METHODOLOGY TO GET PROCESS OPERATING PATHS AND MULTIPLE STEADY STATES.

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ABSTRACT

We present a methodology designed to perform fast and efficient case study analysis of complex processes. This methodology has been implemented in a tool, ProCase, which coupled with a classical commercial process simulator, carries out successive process simulations while varying an operating parameter value. The parameter variation policy uses a predictor-corrector type method using a curvilinear distance. An automatic adjustment of the parameter step helps to track process operating paths and overcome convergence problems.
The case study of an industrial heterogeneous azeotropic distillation process allowed to simulate the suspected multiple steady states in a one day work, providing numerous information suitable for better process operations.

INTRODUCTION

Steady-state process simulators are nowadays well-developed tools routinely used in industry (LIEN and PERRIS, 1996) for process design and analysis. But modeling difficulties may arise and their use remains arduous for complex processes such as heterogeneous azeotropic distillation columns. Simulation (MAGNUSSEN *et al.*, 1979) and simulation coupled with experimental studies (KOVACH and SEIDER, 1987b; MULLER and MARQUARDT, 1997) have shown that for such a process multiple process outputs occur for an identical set of operating parameters. However, multiple steady states are often difficult to obtain by simulation since classical numerical methods (Newton-Raphson, ...) often converge towards the most attractive steady state points. Other solution points may be associated with narrow convergence domains difficult to reach during the convergence procedure.
Homotopy-continuation methods solve this problem and give exhaustively the whole set of solution points (KOVACH and SEIDER, 1987a). However they are so computer intensive that to our knowledge, no general tool applicable to real industrial problems is available. A more pragmatic approach consists in developing a methodology capable of easily detecting possible multiple steady states.

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METHODS

The basic principle consists in making a case study: successive simulations using a classical commercial process simulator with a variation of an input parameter. Convergence is easily obtained by using results of the previous simulation as initialization of the next step outputs. A procedure carrying out constant steps of an operating parameter proved to be inadequate for getting several multiple steady-states and obliged the user to run numerous attempts with different step values. Thus we have developed a procedure able to perform a case study by following an operating path. An operating path is a set of successive steady-states, characterized by continuously derivable output variables. This C_2 set is a good compromise between the physically continuous characteristics of a real system and the inherent limitations of a mathematical model.

The new procedure follows the system evolution according to non-constant steps of the operating parameter. For this purpose a predictor-corrector type method is developed. A priori, the study concerns a single input variable and several output variables. However, our experience has shown that it is better to use a well chosen output variable rather than all output variables because of physical discontinuities like phase splitting. Nevertheless, non chosen output variables may be referred to.

Evaluation of the operating parameter step uses a second order Taylor approximation, the best to cope with the operating path definition:

$$f(u+du) = f(u) + du.\frac{\partial f}{\partial u}(u) + \frac{(du)^2}{2}.\frac{\partial^2 f}{\partial u^2}(u) + o\left((du)^2\right) \qquad (1)$$

As f is unknown, so are $\frac{\partial f}{\partial u}$ and $\frac{\partial^2 f}{\partial u^2}$. However this expression shows that f could be approximated by a second order polynomial function:

$$f(u) \equiv A.u^2 + B.u + C \qquad (2)$$

Parameters A, B, C are evaluated with the three previous points on the path.

As the purpose is to follow an operating path, it appeared more efficient to work with a curvilinear step (Cf. Figure 1). Thus this facilitates the management of large gradient variations of f. The mathematical expression is:

$$(ds)^2=(du)^2+(df)^2 \qquad (3)$$

With the derivative of (2),

$$df \cong 2.A.u.du + B.du \qquad (4)$$

this expression becomes:

$$du = \frac{ds}{\sqrt{1 + A.u + B}} \qquad (5)$$

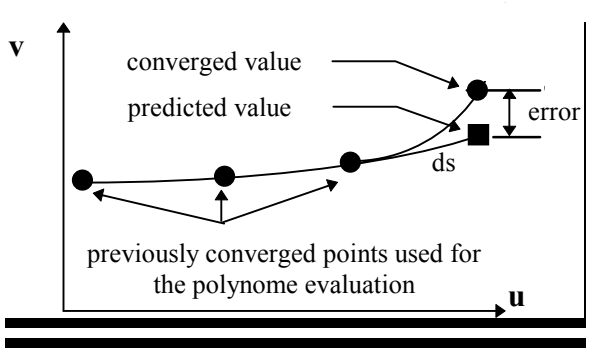


Figure 1: Parameter operation path and curvilinear coordinate.

At the beginning three initial simulations are necessary to obtain the parameters A, B, C. The smaller the operating parameter step is, the better odds to get the three points on the same operating path. That is why these three simulations are made within a unit step *ds* of the operating parameter.

The point given by the simulation with the new variable command value *f(u+du)* is compared with the predicted point. This comparison could be done with several criteria among which we prefer the absolute difference proportional to the step, $c = \left| \frac{f_{calculated} - f_{evaluated}}{ds} \right|$. If the criterion is smaller than a reference value, the point is validated and the procedure is done again starting from this new point, with a new operating parameter value $u=u+du$. If the criterion is bigger than a reference value, we may face an operating path discontinuity. In this case, the new simulated point is stored and the procedure is done again from the last converged point with a step divided by two.

The other case of failure is related to non convergence of the simulation: the step is divided by four. Besides, the procedure may speed up the computation: when several simulations converge on the same operating path, the step size is multiplied by two. These classical numerical choices for a predictor-corrector method are default values that have been validated on studied examples and which may be changed on specific cases.

Off-path points are used to get other operating paths using a restart function. We may restart either from a point which is used as a simulation initialization or with three points which give a direction with the prediction function. Tracking different operating paths gives multiple steady-states.

Notice that we not only obtain multiple steady state points but also investigate their interconnections.

This methodology has been implemented in a tool, ProCase, which is coupled with a classical process simulator ProSim. Through its friendly graphical user interface, ProCase allows to select the desired operating parameter and the output variable monitored to detect possible new operating paths. Various text and Excel format files contain the case study results and parameters. Its interest has been validated on several examples.

APPLICATION EXAMPLE

As an example, a pilot scale industrial heterogeneous azeotropic distillation column that purifies n-butyl acrylate has been considered (see Figure 2). Column feed is coming from an esterification reactor and four components are considered: n-butyl acrylate (BA), acrylic acid (AA), water and

1-butanol (BuOH). The pilot column is modeled by 20 theoretical trays including a reboiler, a total condenser and a supercooled 20°C decanter.

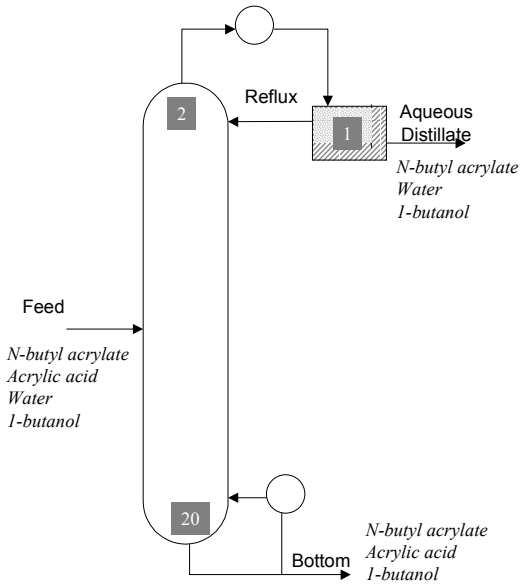


Figure 2: Colonne of butyl acrylate purification

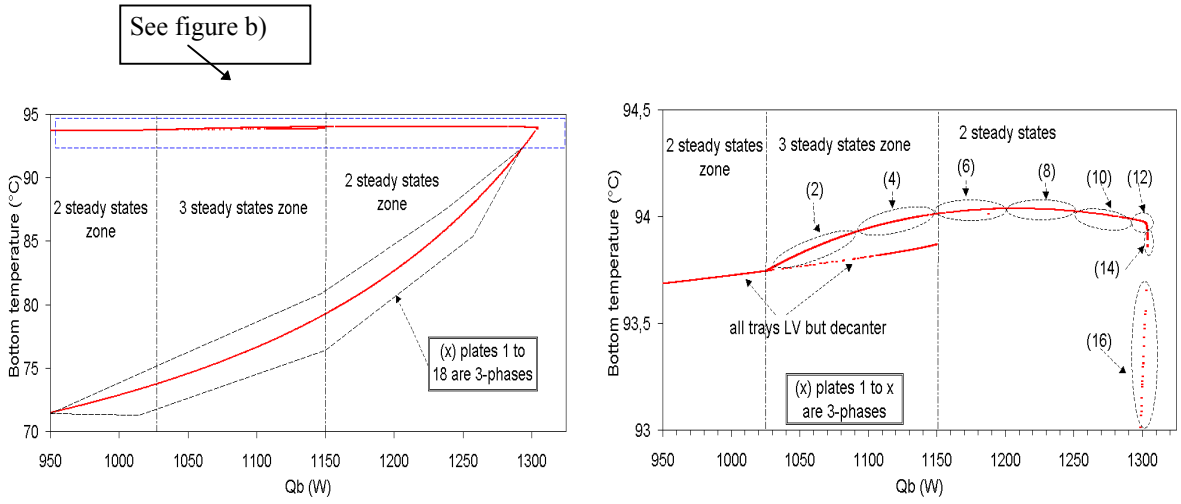
The NRTL thermodynamic model with extended temperature coefficients is chosen to describe the liquid liquid vapor equilibrium. Two proprietary industrial thermodynamic parameter sets are used, one for the mildly hot column where liquid phase split may occur, and one specifically fitted on liquid-liquid equilibrium data for the decanter. Its consistency was checked against experimental data available from the literature at 100 mmHg (BAUER and CHAPMAN, 1997) and 200 mmHg (RESHETV *et al.*, 1988). The thermodynamic phase diagram (not shown) displays a large type II demixion region for the BA-water-BuOH plane. Addition of acrylic acid reduces the demixion zone to complete disappearance above 70 w% acrylic acid. The ternary heteroazeotrope (~31w% BA, ~37w% water, ~32w% BuOH; 54.3°C[1]) boils first, followed by two binary heteroazeotropes (~48w% water, ~52w% BuOH; 55.4°C[1] and ~62w% BA, ~38w% water; 55.8°C[1]). Water is the next low-boiling component (~60°C[1]). A homoazeotrope (~15w% BA, ~85w% BuOH; 77.9°C[1]), BuOH (~78.2°C[1]), AA (~95.1°C[1]) and BA (95.9°C[1]) follow. The organic phase of the decanter is totally refluxed to the column while its aqueous phase is recovered as the distillate. This leaves a single degree of freedom for the case study analysis.

The case study is carried out using ProCase as follow. The operating parameter is the reboiler heat, Q_b. It was varied from 600W to 1500W. The step size is adjusted automatically by ProCase. Path detection is linked to changes in the overhead vapor flow rate value. Around 750W, 979W, 1278W, process simulations converged on new paths and were stored as such. For Q_b greater than 1303.38W, no simulation converged and ProCase stopped while storing the last point. Restarts were made from the singular points and allowed to obtain the operating paths described below.

[1] Computed values at P = 150 mmHg

Figure 3 displays the evolution of the bottom temperature as the boiler heat Q_b increases. Two or three steady states are detected over the Q_b range studied. In the literature, two multiple steady states have been proved by both experimentation and simulation for a similar distillation column dealing with the same 4-components mixture (BAUER and CHAPMAN, 1997) but with a different feed. In our case, for Q_b below 1025W, there exist two steady states. Path 1, the lower path on figure 3, is characterized by a low column temperature profile and by the presence of water in significant concentration on all trays as trays 1 to 18 host two liquid phases (aqueous and organic) and a vapor phase. Path 2 exhibits a high temperature profile in the column and only diphasic trays that restrain the presence of water to the top of the column. Notice that BAUER and CHAPMAN (1997) nicknamed their two experimental steady states by «aqueous» and «organic» to stress the presence/absence of water in most parts of their column. For $Q_b > 1025$ W a new path, path 3 appears (fig. 3.b)) featuring a liquid phase split on tray 2. The number of heterogeneous trays increases with Q_b increasing the water concentration further down the column. Path 1 and 3 join together at 1303.38W, defining a turn back point. Path 2 ends at 1148W and no simulations could be carried further on this path. We suspect that the ending branch of path 2 after the path splitting at 1025 W bears no physical meaning. As the process simulator solves the complete material and heat balances and has very tight convergence criteria ($<10^{-9}$), we are currently investigating elsewhere the reasons of its occurrence during our simulations.

The pinch point at 1303.38 W is characterized by the ternary heteroazeotrope BA-water-BuOH coming out of the column top and by all the trays but the reboiler experiencing a liquid demixion. In the process studied, the feed composition and flow rate are fixed. Therefore once the ternary heteroazeotrope composition and temperature are reached, the overhead vapor flow rate, the - organic phase only - reflux flow rate and composition values are limited by the material and energetic balances. These constraints are met at Q_b = 1303.38W. More heat would violate the equilibrium conditions that the process simulator postulates.



a) whole set of computed points b) zoom of the upper part of figure a)

Figure 3: Bottom temperature versus heat boiler flux Q_b.

CONCLUSION

A procedure, based on a case study analysis have been developed. An automatic adjustment of the parameter step, using a predictor-corrector type method, helps to track process operating paths and overcome convergence problems. This procedure gives multiple-states without guaranty of been exhaustive, but with a very simple use and few computational time, it manages to get physical multiple steady-states. Moreover, the connections between the steady states, operating paths, provides a lot of information suitable for process understanding. Some case studies have shown that it also eases convergence for numerically very unstable simulations. As a whole, this makes the developed procedure and the associated tool, ProCase, readily usable for the study of real industrial problems. We have shown on an example its capability to simulate the operation of an industrial process dedicated to the purification of n-butyl acrylate. Two physical steady states have been computed and linked to experimental ones published in the literature for a closely related process. A third steady state has also been computed. Its peculiar behavior questions its physical consistency and further work is under progress to investigate its occurrence.

NOTATIONS

A, B, C	Parameters of polynomial function
f	Reference output variable
Qb	Boiler heat
s	Curvilinear coordinate
u	Operating parameter

REFERENCES

BAUER W. and CHAPMAN J.T. Process for producing alkyl acrylate. *European Patent EP 0 779 268 A1*, 1997

KOVACH J. and W. SEIDER. Heterogeneous Azeotropic Distillation: - Homotopy-Continuation Methods. *AIChE J.*, 33, 593-605 (1987a).

KOVACH J. and W. SEIDER. Heterogeneous Azeotropic Distillation: Experimental and Simulation Results. *AIChE J.*, **33**, 1300-1314 (1987b).

LIEN K. and T. PERRIS. Industry and Academia Rebuilding the Partnership, *Comp. and Chem. Eng.*, **20** S1545-S1550 (1996).

MAGNUSSEN T., M. MICHELSEN and A. FREDENSLUND. Azeotropic Distillation Using UNIFAC. *Inst. Chem. Eng. Symp. Ser.*, **56**, (1), (1979).

MULLER D. and W. MARQUARDT, Experimental Verification of Multiple Steady States in Heterogeneous Azeotropic Distillation. *Ind. Eng. Chem. Res.*, **36** (12), 5410-5418 (1997).

RESHETV S.A., ZHVANETSKY I.B. *et al.*, *Zh. Prikl. Khim. (Leningrad)*, **67**, 97 (1988) cited in *Azeotropic Data*, Eds. GMEHLING J., MENKE J., KRAFTCZYK J. and K. FISCHER (1994)