

# Design of Operation Policies for Batch Distillation

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**Abstract:** The batch distillation process is briefly reviewed. Control variables, operating decisions and objectives are identified. Modeling aspects are discussed and a suitable representation for operations is introduced. Techniques for the dynamic simulation and optimization of the operation are reviewed, in particular the control vector parameterization method. Optimization formulations and results are presented for typical problems: optimization of a single distillation step, distillation with recycle of off-cuts, multiperiod optimization, reactive batch distillation and the online optimization of a sequence of batches in a campaign. Outstanding research issues are identified.

**Keywords:** Batch Distillation, Modeling, Operation, Dynamic Simulation, Optimization, Optimal Control.

## Introduction

Batch distillation is perhaps one of the oldest unit operations. It was discovered by many ancient cultures as a way to produce alcoholic beverages, essential oils and perfume, and its basic operation had been perfected long before the advent of phase equilibrium thermodynamics, let alone of computer technology. Today, batch distillation is widely used in the production of fine chemicals and for specialized productions and is the most frequent separation method in batch processes [49]. Its main advantages are the ability of separating several fractions of a feed mixture in a single column and of processing several mixtures in the same column. When coupled with reaction, batch distillation of one or more products permits achieving much higher conversions than otherwise possible.

Although distillation is one of the most intensely studied and better understood processes in the chemical industry, its batch version still represents an interesting field for academic and industrial research, for a variety of reasons: i) even for a simple binary mixture there are many

alternative operations possible, with complex trade-offs as a result of the many degrees of freedom available, hence there is ample scope for optimization ii) the process is intrinsically dynamic, hence its optimization naturally results in an optimal control problem, for which problem formulations and numerical solution techniques are not yet well established. However, advances made both in dynamic optimization techniques and computing speeds make it possible to consider rather more complex operation policies iii) advances in plant control make it now feasible to implement much more sophisticated control policies that was possible with earlier control technology and hence to achieve in practice any potential benefits predicted iv) finally, batch distillation is also of interest as merely an excellent representative example of a whole class of complex dynamic optimization problems.

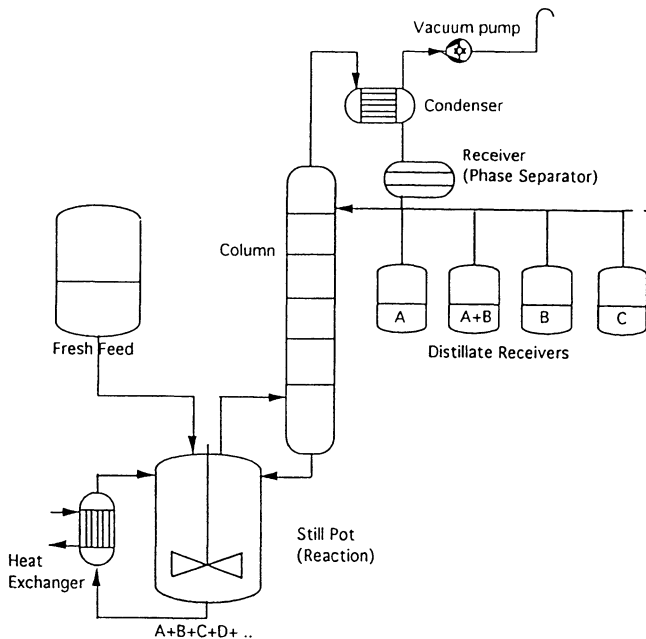
The purposes of this paper are i) to summarize some recent advances in the development of optimal operation policies for a variety of batch distillation applications and ii) to highlight some research issues which are still outstanding. Although, there are obvious interactions between a batch column design and its operation [52], in the following coverage it will be assumed that the column design is given a priori and that an adequate dynamic model (including thermodynamic and physical properties) has been developed. Attention will be focused on the problem of establishing a priori the optimal values and time profiles of the variables controlling the operation for a given feed mixture. It is assumed that a suitable control system can be separately designed later for accurately tracking the optimal profiles predicted. It is in this sense that we talk of "design of operation policies". The control approach, of establishing the optimal policies on-line in conjunction with a state estimator, to take into account model mismatch and disturbances, will not be considered here. Finally, we will concentrate mainly on the optimal operation of a single batch, rather than of an entire campaign.

The paper is structured as follows: first, a brief reminder is given of the batch distillation process and of the main control and operation decision choices available. Some representation and modeling aspects are considered next, followed by simulation issues and optimization issues. Finally, a set of illustrative examples are given for the optimization of typical batch distillation problems involving single and multiple distillation steps, the optimization of off-cut recycles, of a whole batch and of reactive batch distillation. An example is also given of the use of the above techniques in conjunction with an on-line control system, for the automation of a batch campaign. Many of the examples summarized here have been presented in detail elsewhere. Suitable references are given in the main body of the paper.

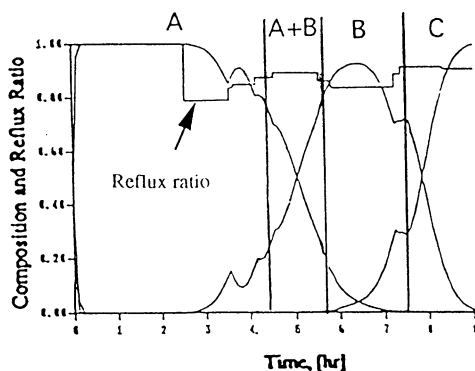
## The Process - A Brief Review

### The Batch Distillation Process

The basic *operation* for processing of a charge in a batch column (a *batch*) is illustrated with reference to the *equipment* in Figure 1 (a general introduction is given in [79]). A quantity of fresh feed is *charged* (typically cold) into a still pot and *heated* to its boiling point. The column is brought to the right pressure and temperature during an initial *startup period*, often carried out at total reflux, during which a liquid holdup builds up in the top condensate receiver and internally in the column. Initial pressure, flow, temperature and composition profiles are established. A *production period* follows when distillate is withdrawn and collected in one or more fractions or "cuts". The order of appearance of species in the distillate is determined by the phase equilibria characteristics of the mixture to be separated (for simple distillation, the composition profiles will follow well defined distillation curves [84, 9]. A typical instant distillate composition profile is given in Figure 2. The distillate is initially rich in the lowest boiling component (or azeotropic mixture), which is then progressively depleted. It then becomes richer in the next lowest boiling



**Figure 1.** Typical Configuration of a Conventional Batch Distillation Column



**Figure 2.** Typical Distillate Composition (mole fraction) Profiles vs. Time, with Fractions Collected

component, etc. Diverting the distillate flow to different receivers permits collecting distillate product cuts meeting desired purity specifications. Intermediate cuts ("off cuts" or "slop cuts") may also be collected which will typically contain material not meeting purity specifications. The operation is completed by a brief *shut down* period, when the heat supply to the reboiler is terminated and the liquid holdups in the column collapse to the bottom. The heavy fraction remaining in the pot may be one of the desired products. Valuable constituents in the offcuts may be recovered by reprocessing the offcut fractions in variety of ways. The column is then prepared for the next batch. Several variations of the basic process are possible. Additional material may be charged to the pot during the batch. Reaction may occur in the pot, or sometimes in the entire column. Esterification reactions are often conducted this way [21, 20, 6]. Vacuum may be applied to facilitate separation and keep boiling temperatures low, so as to avoid thermal degradation problems. Two liquid phases may be present in the distillate, in which case the condensate receiver has the function of a two phase separator. In some cases, the fresh feed is charged to an enlarged condenser reflux drum which thus acts as the pot and the column is used in a stripping mode (inverted column), with high boiling products withdrawn from the bottom, as described by Robinson and Gilliland [77]. Alternative configurations involving feeding the fresh feed in the middle of the column (which therefore has both stripping and a rectifying sections) were also mentioned by [11, 2, 41]. In this paper, attention will be concentrated on the conventional batch distillation system (Figure 1) since the techniques discussed are broadly applicable to those alternative configurations with only minor extensions.

## Operation Objectives

The purpose of batch distillation is typically to produce selected product fractions having desired specifications. For each product, these specifications are expressed in terms of the mole fraction of a key component meeting or exceeding a specified value. Additionally, the mole fraction of one or more other species (individually or cumulatively) in some fractions should often not exceed specified values. These quality specifications are therefore naturally expressed as (hard) inequality constraints.

Additionally, it is typically of interest to maximize the recovery of (the most) valuable species, to minimize energy requirements and to minimize the time required for all operations (not just for fresh feed batches, but also for reprocessing off-cuts, if any). Each of these quantities (recoveries, energy requirements, time) may also have defined upper and/or lower limits. Clearly, there may be conflicting requirements. We may observe that rather than posing a multiobjective optimization problem, it is much easier to select just one of the desired quantities as the objective function and define the others as constraints (e.g. maximize recovery subject to purity, time and energy limits). In fact, the easiest way to combine multiple objectives is to formulate an overall economic objective function which properly weighs all factors of interest in common, in well understood monetary terms.

## Operation Variables and Trade-offs

The maximum vapor boilup and condensate rate that can be produced for a given feed mixture and the liquid holdups in the column are essentially established by the column design characteristics, fixed a priori (column diameter, number of equilibrium stages and column internals, pot, reboiler and condenser type and geometry). For a given charge, the main operation variables available for control are the reflux ratio, the heating medium flow rate (or energy input to the reboiler or vapor boilup rate, varied by means of the energy input to the reboiler), the column top pressure and the times during which distillate is collected in each of the different distillate receivers. Specifying all these variables determines the amount and composition of each of the fraction collected (hence recoveries) and other performance measures (e.g. total time, energy used, etc.). A number of trade-offs must be considered.

Increasing *reflux ratio* will increase the instant distillate purity, giving a smaller distillate flow rate and thus requiring longer time to produce a given amount of distillate, with higher energy

requirements for reboiler and condenser. On the other hand, a larger amount of distillate meeting given purity specifications may be collected this way. Productivity (in terms of the amount of distillate produced over the batch time) may go down as well as up with increasing reflux ratio, presenting an interesting optimization problem. A useful upper bound for the top distillate composition achievable at any one time is given by the total reflux operation.

Traditionally, *constant reflux ratio* (on grounds of simplicity of application) and *constant distillate purity* (requiring progressively increasing reflux ratio) have been considered. In order to achieve a given final composition in a specific accumulated distillate fraction, initially richer distillate may be mixed with lower quality distillate near the end of the production cut. This is obtained with the constant reflux policy. Thermodynamic considerations suggest that any mixing is a source of irreversibility and hence will have to be paid for somehow, providing a justification for the constant distillate composition operation. This argument however ignores the relative costs of product, column time and energy. In general, some intermediate reflux ratio policy will be optimal. Other reflux ratio strategies have been used in practice, for example one characterized by alternating total reflux (no distillate) and distillate product withdrawal (no reflux) [5].

With regards to the *vapor boilup rate*, it is usually optimal to operate at the highest possible energy input, except when hydraulic considerations become limiting (entrainment). When hydraulics is not considered (at one's own risk), the optimal policy can thus be established a priori.

A constant (top) *pressure* level is often selected once for the entire batch distillation, or different but constant pressure levels, if necessary, may be used during each production cut. Pressure may be decreased as the batch progresses as a way to maintain the boiling point in the pot below or at a given limit for heat labile mixtures or to increase relative volatility for difficult separations.

The choice of the *timing for each production cut* is important. With reference to Figure 2, two rather obvious points may be noted. First, it is possible to achieve a high purity specification on one component in an individual fraction by choosing its beginning and end time so as to remove the lower purity front and tail, respectively, in the previous and in the subsequent cut. This, however, may make achieving any specifications on the earlier and subsequent cuts much harder and even impossible. Thus, the operations of all cuts are interacting rather strongly. Second, as already observed, it is possible to eliminate fronts and tails of undesired components as off-cut fractions. This however will affect recoveries and will make offcut reprocessing important.

With respect to the *offcuts*, several choices are available. A fraction not meeting product

specifications may be simply a waste (with associated loss of material and possibly a disposal cost) or it may be a lower quality by-product, with some residual value. Offcuts may also be reprocessed. Here, several alternatives are possible. The simplest strategy is to collect all off-cuts produced during one batch in a single distillate receiver and then add the entire amount to the pot, together with fresh feed, to make up the next charge. This will increase recovery of valuable species, at the expense of a reduction in the amount of fresh feed that can be processed in each batch, leading again to an interesting trade-off [51]. For each offcut, the reflux ratio profile used and the duration of the off-cut production step (hence, the amount and composition of the accumulated offcut) must be defined. The addition of the offcuts from one batch to the pot may be done either at the beginning of or during the subsequent batch, the time of addition representing one further degree of operational freedom. The second principle of thermodynamics gives us again useful indications. Since mixing is accompanied by irreversibility, the addition of an offcut to the pot should be done when the compositions of the two are closest. This also suggests an altogether different reprocessing policy, whereby distinct off-cut fractions from a batch charge are not mixed in the same distillate receiver, but rather collected in separate receivers (assuming sufficient storage capacity is available). Each off-cut fraction can then be individually recycled to the pot at different times during the next batch. In fact, re-mixing of fractions already separated can also be reduced if the same off-cut material produced in successive batches is collected (in a much larger distillate storage) and then reprocessed later as one or more batches, with the full charge made up by the stored off-cut [59, 73]. This strategy is motivated by the fact that each off-cut is typically rich in just a couple of components, and hence their separation can be much easier this way. In practice, the choice of a reprocessing policy will depend on the number and capacity of storage vessels.

It may also be noted that unlike its continuous counterpart, a batch distillation column can give a very high separation even with few separation stages. If a desired purity cannot be achieved in one distillation pass, an intermediate distillate off-cut can be collected and distilled a second (and third, etc.) time.

In summary, we may identify two types of operation choices to be made. Some choices define the *structure* of the operation (the sequence of products to be collected, whether to produce intermediate cuts or not, whether to reprocess off-cut fractions immediately or store them for subsequent distillation, whether to collect off-cuts in a single vessel, thereby re-mixing material already separated, or to store them individually in distinct vessels. These are *discrete* (yes/no) decisions. For a specific instance of these decisions (which we will call an *operation strategy*),

there are continuous decision variables, the main ones being the reflux ratio profiles and the duration of each processing step, with possibly pressure and vapor boilup rate as additional control variables.

Even for simple binary mixtures, there are clearly many possible operation strategies. With multicomponent mixtures, the number of such structural options increases dramatically. For each strategy, the (time dependent and time independent) continuous control variables are highly interrelated. Selecting the best operation thus presents a rather formidable problem, the solution of which clearly requires a systematic approach. Formally, the overall problem could be posed as a mixed integer nonlinear dynamic process optimization problem (MINDPOP), with a general economic objective function and all structural and continuous operation variables to be optimized simultaneously. So far, however, only very much simpler subsets of this problem have been reported. The operation strategy is typically fixed a priori, and just (some) continuous operation variables are optimized. This approach will be followed in this paper as well. Fixed structure operations for which optimization solutions have been proposed include the already mentioned minimum time problem (P1), maximum distillate problem (P2), and maximum profit problem (P3) (Table 1).

**Table 1.** Selected References on a priori Control Profile Optimization-Conventional Batch Distillation Columns

Reference	Column Model	Mixture	Phase Equilibria	Optimisation Problem
Converse & Gross (1963)	Simple	Binary	CRV	P2
Converse & Huber (1965)	"	"	"	"
Coward (1967)	"	"	"	P1
Robinson (1969)	"	"	"	"
Robinson (1970)	"	Multicomponent	"	"
Mayur and Jackson (1971)	"	"	"	"
Kerkhof and Vissers (1978)	"	Binary	"	P3
Murty et al. (1980)	"	"	"	P2
Hansen and Jorgensen (1986)	"	"	"	P1
Diwekar et al. (1987)	Simple <sup>1</sup>	Multicomponent	"	P2
Mujtaba (1989)	Rigorous	"	Rigorous	P1/P2/P3
Fahrat et al. (1990)	Simple <sup>3</sup>	"	Simple	P2-multiperiod
Mujtaba and Macchietto (1991)	"	Binary	Rigorous	P1
Diwekar and Madhavan (1991)	"	"	"	P3
Logsdon & Biegler (1992)	Simple <sup>1</sup>	"	CRV	P2
Jang (1992)	Rigorous	Multicomponent	Rigorous	P1/P2
Diwekar (1992)	Simple <sup>2</sup>	"	CRV	P1/P2/P3
Mujtaba and Macchietto (1992b)	Rigorous	"	Rigorous	P3-multiperiod

CRV = Constant Relative Volatility. 1 - short-cut model of continuous distillation. 2 - same as 1 but modified for column holdup and tuned for nonideality. 3.- short-cut model, no holdups.



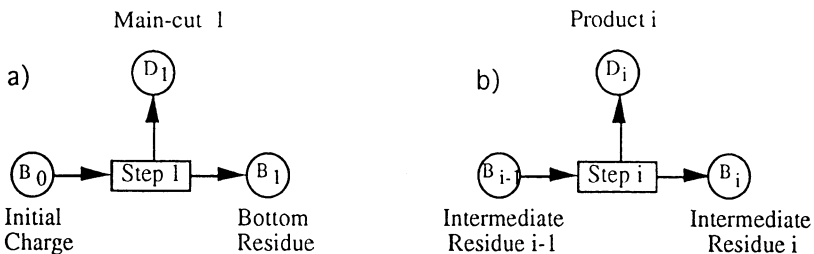
## Benefits

That improved performance batch distillation should be achieved by clever manipulation of the available operation parameters (relatively to simpler, constant control) is intuitively appealing. However, reviews of previous optimization studies have indicated that benefits are often small [78]. This argument has been used to dismiss the need for sophisticated operation policies. On the other hand, these results were often obtained using highly simplified models and optimization techniques, a limited subset of alternative policies (constant distillate composition vs. constant reflux ratio) and objective functions only indirectly related to economic performance. Different benefits are calculated with different objective functions. Kerchief and Vassar [46], for example, showed that small increases in distillate *yield* (order 5%) can translate into 20–40% higher profit. This clearly calls for more comprehensive consideration of operating choices, dynamic models, objective functions, and constraints.

## Representation and Modeling Issues

### Representation

There is a need to formalize the description of the operating procedures. It may be convenient to consider a batch distillation operation as composed by a series of steps, each terminated by a significant event (e.g. completion of a production cut and switch to a different distillate receiver). Following [64] the main structural aspects of a batch distillation operation are schematically represented here as a State Task Network (STN) where a state (denoted by a circle) represents a specified material, and a task (rectangular box) represents the operation (task) which transforms

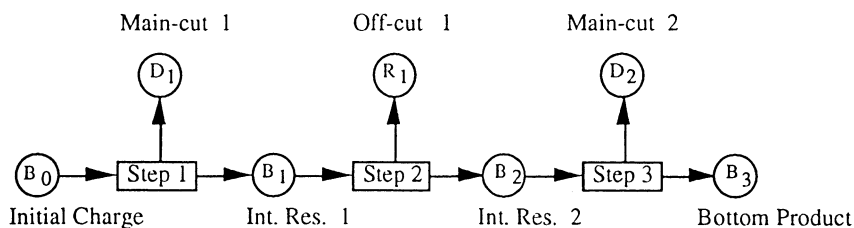


**Figure 3.** a) State Task network for a Simple Batch Distillation Operation Producing Two Fractions  
b) Basic Operation Module for Separation into One Distillate and One Residue Fractions

the input state(s) into the output state(s). A task may consist of one or more steps. For example, Figure 3 shows a simple batch distillation operation with one task (Step 1) producing the two fractions Main-cut 1 and Bottom Residue from the state Initial Charge.

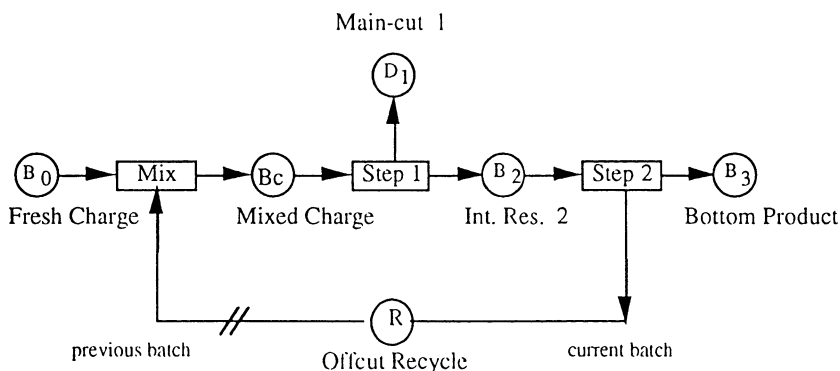
States are characterized by a name an amount and a composition vector for the mixture in that state. Tasks are characterized by an associated dynamic model and operational attributes such as duration the time profiles of reflux ratio and other control variables used during the task etc. Additional attributes of a distillation task are the values of all variables in the dynamic model at the beginning and at the end of the step. The states in the STN representation should not be confused with any state variables present in the dynamic model. For example, in Figure 1 the overall amount and composition ( $B_0$  and  $x_{B0}$  respectively) of the Initial Charge STN state are distinct from the initial pot holdup and composition. The latter may be assigned the same numerical value as the former (a specific model initialization procedure). It is also possible for simulation and optimization purposes to neglect the startup period altogether and initialize the distillation task Step 1 by assuming that some portion of the charge is initially distributed along the column or that the initial column profiles (holdups composition etc.) are those obtained at total reflux (two other distinct initialization procedures). Of course, whatever initialization procedure is used the initial column profiles must be consistent (i.e. mass balance) with the amount and composition of the Initial Charge state in the STN. The initialization procedure is therefore a mapping between the STN states and the initial states in the dynamic model for that task. Similarly the amount and composition  $B_1$  and  $x_{B1}$  of the STN state Bottom Residue are not the holdup and composition of the reboiler at the end of Step 1 but those which are obtained if all holdups in the column at the end of Step 1 are collected as the Bottom Residue STN state. The STN representation originally proposed in. [45] for scheduling is extended by the use of a dynamic model for a task in the place of a simple fixed time split fraction model.

The advantages of the above representation are: makes the structure of the operation quite explicit ii) it enables writing overall mass balances around an individual task (or a sequence of tasks) iii) suitable definition of selected subsets of states and task attributes make it possible to easily define a mix of dynamic simulation and optimization problems for a given operation strategy (STN structure) iv) different initialization procedures or even model equations may be defined for different tasks v) it enables the easy definition of alternative operation strategies by adjoining a small set of basic task modules used as building blocks. As an example the batch distillation of a multicomponent mixture is represented in Figure 4 as the combination of 2 main distillate and 1



**Figure 4.** STN for Batch Distillation Operation with Two Main Distillate Cuts and One Intermediate Off-cut

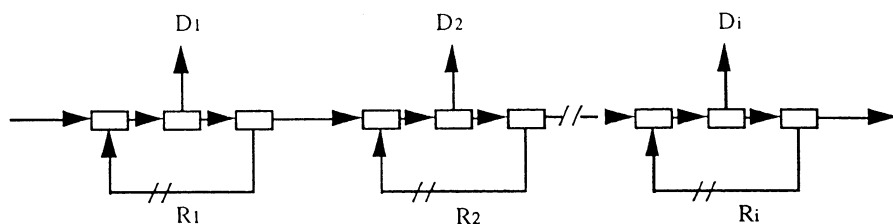
off-cut production steps each of these steps being represented by essentially the same generic "module" given in Figure 3b. Similarly, an operation is shown in Figure 5 consisting of a distillate product cut (Step 1) followed by an off-cut production step (Step 2). The off-cut produced in a batch (state Off-cut Recycle of amount  $R$  and composition  $X_R$ ) is recycled by mixing it in the pot residue with the next batch immediately before performing the main cut step to give an overall mixed charge amount  $B_c$  (of composition  $x_{BC}$ ). This operation (with states and tasks suitably indexed as in Figure 3b.) can be used as a building block to define for example the cyclic batch operation strategy for a multicomponent mixture defined in Figure 6 (states omitted) [63].



**Figure 5.** Basic Module for Separation Operation into One Distillate and One Residue Fractions, with Recycle of an Intermediate Off-cut to the next Batch

## Modeling

Distillation modeling issues have been extensively discussed both for continuous and batch applications (e.g. [27, 44, 69, 4]) and will not be reviewed here in detail. The models required for



**Figure 6.** Operation Strategy for Multicomponent Batch Distillation with Separate Storage of Off-cuts and Sequential Off-cut Recycle to the Next Batch

batch distillation are in principle no different than those required for continuous distillation dynamics. What is of interest is the ability to predict the time responses of temperatures compositions and amounts collected for generic mixtures, columns and operations. It may be argued that models for batch distillation must cover a wider operations range, since startup and shutdown are part of the normal operation. For optimization purposes, the models must often be integrated many times and, hence, speed of execution is important. Some issues particularly relevant to batch columns are:

*Modeling detail - Short-Cut vs. "Rigorous".* As with any modeling exercise, a balance must be struck between the accuracy of the predicted responses availability of data, and speed of execution. Therefore, the "right" level of "rigorousness" depends on advances in thermophysical property predictions, numerical algorithms and computer hardware, and on purpose of use. In the past, most work on batch distillation used fairly simple short-cut models which relied on a number of assumptions such as constant relative volatility equimolar overflow no holdup and no hydraulic models etc. When used, the dynamic mass and energy balances have also been simplified in many ways. In some cases, accumulation terms have been neglected selectively or even altogether with dynamics approximated by a sequence of steady state calculations (e.g. [67, 35] for recent examples). These simplifications were dictated by the available technology and lead to useful results (e.g. [28]). At the other end of the spectrum, full dynamic distillation models have been proposed with very detailed phenomena described (e.g. [80]).

Without entering into a lengthy discussion, it appears that at present fairly "rigorous" dynamic models with full dynamic mass and energy balances for all plates and thermophysical properties predicted from generic comprehensive thermophysical packages can be readily integrated for use in batch simulation and optimization. The main justifications for shortcut models (simplicity, speed

of solution, and ability to tailor special solution algorithms) appear to be less and less valid particularly in the light of the effort needed to validate the short cut approximations. Simplified thermodynamic and column models may still be necessary for mixtures for which a relative volatility is all that can be estimated, or for very demanding optimization applications (e.g. [48]). The desirable approach to follow, however, is no doubt to develop simulation and optimization tools suitable for as generic a model form as possible, but to leave the user the possibility to adopt simplifying assumptions which may be appropriate for specific instances.

*Production period.* Standard continuous dynamic distillation models can be used, represented by the general form:

$$f(x, x', t, u, v) = 0 \quad t_0 \leq t \leq t_f \quad (\text{eq. 1})$$

with initial conditions  $x_0 = x(t_0)$  and  $x'_0 = x'(t_0)$ . In eq. 1,  $f$  is a vector of differential and algebraic equations (DAEs), (mass and energy balances, vapor liquid equilibrium relations, thermophysical property defining equations, reaction kinetic equations, etc.),  $x$  and  $x'$  are vectors of (differential and algebraic) state variables and their time derivatives (differential variables only),  $t$  is the time,  $u$  is a vector of time varying control variables (e.g the reflux ratio) and  $v$  is a vector of time independent control variables (e.g. pressure).

A modeling issue particularly important for batch distillation regards the treatment of liquid holdups. Holdups may have quite significant effects on the dynamic response of the column (e.g. [19, 62]), and therefore should be considered whenever possible (zero liquid holdup means that a composition change in the liquid reflux reaches the still infinitely fast, clearly not the case). Assumptions of constant (mass, molar or volume) holdup are often used, and these already account for the major dynamic effects (delay in composition responses). Where necessary, (i.e. low pressure drop per plate) more detailed hydraulic models for plates and downcomers should be used. The extra information added to the model should be considered in light of the low accuracy often attached to generic hydraulic models and other estimated (guessed?) quantities (e.g. Murphee efficiencies). High quality relations, regressed from experimental data, are however often available for proprietary applications and their use is then justified. Vapor-liquid equilibrium has been invariably assumed so far for batch distillation, but there is no reason in principle why rate models cannot be used.

Similar arguments apply to the modeling of heat transfer aspects (reboiler, heat losses) and control loops. If the heat exchange area decreases as the pot holdup decreases, or the heat transfer

coefficients vary significantly during a batch, for example, the assumptions of constant heat supply or constant vapor boilup rate may no longer be valid and it may be necessary to use a more detailed heat transfer model, accounting for the reboiler geometry [3]. If perfect control action (say, on the reflux ratio) is not a good assumption, equations describing the control loop dynamics may be included in eq. 1. In this case, the controller set-points will become the manipulated quantities and possible optimization variables.

*Startup period.* This may be defined as the period up to the time when the first distillate is drawn. It may be divided into two steps. In the first step, the column fills up and some initial profiles are established. In the second step total reflux is used until the top distillate is suitably enriched. For the first step, a model must be able to describe the establishment of initial liquid and vapor profiles, holdups and compositions along the column and in the condenser from an empty, cold column. Flows may be intermittent and mixing behavior on the plates and in the downcomers will be initially very different from the fully established situation, with vapor channeling weeping of liquid, sealing of downcomers, etc. This would demand accurate representation of hydraulic and phase behavior in rather extreme conditions. The use of vapor-liquid models based on perfect mixing and equilibrium under these circumstances is clearly suspect. Thermal effects due to the column being initially cold may be as important as other effects and the exact geometry of the column is clearly important [57]. Some of these aspects have been modeled in detail in [80], based on work for continuous distillation [36].

What is more usually done is to assume some far simpler mechanism for the establishment of the initial vapor and liquid profiles which does not need a detailed mechanistic model. For example: i) finite initial plate and condenser liquid holdups may be assigned at time zero at the same conditions as the pot (boiling point) (e.g. [19, 48]); ii) the column is considered initially (as a single theoretical stage, with the vapor accumulating in the condenser receiver at zero reflux. When sufficient liquid has been accumulated, this is redistributed as the internal plate holdups, filling the plates from the top down (e.g. [50, 38]) or from the bottom up [3]).

For the second startup step the same dynamic model may be used for the production steps. From an operation point of view, the practical question is whether a total reflux operation should be used at all, and if so, for how long. The duration of the total reflux operation (if at all necessary) can be optimized [19, 59].

An even cruder approximation is to ignore the startup period altogether, consider it as an instantaneous event and initialize the column model using the assumption of total reflux,

steady-state (or as in [4], at the steady-state corresponding to a finite reflux ratio with no distillate production, obtained by returning the distillate to the pot). Of course, this procedure does not permit calculating the startup time.

Clearly, different startup models will provide different starting values for the column dynamic profiles in the first production step. Whether this matters was considered [1], comparing simulation results with four different models of increasing complexity for the first startup a stage. In all four cases, the procedure was followed by a second startup step at total reflux until stable profiles were achieved (steady state). The main conclusions were that the (simulated) startup time can be significant (especially for difficult separations), is essentially due to the second step, is roughly proportional to the major holdups (in the condenser drum and, for difficult separations, those in the column) and that all four models gave approximately the same results (startup time and column conditions).

In the absence of experimental data to confirm or reject either approach, the use of the simpler procedures (i and ii above) to model the first step of the startup period would appear to be a reasonable compromise.

*Shut down period.* This period is typically not modeled in detail, since draining of the column and condenser following interruption of heating is usually very rapid compared to all other periods and separation is no longer affected. However, the final condenser receiver holdup may be mixed with the last distillate fraction, collected separately or mixed with the bottoms fraction, thus the exact procedure followed should be clearly defined (this is clearly irrelevant when holdups are ignored).

*Transfers, additions, etc.* Fresh feed or recycle addition are often modeled as instantaneous events. Adding side streams with finite flow rates to a generic column model, if required, is however a simple matter. These additional feeds (if any) may then be chosen as additional control variables.

In principle, different models of the type defined by eq. 1 may be defined for distinct distillation tasks. For example, referring to the operation in Figure 4, the number of species present in the final separation task (Step 3) may involve only a small subset of the species present in the initial charge. For numerical reasons, it may well be better to eliminate the equations related to the depleted species, giving a different set of equations for Step 1 and Step 3. Other modeling formulation details affect the numerical solution. For example, we found it is better to use an internal reflux ratio definition ( $L/V$ , with range 0-1 ) rather than the usual external one ( $L/D$ , ranged 0-infinity).

## Simulation Issues

The simulation problem may be defined as follows:

Given: A DAE batch distillation model	$f(x, x', t, u, v)=0$	(eq. 1)
Values for all control variables	$u(t), v$	
Initial conditions	$t_0, x_0$ and $x'_0$	
Termination conditions	based on $t_f, x(t_f), x'(t_f), u(t_f)$	
Calculate: Time profiles of all state variables	$x(t), x'(t)$	

Dynamic models used in batch distillation are usually stiff. The main techniques used to integrate the above DAE system are BDF (Gear's) methods [37, 43] and orthogonal collocation methods [85]. Discontinuities will typically be present due to *discrete* events such as the instantaneous change in a control variable (e.g. a reflux ratio being changed between two values) and the switching of receivers at the end of a step. The presence of algebraic equations adds constraints between the state variables and their derivatives (and a number of complications). With respect to the initial conditions, only a subset of all  $x_0$  and  $x'_0$  variables may then be fixed independently, the remaining ones having to satisfy eq. 1 at the initial time (consistent initialization). A similar situation occurs with the discrete changes. If an algebraic variable can only be calculated from the right hand side of a differential equation (for example, the vapor leaving the stage from the energy balance), then some algebraic equation may have to be differentiated before the algebraic variable can be calculated (the number of differentiations required being called the index of the DAE system). A number of ad-hoc solutions had been worked out in the past to overcome these problems. For example, the derivative term in the energy balance could be approximated (e.g by a backwards finite difference, yielding an algebraic equation). To avoid discontinuities when changing reflux ratios, a continuous connecting function may be used [25]. These aspects are now far better understood, and even if it is still not possible to always solve higher index systems, it is usually possible to reformulate the equations so as to produce index 1 systems in the first place and to address implicit and explicit discontinuities. Requirements related to the consistent definition of the initial conditions, solvability of the system, DAE index, model formulation so as to avoid index higher than one and (re)initialization procedures with discontinuities were discussed in particular by [69, 4].

General purpose simulation packages such as BATCHES [17] and gPROMS [8] allow the process engineer to build combined discrete-event/differential algebraic models for simulation



studies and have built in integration algorithms dealing with the above issues. In particular, they are able to deal effectively with model changes between different stages and discrete events. They are therefore suitable for general batch distillation simulations. General purpose dynamic simulators for essentially continuous systems such as SPEEDUP [68] can also be used, although the ability to handle generic events and model changes is more limited. A number of codes have also been developed specifically for batch distillation simulation (e.g. [4, 31, 35]) or adapted from continuous distillation [80]. A batch simulation "module" is available in several commercial steady state process simulators (e.g. the BATCHFRAC program [12], Chemcad III, ProsimBatch [71]). These are tailored to handle the specific events involved (switching of receivers, intermediate addition of materials, etc.) and in general use a single equation model for the entire batch operation and generic thermophysical property packages.

## Optimization Issues

As noted, there are both discrete and continuous operation decisions to be optimized. At present dynamic optimization solutions have only been presented dealing with problems with fixed operation structure and with the same model equations for all separation stages. In the following we will therefore consider the optimization of the continuous operating decisions for an operation strategy selected a priori. Some work on the optimization of the operations structure is briefly discussed in the last section.

Equations and variables may be easily introduced into eq. 1 to define integral performance measures, for example, the total energy used over a distillation step. This permits calculating additional functions of all the states, controls, etc. and to define additional inequality constraints and an objective function, in a general form:

$$\text{Inequality constraints} \quad g = g(t_f, x(t_f), x'(t_f), u, v) \quad (\text{eq. 2})$$

$$\text{Objective function} \quad J = J(t_f, x(t_f), x'(t_f), u, v) \quad (\text{eq. 3})$$

The optimization problem may then be defined as follows:

$$\begin{array}{ll} \text{Given: Initial conditions} & t_0, x_0 \text{ and } x'_0 \\ \text{Find: Values of all control variables} & v, u(t) \\ \text{So as to: Minimize the objective function} & \text{Min } J \end{array} \quad (\text{eq. 3})$$

$$\text{Subject to: Equality constraints (DAE model)} \quad f(x, x', t, u, v) = 0 \quad (\text{eq. 1})$$

$$\text{Inequality constraints} \quad g(t_f, x(t_f), x'(t_f), u, v) \leq 0 \quad (\text{eq. 2})$$

Upper and lower bounds may be defined on the control variables,  $u(t)$  and  $v$ , and on the final time. Termination conditions may be implicitly or explicitly defined as constraints. Additional inequality constraints may be defined for state variables not just at the end, but also at interior points (*path constraints*). For example, a bottom temperature may be bounded at all times. Some initial conditions may also have to be optimized.

The main problem in this formulation is the need to find optimum *functions*  $u(t)$  i.e. an infinite set of values of the controls over time. The main numerical techniques used to solve the above optimal control problem are the control vector parameterization (CVP) method (e.g. [58, 34]) and the collocation method (e.g. [10, 26, 74, 48]). Both transform the control functions into discrete forms approximated by a finite number of parameters.

The CVP method (used in this paper) discretizes each continuous control function over a finite number, defined a priori, of *control intervals* using a simple basis function (parametric in a small number of parameters) to approximate the control profile in each interval. For example, Figure 7 shows a piecewise constant approximation to a control profile with 5 intervals. With the initial time given, two parameters are sufficient to describe the control profile in each interval a control level and the final time of the interval. Thus the entire control profile in Figure 7 is defined by 10 parameters. These can then be added to any other decision variable in the optimization problem to form a finite set of decision variables. The optimal control problem is then solved using a nested procedure: the decision variables are set by an optimizer in an outer level and, for a given instance of these variables, a dynamic simulation is carried out to calculate objective function and constraints (eqs. 1-3). The outer problem is a standard (small scale) nonlinear programming problem (NLP), solvable using a suitable method such as Sequential Quadratic Programming (SQP). Parameterizations with linear, exponential, etc. basis functions may be used [34]. Since the

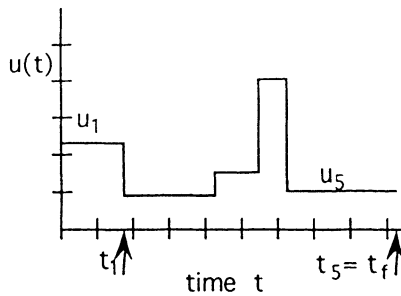


Figure 7. Piecewise Constant Discretization of Continuous Control Function

DAEs are solved for each function evaluation, this has been called a feasible path approach. Its main advantage is that the approach is very flexible. General purpose optimizers and integrators may be used, and the set of equations and constraints may be very easily changed.

The collocation methods discretize both the control functions and the ordinary differential equations in the original DAE model, using collocation over finite elements. The profiles of all variables are approximated using a set of basis functions, with coefficients calculated to match any specified initial conditions, final conditions and interior conditions (additional conditions being provided by the continuity of profiles across the finite elements). The end result is a large system of algebraic equations, which together with constraints and objective function form a large NLP problem. For the same problem, however, the degree of freedom for this large scale NLP is the same as for the small scale NLP in the CVP approach. The optimization may be solved using suitable NLP algorithms, such as a SQP with Hessian decomposition [48]. Since the DAEs are solved at the same time as the optimization problem, this has been called an infeasible path approach. The main advantage claimed for this approach is that it avoids the repeated integrations of the two level CVP method, hence it should be faster. However, comprehensive comparisons between the collocation and the CVP methods have not been published, so it is not possible to make definite statements about the relative merit.

The *path constraints* require particular treatment. Gritsis [39] and Logsdon and Biegler [48] have shown that they can be handled in practice both by the CVP and orthogonal collocation methods (in particular, by requiring the constraints to hold at a finite number of points, coincident with control interval end points or collocation points). A general treatment of the optimal control of constrained DAE systems is presented in [70].

Computer codes for the *optimization* of generic batch distillation operations have been developed by [59, 31]. To my knowledge, no commercial code is presently available.

## Application Examples

In this section, some examples are given of the application of the ideas and methods outlined above, drawn from our own work over the last few years. The examples are used to illustrate the current progress and capabilities, in particular with respect to the generality of operation strategies, column and thermodynamic models and objective functions and constraints that can be handled.

## Solution Models and Techniques

All examples were produced using a program developed specifically for batch distillation simulation and optimization by [68] and successively extended to handle more features. For a particular problem, a user supplies the definition of a batch *column configuration* (number of theoretical stages, pot capacity, etc.), defines the fresh charge mixture to be processed and selects a *distillation model* and *thermodynamic options*. Two column models have been used, mainly to show that the solution techniques are not tied to a specific form of the model. The simpler column model (MC1) is based on constant relative volatility and equimolar overflow assumptions. A more rigorous model (MC2) includes dynamic mass balances and general thermodynamics, with the usual assumptions of negligible vapor holdup, adiabatic plates, perfect mixing for all liquid holdups, fixed pressure and equilibrium between vapor-liquid. A total condenser is used with no sub-cooling and finite, constant molar holdups are used on the plates and in the condenser receiver. To maintain solution time reasonably low, the energy balances are modeled as algebraic equations (i.e. energy dynamics is assumed to be much faster than composition dynamics). Thermodynamic models, vapor liquid equilibria calculations and kinetic reaction models are supplied as subroutines (with analytical derivatives, if available). Rigorous, general purpose thermodynamic models, including equations of state and activity coefficient models may therefore be used for nonideal mixtures. A simple constant relative volatility model (MT1) may still be used, if desired, in conjunction with the more rigorous dynamic model MC2.

A desired *operation strategy* (number and sequence of product cuts, off-cuts, etc) is defined *a priori*. A simple initialization strategy is used for the first distillation task. The fresh charge is assumed to be at its boiling point and a fraction of the initial charge is distributed on the plates and in the condenser (according to the specified molar holdups). For successive tasks, the initial column profiles are initialized to be the same as the final column profiles in the preceding task. Adjustments may be made for secondary charges and to drop depleted component equations from the model. For each STN task, the *control variables* are identified and the number of discretization *control intervals* is selected (a CVP method with piecewise constant parameterization is used) and initial values are supplied for all control levels and control switching times. Reflux ratio, vapor boilup rate and times are available as possible control variables (additional quantities, if present, may also be used for control, such as the rate of a continuous feed to an intermediate stage). A variety of *specifications* may be set for individual distillation steps, including constraints on selected end

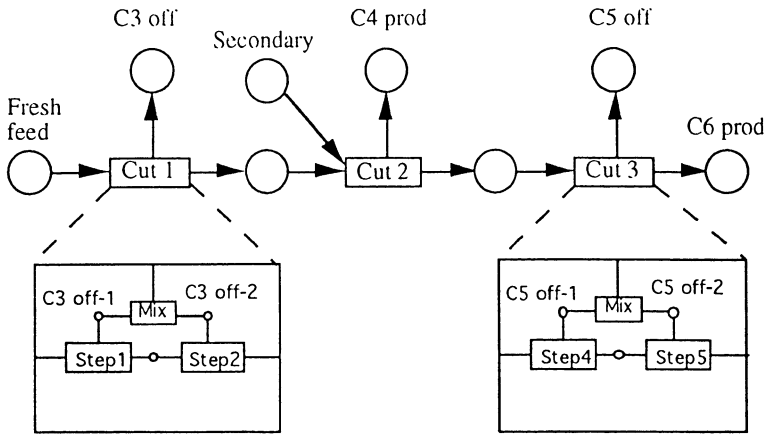
purities and amounts collected (other specifications are described in the examples). Finally, an *objective function* is selected, which may include those traditionally used (max distillate, min time), one based on productivity (amounts over time) or on economics (max profit). In the latter case, suitable cost coefficients must also be supplied for products, off-cuts, feed materials and utilities. From these problem definitions, programs are generated for computing all required equation residuals and the analytical Jacobians, together with a driver for the specific simulation/optimization case.

A robust general purpose SQP code [15] is used to solve the nonlinear programming optimization. A full matrix version is used here, although a sparse version for large scale problems (with decomposition) is also available. The DAEs system is integrated by a robust general purpose code, DAEINT, based on Gear's BDF method. The code includes procedures for the consistent initialization of the DAE variables and efficient handling of discontinuities. The gradients needed by the SQP method for optimization are efficiently calculated using adjoint variables [58], requiring the equivalent of approximately only two integrations of eq. 1 to calculate all gradients (an alternative, method for generating the gradients would be to integrate the dynamic sensitivity equations alongside the model equations, [13]. Outputs are in tabular and simple graphical form.

### **Simulation and Sequential Optimization of Individual Distillation Steps**

The first example deals with a four component mixture (propane, butane, pentane and hexane) to be separated in a 10 equilibrium stage column and was initially presented in [12]. The operation consists of 5 distillation steps with two desired products. A fraction with high propane purity is collected first, followed by a step where the remaining propane is removed. A high purity butane fraction is then collected, with removal of pentane in an off-cut in the fourth step. The final step removes the remaining pentane in the distillate and leaves a high purity hexane fraction as the bottom residue. A secondary charge is made to the pot after the second step (Figure 8).

Boston et al. presented [12] simulation results for an operation with constant reflux ratio during each step and different values in distinct steps. Simulations of their operation (same reflux ratio and duration for each step) were carried out in [59] with two thermodynamic models, MT2 (an ideal mixture model with VLE equilibrium calculated using Raoult's law and Antoine's model for vapor pressure, ideal gas heat capacities for vapor enthalpies from which liquid enthalpies were obtained by subtracting the heat of vaporization) and MT3 (SRK equation of state). Results with the former thermodynamic model and with the more rigorous dynamic column model MC2 are



**Figure 8.** Batch Distillation of Quaternary Mixture [12]-Operating Strategy. The two distillation tasks Cut1 and Cut3 are composed of two off-cut production steps each

reproduced in Table 2. They are very similar to those reported in the original reference, with inevitable minor differences that are due to difference in thermodynamic models, integration tolerances, etc. This operation was taken as a base case.

Mujtaba [12] considered the optimization of the same process, using the above operating policy as a base case, as follows. In the absence of an economic objective function in the original reference, it was assumed that the purities obtained in each of the cuts (in terms of the molar fraction of the key component in that cut) were the desired ones and that the reflux ratio policy could be varied. A variety of objective functions were defined. Table 3 reproduces the results obtained for the *first* distillation step with three objective functions: minimum time, maximum distillate and maximum productivity, with an end constraint on the mole fraction of propane in the accumulated distillate ( $x_{\text{propane}} = 0.981$ ). All results are reported in terms of a common measure of productivity, the amount of C3 off-1 distillate produced over the time for Step 1 and for two ways of discretizing the control variable, into a single interval and five intervals, respectively. As expected, the productivity of this Step varies depending on the objective function used, increases when more control intervals are used and is maximum when productivity itself is used as the objective function. As a comparison, the base case operation had a productivity of 2.0 lbmol/hr for Step 1 (8.139 lbmole produced in 4.07 hr). With a single reflux ratio level, the minimum time problem and the maximum distillate problem resulted (within tolerances) in the same operation as

**Table 2.** Batch Distillation of Quaternary Mixture [12]. Simulation Results with MC2 Column Model (dynamic, more rigorous) and MT2 Thermo Model(ideal). Total Time  $T_f=30.20$  hr; Overall Productivity  $(A+B)/T_f=3.17$  lbmol/hr

Column					
No. of Internal Stages (ideal)	8				
Condenser	total	no	subcooling		
Liquid Holdup - stage (lbmol)	4.93 10 <sup>-3</sup>				
Liquid Holdup - cond. (lbmol)	4.93 10 <sup>-2</sup>				
Charges	Fresh feed	Secondary			
(1) Propane	0.1	0.0			
(2) Butane	0.3	0.4			
(3) Pentane	0.1	0.0			
(4) Hexane	0.5	0.6			
Amount (lbmol)	100	20			
at time	initial	after Step2			
Operation - Specified					
Task	Step1	Step2	Cut2	Step4	Step5
Products	C3 off-1	C3 off-2	C4 prod	C5 off-1	C5 off-2 C6 prod
Specified:					
Reflux ratio (external)	5	20	25	15	25
Time (hr)	4.07	1.81	18.27	4.31	1.78
Distillate rate (lbmol/hr)	2	2	2	2	2
Pressure (bar)	1.03	1.03	1.03	1.03	1.03
Operation - Results					
Top Vapour rate (lbmol/hr)	12	42	52	32	52
Instant Distillate (mole fraction)					
Propane	0.754	0.031	....	....	....
Butane	0.246	0.969	0.254	....	....
Pentane	....	....	0.745	0.613	0.091
Hexane	....	....	....	0.387	0.909
Accum. Distillate (mole fraction)					
Propane	0.981	0.850	....	....	....
Butane	0.019	0.150	0.988	0.017	0.012
Pentane	....	....	0.012	0.940	0.778
Hexane	....	....	....	0.043	0.210
Amount (lbmol)	8.139	11.760	36.548=A	8.619	12.180
Still Pot (mole fraction)					
Propane	0.021	....	....	....	....
Butane	0.325	0.319	0.001	....	....
Pentane	0.109	0.113	0.133	0.023	0.002
Hexane	0.545	0.567	0.866	0.977	0.998
Amount (lbmol)	91.860	88.240	71.680	63.061	59.380=B

the base case (for the required purity, the system behaves as a binary and the optimization essentially solves a two-point boundary value problem). Taking both the amount produced and the time required into account (i.e. the productivity objective function), however, permits improving this step by over 50%. Further improvements are achieved with more control intervals. Two of the optimum control policies calculated for the maximum productivity problem are also reported in Table 3. The desired propane purity is achieved in all cases.

**Table 3.** Batch Distillation of Quaternary Mixture [12]-Optimization of Step 1 with MC2 Column Model (dynamic, more rigorous) and MT2 Thermo Model (ideal)

Problem - Optimise Step 1	Min Time	Max Distillate	Max Productivity
Specified:			
Top Vapour rate (lbmol/hr)	12	12	12
Pressure (bar)	1.03	1.03	1.03
Product state C3 off 1 - mole fraction C3	0.981	0.981	0.981
Amount(lbmol)	8.139		
Time (hr)		4.07	
Controls:			
Reflux ratio (external) (r): End time (t1)	r, t1	r	r, t1
<b>Optimal Operation</b>			
<b>1 control interval</b>			a)
End Time: t1 (hr)	4.01		1.75
Amount of C3 off-1: C (lbmol)		8.15	5.67
Productivity = A/t1 (lbmol/hr)	2.02	2.00	3.24
<b>5 control intervals</b>			b)
End Time: t1 (hr)	2.82		1.64
Amount of C3 off-1: C (lbmol)		9.26	5.88
Productivity = C/t1 (lbmol/hr)	2.881	2.275	3.59
Optimal reflux ratio policies (control level/end time, level/time, ...)			
a) (r, t) = (0.73/1.75)			
b) (r, t) = (0.30/0.636, 0.664/0.59, 0.695/0.91, 0.727/1.22, 0.758/1.64)			

Optimization of the first step, as described, provided not only the optimal values of the control parameters for the step, but also values of all state variables in the column model at the end of the step. These are used to calculate the initial values of all the state variables in the model for the next step. If the same equations model is used in the two steps, the simplest initialization policy for step 2 is simply to set the initial values for step 2 to the final values of step 1 (used in all examples, unless noted). However, it is also possible to change the model (for example, to use a different thermodynamic option, to eliminate equations for components no longer present) or to carry out calculations for impulsive events defined at the transition between the two steps (for example, to determine the new pot amount and composition upon instantaneous addition of a secondary charge). The next step may then be either simulated (if all controls are specified) or optimized (if there are some degrees of freedom). In principle, a different objective function could be used for each step.

Results for such a sequential optimization of the five distillation steps in the operation, using the same distillation model throughout, minimum time as the objective function for each step and the same purity specifications as in the base case gave the results summarized in Table 4, in terms of overall productivity (total amount of the two desired products/ total time). Significant increases



**Table 4.** Batch Distillation of Quaternary Mixture [12] - Optimization of 5 Steps in Sequence (min. time for each step) with MC2 Column Model (dynamic, more rigorous) and MT2 Thermo Model (ideal)

Problem: Sequential Optimisation (min time for each step)	Step1	Step2	Step3	Step4	Step5	Overall
Specified:						
Top Vapour rate (lbmol/hr)	12	42	52	32	52	
Pressure (bar)	1.03	1.03	1.03	1.03	1.03	
Product state	C3 off1	C3 off-2	C4 prod	C5 off-1	C6 prod	
(Key component) mole fraction	(1)0.981	(1)0.850	(2)0.988	(3)0.940	(4)0.998	
Amount (lbmol)	8.139	11.760	36.548	8.619	59.380	
Controls:						
Reflux ratio (external), r; times	r, t1	r, t2	r, t3	r, t4	r, t5	
Optimal Operation						
1 control interval per step:						
Time (hr)	4.01	1.56	9.20	3.49	1.55	19.31
Amount (lbmol) A=C4 prod, B=C6 prod			36.566=A		59.44=B	
Productivity = (A+B)/Tf (lbmol/hr)						4.84
5 control intervals per step:						
Time (hr)	2.82	1.37	2.57	2.83	1.54	11.13
Amount (lbmol) A=C4 prod, B=C6 prod			36.567=A		59.44=B	
Productivity = (A+B)/Tf (lbmol/hr)						8.62

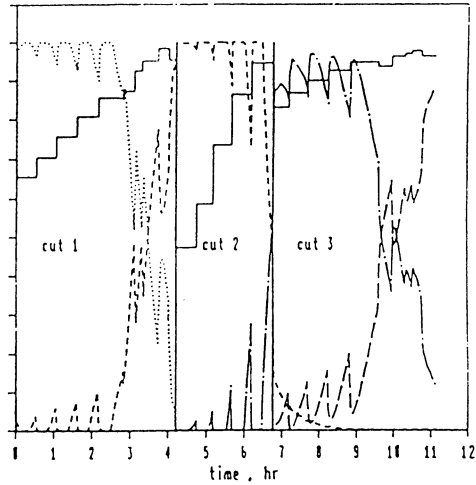
in performance (over 50%) relative to the base case are achieved even with a single (but optimal) profiles are given in Figure 9 for the whole operation. The dynamic model used does not include hydraulic equations, therefore, the optimal operation should be checked for weeping, entrainment, flooding, etc.

### Recycle Optimization

Policies for recycles were discussed in general terms in the initial sections. Off-cut recycle optimization methods have been discussed for the simpler, binary case in [56, 16, 60], as well [51, 72, 63] as different special cases of multicomponent mixtures.

With reference to the specific operation strategy in Figure 5, if the off-cut produced in Step 2 in one batch is characterized by the same amount and composition as that charged to the pot in the *previous* batch, then, for constant fresh charge and with the same control policies applied in subsequent batches, the operation described in Figure 5 will be a quasi-steady state one, that is subsequent batches will follow the same trajectories, produce the same product and intermediate states, etc. This cyclic condition may be stated in several ways, for example by writing the composition balance for the charge mixing step (Mix) as:

Instant Distillate Composition Minimum  
Time Problem



Accumulated Distillate Composition Minimum  
Time Problem

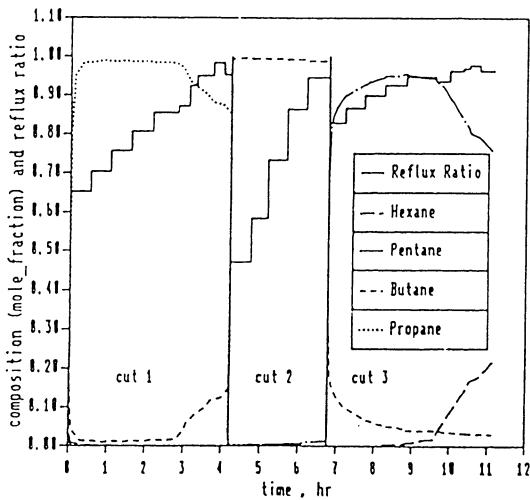


Figure 9. Batch Distillation of Quaternary Mixture[12]-Sequential Optimization of all 5 Steps.Optimum Reflux ratio Profile and Distillate Composition (mole fractions)

$$B_0 x_{B0} + R x_R = B_c x_{Bc} \quad (\text{eq. 5})$$

where  $B_0$ ,  $x_{B0}$  and  $B_c$ ,  $x_{Bc}$  the fresh feed and mixed charge amounts and composition, supply the *initial* conditions for Step 1 and  $R$ ,  $x_R$  are the amount and composition of the collected off-cut at the *final* time of Step 2. Different cyclic operations may be obtained corresponding to different off-cut fraction amount and composition. An optimal recycle policy can be found by manipulating simultaneously the available controls (e.g. reflux ratio profile and duration) of all distillation steps within the loop (Step 1 and Step 2), so as to optimize a selected objective function, while satisfying constraints 5 (or equivalent ones) in addition to other constraints (on product purity, etc.). A solution of this problem for binary mixtures was presented [60] using a two level problem formulation, with minimum time for the cyclic operation as the objective function. For given values of  $R$  and  $x_R$ , a sequence of two optimal control problems is solved in an inner loop. The minimum time operation of Step 1 is calculated as described above, followed by the minimum time operation for Step 2, with purity and amount of the off-cut constraints to match the given values. In an outer loop, the total time is minimized by manipulating  $R$  and  $x_R$  as the (bounded) decision variables.

An alternative, single level formulation for this problem was also developed by [59] where the total time is minimized directly using the mixed charge quantities ( $B_c$  and  $x_{Bc}$ ) as decision variables, together with reflux ratio as control variable, as follows:

$$\text{Min} \quad J = t_1 + t_2 = t_f$$

$$B_c, x_{Bc}, r(t)$$

subject to: DAE model

bounds on all control variables

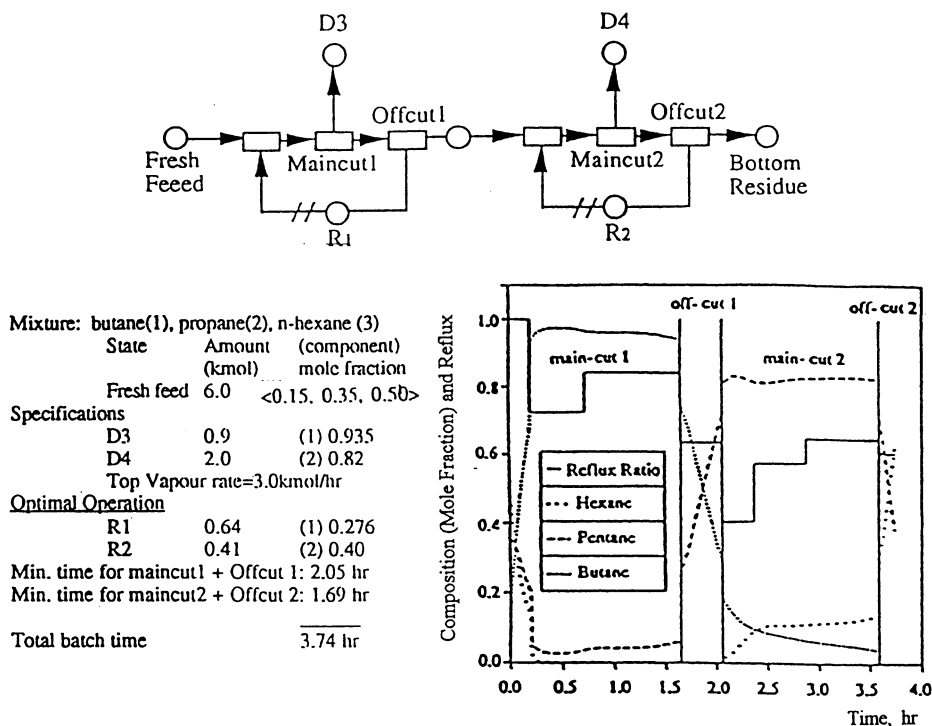
$$\text{interior point constraints, e.g.:} \quad x_{D1}(t_1) \geq x_{D1}^*$$

$$D_1(t_1) \geq D_1^*$$

$$\text{end point constraints, e.g.:} \quad x_{B3}(t_f) \geq x_{B3}^*$$

$$\text{cyclic conditions} \quad (\text{eq. 5})$$

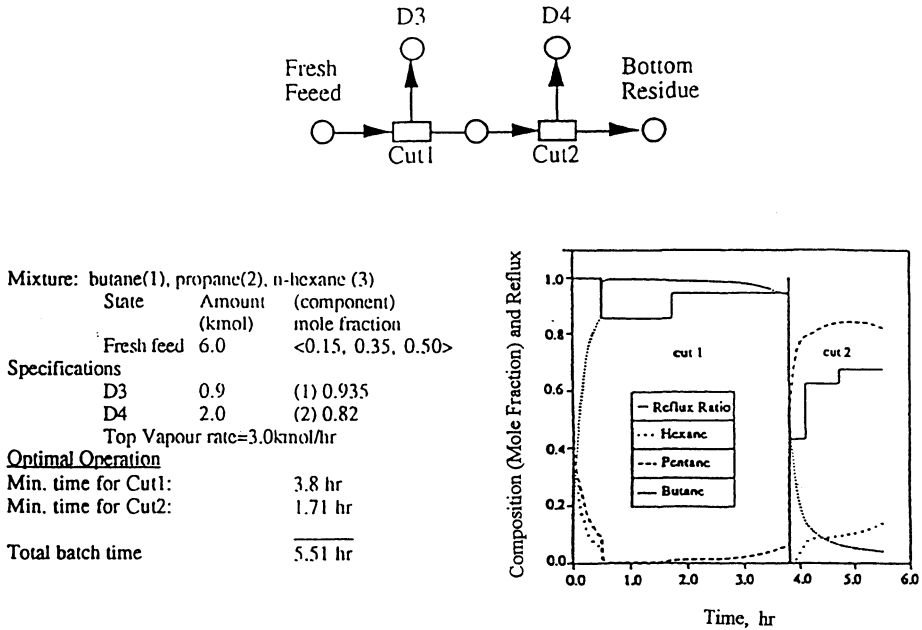
Here  $t_1$  and  $t_2$  are the duration of production Steps 1 and 2, respectively and  $t_f$  is the total time of the cyclic operation. The starred values are specifications (only two of which are independent, the other two being obtained from a material balance over the STN states Fresh Charge, Maincut 1 and Bottom Product in Figure 5). The control vector is discretized, as usual, into a number of control intervals. However, the end time of Step 1,  $t_1$ , is defined to correspond to one of the control interval boundaries. The constraints on the main distillate fraction are now treated as interior point constraints and the cyclic conditions are treated as end point constraints. This



**Figure 10.** Batch Distillation of Ternary Mixture with production and recycle of intermediate off-cut. Thermodynamic model MT2 (ideal), Column Model MC2 (dynamic, more rigorous)

formulation was found to result in rather faster solution than the two level formulation, while giving the same results.

This approach may also be used for multicomponent mixtures and more complex operation strategies, such as that shown in Figure 6. An example for a ternary mixture (butane, pentane and hexane) with specifications on two main products was reported in [63]. The production strategy involves four steps (two main product fractions, each followed by an off-cut production step, with each off-cut recycled independently), as shown in Figure 10. Using the single level formulation, the minimum distillation time for the first recycle loop was calculated first, providing initial column conditions for the second loop, for which the minimum time was then also calculated. The results for this *sequential* optimization of individual recycle loops are summarized in Figure 10. Comparison of the total time required with that for the optimal operation involving just two product steps and no off-cuts (Figure 11) shows a significant reduction of 32% in the batch time. The same products (amounts and compositions) are obtained with both operations.



**Figure 11.** Batch Distillation of Ternary Mixture with no Off-Cuts. Thermodynamic Model MT2 (ideal), Column Model MC2 (dynamic, more rigorous)

### Multiperiod Optimization

In the above examples, optimization was performed of distillation steps individually and sequentially. Clearly, this is not the same as optimizing an overall objective function (say, minimum total time), nor are overall constraints taken into account (say, a bound on overall energy consumption). An *overall* optimization was however discussed for all steps in a single recycle loop and the same two approaches in that section may also be used to optimize several adjacent steps or even all the production periods in an operation. We refer to this as multiperiod optimization. This has been discussed by Fahrat et al. [34], however with shortcut models and simple thermodynamics and in [64] with more general models.

Only a small set of decision variables is required to define a well posed optimal control problem for individual steps. With the fresh feed charge given, specification of a key component purity and an extensive quantity (amount of distillate or residue, or a recovery) for each distillation step permits calculating the minimum time operation for that step, and hence for all steps in

sequence. Typical quantities of interest for overall economic evaluation of the operation (amounts produced, energy and total time used, recoveries, etc.) are then explicitly available. A general overall economic objective function may be calculated utilizing unit value/cost (\$/ kmol) of all products, off-cut materials, primary and (if any) secondary feeds and unit costs of utilities (steam, cooling water). For example an overall profit (\$/batch) may be defined as:

$$J1 = \text{Sum (product/off-cut values)} - \text{Sum (feed costs)} - \text{Sum (utility, setup, changeover costs)} \quad (\text{eq. 6})$$

or in terms of profit per unit time (\$/batch):

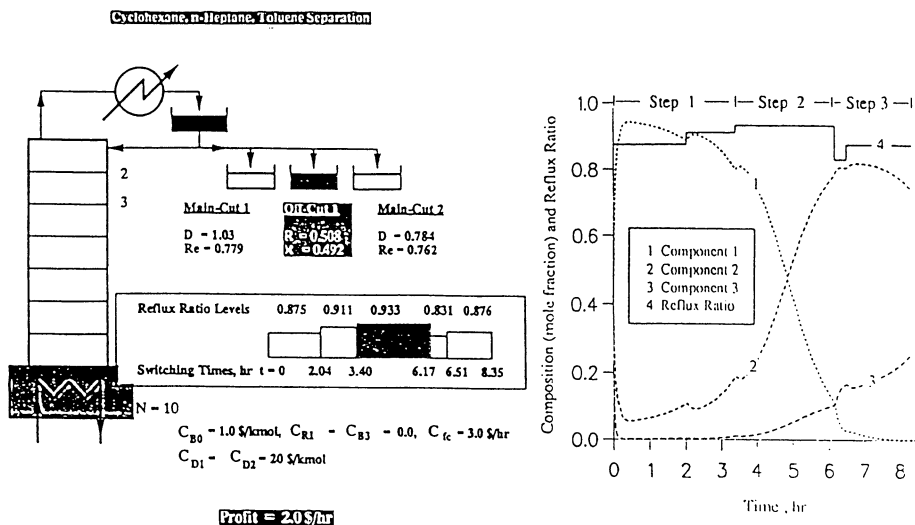
$$J2 = J1 / \text{batch time} \quad (\text{eq. 7})$$

with significant changeover and setup times also included in the batch time. Overall equality and inequality constraints may be similarly written.

The decision variables may then be selected in an outer optimization step to maximize an overall objective function subject to the overall constraints. Many purities are typically specified as part of the problem definition and recoveries represent sensible engineering quantities for which reasonably good initial guesses can often be provided. The outer level problem is therefore a small nonlinear programming problem solvable using conventional techniques. The inner problem has a block diagonal structure and can be solved as a sequence of small scale optimal control problems one for each STN task.

This solution method was proposed in [64] who presented results for batch distillation of a ternary mixture in a 10 stage column with two distillate product fractions (with purity specification) and one intermediate off-cut distillate (with a recovery specified). Here, the more rigorous dynamic model was used with thermodynamic described by the SRK equation of state (Thermo model MT3). The amounts of all fractions the composition of the recycle off-cut and the reflux ratio profiles were optimized so as to maximize the *hourly profit*, taking into account energy costs. The optimal operation is summarized in Figure 12 with details given in the original reference. The required gradients of objective functions and constraints for the outer problem were obtained by finite difference (however exploiting the block diagonal structure of the problem) with small effort. Analytic sensitivity information could be used if available.

For the quaternary example [12] previously discussed the operation in Figure 8 is considered again this time with Step 1 and Step 2 merged into the single task Cut 1 (propane elimination) and Step 4 and 5 merged into the single task Cut 3 (pentane elimination). A problem is formulated whereby the overall productivity (amounts of states C4 prod and C6 produced over the total time)



**Figure 12.** Multi-period Optimization with Ternary Mixture - Maximum hourly profit, SRK EOS, dynamic column model MC2, Specifications on maincut 1 and maincut 2 product purity and Cyclohexane recovery in Off-cut. Optimal operation and instant distillate composition profiles are shown

is maximized subject to the same product purity constraints considered in the sequential optimization (Table 4). The pentane purity in the C3 off-fraction butane recovery in Cut 2 and hexane recovery in Cut 3 are now considered as variables to be optimized in addition to the reflux ratio profiles and times. A two level multi-period solution leads to the optimal operation detailed in Table 5. Smaller amounts of product are produced, however in far less time, leading to an overall productivity almost twice as high as for the optimal sequential solution and four times higher than the base case. This is no doubt also due to the use here for all times of the largest vapor rate (52 lbmol/hr) which was utilized in the previous cases (only in Steps 3 and 5). This optimization required 4 functions and 3 gradient evaluations for the outer loop optimization and less than 5 hrs CPU time on a SUN SPARC10 machine.

**Table 5.** Multiperiod Optimization of Quaternary Mixture [12] with 3 Separation tasks. Maximum overall productivity, MC2 column model (dynamic, more rigorous) and MT2 thermo model (ideal)

Multiperiod Optimisation max Productivity = (A+B)/Tf	Cut1	Cut2	Cut3	Overall
Specified: Top Vapour rate (lbmol/hr) Pressure (bar) State (Key comp.) mole fraction State (Key comp.) task recovery	52 1.03  C3 off (1) 0.996	52 1.03 C4 prod (2) 0.988	52 1.03 C6 prod (4) 0.998	
Optimised: State (Key comp.) mole fraction (Key comp.) recovery for task Controls Variables (No. contr. intervals) Initial guess control level end time	initial <bounds> C3 off (1)0.981<0.8-0.95>	initial <bounds> C4 prod (2)0.90<0.85-0.95>	initial <bounds> C6 prod (4)0.95<0.90-0.98>	
Optimal Operation Time (hr) Productivity=(A+B)/Tf (lbmol/hr)	1.66	1.28	3.05	5.99=Tf 14.55
Product State (mole fraction) Propane Butane Pentane Hexane Amount (lbmol)	C3 off 0.869 0.131 ... ... 11.433	C4 prod 0.001 0.988 0.011 ... 31.361=A	C5 off C6 prod ... ... 0.258 ... 0.450....0.002 0.292 0.998 21.186 55.814=B	
Optimal control level end time	0.711,0.987,0.969 0.37, 0.90, 1.66	0.469,0.599,0.723 0.57, 0.96, 1.28	0.648,0.877,0.945 0.59, 1.44, 3.05	

As with recycles, it is possible to utilize the single level problem formulation for the general multiperiod case.

### Reactive Batch Distillation

Reactive batch distillation is used to eliminate some of the products of a reaction by distillation as they are produced rather than in a downstream operation. This permits staying away from (reaction) equilibrium and achieving larger conversions of the reactants than possible in a reactor followed by separation. With reference to Figure 1, reaction may occur just in the pot/reactor (for example, when a solid catalyst is used) or in the column and condenser as well (as with liquid phase reactions). Suitable reactions systems are available in literature [6].

With the batch distillation model (eq. 1), written in general form, extensions to model the reactive case amount to just small changes in the mass and energy balances to include a generation term and to the addition of reaction kinetic or equilibrium equations for all stages where reaction



occurs (pot, or all stages). Energy balances do not even need changing if written in terms of total enthalpy. Modeling details and simulation aspects are given in many references (i.e. [25, 4]).

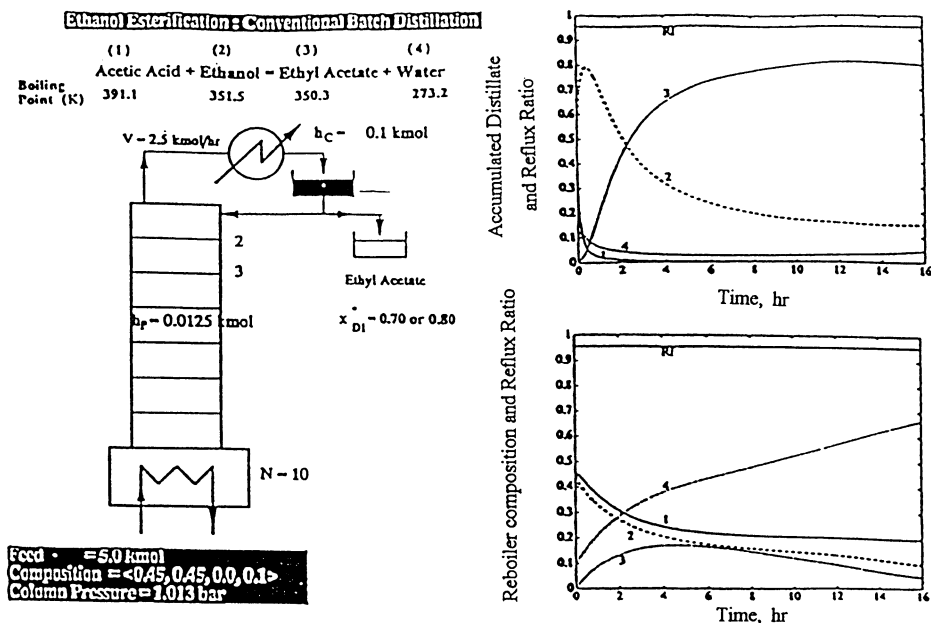
From the operation point of view, there are some interesting new aspects with respect to ordinary batch distillation. Reaction and separation are tightly coupled (reaction will affect temperatures, distillate and residue purities, batch time, etc. while the separation will affect reaction rates and equilibrium, reactant losses, etc.). There is one more objective, essentially the extent of reaction, but no new variables to manipulate (unless some reactants are fed semi-continuously, in which case the addition of time and rate may be new controls), making this an interesting dynamic optimization problem. Optimization aspects were first discussed in [33] and more recently in [86, 40, 65] who also review recent literature.

With the optimal control problem formulated as above, no change is needed to handle the reactive case, other than to supply a slightly modified model and constraints. Optimal operating policies were presented in [65] for several reaction systems and column configurations. Typical results are summarized in Figure 13 for the esterification of ethanol and acetic acid to ethyl acetate and water, with *maximum conversion* of the limiting reactant used as the objective function, reflux ratio as the control variable, given batch time and a constraint on the final purity of the main reaction product (80% molar ethyl acetate, separated in a single distillate fraction). This formulation is the equivalent of the maximum distillate problem in ordinary batch distillation. Similar results were also calculated for maximization of a general economic objective function, *hourly profit* = (value of products - cost of raw materials - cost of utilities)/ batch time, with the batch time also used as a control variable. Again, profit improvements in excess of 40% were achieved by the optimal operation with respect to quite reasonable base cases, obtained manually by repeated simulations.

### **On-Line Application - Optimization of All Batches in a Distillation Campaign**

The above examples involved the a priori definition of the optimal control profiles for a batch, assuming that all batches would be carried out in the same way. Here, we wish to show how such techniques may be applied in an automated, flexible batch production environment.

The application was developed for demonstration purposes and involves a simple binary mixture of Benzene and Toluene, to be separated into a distillate fraction and a bottom residue, each with specified minimum purity (benzene mole fraction = 0.9 in the distillate, toluene mole fraction = 0.9 in the residue). A batch column is available, of given configuration. A quantity of



**Figure 13.** Reactive Batch Distillation - Maximum Conversion of Acetic Acid to Ethyl Acetate, with purity specification on the Ethyl Acetate (Distillate) product. Column model MC2, correlated K-values and kinetic rates

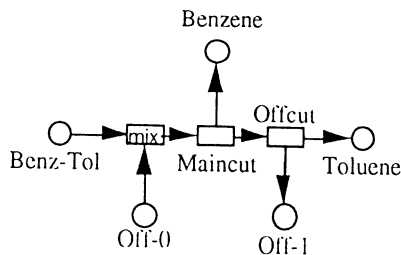
feed material becomes available, its exact composition being measured from the feed tank. Other tanks (one for each product plus one for an intermediate) are assumed initially empty. The quantity of feed is such that a large number of batches are required. The following procedure is adopted:

1. An operation structure is selected for the typical batch, in this case involving an off-cut production and recycle to the next batch (Figure 5). Given the measured fresh feed charge composition (mole fraction benzene = 0.6), pot capacity and product purity specifications, the *minimum total time*, cyclic operation (reflux ratios profiles, times, etc.) is calculated as 0.6 kmol of distillate, optimal off-cut of 0.197 kmol at mole fraction benzene = 0.63, reflux ratio  $r = 0.631$  for 2.64 hr (benzene production) then  $r = 0.385$  for 0.51 hr (off-cut production), leaving 0.6 kmol of bottom product. A single control level was chosen for each step for simplicity, with a multiperiod, single level formulation for the optimization problem.
2. First batch - Since the off-cut recycle tank is initially empty, the cyclic policy cannot be implemented at the beginning and some way must be established to carry out one or more initial

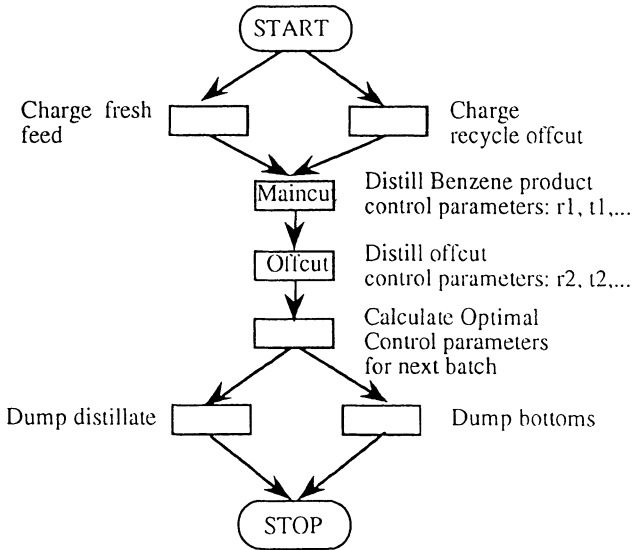
batches so as to reach it. One way (not necessarily the best one), is to run the first batch (according to the operation strategy in Figure 14 (*secondary charge and off-cut production*)). The off-cut from the previous batch, OFF-0 is known (zero for the first batch). The desired off-cut OFF-1, is specified as having the optimal cyclic amount and composition determined in 1 above. With distillate and residue product purities specified, a material balance gives the target values for distillate and product amounts (e.g. 0.4744 kmol of distillate for the first batch). With these targets, a minimum total time operation for this batch is calculated. In an ideal world, the cyclic operation could then be run from batch two onward.

3. The optimal operation parameters for this batch are passed to a control system and the batch is carried out. The actual amounts and compositions produced (distillate cut, off-cut and residue cut) will no doubt be slightly different than the optimal targets, due to model mismatch, imperfect control, disturbances on utilities, etc. Product cuts from the batch are discharged to their respective tanks. The actual composition in the product and in the off-cut tanks is measured.

4. The optimal operation for the next batch is calculated again using the operation structure in Figure 14 and the calculation procedure outlined for the first batch but using the measured amounts and composition of the off-cut produced in the previous batch. Because of this, the optimal policy for the batch will be slightly different from that calculated in step 1. Any variations due to disturbances control problems missed targets etc. in previous batches will also be compensated by the control policy in the current batch. Steps 3 and 4 are repeated until all the fresh feed is processed (a special operation could be calculated for the last batch so as to leave the off-cut tank



**Figure 14.** Batch Distillation of Binary Mixture (Benzene, Toluene)-Operating strategy with addition of secondary charge ( off-cut from previous batch) and production of intermediate off-cut. Column model MC2 (dynamic, more rigorous), thermo model MT2 (ideal)



**Figure 15.** Control Procedure for the Automatic Execution of one Batch by the Control System

empty).

The procedure controlling the actual batch execution is shown schematically in Figure 15. The main control phases correspond to the distillation tasks in the STN definition of the operation with additional control phases for all transfers and details with regards to the operation of individual valves control loops etc. After the main distillation steps (and quality measurements on the fractions produced) the sequence automatically executes an optimal control phase kicking off the program for the numerical calculation of the optimal policy for the next batch. The resulting parameters are stored in the control system database and used in the control phases for the next batch.

A complete implementation of this strategy within an industrial real time environment (the RTPMS real time plant management and control system by IBM) was presented in [53] with the optimal control policies calculated as previously discussed batch management carried out by the SUPERBATCH system [22, 23, 54] and standard control configurations (ratio control on reflux rate and level control on the condenser receiver all PID type). Actual plant behavior was simulated by a detailed dynamic model implemented in a version of the Speedup general purpose simulator directly interfaced to the control system [68].

This application indicates that the dynamic optimization techniques discussed can indeed be used in an on-line environment to provide a reactive batch-to-batch adjustment capability. Again, the operation strategy for each batch was defined a priori and optimization of individual batches in sequence, as just described, is not the same as a simultaneous optimization of all the batches in the campaign, so there should be scope for further improvements.

## Discussion and Conclusions

We may now draw a number of general conclusions and highlight some outstanding problems.

- 1) With regards to modeling and simulation, recent advances in handling mixed systems of algebraic and differential equations with discrete events should now make it possible to develop and solve without (too many) problems the equations required to model in some detail all the operations present in batch distillation. The question remains, in my opinion, of how detailed the models need be in particular to represent the startup period, heat transfer effects in the reboiler, and hydraulic behavior in *sufficient* detail.
- 2) It is presently possible to formulate and solve a rather general class of dynamic optimization problems with equations modeled as DAEs, for the optimization of individual batch distillation steps. Both the control vector parameterization method utilized in this paper and collocation over finite elements appear to work well. These solution techniques are reaching a certain maturity, that is, are usefully robust and fast (a few minutes to a few hours for large problems). Algorithmic improvements are still needed to handle more efficiently very large scale problems and for some special cases (e.g. high index problems). Some attention is also required to formulation of constraints and specifications so that the dynamic optimization problem is well posed. A variety of problems for which specialized solution methods were previously developed can now be all effectively solved in a way which is largely independent from the specific column and thermodynamic models objective function and specifications used. These advances should shift the focus of batch distillation studies towards the use of more detailed dynamic column models and towards optimization of more difficult processes (reactive azeotropic extractive with two liquid phases etc.) which did not easily match the assumptions (simple thermodynamics etc.) of the short cut methods.
- 3) With regards to the optimization of several batch distillation steps in a specified sequence (multiperiod problem), two approaches were presented here, one based on a two level

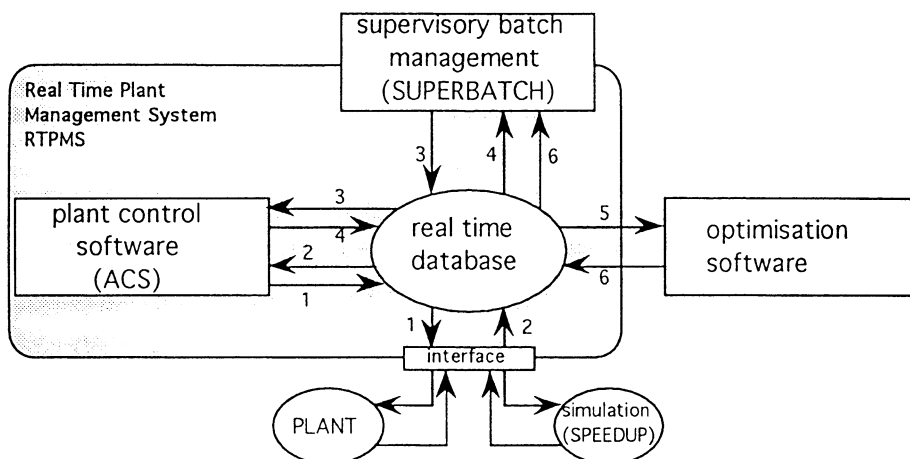
decomposition, taking advantage of the natural structure of batch distillation, the other on a single level formulation. In this area, further work is needed to establish whether one approach is better than the other or indeed for altogether new approaches.

4) The problem of choosing the optimal sequence of steps for the processing of one batch (an operation strategy), as well as the control variables for each step, has not been given much attention, no doubt because of the difficulty of the mathematical problem involved. Systematic methods are needed to select in particular the best strategy for reprocessing off-cuts and more in general, for processing multiple mixtures. Some initial results were presented in literature [82, 83] where a nonlinear programming (NLP) formulation was proposed. The use MINLP for simulation and solution was suggested, but not developed. In this area, there is clearly scope for novel problem formulations and solutions. Similarly, the optimization of each batch in a campaign so as to maximize the performance of the whole campaign does not appear to have been considered other than in the context of scheduling, with extremely simplified "split fraction" and fixed time models, e.g. in [45].

5) One of the assumptions made initially was that of perfect control response. The integration of open loop operation design and closed loop optimization is clearly relevant, as are the sensitivity, controllability and robustness properties of any optimal operation policies. These issues are beyond the scope of this paper, but some initial results are discussed in [73, 81], while an interesting method for model based control of a column startup was presented in [7].

6) Current developments in hardware speed, optimal control algorithms and control and supervisory batch management systems are such that sophisticated optimal operations can be calculated and implemented on-line, not only with respect to the optimal control policies for a batch, but also with regards to batch-to-batch variations, as demonstrated by the last application example. "Keeping it constant", which used to be a practical advantage, is no longer a constraint.

7) Finally, while a number of earlier studies indicated that performance improvements obtained by optimizing the reflux ratio policies were often small, if not marginal, more recent work appears to point to double digit benefits in many cases. As discussed above in one of the examples, this is possibly due to the consideration of a wider range of operating choices, more realistic models and objective functions. Whether the benefits predicted using the more advanced operation policies are indeed achieved in practice is an interesting question which awaits confirmation by the presentation of more experimental, as well as simulated results.



#### Data flows

- 1 control commands and parameters
- 2 measurements
- 3 phase commands and parameters
- 4 phase status
- 5 optimal control requests and problem data
- 6 optimal control solutions (phase parameters) for next batch

**Figure 16.** Schematic Structure of Control Software

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