© 2006 IChemE

STRATEGIES FOR IDENTIFYING MULTIPLICITIES IN DISTILLATION SYSTEMS USING PROCESS SIMULATORS

Setu Chokshi[1] and Ranjan K. Malik[2]
Department of Chemical Engineering, Indian Institute of Technology – Bombay Powai, Mumbai, 400076, India

The complexity and difficulty of determination of Multiple Steady States (MSS) in azeotropic and reactive distillation have remained a matter of concern for the development of a systematic and easily verifiable criterion for the detection and characterization of MSS. This has resulted in a plethora of methods that are either experimental or model-based in nature adapting different solution strategies. However, no single methodology is solely suitable for all systems. A sensible approach would be to apply together several solution methodologies for consistent and accurate solutions. It is then obviously desirable to have a framework that enables such a bouquet of tools to be used in an easy and efficient manner. In this paper, one such framework is proposed that relies on model based methodologies, and uses the process models and the property equations already present in the commercial simulators such as Aspen Plus and Aspen Hysys. A developed tool has also been demonstrated to study the sensitivity of the parameters incorporated together with the solution strategy while solving the system of equations representing the distillation column.

KEYWORDS: azeotropic distillation, solution multiplicity, detection of multiple steady states, process simulators

INTRODUCTION
An important problem in the design and optimisation of azeotropic and/or reactive distillation systems is the determination of Multiple Steady States (MSS) and associated limit cycles (see, for example, Jacobsen and Skogestad [1991]; Bekiaris et al. [1993]). The usefulness of process models in determination of MSS has been established by many researchers in the recent past. They are more accurate than the analytical methods and cheaper to work with than experiments (Bossen et al. [1993]; Vadapalli and Seader [2001]). Unfortunately, widespread use of rigorous models for detection of MSS has not been seen much in the literature which may be due to an extensive requirement of computational power. Several simplifying assumptions (e.g. infinite reflux/stages, fixed stage efficiency) with binary or ternary mixtures make the problem traceable with simple computational resources, but pose a challenge while extending it to real columns. Such tractability is however gained at the expense of accuracy that is critically important in the detection and characterization of MSS.

[1]Currently with GE, John F Welch Technology Center, Bangalore 560066, India
[2]Author to whom all correspondence should be addressed, Email: rkmalik@che.iitb.ac.in

A recent development that holds promise is the maturing of commercial simulation platforms like Aspen Plus and Aspen Hysys, Prosim, etc., into powerful broad based, and efficient steady-state/dynamic process simulation environments. It was thus decided to take advantage of existing process models and solution algorithms in the commercial simulators to propose a technique for detection of multiple solutions, if present, for a distillation model. The multiple solutions obtained using the process simulators, by nature of their design, may point towards existence of MSS in real columns, thus eliminating the issue of imaginary solutions that has appeared in literature occasionally. The proposed technique is based on the well-known branch and bound algorithm, which provides the feature of tracking observed variables with respect to the bifurcation parameter, on which the bounds are repetitively provided and adjusted to enable it to converge. The efficacy of the proposed methodology is illustrated by its application to three widely used case studies. Prediction of MSS by ∞/∞ analysis is compared with solution obtained by this methodology for the Methanol–Methyl Butyrate–Toluene (MMBT) system. Validation of the Ethanol–Water–Cyclohexane (EWC) MSS obtained from simulations with that obtained using experimental column is also shown.

The complexity of determining multiplicities is compounded further by the extreme sensitivity of the solutions to errors in parameters. Bekiaris et al. (2000) have demonstrated the implication of the inaccuracies in the reported thermodynamics on the existence of MSS. Not much work has been done to study the impact of parametric sensitivity on determination of MSS, though a few analytical results are available in the literature (Benz and Scenna [1997], Bekiaris et al. [1993, 1996]). Though the latter reference gives necessary and sufficient conditions for the existence of MSS, the applicability of these conditions is rather restricted to ternary systems. No easily verifiable conditions seem to exist in general for determining multiplicity in steady states accounting for numerical sensitivity. This is an important problem for distillation design, simulation, and operation, for example under-predicting the azeotropic composition may result in a poor column design, while an over-prediction may result in an infeasible column. In this paper we additionally propose a tool to study this problem that is configured for easy use with commercial simulators like Aspen Plus. This tool complements the methodology proposed for determination and characterization of MSS, enabling the study of not only the influence of adopted modelling hypotheses, but also the parametric sensitivity, simultaneously. A case study using the ternary system of Acetone–Heptane–Benzene (ABH) is presented to illustrate the features of this tool.

METHODOLOGY TO OBTAIN MSS USING PROCESS SIMULATORS

Consider a typical bifurcation curve often encountered in chemical processes (Figure 1). The plot shown can be characterized by a state variable u_i (from a vector of state variable **u**) on y-axis, while the bifurcation parameter, λ is given on the x-axis. The variable u_i represents the state variable like temperature or component mole fraction in bottoms or distillate, and λ represents an input or equipment variable that is being varied over the range of values. The S shaped curve consists of three steady state solutions branches
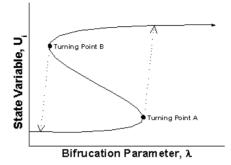
Figure 1. A typical bifurcation curve encountered in chemical processes

that change direction at the two turning points (bifurcation points), and hence there are three sets of state variables that satisfy the process model, also known as region of multiplicity. The technique presented in this paper uses the distillation models and the thermodynamic equations already present in the commercial process simulator to identify, detect and track all possible solutions in a region of multiplicity.

1. Configure the column and run the simulation so that the column has converged to a valid solution. It is preferable to choose the bifurcation parameter (Specification 1) as specification to satisfy the degree of freedom for the column. Choose any other variable as second specification (Specification 2).
2. Find the region of multiplicity. This can either be obtained using an ∞/∞ analysis, or by carrying out an analysis using the developed bifurcation tool.
3. Alter the specification values, such that the converged solution lies in the region of multiplicity.
4. Select a state variable u_i for which the bifurcation diagram has to be constructed. Preferable variables include the component mole fractions of the product streams as the upper (x^{UBD}) and lower bounds (x^{LBD}) for mole fractions are known a priori, i.e. 1 and 0 respectively. This range between upper and lower bounds becomes the search region.
5. Replace Specification 2 with the specification involving the state variable and update the upper, x^{UBD}, and lower bounds, x^{LBD}, appropriately. For the first iteration, the local bounds $x^{L,iter}$, $x^{U,iter}$ are set equal to the global ones, i.e. $x^{L,iter} = x^{LBD} = u^I$ and $x^{U,iter} = x^{UBD} = u^{II}$. This is particularly important while implementing this strategy using Aspen Plus simulator (version 11.1). The column is now configured with two specifications, one with the state variable (Specification 1), while the other with the bifurcation parameter (Specification 2).
6. Run the simulation, so the column converges with the new set of specifications. Let the value of the state variable be $u^{converged}$, such that $u^I \leq u^{converged} \leq u^{II}$.

SYMPOSIUM SERIES NO. 152 © 2006 IChemE

7. Bisect the search region in two. One with bounds given by $x_1^{L,iter} = u^I$, $x_1^{U,iter} = u^{converged}$ and the other with bounds given by $x_2^{L,iter} = u^{converged}$, $x_2^{U,iter} = u^{II}$. Run the simulation for both the regions successively. For each converged simulation in a region repeat Step 7 until no further convergence is possible, or till the limit points are reached.

IMPLEMENTATION IN HYSYS PROCESS SIMULATOR

The reason that makes Hysys suitable for implementing the above strategy is because of a unique feature called "*Ranged Specification*". As the name suggests, a ranged specification requires both upper and lower bounds together with the specification value. The solver attempts to meet the specified value, but if convergence fails, the specification is perturbed within the interval until the column reaches convergence. This feature helps us setting the upper bound, x^{UBD}, and lower bound, x^{LBD}, appropriately. Another feature that aids in the implementation of the strategy is the "*Alternate Specification*". This requires specifying two alternate specifications, one of which will be active while the other will be inactive. The solver first attempts to meet an active Alternate specification value, but if the value is not solved after a minimum number of iterations, the active alternate specification is replaced by an inactive Alternate specification. This feature is particularly useful when there are no solutions possible in a particular region, during which the specification on the state variable can be ignored (enabling another) to meet the rest of the specifications and converge the column. These features are not enabled by default and have to be configured before they can be applied to the column. The ranged specification is only available with "Hysim Inside–Out" and "Modified Hysim Inside–Out" algorithms. Hysys also supports *automation*, i.e., it is possible to interact with Hysys through exposed objects which make it possible to perform nearly any action that is accomplished through the Hysys graphical user interface, thereby enabling automation of the whole process (implemented in bifurcation tool).

IMPLEMENTATION IN ASPEN PLUS PROCESS SIMULATOR

The introduction of Equation Oriented (EO) solving strategy in Aspen Plus (version 11 and higher) makes it suitable for the implementation of the algorithm described earlier to find MSS when they exist. EO modeling is an additional strategy to Sequential Modular modeling for solving flow sheet simulations. Instead of solving each block in sequence, EO gathers all the model equations together and solves them at the same time. EO modeling strategy works well when all the variables are "near" the solution. Hence the initialization is done using SM. DMO and LSSQP are the two solvers available under the EO mode. Both solvers implement a variant of the successive quadratic programming (SQP) algorithm to solve large-scale optimization problems, by solving a sequence of quadratic programming sub-problems. One important difference between DMO and LSSQP is that DMO ignores all bounds on variables during the equation oriented simulation and parameter estimation, i.e., modes with no degrees of freedom. Hence this makes the DMO solver unsuitable for our purpose. MSS in this study were worked out using the LSSQP solver in the EO mode by *repeatedly setting bounds* as required by the algorithm.

BIFURCATION TOOL DEVELOPED IN THIS WORK

The importance of thermodynamic procedures and their parameters in the detection of MSS for a distillation system cannot be emphasized enough. Operatively, different numeric resolution strategies, and use of different ways of initializing the methods, can influence the detection of multiple solutions. In order to study such effects, a user-friendly tool has been developed. The need for such a tool arises because of the absence of an *a priori* criterion that establishes whether a system can, or cannot present multiple solutions. Also, there is no criterion available that allows the detection of all possible steady states. Thus the focus is on the influence of the adopted hypotheses (simplification used in the model) or the strategy for the numerical resolutions of specific aspects, as these are not sufficiently developed in the published literature till date. The developed tool carries out the analysis and the resolution of multiple steady states based on various parameters that include thermodynamic methods (equations of state, and activity coefficient models), column convergence methods, and column configuration parameters. The tool also identifies the turning points based on the criteria (Seader and Vadapalli [2001]) using the two most recently converged simulations:

$$\lim_{\Delta\lambda\to 0} \tan^{-1}\left(\frac{du}{d\lambda}\right) \longrightarrow 90\,\text{deg}$$

CASE STUDY I: ACETONE–HEPTANE–BENZENE SYSTEM

The ternary homogeneous mixture Acetone–Heptane–Benzene is quite popular for simulation studies [see, Laroche et al. (1992) and Bekiaris et al. (1993)]. We have selected a known case reported in the paper of Bekiaris et al. (1993) that presents multiple solutions. This mixture belongs to class 001. The minimum boiling binary azeotrope between acetone and heptane is at 93.56-mol% acetone. Although they did not describe the algorithm to solve the distillation column, it was mentioned that the hypothesis of constant molar overflow (CMO) along the column was adopted. This is an important simplification in the equation modeling implying that the column energy balance was not applied. The liquid activity coefficients and vapor pressures were calculated using Van Laar and Antoine equations, respectively. The system consists of a distillation column that receives a feed of an azeotropic mixture of acetone and heptane and uses benzene as an entrainer. The split into two liquid phases in the condenser was not considered. In a later paper, Bekiaris et al. (1995) included these latter phenomena in the model. Multiple solutions were obtained by varying the reflux flow and the distillate flow (bifurcation parameters). The numbers of trays of the column and the entrainer flow were also used as bifurcation parameters. The column consisted of 44 plates and the feed enters on tray 40. The system represents a binary azeotropic feed with molar composition 93% acetone and 7% heptane. Benzene is used as an entrainer for the separation of the azeotrope. The presence of a single phase (checking its existence) along the column is assumed, but the separation of the liquid phases in decanter (heterogeneous model) is not included in the model (Bekiaris et al., 1995). The activity coefficients in the liquid phase are calculated with UNIQUAC
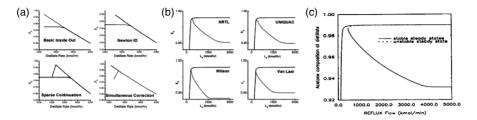
Figure 2. a) Effect of Solvers on the detection of multiplicity; b) Effect of column solving parameters and exact detection of multiplicity; c) Bifurcation diagram reported in Bekiaris et al. (1993)

and eventually with Wilson, NRTL and Van Laar. The vapor phase is assumed to be ideal. In this case, both the azeotropic feed and the entrainer flow are maintained at 100 kmol/min. The bifurcation tool is used to carry out the analysis and the resolution of multiple steady states based on various parameters that include thermodynamic methods, column convergence methods, and column configuration parameters. The results of these are shown in Figure 2. It can bee seen that not all solvers are able to resolve the multiplicity in the column and location too varies with the thermodynamic method used. The region of multiplicity identified by the tool is between 90 kmol/min and 95 kmol/min as reported in the literature. In order to study the effect of various specifications that are used to solve the column, analysis using the tool for various combinations of reflux rate and distillate rate were carried out. Figure 3 also shows the region of multiplicity as input and output.

In order to validate the methodology we decided to carry out the simulations using the values reported in the literature. Distillate rate was taken as the bifurcation parameter and allowed to vary. A specification value of 92.2 kmol/min (which lies in the multiplicity region identified earlier) was specified and the variable was treated as inactive Alternate specification. Mole fraction of acetone in the distillate was treated as the state variable and treated as the active Alternate specification. It is also treated as a Ranged specification and the upper and lower bounds are fixed as 1 and 0 respectively.
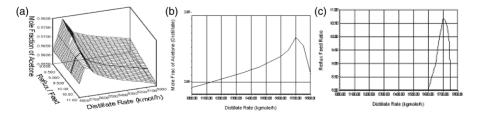

Figure 3. Multiplicities: b) Output (reflux/feed = 9.5); c) Input (mole fraction of acetone in distillate = 0.971)
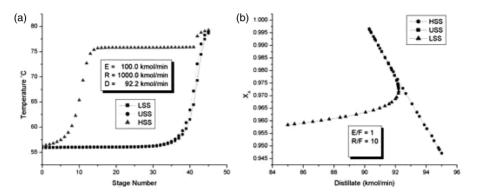
Figure 4. a) Temperature profiles for the ABH system; b) Bifurcation diagram, showing the effect of the distillate rate on the purity of acetone in distillate

Another primary specification is that of the reflux rate, the value for which is fixed at 1000 kmol/min. With these in place, the algorithm for the identification of MSS is applied. The results for the same are shown in the Figure 4 and are similar to the ones reported in the literature.

CASE STUDY II: METHANOL–METHYL BUTYRATE–TOLUENE SYSTEM

Until today, the mixture methanol–methyl butyrate–toluene (MMBT) is the only homogeneous mixture reported in the literature for which the existence of MSS is reportedly caused by VLE (Guttinger et al., 1997). This mixture has also been studied experimentally (Guttinger and Morari, 1997; Dorn et al., 1998) which is demonstrated in this study. Further, it was the first mixture for which simulations were published showing the existence of limit cycles in the open – loop models of homogeneous azeotropic distillation columns (Lee et al., 1999). The mixture belongs to the class 001. The binary minimum boiling azeotrope between methanol and toluene is located at 88 mol% methanol. The activity coefficients in the liquid phase are calculated with Wilson equation. The vapor phase is assumed to be ideal. Distillate rate was taken as the bifurcation parameter and was allowed to vary. A specification value of 3.1 kg/h was specified and the variable was treated as inactive Alternate specification. Mole fraction of acetone in the distillate was treated as the state variable and treated as the active Alternate specification. It is also treated as a Ranged specification and the upper and lower bounds are fixed as 1 and 0 respectively. Another primary specification is that of the reflux rate, the value for which is fixed at 13.5 kg/h. With these in place, the algorithm for the identification of MSS is applied. The results for the same are shown in the Figure 5a, and these can be compared to the theoretical ∞/∞ predictions in Figure 5b. The temperature profile so obtained is similar to the one obtained by implementing the pseudo arc length continuation method in Aspen Plus.
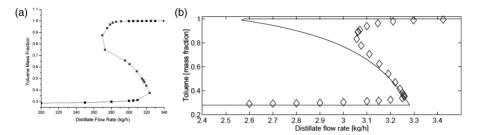
Figure 5. a) Bifurcation diagram for MMBT system; b) Steady stage bifurcation diagram showing the bottoms composition of toluene from the theoretical ∞/∞ predictions (Dorn et al., 1997)

CASE STUDY III: ETHANOL–WATER–CYCLOHEXANE SYSTEM

The analysis of a three-phase distillation process presented in this section is motivated by the economic potential of heterogeneous azeotropic distillation processes to separate azeotropic mixtures. The potential is based on the low energy consumption of the process and the low temperature level at which external energy is required. In industrial applications, however, alternative processes such as extractive distillation and zeolites are often preferred, and the potential of heterogeneous azeotropic distillation is not used. The reason is the extremely high sensitivity and the complex dynamic behavior of the process. For a model based development of the process structures, operating conditions and control systems a validated process model is needed which describes the liquid splitting on individual trays. This not only necessitates the need for a good set of binary interaction parameters but also the three phase distillation models which should be flexible enough to support phase splitting and characterization of the same which are available in the simulators available in the market. Bekiaris et al. (2000) have pointed out various inaccuracies reported in the simulation of Ethanol–Water–Benzene and it was decided the extreme caution be taken to ensure that the correct thermodynamic description is included to determine correct output multiplicity. Hence, at first the simulation results were compared to
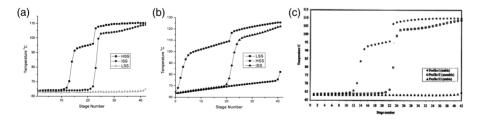

Figure 6. a, b) Temperature Profiles for the three steady states at different R/F; c) Results from Seader and Vadapalli (2001)
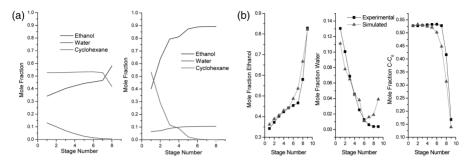
Figure 7. a) Two Steady States obtained for Ethanol Water Cyclohexane System; b) Comparison of experimental results with simulated results (Vasconcelos [2004])

the experimental values reported in the literature and then the steps, aforementioned, were carried out to obtain multiple solutions. The binary interaction parameters for Water–Cyclohexane itself were fitted using experimental data (Vasconcelos [2004]). The column simulation was carried out using the three-phase distillation column in Hysys in an attempt to reproduce the results in paper of Muller and Marquardt (1997). Benzene was used earlier instead of Cyclohexane, but due to the carcinogenic properties of the former entrainer, the latter, Cyclohexane, is used. In either case the structure of the RCM is the same. The Ethanol–Water mixture either with Benzene or Cyclohexane is the widely studied example. Three MSS are reported in the literature with volumetric distillate flow rate (in some cases, more MSS have been reported). In our case, bottoms ethanol composition was taken to be the manipulated variable. The solution is obtained using Sparse Continuation Solver for a Three Phase Distillation column of Hysys. The results so obtained compare well with the experimental results (see Figure 7).

CONCLUSIONS

In light of the results obtained above it can be concluded that the technique proposed is successful with both heterogeneous and homogeneous systems. It is clear, at least by simulations, that it is possible to leverage the existing process simulators to aid in the detection of MSS. The tool demonstrated in this paper complements the methodology proposed for determination and characterization of MSS in that not only the influence of adopted modeling hypotheses, but also parametric sensitivity can be studied simultaneously. The algorithm is simple to implement and no additional code is to be written by the user. Hence systematic identification of the steady states is possible even when there is no bifurcation curve generated, e.g. Ethanol–Water–Cyclohexane system has its three solutions in two separate regions. The algorithm is limited by the fact that it cannot indicate immediately whether the solution is stable or unstable. This shortcoming can be overcome to some extent by noting that the branches change stability at every turning point, in case where the bifurcation diagram is generated. A further extension to the algorithm implemented

in Aspen Plus is possible to detect exact bifurcation points as some new features allow computing the same. The solution strategy works well on variety of two product columns. The strategy can also be extended to reactive distillation, and is only limited by the solution methods offered by the simulators and the theory related to them.

REFERENCES

Bekiaris, N., Meski, G., Radu, C. and Morari, M. (1993), Multiple Steady States in Homogeneous Azeotropic Distillation, Ind. Eng. Chem. Res. 32(9): 2023–2038.

Bekiaris, N., Meski, G. and Morari, M. (1996), Multiple Steady States in Heterogeneous Azeotropic Distillation, Ind. Eng. Chem. Res. 35(1): 207–227.

Bekiaris, N., Guttinger, T. and Morari, M. (2000), Multiple Steady States in Distillation – VLLE Inaccuracies, Multiplicities and ∞/∞ Predictions, AIChE Journal 46(5): 955–978.

Benz, S. J. and Scenna, N. J. (1997), The Influence of Different Models in Obtaining Multiple Solutions in Distillation Columns, Can. J. of Chem. Eng. 75(12): 1142–1152.

Bossen, S., Jorgensen, S. and Gani, R. (1993), Simulation, Design, and Analysis of Azeotropic Distillation Operations, Ind. Eng. Chem. Res. 32: 620–633.

Dorn, C., Guttinger, T. and Morari, M. (1997), Experimental Study of Multiple Steady States in Homogeneous Azeotropic Distillation, in R. Darton (ed.), Distillation and Absorption'97, Vol. I, IChemE Symposium Series No. 142, IChemE, Rugby, UK, 217–226.

Dorn, C., Guttinger, T., Wells, J., Morari, M., Kienle, A., Klein, E. and Gilles, E. (1998), Stabilization of an Azeotropic Distillation Column, Ind. Eng. Chem. Res. 37(2): 506–515.

Guttinger, T. and Morari, M. (1997), Predicting Multiple Steady States in Distillation: Singularity Analysis and Reactive Systems, Comput. Chem. Eng. 21: Supplement S995–S1000.

Jacobsen, E. and Skogestad, S. (1991), Multiple Steady States in Ideal Two-Product Distillation, AIChE Journal 37(4): 499–511.

Laroche, L., Bekiaris, N., Andersen, H. and Morari, M. (1992), Homogeneous Azeotropic Distillation: Separability and Flowsheet Synthesis, Ind. Eng. Chem. Res. 31(9): 2190–2209.

Lee, M., Dorn, C., Meski, G. and Morari, M. (1999), Limit Cycles in Homogeneous Azeotropic Distillation, Ind. Eng. Chem. Res. 38(5): 2021–2027.

Muller, D. and Marquardt, W. (1997), Experimental Verification of Multiple Steady States in Heterogeneous Azeotropic Distillation, Ind. Eng. Chem. Res. 36(12): 5410–5418.

Vadapalli, A. and Seader, J. (2001), A generalized framework for computing bifurcation diagrams using a process simulation programs, Comput. Chem. Eng. 25(2): 445–464.

Vasconcelos, C. (2004), Personal communication, By email.