STARTUP OPERATION OF A CYCLIC MIDDLE VESSEL BATCH DISTILLATION

S. Gruetzmann[1], G. Niggemann[1], Th. Kapala[2], and G. Fieg[1]
[1]Hamburg University of Technology, Institute of Process and Plant Engineering
Schwarzenbergstr. 95 C, 21073 Hamburg, Germany, E-mail: gruetzmann@tuhh.de
[2]Cognis Deutschland GmbH & Co.KG, 40551 Düsseldorf, Germany

Batch distillation is one of the most important unit operations for the small-scale production of specialty and fine chemicals. The so called Middle Vessel Batch Distillation (MVBD) with total reflux offers many advantages compared to conventional batch distillation. It is favourable due to the simultaneous production of three products of high purity. In this work, we present a thorough analysis of the startup of a MVBD column for the first time. The column is initially at ambient conditions. Therefore, we present an accurate dynamic model that includes the heating of the distillation column and peripheral equipment as well as the formation and propagation of the hydraulic and thermodynamic profiles. Finally, we compare two startup procedures on the basis of simulation studies. The results impressively point out that switching of important manipulated variables during startup can increase the process performance.

KEYWORDS: middle vessel batch distillation, startup procedures, total reflux, ambient conditions

INTRODUCTION

Batch distillation is a unit operation, which has arisen increasing interest in industry over the past decade. The reason is a significant change in the market from a quantity-oriented to a quality-oriented demand. It is favourable in the separation of multicomponent mixtures if the amount of feed is small and high purity products are demanded. Recent investigations focus on complex batch distillation columns, namely, the middle vessel column (*Barolo and Botteon 1997, Gruetzmann et al. 2006a*) and multivessel column (*Furlonge et al. 1999*, *Low et al. 2005*, *Skogestad et al. 1997*). The main difference between the conventional and complex batch distillation column is the installation of additional product vessels along the column. Then, the process unit consists of a reboiler, *n* product vessels, *n-1* column sections and a condenser. Figure 1 illustrates the principle structure of a MVBD.

The startup of distillation columns has been discussed in many publications in the open literature. A widely accepted model for the startup of continuous distillation columns has been proposed by *Ruiz et al. 1988*. There, the startup is subdivided into a discontinuous, semi-continuous and continuous period. Indeed, there is also a continuous period in the process of cyclic batch distillation when all state variables remain constant. However, experimental studies by *Gruetzmann et al. 2005* recently indicate that the deliberate

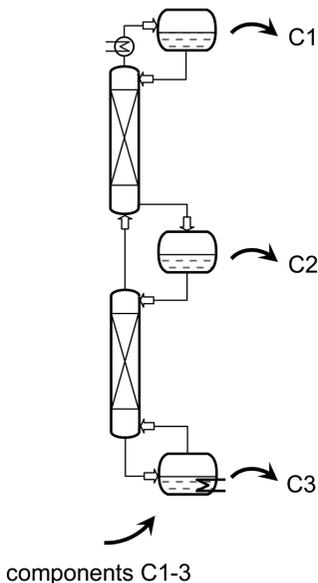Dedicated to Prof. Dr.-Ing. W. Roetzel on the occasion of the 70th anniversary of his birthday.

Figure 1. Middle vessel batch distillation

switching of discrete decision variables (e.g. reflux flow) can lead to a shorter startup period. In terms of optimisation, a focus on the first and second period, where hydraulic and thermodynamic profiles are formulated, is reasonable. Large changes in the state variables indicate these periods.

A detailed analysis of the startup phase has been considered only in few cases (e.g. *Wang et al. 2003*, *Elgue et al. 2004*). To the best of our knowledge no publication deals with the analysis and optimisation of a complex batch distillation column taking the startup phase into account. Therefore, the objective of this contribution is twofold. Firstly, we present a mathematical model that is capable of handling the physical phenomena occurring during the startup of a complex batch distillation column. Secondly, we analyse the startup of a middle vessel batch distillation and compare two startup procedures. The simulation results emphasize the necessity of the sophisticated model.

MATHEMATICAL MODEL
In this section, the complex rigorous dynamic model will be partially presented. The entire differential-algebraic set of equations for a theoretical stage can be found in the appendix. The process model has been implemented in the modelling and simulation software Aspen Custom Modeler. The dynamic modelling of the startup behaviour of distillation columns from ambient conditions is a very challenging task due to the discrete-continuous

character of the process. Besides the usual description of a distillation column, the process model has to consider the variable vapour flow, heat accumulation of the column wall and the column internals, variable liquid flow and non-adiabatic operation additionally. However, some reasonable assumptions, such as neglecting vapour holdup, have been made. The high stiffness and discrete state transitions result in numerical problems. For each process unit an elaborate DAE system of form

$$\dot{x} = g(x, u) \tag{1}$$

$$0 = f(x, u) \tag{2}$$

has been developed to overcome these problems, where x and u denote the time-variant process variables, t the process time and g, f non-linear algebraic functions. Specific techniques have been used to model the discrete transitions shown in the Petri-net representation of the tray hydraulics (Figure 2).

At the initial state (stage 0) the column is at ambient conditions. Thus, tray j is empty and no stream enters or leaves the tray. During stage 1 a vapour stream V_{j+1} enters the empty tray. With the vapour condensing at the column wall and internals, the tray is filled up to its maximum liquid holdup HU_{max}. Heat losses over the column wall and accumulation have been considered in the energy balance. HU_{max} can be optionally calculated by various correlations from the open literature (*Engel et al. 2001*, *Mackowiak 2003*) or set constant. However, simulation studies reveal, that an *a priori* calculation of the maximum holdup can improve the simulation robustness with no loss of accuracy. If the liquid holdup HU_j exceeds the maximum holdup, a liquid stream L_j flows down the column during stage 2. The rising vapour stream still heats up the tray until the liquid reaches boiling temperature. In this stage, a vapour-liquid equilibrium is calculated, following equation 3

$$y_{i, j} = K \cdot x_{i, j}, \tag{3}$$

with y_i and x_i as molar vapour fraction and molar liquid fraction, respectively. K denotes the equilibrium constant that is called from Aspen Properties depending on the chosen
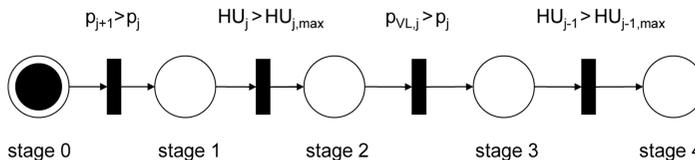

Figure 2. Petri-net representation of the tray hydraulics

physical equilibrium method. If the vapour pressure $p_{VL,j}$ is larger than the pressure on the tray p_j, a vapour outlet stream V_j is computed.

$$V_j = const \cdot \frac{p_j^{VL} - p_j}{p_j} \ \text{if} \ p_j^{VL} > p_j \tag{4}$$

This indicates the beginning of stage 3. During stage 4, liquid from the upper tray flows downwards (L_{j-1}). Simulation results have clearly shown the physical consistency of the model. The validity of the model has been proven by comparison with experiments and has been presented by *Gruetzmann et al. 2006b*. The overall complex batch distillation model includes the reboiler, packing sections, a total condenser with adjustable subcooling, the reflux drum, the middle vessel and optional liquid accumulators and distributors. Control models are provided by the software tool and can be easily added to the model. Implicit Euler's method with variable step size and Newton's method has been used to solve the DAE system. Explicit numerical solvers are not appropriate as to little step size is required in order to guarantee stability.

STARTUP PROCEDURE

To accentuate the need for the proposed model, two simulation studies are presented in the next chapter. We observe the startup of the regular procedure and a modified one. Initially, the propagation of the temperature profile is used to characterise the process. It can be divided into three parts. Then, a modified startup procedure that is based on simple temperature measurements is introduced and compared to the regular one.

Within the simulations, the separation of a ternary mixture of hexanol, octanol and decanol has been investigated. The feed is rich in the middle boiling component octanol, which is a typical task in industry. The components show a nearly ideal thermodynamic behaviour. The easy separation (relative volatilities > 4) is performed under vacuum, while the mass fraction w_i of the key components in the three product vessels has been subject to tight conditions, that is, $w_i \geq 0.99 \ \forall \ i \ \in \{C1,C2,C3\}$. The most important simulation parameters are reported in Table 1.

Table 1. Simulation parameters of the middle vessel batch column

Process parameter	Unit	Value
number of theoretical stages	–	2×8
reboiler duty	W	750
feed amount	kg	5
feed composition	wt%	{15;70;15}
pressure (top)	kPa	1.5
pressure drop (overall)	kPa	0.37

The levels in the distillate receiver and middle vessel have been controlled by PI controllers using the liquid holdup in the product vessels. The controller parameters have been adjusted in a way that a smooth operation has been assured. In all simulations, only heating of the column wall and internals has been taken into consideration. As a first approach, the heat losses have been set to zero.

Figure 3 shows the temperature profile at various time points in the range between startup and steady state. The process can be subdivided into three parts. At the beginning of the first part (Figure 3a), the column is at ambient conditions, that is, it is cold and trays are empty. The vapour heats up the column and reaches the head after 45min. Of course, no stable wave that could be described mathematically has been formed so far. Condensed liquid is afterwards accumulated in the distillate receiver. While the least volatile component exhales from the reboiler, the middle boiler reaches the condenser, too, with the result that the temperature profile raises further (Figure 3b). The upper set point (liquid holdup in the distillate receiver) is reached after 57min. The reflux valve is
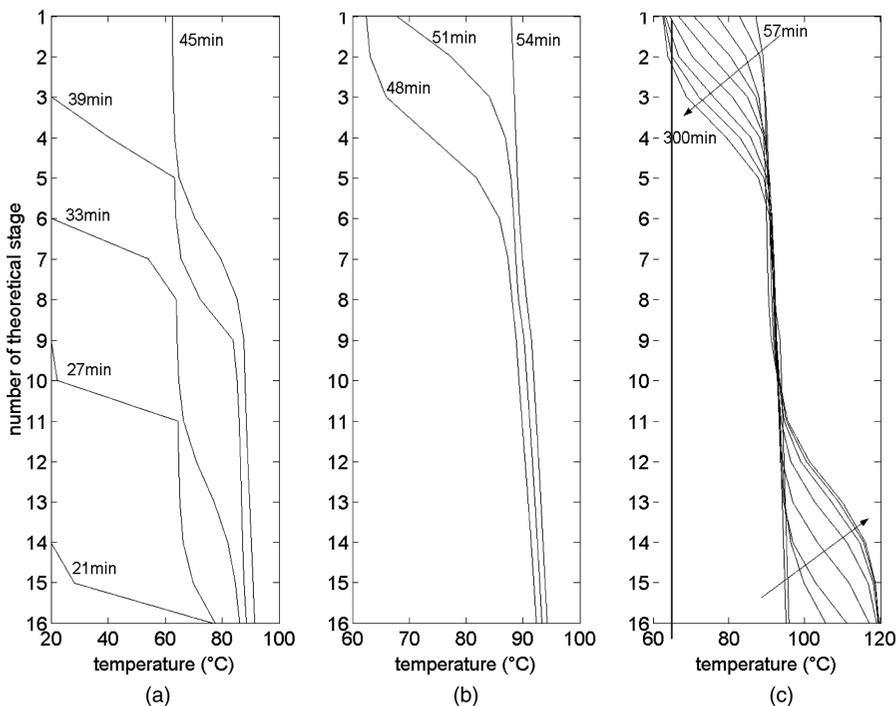

Figure 3. Propagation of the temperature profile during startup, divided into three parts (numbering from the top to the bottom)

opened and liquid fills the theoretical stages. Figure 3c clearly shows the starting separation effect and the formation of a steady state profile after 300 min. Although, the first two parts of the process are very short compared to the third one, it is obvious that the first important control actions take place during part two. Consequently, the development of new startup procedures is only possible with an accurate mathematical model.

Former experimental results presented by *Gruetzmann et al. 2005* have indicated the opportunity to accelerate the process of a MVBD with total reflux applying the so called MT-algorithm. The startup procedure is based on simple temperature measurements. Denoting T^* as measured temperature at time t^* and T^{ss} as temperature at steady state, one can compute the *MT* value of a column section (stages 1 to n) as the sum of absolute values of temperature differences:

$$MT = \sum_{j=1}^{n} \left| T_j^* - T_j^{ss} \right| \tag{5}$$

Following the algorithm, total reflux from the distillate receiver is activated when the *MT* value reaches a characteristic minimum for the first time. In our simulation studies the *MT* value has been computed using the temperatures in the upper column section. Previous simulations have shown that the minimum appears before the holdup in the distillate receiver reaches the nominal liquid holdup. However, one has to accumulate a specific amount of liquid in the product tanks, which is obviously not possible with total reflux. Therefore, only the minimum amount of liquid has been sent back to the column. The reflux has been determined computing the minimum liquid load of approximately 0.5 m^3/m^2h to guarantee packing separation performance. The upper level controller and total reflux is activated when the set point is reached. The second (middle) product tank is filled without any specific algorithm and the reflux valve is opened when the nominal liquid level is attained. The comparison of the two startup procedures is illustrated in Figure 4.

In Figure 4d, the progress of the *MT* value is shown. The switching action of the modified procedure takes place after 48 min, which is during the second part referring to Figure 3b. Figure 4a-c show the progress of the key component mass fractions in the distillate vessel (a), the middle vessel (b) and the reboiler (c). In all cases, the modified process is faster than the regular process. This is due to the early activation of the reflux avoiding that middle boiler impurifies the distillate product. The simulation results impressively show that an optimisation of the process is possible by means of exact dynamic simulation of the physical phenomena during startup.

CONCLUSION

The contribution deals with the startup operation of a middle vessel batch distillation column. The column is initially at ambient conditions, that is, the column wall and the column internals are cold and no liquid is on the trays. Describing the startup operation
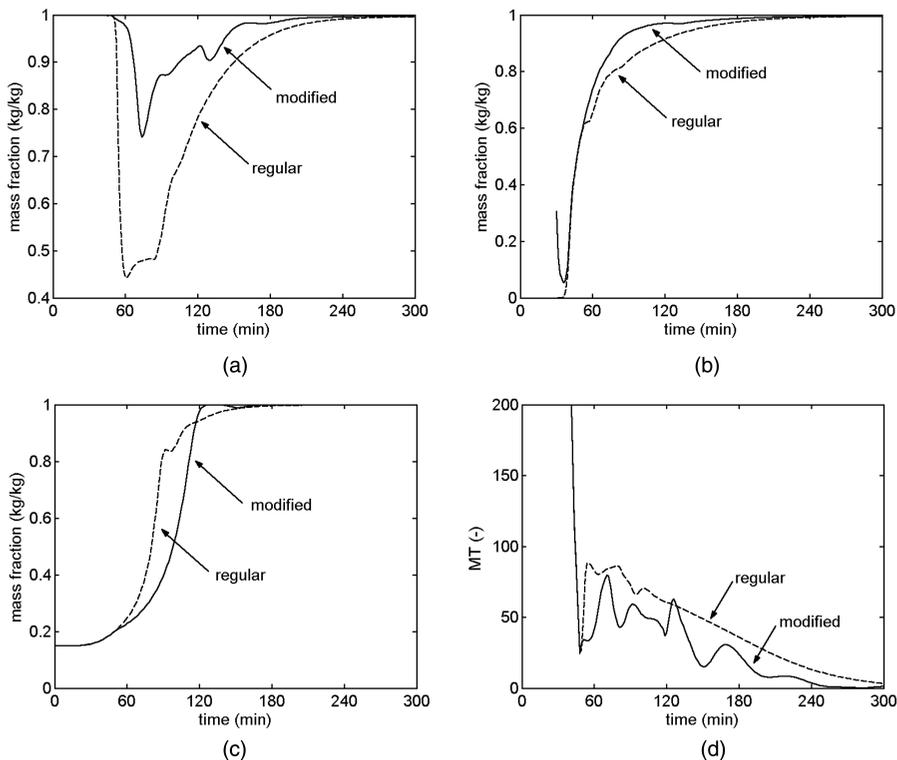
Figure 4. Comparison of the regular (dashed line) and the modified (solid line) startup procedure

theoretically, a structured rigorous dynamic model has been set up and presented. The model is capable of dealing with the discrete-continuous characteristics of the process during the heating and filling of the column. A physical consistency check has been performed successfully and comparison of simulation results and experimental data has revealed a very good agreement. The necessity of the developed model is illustrated presenting and comparing two startup procedures. The simulation results reveal some new optimisation approaches that are focus of further investigations.

ACKNOWLEDGMENTS

REFERENCES

M. Barolo, F. Botteon, 1997, A Simple Method of Obtaining Pure Products by Batch Distillation, AIChE J., 43, 10, 2601-2604

S. Elgue, L. Prat, M. Cabassud, J.M. Le Lann, J. C'ezerac, 2004, Dynamic Models for Start-up Operations of Batch Distillation Columns with Experimental Validation, Comp. Chem. Eng., 28, 2735-2747

V. Engel, J. Stichlmair, W. Geipel, 2001, Fluiddynamics of packings for gas-liquid-contactors, Chem. Eng. Techn., 24(5), 549-462

H.I. Furlonge, C.C. Pantelides, E. Sørensen, 1999, Optimal Operation of Multivessel Batch Distillation Columns, AIChE J., 45, 4, 781-801

K.H. Low, E. Sørensen, 2005, Simultaneous Optimal Configuration, Design and Operation of Batch Distillation, AIChE J., 581, 6, 1700-1713

J. Mackowiak, Fluiddynamik von Füllkörpern und Packungen, 2003, Springer Verlag, Berlin Heidelberg

S. Gruetzmann, M. Temprano, G. Fieg, Th. Kapala, 2005, Führungskonzepte zur Minimierung der Prozessdauer der zyklischen Batch-Rektifikation, Chem. Ing. Techn., 77, 8, 1101-1102

S. Gruetzmann, G. Fieg, Th. Kapala, 2006a, Theoretical Analysis and Operating Behaviour of a Middle Vessel Batch Distillation with Cyclic Operation, Chem. Eng. Process., 45, 1, 46-54

S. Gruetzmann, Th. Kapala, G. Fieg, 2006b, Dynamic Modeling of Complex Batch Distillation Starting from Ambient Conditions, ESCAPE-16, accepted

C.A. Ruiz, I.T. Cameron, R. Gani, 1988, A Generalized Dynamic Model for Distillation Columns - III. Study of Startup Operations, Comp. Chem. Eng., 12, 1-14

S. Skogestad, B. Wittgens, R. Litto, E. Sørensen, 1997, Multivessel Batch Distillation, AIChE J., 43, 4, 971-978

L. Wang, P. Li, G. Wozny, S. Wang, 2003, A Startup Model for Simulation of Batch Distillation Starting from a Cold State, Comp. Chem. Eng., 1485-1497

APPENDIX

In this section, the mathematical model that have been used is presented for a theoretical stage. Similar DAE systems have been set up to describe the reboiler, the condenser, the distillate receiver and the middle vessel. Optional modules have been provided to describe the behaviour of liquid accumulators and distributors. The index i denotes the components and j the theoretical stages, numbering from the top to the bottom. The heat capacity of the column wall and the internals is considered by the heat capacity-flowrate (mc_p) with indices *internals* and *wall*, respectively.

Overall mass balance:

$$\frac{dHU_j}{dt} = L_{j-1} + V_{j+1} - L_j - V_j \tag{1}$$

Component mass balance:

$$\frac{d(HU_j x_{i,j})}{dt} = L_{j-1} x_{i,j-1} + V_{j+1} y_{i,j+1} - L_j x_{i,j} - V_j y_{i,j} \tag{2}$$

SYMPOSIUM SERIES NO. 152 © 2006 IChemE

Energy balance:

$$\frac{d(HU_j h_j^{liq})}{dt} + \frac{d(mc_p T)_{j,\,internals}}{dt} + \frac{d(mc_p T_m)_{j,\,walls}}{dt} = L_{j-1} h_{j-1}^{liq} + V_{j+1} h_{j-1}^{vap}$$
$$- L_j h_i^{liq} - V_j h_j^{vap} - Q_{j,\,loss} \tag{3}$$

with

$$T_{j,\,m} = \frac{T_j + T_{ambient}}{2}, \tag{4}$$

where $T_{j,m}$ is called the average temperature of the wall.

Summation equation:

$$\sum_i y_{i,\,j} = 1 \tag{5}$$

Vapour-liquid equilibrium:

$$y_{i,\,j} = K_i x_{i,\,j} \tag{6}$$

Pressure model:

$$p_j = p_{j-1} + \Delta p_j = f(\text{geometry, physical properties, tray hydraulics}) \tag{7}$$

Holdup model:

$$HU_{j,\,max} = f(\text{geometry, physical properties, tray hydraulics}) \tag{8}$$

Heat losses:

$$Q_{j,loss} = kA(T_j - T_{ambient}) \tag{9}$$

with A as surface of the column shell.