# EFFECT OF VAPOR-LIQUID EQUILIBRIUM DATA ON THE DESIGN OF SEPARATION SEQUENCES BY DISTILLATION

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*Abstract— An evaluation of the effect of vapor-liquid equilibrium experimental data on the design of separation sequences by distillation was done using computer simulation. Separation of a mixture of acetone-chloroform-benzene was chosen as an example problem. Two sequences were compared. To quantify the thermodynamic data uncertainties for each sequence two sets of binary vapor-liquid equilibrium data were chosen. These two sets of data were used to generate simulation cases as in classical two-level factorial design of experiments. A third set of binary vapor-liquid experimental data allows comparing phase liquid models. For the two-column sequence, analysis done to each column alone or to the whole sequence gave the same results. In the three-column sequence, results were different and simulation of the whole sequence gave a complete different account that simulation of each column alone.*

*Keywords— Azeotropic distillation, sensitivity analysis, phase equilibrium, azeotrope.*

## I. INTRODUCTION

The design of chemical processes involves computer simulations. The results of these simulations are strongly dependent on the thermodynamic models for the phase equilibrium. While proper choice of the thermodynamic model is important, the uncertainties in experimental data that are used to regress the model parameters are also significant. Techniques for assessing these effects are required for improving thermodynamic modeling, designing experiments and selecting data. The effect of property inaccuracies on process design is therefore of great importance in the chemical industry. Studies of this problem have been reported earlier (Streich and Kistenmacher, 1979; Nelson *et al.*, 1983; Hernandez *et al.*, 1984). More recent studies have analyzed the effect of model (Mandagarán *et al.*, 1999) and of thermodynamic data (Whiting *et al.*, 1999) on calculated process performance. On the other hand new design methods have been introduced that allows screening of distillation sequences (Thong and Jobson, 2001; Brüggemann and Marquardt, 2004; Liu *et al.*, 2005).

The purpose of the present work is to study the effect of the uncertainties of the vapor-liquid equilibrium data on the design of the separation process of a mixture of acetone, chloroform, and benzene. Through a series of case studies we present how thermodynamic models and uncertainties of the thermodynamic data impact the design of the process. The case studies belong to two distillation sequences to obtain benzene, acetone, and chloroform under certain specifications from a ternary mixture of all three components.

## II. PROCESSES STUDIED AND CALCULATION DESCRIPTION

We consider the problem of separation of a mixture of acetone, chloroform, and benzene as it was posed in the literature (Westerberg and Wahnschafft, 1996). A 100 kmol/h feed of 36 % of acetone (1), 24 % of chloroform (2), and 40 % of benzene (3) is to be separated into three products with the following specification: one stream with a acetone molar concentration better than 99.9%, one stream with a benzene molar concentration better than 99.9 % and one stream rich in chloroform (> 99 %) with no more than 0.0001 % of benzene.

To accomplish the proposed separation we have used the two alternatives of Fig. 1 and Fig. 2 and specifications set in Table 1. In the alternative of Fig. 1 benzene is mixed with the feed and introduced to column 1, yielding a pure acetone top product and a bottom of almost all the benzene and chloroform in its feed plus a trace of acetone. This bottom product is fed to column 2, where it is separated into benzene and chloroform. Part of the benzene is then recycled to mix with the original feed. In the alternative of Fig. 2, we start with the direct split, where we take pure acetone off as a product from the first column. The first column produces nearly pure acetone from the top and a mixture of all three species in the bottom. This mixture is near to the distillation boundary. We feed the bottom product to a second column, which separates benzene (bottom product) from the acetone and chloroform (top product). This top product from the second column is separated in a third column into pure chloroform (top product) and a mixture of acetone and chloroform very near to the azeotrope (bottom product). Finally, the azeotropic mixture is recycled to feed column 1.

Simulations of the processes were performed with the program HYSYS (Hyprotech software) version 2.4.1. Distillation columns have a partial reboiler and a total condenser. Pressure at the top and bottom of the columns was 1 atm. Table 1 presents specification and design parameters for each column in the two sequences under analysis. Our aim was to compare the results of separation in each case study obtained on the basis of different data for the phase equilibrium. For representing

the liquid-vapor equilibrium, we assumed ideal gas behavior for the gas phase and we modeled the liquid phase with the Wilson equation (Prausnitz *et al.*, 1999). Also, results using UNIQUAC and NRTL equations (Prausnitz *et al.*, 1999) for the liquid phase are included in the study. As we did the calculation with HYSYS all the auxiliary data used in the simulation are from its database. To quantify vapor-liquid equilibrium data uncertainties we used a factorial design of experiment (Gunter, 1993) type of approach. We used three different sets (called levels) of binary vapor liquid equilib

Table 1. Summary of column design parameters and specifications.

| PARAMETER | Two - column | | Three - column | | |
|---|---|---|---|---|---|
| | Col. 1 | Col. 2 | Col. 1 | Col. 2 | Col. 3 |
| Number of stages | 68 | 60 | 40 | 54 | 36 |
| Feed stage (from top) | 26 | 30 | 18 | 27 | 21 |
| Acetone recovery | 99.5 % | - | - | - | - |
| Distillate rate (kmol/h) | - | - | 35.7 | - | 24.0 |
| Distillate acetone molar fraction | 0.999 | - | 0.999 | - | - |
| Distillate chloroform molar fraction | - | 0.990 | - | - | 0.990 |
| Bottom rate (kmol/h) | - | - | - | 40.0 | - |
| Bottom benzene molar fraction | - | 0.999 | - | 0.999 | - |

Table 2. Wilson binary parameters [a] for the system acetone (1) – chloroform (2) – benzene (3)

| i | j | $a_{ij}$ (cal/mol) | $a_{ij}$ (cal/mol) | Reference |
|---|---|---|---|---|
| | | Level 0 | | |
| 1 | 2 | 116.1171 | -506.8518 | Gmehling and Onken, 1979 a |
| 1 | 3 | 682.4061 | -243.9651 | Gmehling and Onken, 1979 b |
| 2 | 3 | -71.81089 | -11.821 | Gmehling and Onken, 1997 |
| | | Level + | | |
| 1 | 2 | -107.2916 | -394.53953 | Fredenslund *et al.*, 1977 |
| 1 | 3 | 120.68724 | 203.32064 | Fredenslund *et al.*, 1977 |
| 2 | 3 | -217.86487 | 34.59343 | Fredenslund *et al.*, 1977 |
| | | Level – | | |
| 1 | 2 | 37.087174 | -453.83994 | Kojima et al., 1991 |
| 1 | 3 | 468.67944 | -155.58156 | Kojima et al., 1991 |
| 2 | 3 | -296.68263 | 225.73953 | Kojima et al., 1991 |

a)  $ln\ \gamma_i = 1 - ln\ \sum_i x_j A_{ij} - \sum_k ( x_k A_{ki} / \sum_j x_j A_{kj} )$ ; $A_{ij} = ( v_j / v_i ) \exp (-a_{ij} / RT )$; i,j,k = 1,..., n

Table 3. Comparison of data and Mc Cabe-Thiele results at P = 1 atm.

| FACTOR | DESCRIPTION | EFFECT [a] | | | | |
|---|---|---|---|---|---|---|
| | | 1 [b] | 2 | 3 | 4 | 5 |
| A | Acetone – chloroform binary | -46.91 | -37.40 | -0.82 | 17.87 | 34.39 |
| B | Chloroform – benzene binary | -11.72 | -20.35 | -15.01 | -8.95 | -1.75 |
| C | Acetone – benzene binary | -12.14 | -10.07 | -14.09 | -16.7 | -21.50 |

a)  % variation in reflux ratio of column i ($R_i$); [($R_i$ (level – ) – $R_i$ (level + )) / $R_i$ (level +)] * 100
b)  Molar fraction of more volatile component: 1) x = 0.2,  2) x = 0.35, 3) x = 0.5, 4) x = 0.65, 5) x = 0.8.
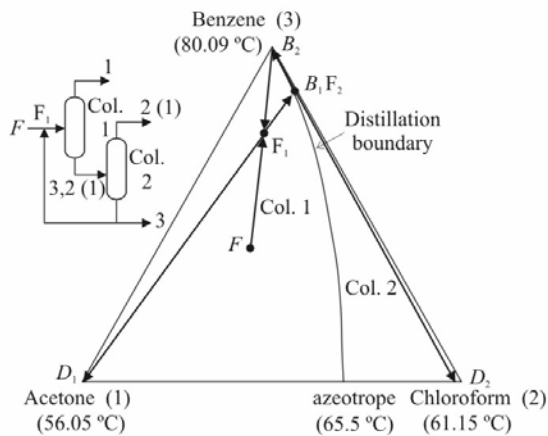


Figure 1. Two – column flowsheet for the acetone (1) – chloroform (2) – benzene (3) separation
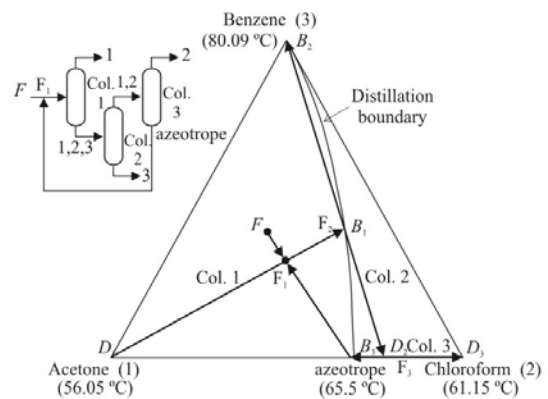


Figure 2. Three – column flowsheet for the acetone (1) – chloroform (2) – benzene (3) separation.

rium data to make the analysis. The experimental data references for the binary vapor-liquid equilibrium are presented in Table 2 that also shows the values of Wilson binary parameters. Three levels of data were used: "0" level to compare phase liquid models, and "+" and "−" levels in the factorial approach. Figure 3 shows the setting in three factor two level design involving 9 simulations.

Figures 4, 5 and 6 display the difference between the level + and − of the experimental data. The level + is obtained when UNIFAC (Fredenslund *et al.*, 1977) is used to get the Wilson parameters. UNIFAC represents an "average" set of experimental data, as UNIFAC is a
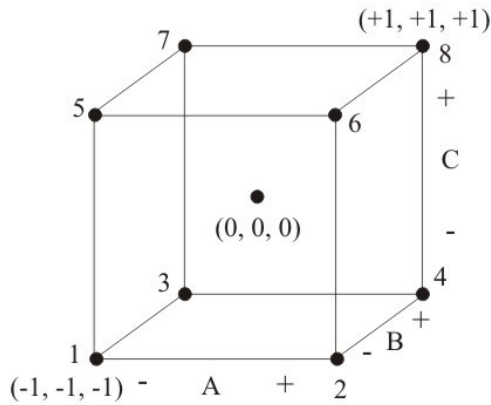


Figure 3. Points describing the settings in three factor design. Points at the center and corners of the cube are the cases of Table 4.
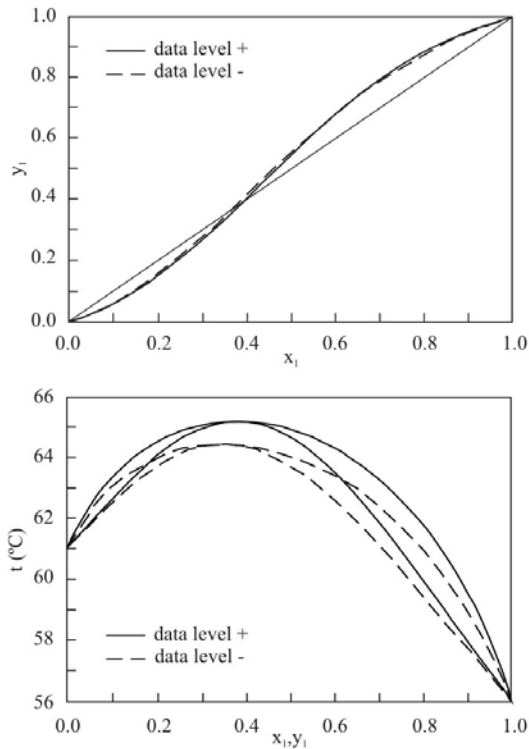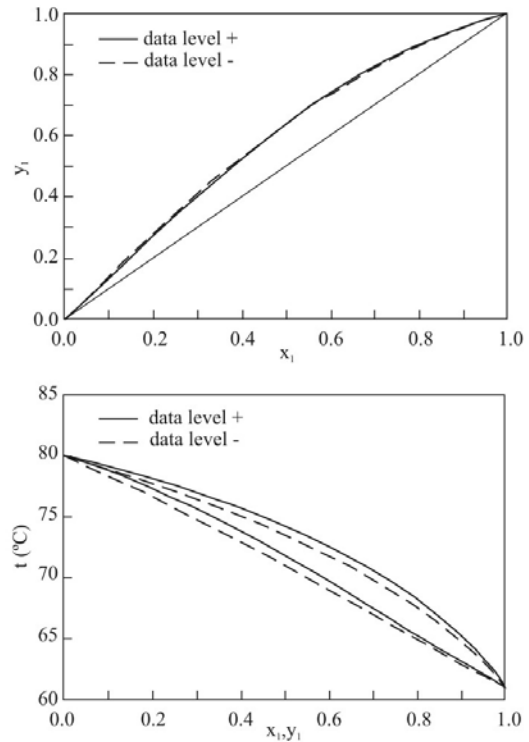


Figure 5. Comparison of x–y and t–x diagrams of isobaric data level + and level − for the system chloroform (1) – benzene (2). Binary parameters values in Table 2.



Figure 4. Comparison of x–y and t–x diagrams of isobaric data level + and level − for the system acetone (1) –chloroform (2). Binary parameters values in Table 2.
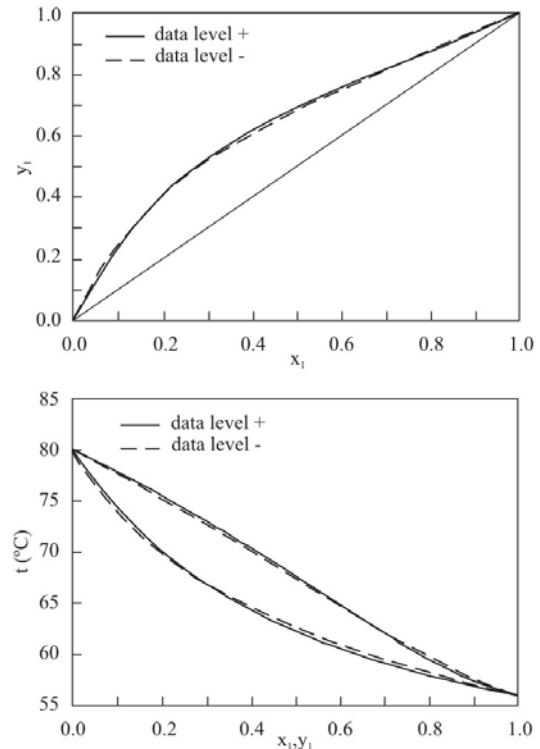


Figure 6. Comparison of x–y and t–x diagrams of isobaric data level + and level − for the system acetone (1) – benzene (2). Binary parameters values in Table 2.

predictive method that summarized a big number of experimental data. The level – is a set of data reported by Kojima *et al.* (1991). Then, the difference between the "average" data and the Kojima's data is used to represent the experiment uncertainties of the binary vapor-liquid data. The level 0 is a set reported by Gmehling and Onken (1979 a, b and 1997), these data are included in HYSYS and are used with the three models: NRTL, Wilson and UNIQUAC. The set represents a unique set of data that is used to get binary parameters for all models. It is expected to obtain similar results with Wilson, NRTL and UNIQUAC. All experimental data passed Herrington consistency test.

Another way to see the difference between level – and level + is considering the separation of the three binaries mixtures that made the ternary mixture. Each binary system is one factor in the factorial approach of studying data sensitivity. Results of a McCabe-Thiele distillation analysis for each factor (binary system) are given in Table 3. We considered several mixtures for each binary, with a desired distillation purity of 99.5 % and bottom purity of 99.5 % (or 99.5 % of azeotropic composition for the acetone- chloroform binary). Reflux rate varies from 34.39 % to -46.91 %, at fixed stage numbers. These results show that the difference between levels +/– , that seems small in Figures 4, 5 and 6, is significant for distillation column design.

## III. RESULTS AND DISCUSSION

We simulated the cases of Figs. 1 and 2 matching column specifications, as set in Table 1, using different va-por-liquid equilibrium data and considering the effect on column reflux ratio. For each binary system (factor), we considered two levels of experimental data as mentioned. The binary parameters obtained with those data and used in the simulation are displayed in Table 2. For each case, we did simulations that combined three factors at two levels in the traditional two-level factorial design (Gunter, 1993). Table 4 displays the reflux ratio for the different cases. The 0 cases are used to compare models; in particular the 0 case using Wilson is used as reference to calculate the relative variations in reflux ratio. The 1 to 8 cases are the traditional two-level factor in a factorial design of experiments. The way that parameters (binary experimental data) are changed implies that we have actually performed four little one factor at a time change on one binary system parameter and obtained four separated estimated of binary data effect, each for a combination of setting of the other two binary system vapor-liquid equilibrium data. The calculated effects, % variation in reflux ratio, for the numbers of Table 4 are shown in Table 5. The factorial analysis allows seeing not only the effect of a single factor but also the effect of a combination of factors. Table 5 shows that for Col. 1 in the two-column sequence the variation in reflux ratio is very important for acetone-benzene binary experimental data, factor C, with a value of 70.31 %. However, when the acetone-benzene binary experimental data are considered together with acetone-chloroform binary experimental data, factor AC, variation in reflux ratio is small, 0.29 %.

Table 4. Reflux ratio of Col. 1 of the two sequences using different experimental data.

| CASE [a] | FACTOR [b] | | | REFLUX RATIO | |
|---|---|---|---|---|---|
| | | | | Two - column | Three - column |
| | A | B | C | $R_1$ | $R_1$ |
| 0 (WILSON) | 0 | 0 | 0 | 6.02 | 13.69 |
| 0 (NRTL) | 0 | 0 | 0 | 6.03 | 13.92 |
| 0 (UNIQUAC) | 0 | 0 | 0 | 6.16 | 14.24 |
| 1 | – | – | – | 5.36 | 12.28 |
| 2 | + | – | – | 5.38 | 16.45 |
| 3 | – | + | – | 5.09 | 11.10 |
| 4 | + | + | – | 5.16 | 10.66 |
| 5 | – | – | + | 9.52 | 29.04 |
| 6 | + | – | + | 9.62 | 30.45 |
| 7 | – | + | + | 9.36 | 26.30 |
| 8 | + | + | + | 9.42 | 28.06 |

a)  In parenthesis the model used. Cases 1 to 8: Wilson
b)  A = acetone – chloroform; B = chloroform – benzene; C = acetone – benzene; 0, +, – = defined in Table 2.

Table 5. Estimates of effect for Col. 1 in both sequences.

| FACTOR | DESCRIPTION | EFFECT [a] | |
|---|---|---|---|
| | | Two – column | Three – column |
| | | $R_1$ | $R_1$ |
| A | Acetone – chloroform binary | 1.04 | 12.60 |
| B | Chloroform – benzene binary | -3.53 | -22.10 |
| C | Acetone – benzene binary | 70.31 | 115.70 |
| AB | | 0.04 | -7.78 |
| AC | | 0.29 | -1.02 |
| BC | | 0.54 | 3.36 |

a)  % variation in reflux ratio of column i ($R_i$); ($\Delta R_i$ / $R_i$ (level 0)) * 100

Figure 7. Reflux ratio of Col. 1 in the two – column and three – column sequences.
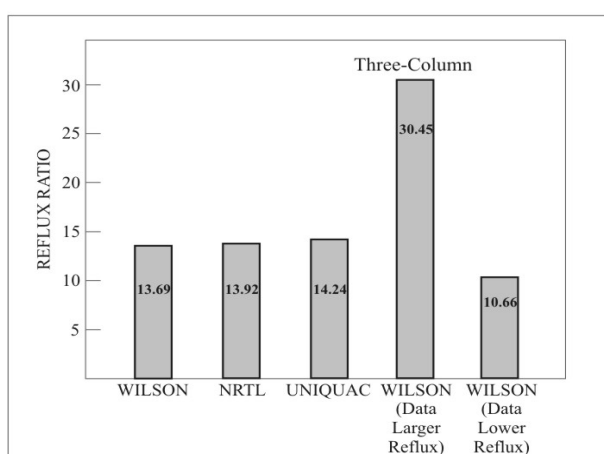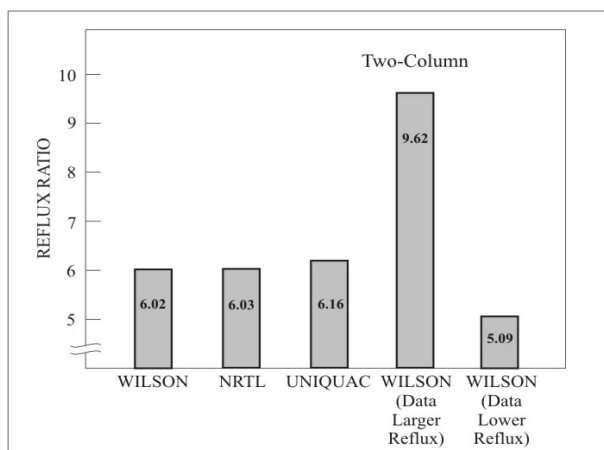




Figure 8. Liquid mole fraction profile inside Col. 1 in the two – column and three – column sequences.

We did the sensitivity analysis of the two sequences in two steps. First, each column was simulated alone. Then, the complete sequences were simulated.

Table 5, Figures 7 and 8 show the numbers for the first column (Col. 1) in each sequence when Col. 1 is simulated alone. The Col. 1 of each sequence is similar, top products are the same (acetone) and bottom products have different compositions but they are close to the distillation boundary. Table 5 reports the effect of each factor, binary experimental data, on reflux ratio values for Col. 1 in each sequence. The numbers indicate that factor C, acetone-benzene binary system data, is the most important. Figure 7 displays the reflux ratio for Col. 1 comparing models (Wilson, NRTL, UNIQUAC) with the larger and lower value of reflux ratio. As expected, the figure shows that for this column model is not important, what it is important is binary experimental data. Figure 8 displays liquid mole fraction profiles for Col. 1. The figure shows that along column, benzene is fractionating against acetone, and chloroform plays the same role, increasing its concentration from condenser to reboiler, reaching a maximum near reboiler. The profiles of Fig. 8 are consistent with the numbers of Table 5; the important binary is the acetone-benzene binary system.
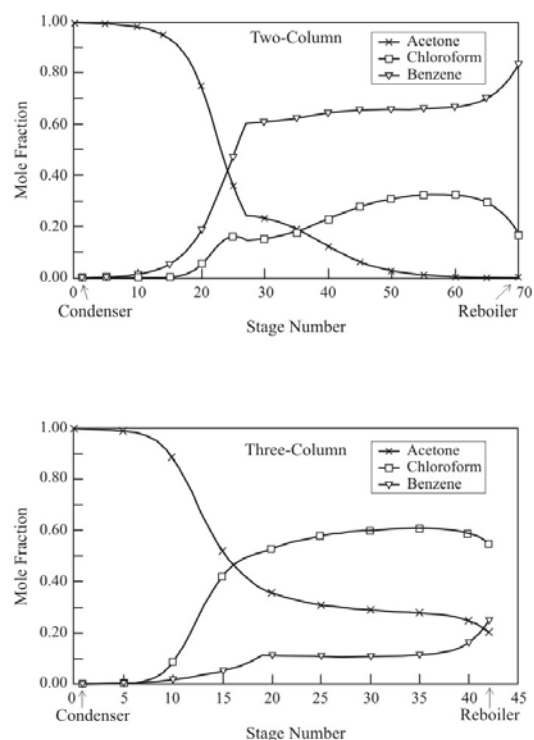
Table 6, Figures 9 and 10 show the numbers for the second column (Col. 2) in each sequence when Col. 2 is simulated alone. Col. 2 of each sequence is similar: top products are the same (benzene), bottom products have different compositions but they are close to the acetone-chloroform axe, and feeds are on one distillation region with the products in the other region. The Col. 2 in both sequences crosses the distillation boundary. Table 6 reports the effect of each factor, binary experimental data, on reflux ratio values for Col. 2 in each sequence. The numbers indicate that factor B, chloroform-benzene binary, is the most important. Figure 9 displays the reflux ratio for Col. 2 in both sequences. The figure compares models (NRTL, Wilson, UNIQUAC) with the larger and lower values of reflux ratio, and shows that for this column model is not important, what it is important is binary experimental data. Figure 10 displays liquid mole fraction profiles for Col. 2. The figure shows that along column benzene is fractionating against chloroform. The profiles of Fig. 10 are consistent with the numbers of Table 6; the important binary is the chloroform-benzene binary system.

Figure 11 shows the numbers for the third column in the three-column sequence. The figure displays the reflux ratio and column liquid mole fraction profiles. The figure compares models (NRTL, Wilson, UNIQUAC) with the larger and the lower value of reflux ratio. For, also, Col. 3 models are not as important as experimental binary data. The figure shows that in Col. 3 chloroform is fractionating against acetone. Numbers are consistent

Table 6. Estimates of effect for Col. 2 in both sequences.

| FACTOR | DESCRIPCION | EFFECT [a] | |
| --- | --- | --- | --- |
| | | Two – column $R_2$ | Three – column $R_2$ |
| A | Acetone – chloroform binary | 0 | 9.27 |
| B | Chloroform – benzene binary | 85.88 | 87.50 |
| C | Acetone – benzene binary | 0 | -3.63 |
| AB | | 0 | -2.42 |
| AC | | 0 | -0.81 |
| BC | | 0 | 0 |

a)     % variation in reflux ratio of column i ($R_i$); ($\Delta R_i / R_i$ (level 0)) * 100





Figure 9. Reflux ratio of Col. 2 in the two – column and three – column sequences.
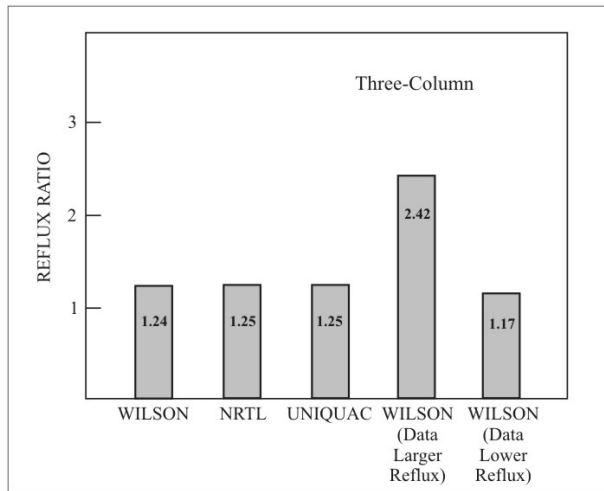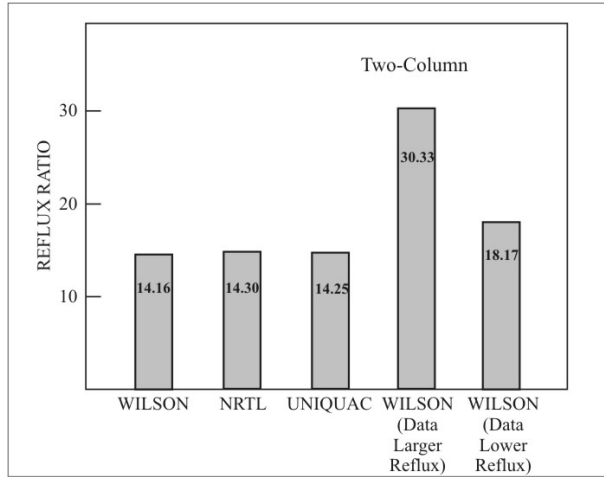




Figure 10. Liquid mole fraction profile inside Col. 2 in the two – column and three – column sequences.

with Fig. 11: -31.45 % variation for factor A (acetone-chloroform binary), -0.01 % variation for factor B (chloroform-benzene binary), and 0.02 % variation for factor C (acetone-benzene binary).

    The second step of the sensitivity analysis was to simulate the complete sequences of columns. The behavior of simulation was different for each sequence. With the two-column sequence, it was possible to fix the recycle flow. Numbers were obtained for several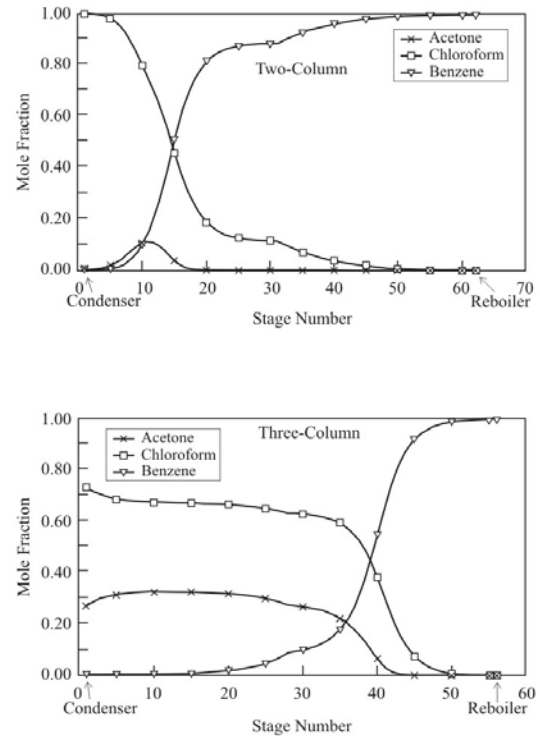 recycle flows, the effect for each one of these flows were identical and this effect was the same effect that was obtained when each individual column was analyzed. Table 7 presents the results. Factor C, acetone-benzene equilibrium vapor-liquid data, is the most important factor for Col. 1, and factor B, chloroform-benzene equilibrium vapor-liquid data, is the most important factor for Col. 2. The numbers of Col. 1 in Table 7 are almost the same that the numbers of Col. 1 in Table 5. This same situation is true for Col. 2, when Table 7 and 6 are examined numbers are the same. Table 7 includes the effect on vapor rate for each column knowing that vapor rate is directly related to column diameter and energy requirement. The factors play the same effect on vapor rate that on reflux ratio. The quantitative differences between variation in reflux ratio and in vapor rate are due to the relation that exists between the reflux ratio and the vapor rate when a mass balance is done around the condenser. This difference goes to zero when distillate rate goes to zero. With the three-column sequence, a

unique recycle flow was not possible to be fixed for all cases. To improve recycle convergence a purge was added to the bottom of the last column. As recycle flow increase iteration after iteration, the purge helps to stabilize the flow. Table 8 presents the numbers for the three-column sequence; each case has a different recycle flow. The numbers of Table 8 are different from the numbers obtained when each column was simulated alone. Table 8 displays that all factors, all binary experimental data, are important in all columns. Even combinations of factors are important. To complete the analysis, simulation were done at fixed recycle flow and reflux ratio in each column. Table 9 presents numbers for the simulation with a recycle flow of 160 kmol/h, a reflux ratio for Col. 1 of 24, for Col. 2 of 14.6, for Col. 3 of 15. Compositions of products are different for each simulated case. In neither of the simulated cases, the specifications were fulfilled.

The two-step analysis done shows that the second step, the simulation of the whole sequence to see the effect of experimental data, is an absolute necessity. The way that recycle is built into sequences could changed how vapor-liquid equilibrium experimental uncertainties affect distillation column simulations.

## IV. CONCLUSION

Several simulations were done to evaluate the effect of vapor-liquid equilibrium data on the conceptual design of a separation sequence by distillation. Three different sets of binary data were used following a two step procedure that involve column simulation, alone or with the sequence. Two sequences for the acetone-chloroform - benzene separation were compared. For the two-column sequence, analysis done to each column alone or to the whole sequence gave the same results. In the three-

Table 7. Estimates of effect for the two – column separation sequence.

| FACTOR | DESCRIPTION | EFFECT [a] | | | |
| --- | --- | --- | --- | --- | --- |
| | | REFLUX RATIO | | VAPOR RATE | |
| | | $R_1$ | $R_2$ | $V_1$ | $V_2$ |
| A | Acetone – chloroform binary | 0.83 | 0.02 | 0.67 | -1.36 |
| B | Chloroform – benzene binary | -2.92 | 85.80 | -2.28 | 81.56 |
| C | Acetone – benzene binary | 70.45 | -0.02 | 60.47 | -1.40 |
| AB | | -0.08 | 0.02 | -0.09 | -1.38 |
| AC | | 0.00 | 0.02 | -0.05 | 1.39 |
| BC | | 0.75 | -0.02 | 0.67 | -1.39 |

a) % variation in reflux ratio of column i ($R_i$); ($\Delta R_i / R_i$ (level 0)) * 100
   % variation in vapor flow leaving reboiler ($V_i$ [kmol/h]); ($\Delta V_i / V_i$ (level 0)) * 100

Table 8. Estimates of effect for the three – column separation sequence.

| FACTOR | DESCRIPTION | EFFECT [a] | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | REFLUX | | | VAPOR RATE | | |
| | | $R_1$ | $R_2$ | $R_3$ | $V_1$ | $V_2$ | $V_3$ |
| A | Acetone – chloroform binary | 10.13 | 4.32 | 1.91 | 9.95 | 9.47 | 1.96 |
| B | Chloroform – benzene binary | -17.11 | 0.58 | -7.80 | -16.48 | -0.23 | -7.34 |
| C | Acetone – benzene binary | 20.77 | 2.19 | 0.76 | 20.09 | 6.54 | 0.73 |
| AB | | 9.90 | -2.67 | -6.41 | 9.51 | -3.71 | -6.02 |
| AC | | -0.16 | 1.47 | -3.61 | -0.09 | 5.01 | -3.39 |
| BC | | 4.26 | -2.53 | 8.64 | 4.15 | -2.00 | 8.18 |

a) % variation in reflux ratio of column i ($R_i$); ($\Delta R_i / R_i$ (level 0)) * 100
   % variation in vapor flow leaving reboiler ($V_i$ [kmol/h]); ($\Delta V_i / V_i$ (level 0)) * 100

Table 9. Composition variation in the three – column separation sequence.

| CASE [a] | FACTOR [b] | | | PRODUCT COMPOSITION [c] | | |
| --- | --- | --- | --- | --- | --- | --- |
| | A | B | C | $x_{Ac,D1}$ | $x_{Be,B2}$ | $x_{Ch,D3}$ |
| 0 (WILSON) | 0 | 0 | 0 | 0.9648 | 0.9979 | 0.9395 |
| 0 (NRTL) | 0 | 0 | 0 | 0.9725 | 0.9975 | 0.9508 |
| 0 (UNIQUAC) | 0 | 0 | 0 | 0.9702 | 0.9976 | 0.9475 |
| 1 | – | – | – | 0.9818 | 0.9990 | 0.9648 |
| 2 | + | – | – | 0.9779 | 0.9982 | 0.9594 |
| 3 | – | + | – | 0.9948 | 0.9996 | 0.9841 |
| 4 | + | + | – | 0.9946 | 0.9993 | 0.9843 |
| 5 | – | – | + | 0.9984 | 0.9986 | 0.9895 |
| 6 | + | – | + | 0.9986 | 0.9987 | 0.9901 |
| 7 | – | + | + | 0.9988 | 0.9989 | 0.9900 |
| 8 | + | + | + | 0.9988 | 0.9990 | 0.9905 |

a) In parenthesis the model used. Cases 1 to 8: Wilson
b) A = acetone–chloroform ; B = chloroform–benzene ; C = acetone–benzene; 0, +, – = defined in Table 2.
c) $x_{Ac,D1}$ = acetone molar fraction in distillate Col. 1
   $x_{Be,B2}$ = benzene molar fraction in bottom Col. 2
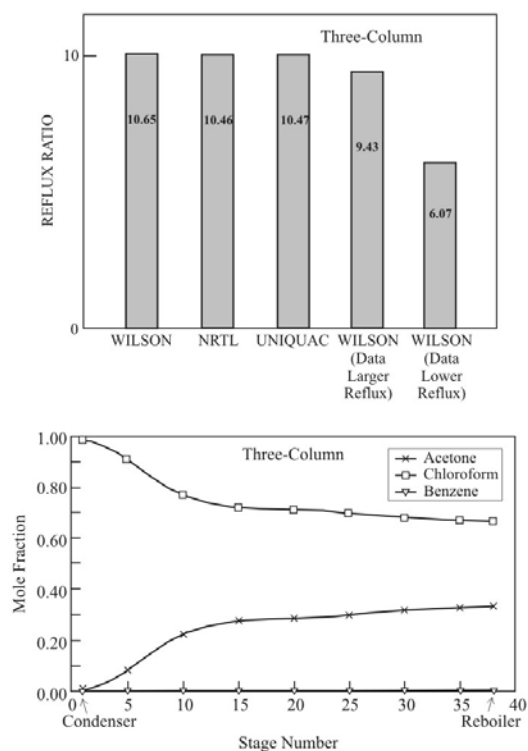   $x_{Ch,D3}$ = chloroform molar fraction in distillate Col. 3

Figure 11. Liquid mole fraction profile and reflux ratio of Col. 3 in the three – column sequence.

column sequence, results were different and simulation of the whole sequence gave in complete different picture that simulation of each column alone. The sensitivity analysis done shows that it is necessary to simulate the whole sequence to see the effect of vapor-liquid equilibrium experimental uncertainties on distillation column simulations.

## NOMENCLATURE

$a_{ij}$, $a_{ji}$ = Wilson binary parameters of the system i-j
A, B, C = factors in the sensitivity analysis
$B_i$ = bottom rate for column i
$D_i$ = distillate rate for column i
$F_i$ = feed rate for column i
P = total pressure
R = universal gas constant
$R_i$ = reflux ratio for column i
t, T = temperature
$v_i$ = molar volume of component I
$V_i$ = vapor rate for column i
$x_i$ = liquid phase mole fraction of component i
$y_i$ = vapor phase mole fraction of component i
$\gamma_i$ = activity coefficient of component i

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