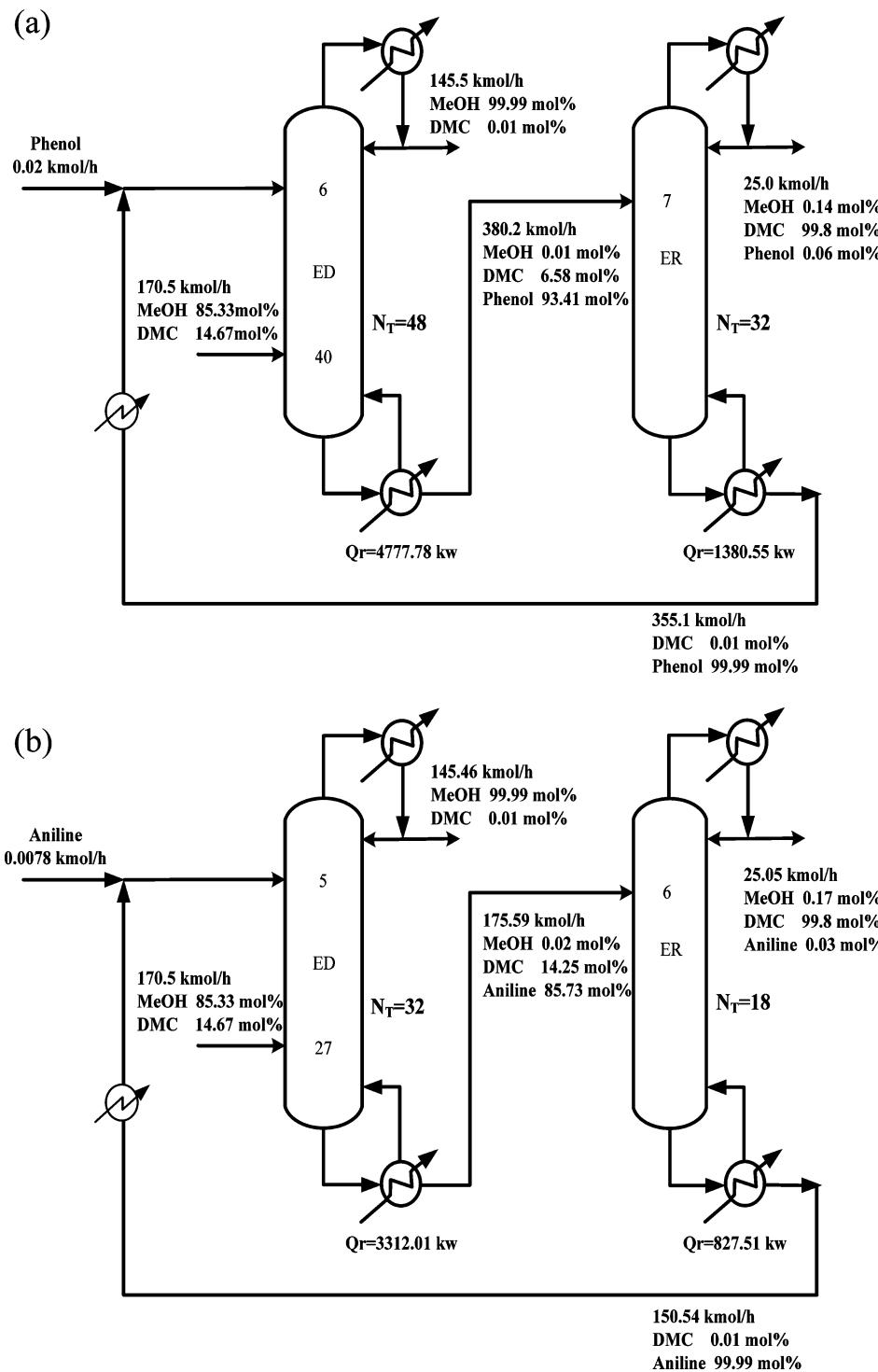


Figure 11. Comparison to Wang et al.⁸ design flow sheet: (a) Wang et al.⁸ flow sheet; (b) flow sheet with aniline as entrainer.

varying the two degrees of freedom in this column (e.g., reboiler duty and reflux flow rate).

Total annual cost (TAC1) of this column is used as the objective function to be minimized, which including annualized capital costs and operating costs. A sequential iterative optimization search procedure is used to find the optimal design with the entrainer feed rate as the outer iterative loop, $N_{\text{T}1}$ as the middle loop, and N_{FE} and N_{FF} as the inner iterative loop. The procedure is to fix entrainer feed rate and $N_{\text{T}1}$ first and then to find the right N_{FE} and N_{FF} to minimize TAC1 at this particular combination of entrainer feed rate and $N_{\text{T}1}$. The procedure is repeated for the other combinations of entrainer feed rate and

$N_{\text{T}1}$. After the optimum solution of $N_{\text{T}1}$, N_{FE} , and N_{FF} at each entrainer feed rate is obtained, the total TAC of this two-column system can be calculated with the entrainer recovery column and the recycle stream included. Additional costs in the total TAC include annualized capital cost for the entrainer recovery column, costs associated with the cooler for the entrainer recycle, operating costs of the steam and cooling water to operate the entrainer recovery column, and entrainer makeup cost.

Figure 9 shows a summary plot of the total TAC of this two-column system at various entrainer feed rates. Any point in this summary plot is a collective result of many simulations in the inner iterative loops to determine the total stages and feed

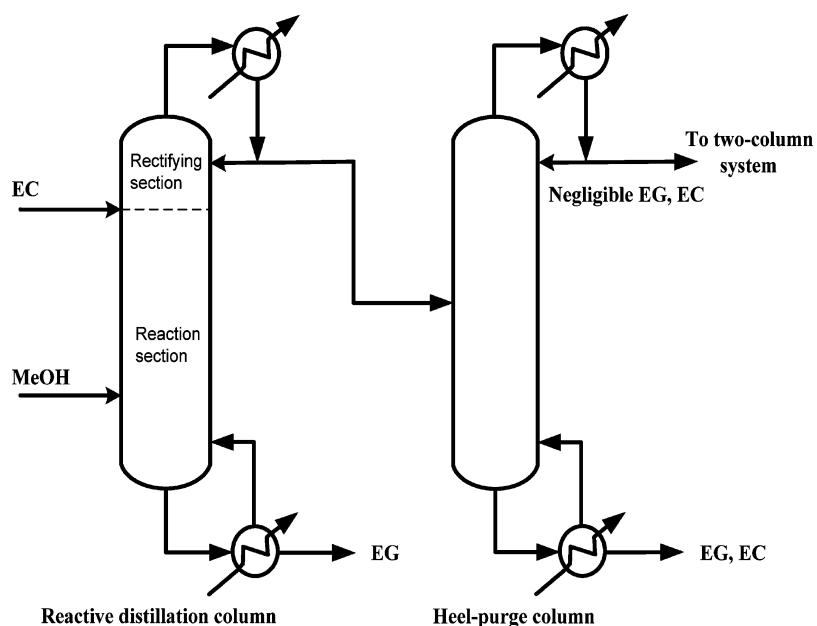


Figure 12. Addition of a heel-purge column in the overall process.

locations of the two-column system. It is observed that the best entrainer feed rate is 60 kmol/h. Table 3 shows the optimal design variables and also the minimized TAC results of this two-column system. The final design flow sheet of this two-column system is shown in Figure 10. It is noticed that the total stages of the extractive distillation column and also the entrainer recovery column are moderate. The ratio between the entrainer feed and MeOH–DMC feed is only 0.883.

3.3. Comparison to Wang et al.⁸ Design. In this section, simulation results with aniline and phenol as entrainer will be compared. The simple analysis in section 3.1 demonstrated that aniline should be a much more effective entrainer for this separation system. We will further strengthen this conclusion with process simulation.

The feed condition as in Wang et al.⁸ is adapted in this comparison, and also all the product purities are set as the same. We will just use the optimization results obtained in the previous section for this separation task with aniline as entrainer; thus feed ratio is set at 0.883, $N_{T1} = 32$, $N_{FE} = 5$, $N_{FF} = 27$, $N_{T2} = 18$, and $N_{F2} = 6$. Figure 11 shows two design flow sheets with either phenol or aniline as entrainer. The simulation result for the case with phenol as entrainer is excerpted from Wang et al.⁸ It is observed that the sum of reboiler duties for our system is reduced by as much as 32.8%. The required feed ratio of the Wang et al.⁸ system is much higher (1.965 vs 0.883 in our system). The extractive distillation column in Wang et al.⁸ is much taller ($N_{T1} = 48$ vs 32 as in our system), as is the entrainer recovery column ($N_{T2} = 32$ vs 18 as in our system). Wang et al.⁸ did not give information on column diameters. However, judging from the much higher reboiler duty, the column diameter should be much larger too. Comparison of TACs for Figure 11 cannot be made because we do not have detailed design information on the Wang et al.⁸ system. However, from the above comparison of column heights and reboiler duties, their capital and utility costs should be much higher.

3.4. Problem with Heavy-Boiler Impurities in the Feed Stream. In Figure 4 of the paper by Wang et al.,⁸ it is noticed that the bottom composition contains small impurities of EC (2.5×10^{-3} mol %) and EG (2.8×10^{-3} mol %). These small impurities are carried into this extractive distillation system via the feed stream (distillate of the RD column). The normal boiling points of these

two components are very high, EC at 248.56 °C and EG at 197.08 °C. Because this bottom stream is recycled back to the extractive distillation column, these two heavy-boiler impurities would not escape from the two distillate streams and therefore will be accumulated in the system. Since this is a very practical situation in an industrial setting, it is worth discussing here.

One way to avoid heavy-boiler impurities in the feed stream of the extractive distillation system is to add a heel-purge column between the RD column and the extractive distillation system. The conceptual design flow sheet can be seen in Figure 12. Conventional wisdom told us that this will not be the economical solution for this problem because a large reboiled ratio resulting in extra reboiler duty is required to vaporize most of the materials to overhead in this new heel-purge column, not to mention additional column equipment and instrumentation will be needed for this design flow sheet.

Another easier solution to solve this problem is to increase the rectifying section of the RD column as in Figure 3 of this paper. Figure 13 shows two design flow sheets of the RD column with varying rectifying sections. Figure 13a shows the design flow sheet of the RD column with minimized TAC. However, because there are only two stages of the rectifying section, small impurities of EC and EG (especially EG) are present in the distillate stream. Upon simple addition of several stages in the rectifying section, as can be seen in Figure 13b, EC and EG become negligible in the distillate stream. Notice the design specifications (purity of EG at bottom set at 0.995 and conversion set at 99.95%) are all met for these two design flow sheets. The TAC of this feasible flow sheet (Figure 13b) is only slightly increased from that of the optimized flow sheet.

4. Control Strategy for the Overall Process

The overall design flow sheet of this process is displayed in Figure 14. There are two recycle streams in the overall process. One is to recycle the excess reactant, methanol, back to the reactive distillation column. The other one is to recycle the entrainer to the extractive distillation column. In this section, the overall control strategy of this complete process will be studied. The purpose is to maintain the purity of the dimethyl carbonate product as well as the coproduct, ethylene glycol. In

the control strategy development, we restrict ourselves to use only tray temperature control loop(s) in each of the three columns to indirectly hold the product purity for wider industrial application purposes.

Pressure-driven simulation in Aspen Dynamics is used in the control strategy development. Ten minutes holdup time with 50% liquid level is used to calculate the volume of each column base and reflux drum of each column. Top pressures of the three columns are all set at atmospheric pressure. The tray rating tool in Aspen Plus is used to automatically calculate the pressure drop along all columns.

The inventory and some simple regulatory control loops are determined first as below:

1. EC feed is flow-controlled. (used as a throughput manipulator).

2. Total MeOH feed is flow-controlled by manipulating a control valve at fresh feed stream. The total MeOH feed set point is changed to maintain MeOH/EC feed ratio into the RD column. This feed ratio can be reset by a tray temperature control loop.

3. RD column base level is controlled by manipulating the bottom flow (EG product flow).

4. RD column reflux drum level is controlled by manipulating the distillate flow.

5. RD column top pressure is controlled by manipulating the condenser duty.

6. RD column reflux is a ratio to EC feed flow.

7. RD column reboiler duty is a ratio to EC feed flow.

8. Base level of the extractive distillation column is controlled by manipulating the bottom flow.

9. Reflux drum level of the extractive distillation column is controlled by manipulating the distillate flow (MeOH recycle flow).

10. Top pressure of the extractive distillation column is controlled by manipulating the condenser duty.

11. Reflux flow of the extractive distillation column is ratio to distillate of RD column.

12. Base level of the entrainer recovery column is controlled by manipulating the aniline makeup flow.

13. The entrainer feed flow to the extractive distillation column is flow-controlled and ratio to distillate of RD column.

14. Reflux drum level of the entrainer recovery column is controlled by manipulating the distillate flow (DMC product flow).

15. Reflux flow of the entrainer recovery column is a ratio to distillate of the RD column.

16. Top pressure of the entrainer recovery column is controlled by manipulating the condenser duty.

17. Entrainer feed temperature is controlled by manipulating cooler duty.

An important inventory control loop in the extractive distillation system is the bottom level of the entrainer recovery column (item 12). The control of this level was suggested by Grassi²³ and Luyben²⁴ to be held by the entrainer makeup flow. However, because this flow is very small, thus bottom level essentially floats indicating whether the entrainer inventory in the system is balanced or not. With this control pairing, the entrainer feed flow to the extractive distillation column is flow-controlled and ratio to distillate of RD column. Another control strategy (items 11 and 15) was adapted from Arifin and Chien,²⁵ where they found that control strategy with fixing R/F ratio is better in rejecting the disturbances than fixing the reflux ratio.

As for the product quality control loops, the simplest control strategy is proposed to use only one tray temperature in each

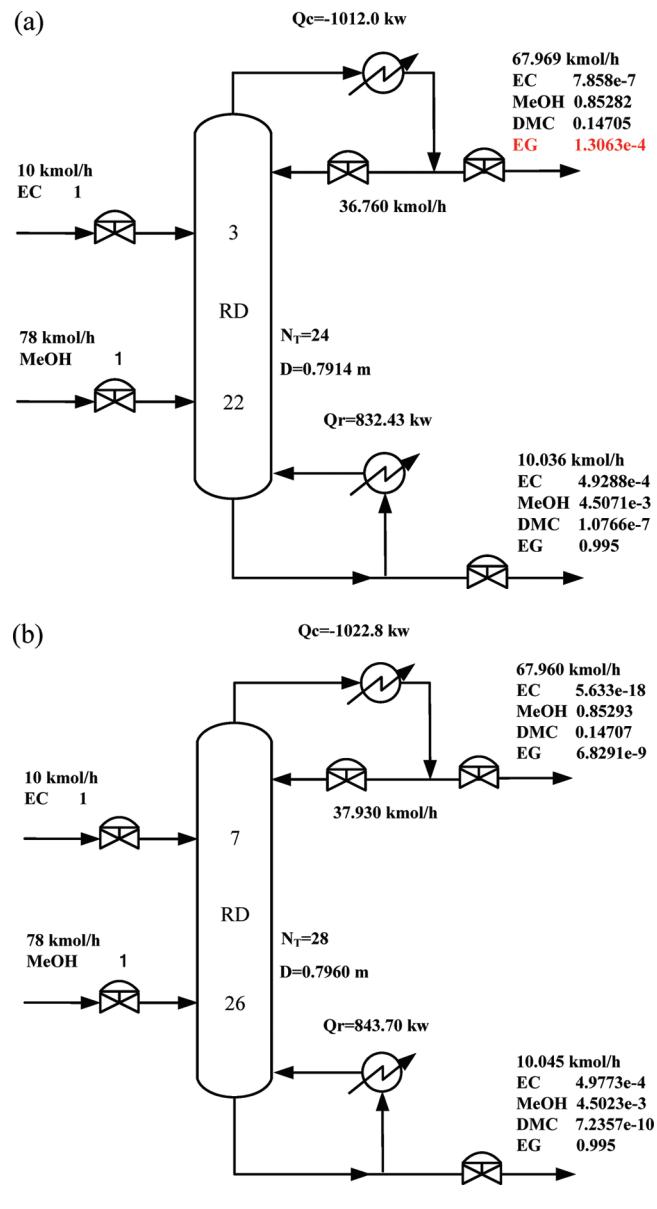


Figure 13. Effect of increasing rectifying section: (a) smaller rectifying section; (b) larger rectifying section.

column to infer the compositions. The manipulated variable selected for the RD temperature loop is the MeOH/EC feed ratio; the ones for the extractive distillation and entrainer recovery columns are their reboiler duties. The open-loop sensitivity analysis was performed to find the temperature control point(s) that is(are) most sensitive to the manipulated variable changes while still exhibiting near-linear behavior. The resulting temperature control points are at 27th, 30th, and fourth stage for the RD, extractive distillation, and entrainer recovery columns, respectively.

Figure 15 displays the overall control strategy of this complete process. In the closed-loop simulation runs, P-only controller is used in all level loops. The reason for using P-only controller is to provide maximum flow smoothing and also because maintaining a liquid level at set point value is often not necessary. $K_c = 2$ as suggested in Luyben²⁶ is used in most of the level loops. For the two bottom level loops in the extractive distillation system, $K_c = 10$ is used so that faster dynamics of the internal flow of the overall process can be achieved and also for faster increase or decrease of entrainer makeup into the system. For the top pressure control loops of the columns,

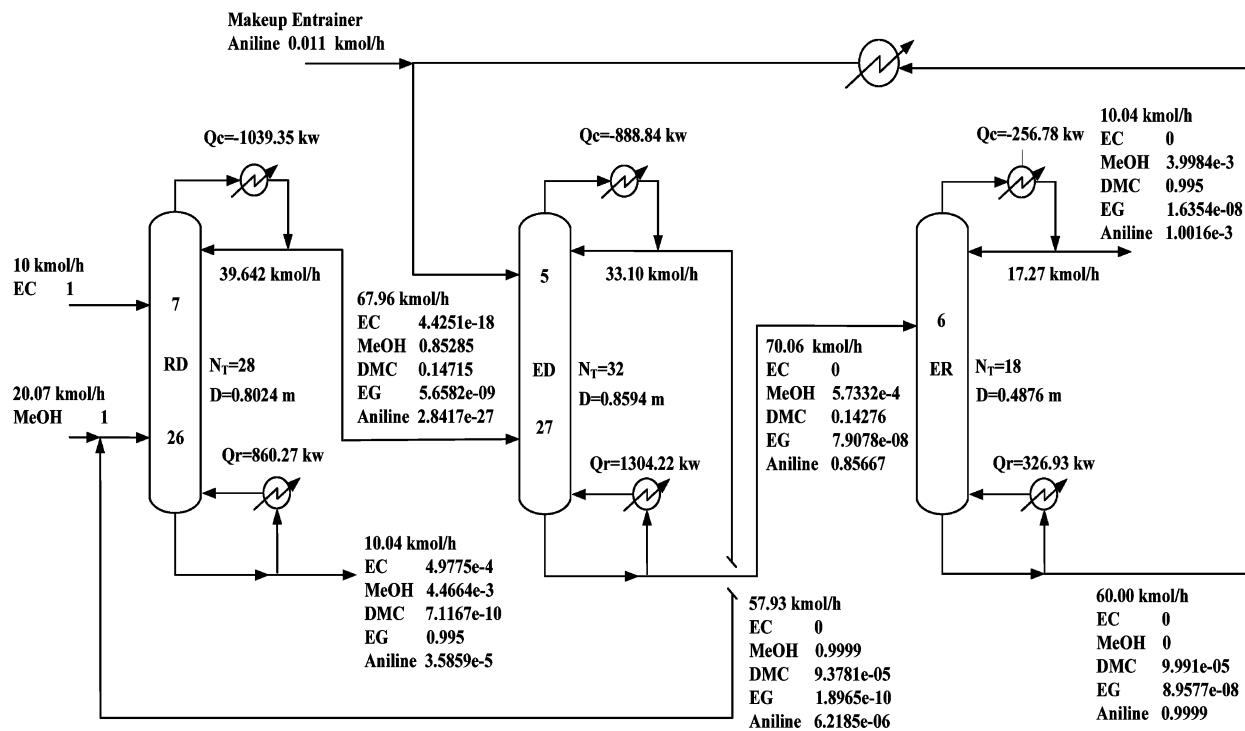


Figure 14. Design flow sheet of the complete process.

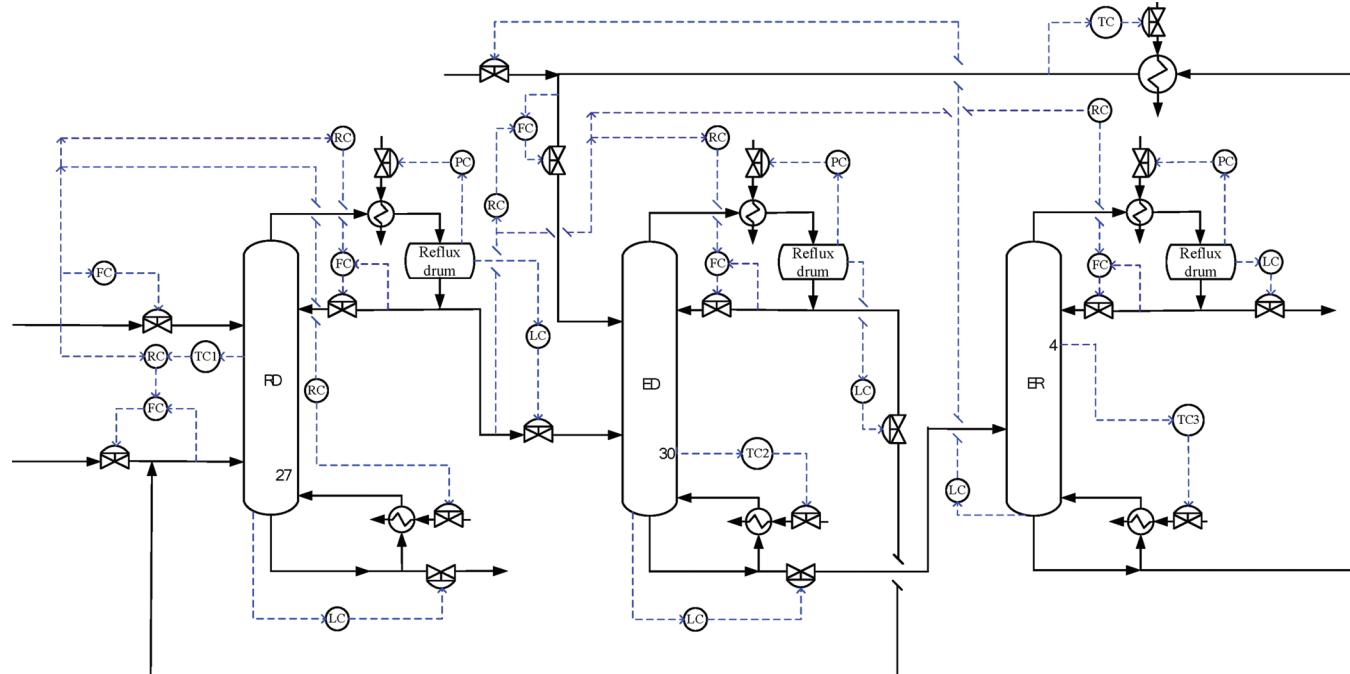


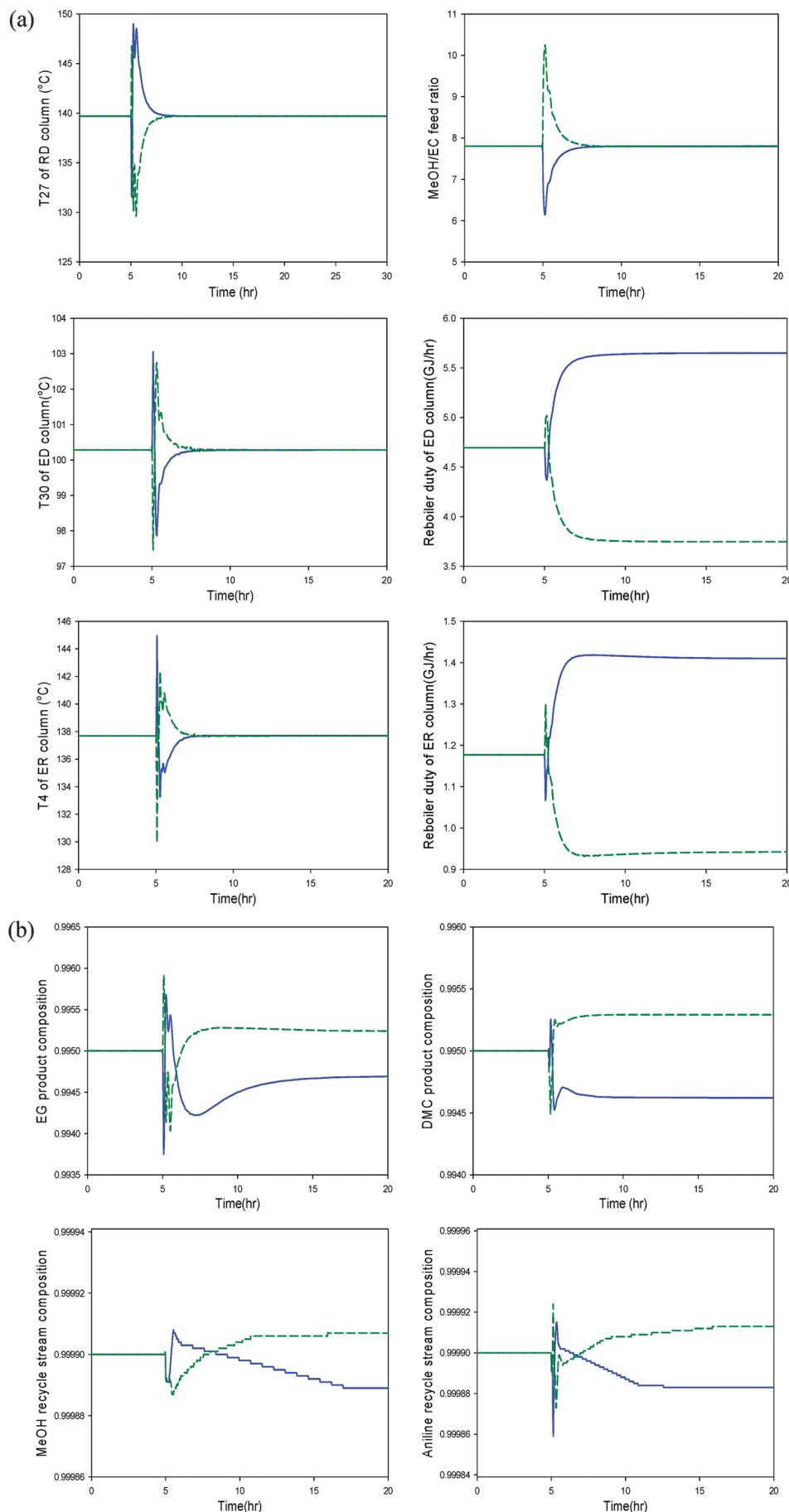
Figure 15. Overall control strategy.

tight PI controller tuning parameters of $K_c = 20$ and $\tau_I = 12$ min are used.

In each temperature loop, an additional 1-min dead time is included for modeling the other neglected dynamics in the system. The tuning constants are determined via relay feedback test provided in Aspen Dynamics with Tyreus and Luyben tuning rules.²⁷ The iterative tuning procedure was to tune the temperature loop in the reactive distillation column first, then the extractive distillation column, and then the entrainer recovery column. The procedure is repeated until the tuning parameters from relay feedback test converged. The resulting PI tuning constants for the tray 27 temperature loop of the reactive

distillation column are $K_c = 0.71$ and $\tau_I = 10.5$ min; the tuning constants for the tray 30 temperature loop of the extractive distillation column are $K_c = 1.2$ and $\tau_I = 3.0$ min; and the tuning constants for the tray 4 temperature loop of the entrainer recovery column are $K_c = 1.3$ and $\tau_I = 5.5$ min.

Two feed disturbances are introduced into the system to test the control strategy. The first one is the $\pm 20\%$ throughput changes. This can be done by changing the set point of the EC feed flow control loop. Figure 16 shows the closed-loop results with the proposed control strategy. From Figure 16a, it is noticed that all three controlled temperatures are returned back to their set point values with smooth manipulated variable changes.

**Figure 16.** Closed-loop results with $\pm 20\%$ throughput changes (solid line, +20%; dashed line, -20%).

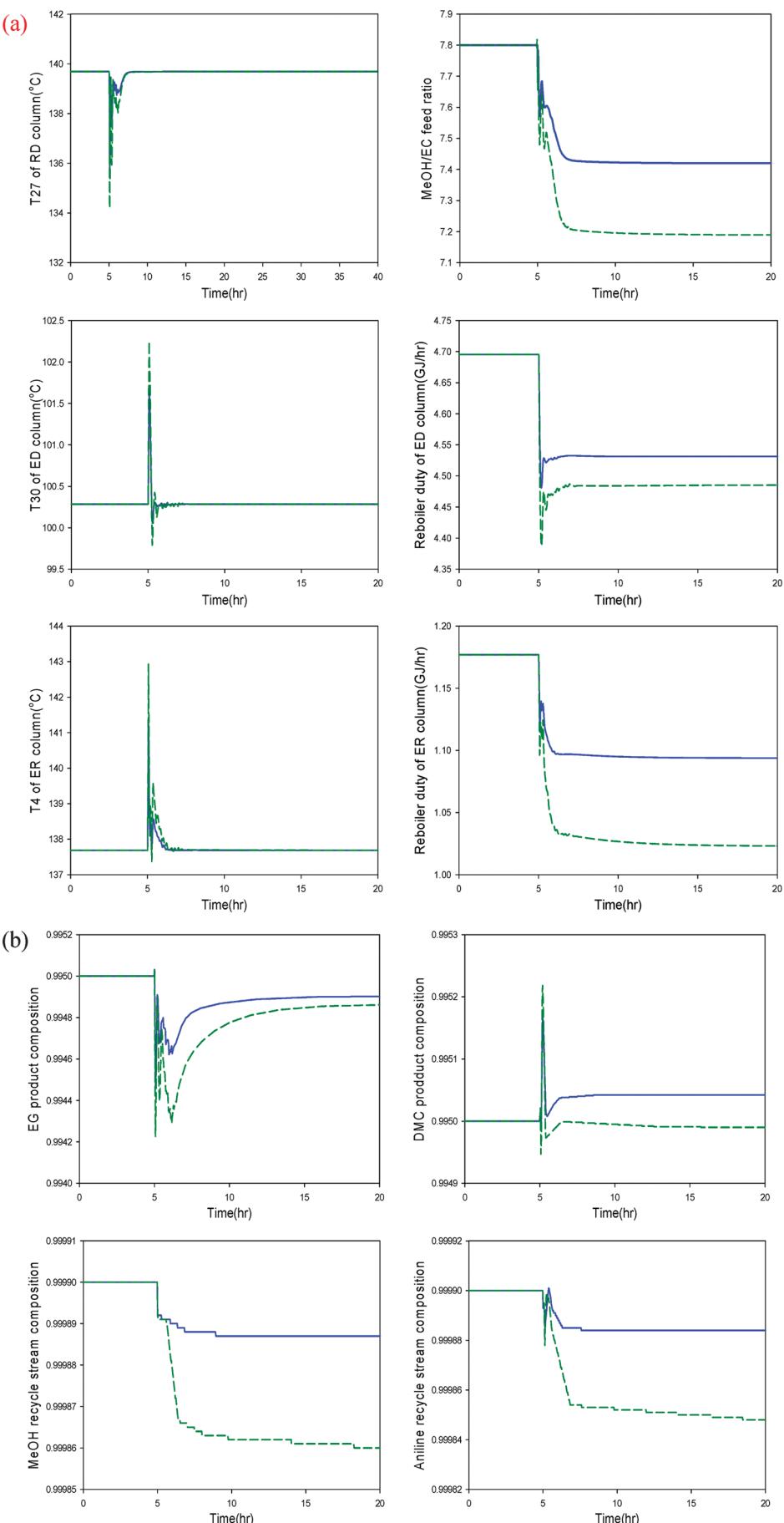


Figure 17. Closed-loop results with EC feed composition changes (solid line, EC feed contains 10% EG; dashed line, EC feed contains 20% EG).

From Figure 16b, the compositions of two products (DMC and EG) as well as the compositions of the two recycle streams (MeOH and aniline) all display only small deviations from their specifications. Notice that because the throughput changes are a known disturbance, it is possible to adjust the temperature set points to make the compositions closer to their specifications.

The second feed disturbance is feed composition changes: it is assumed that the EC feed is not pure but contains 10% or 20% EG in this feed stream. The proposed control strategy should adjust the MeOH/EC feed ratio to accommodate these changes. Figure 17 displays the closed-loop results. It is observed that the MeOH/EC feed ratio is reduced, as was desired. The product compositions show only small deviations from their base case values.

5. Conclusion

In this paper, design and control of the overall process for production of dimethyl carbonate is studied. The focus is particularly on the separation of DMC–MeOH azeotrope via extractive distillation. Since the ability of the entrainer to enhance relative volatility is crucial to the success of the separation task, a very simple procedure is proposed in this paper to quickly compare alternative entrainer candidates before rigorous process simulation is conducted. An isovolatility curve is used to determine the desirable distillate product of the extractive distillation column. Equivolatility curves together with the relative volatility plot, as in Figure 7, can be used to compare the ability of alternative entrainers to enhance the relative volatility of the original two components. The T – xy plots of the entrainer versus one of the original two components should also be examined to confirm ease of separation in the rectifying section of the extractive distillation column and in the entrainer recovery column.

For the system of separating methanol and DMC, aniline was found to be a much more effective entrainer than the one used in open literature. This paper also pointed out a practical problem that may occur in industry when the feed stream of an extractive distillation system contains heavy-boiler impurities. If these impurities are not eliminated from the feed stream, accumulation will occur in the extractive distillation system, causing operational problems. A practical solution for this problem is to increase the rectifying section of the RD column to suppress these heavy-boiler impurities from going up the RD column and showing up in the feed stream of the extractive distillation system.

The design and control of the overall process have also been developed. The overall process contains two recycle streams, one to recycle excess methanol reactant and the other to recycle entrainer. A simple overall control strategy of this process is also proposed to maintain product purity despite various feed disturbances. Only one tray temperature control loop is required for each of the three columns.

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