See also: **I / Distillation:** Historical Development; Modelling and Simulation; Theory of Distillation; Tray Columns: Performance; Tray Columns: Performance; Vapour-Liquid Equilibrium; Correlation and Prediction; Vapour-Liquid Equilibrium: Theory.

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Pilot Plant Batch Distillation

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Introduction

Laboratory distillation encompasses an operating range from millilitres in bench-top devices to pilot units with the capacity for producing several hundred kilograms of product per day. While the design of bench-top assemblies is generally geared towards the achievement of a specified purity grade of the desired product, quantitative predictions are not usually feasible for such equipment and their construction relies a great deal on ingenuity and craftsmanship. For dedicated applications, glassware companies offer off-the-shelf equipment. This article will therefore focus on the pilot-scale units, where the analytical principles of mass and heat transfer can be applied to the operation, design and optimization of the equipment.

The section on theory presents analytical descriptions of batch distillation for three different approaches in order of decreasing complexity. It starts with a comprehensive model for a nonadiabatic, nonzero hold-up, nonconstant molar overflow, nonideal multicomponent column. The second model presented neglects stage hold-ups and assumes adiabatic stages and constant molar overflows to arrive at a set of equations describing the transient behaviour of the equipment, which can be solved for a binary system using a simple spreadsheet. If constant relative volatility and operation at minimum reflux are further assumed, the derivation of a third model is possible, where the transient states within the equipment are given by direct analytical expressions.

The design of a batch column can be a challenging task because batch distillation presents unique considerations that are not addressed in most of the available literature, which is concerned with continuous operation. The section on design is a collection of advice and criteria for the design of batch columns. Specific information is given about equipment for batch distillation and accompanying instrumentation and safety circuitry. Details are drawn from a pilot-scale column that is installed in Penn State University's Department of Chemical Engineering. The section on column operation extends the scope of the two preceding sections by providing information on establishing operating strategies and operating protocols for batch runs. Much of this information is based on hands-on experience acquired with the column described in the subsection on equipment.

The last section is a synopsis of numerical techniques that have been developed in recent years to facilitate the optimization of the operation and design of batch columns. Inherent difficulties associated with the implementation of these numerical techniques into computer codes prevents their widespread use in equipment operation and design. However, it is likely that these techniques will be integrated into commercial simulators in the near future and be readily available to users with little knowledge of programming. The aim here is to introduce the reader to the topic, rather than to offer extensive coverage, providing references for those interested in further reading.

Theory

The theory of batch distillation permits design, operation and optimization calculations by integrating the concepts of thermodynamic equilibrium, mass and heat transfer, energy and material balances to solve the problem of predicting the compositions and flow rates of process streams. The traditional approach to the development of governing equations is to model the equipment as a stack of equilibrium stages. Departures from ideality are taken into account by introducing the concept of stage efficiencies. Modelling in terms of equilibrium stages is convenient because of the availability of extensive equilibrium data for multicomponent systems and the associated predictive thermodynamic models. Packed columns, which do not possess physical mass transfer stages, can be translated into this technical framework by the use of the transfer unit concept (see, for example, McCabe *et al.*, 1993).

Relinquishing or including levels of complexity and interdependence in the fundamental equation and process variables will result in more or less rigorous treatments, with gains in accuracy usually being accompanied by substantial drawbacks in complexity and computational difficulty. Hereunder, three different sets of model equations are presented in decreasing levels of complexity. A rigorous approach to the problem involves the solution of a set of time-dependent differential and algebraic equations for the material and heat balances and for the equilibrium relations. Batch columns are usually constructed so that there is only one section, either above or below the feed stage. The typical column design depicted in **Figure 1** represents the rectifying section. From this simplification it is possible to write the following equations to define the problem completely in each stage except the top stage and the feed drum (reboiler).

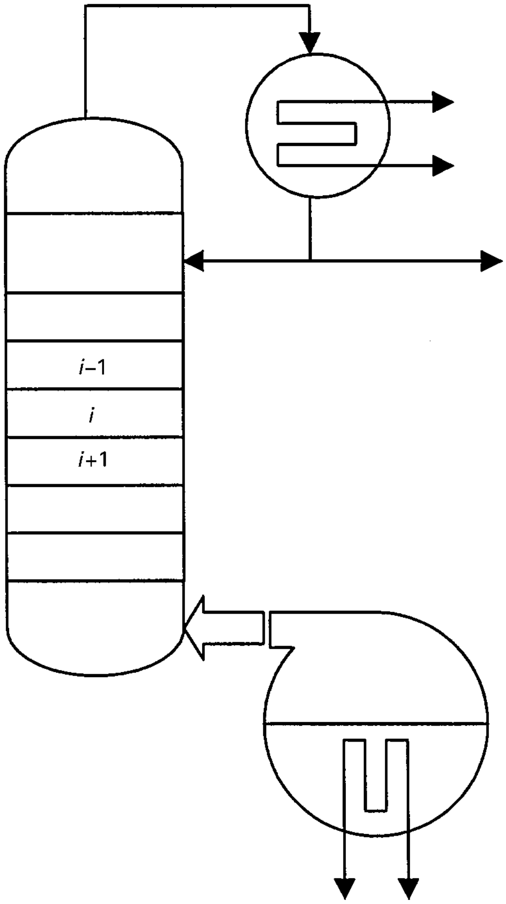

Figure 1 Batch distillation column schematic for a rectifying configuration.

Total material balance

$$\frac{dh^{L}_{tot,i}}{dt} = L_{i-1} + V_{i+1} - L_{i} - V_{i} \qquad [1]$$

Component material balances

$$h^{L}_{tot,i}\frac{dx_{i,j}}{dt} = L_{i-1}x_{i-1,j} + V_{i+1}y_{i+1,j} - L_{i}x_{i,j} - V_{i}y_{i,j}$$

$$i = 1, N_{stage}, j = 1, NC \qquad [2]$$

Energy balance

$$\left(h^{L}_{tot,i}\sum_{x=1}^{NC} x_{i,j}\frac{dH^{L}_{i,j}}{dT}\right)\frac{dT}{dt} = L_{i-1}x_{i-1,j}H^{L}_{i-1,j} + V_{i+1}y_{i+1,j}H^{V}_{i+1,j} - L_{i}x_{i,j}H^{L}_{i,j} - V_{i}y_{i,j}H^{V}_{i,j} + Q_{i}$$

$$i = 1, N_{stage}, j = 1, NC \qquad [3]$$

Vapour liquid equilibrium relation

$$y_{i,j} = f(x_{i,j}) \qquad [4]$$

Summation of liquid mole fractions

$$\sum_{j=1}^{NC} x_{i,j} = 1 \qquad [5]$$

Summation of vapour mole fractions

$$\sum_{j=1}^{NC} y_{i,j} = 1 \qquad [6]$$

Liquid total hold-up constraint

$$h^{\mathrm{L}}_{\mathrm{tot,i}}\left(\sum_{\mathrm{j}=1}^{\mathrm{NC}} x_{\mathrm{i,j}}v_{\mathrm{j}}\right) = Vol \qquad [7]$$

Eqns [1]–[7] ignore the tray hydraulic behaviour and assume identical compositions for the liquid hold-up within a stage and the liquid outflow out of the stage. Other major features and assumptions of the model are nonadiabatic stages, negligible vapour hold-up and constant volumetric liquid hold-up. The assumptions concerning the hold-up are very reasonable and the equations can be readily translated to real stages by the introduction of Murphree tray efficiencies as correction factors for either the liquid or the vapour compositions.

For the top stage, the liquid inflow is related to the distillate outflow by the reflux ratio, and for the feed drum, the depletion of material should be taken into account. There is also no liquid outflow for the reboiler, thereby decreasing the number of necessary equations by one (eqn [7]). The following equations are the modified set for the situation in the top stage and reboiler.

Top stage: total material balance

$$\frac{dh^{\mathrm{L}}_{\mathrm{tot,1}}}{dt} = DR_{\mathrm{D}} + V_2 - L_1 - V_1 \qquad [8]$$

Component material balances

$$h^{\mathrm{L}}_{\mathrm{tot,1}}\frac{dx_{1,\mathrm{j}}}{dt} = DR_{\mathrm{D}}x_{\mathrm{D,j}} + V_2y_{2,\mathrm{j}} - L_1x_{1,\mathrm{j}} - V_1y_{1,\mathrm{j}} \qquad [9]$$

Energy balance

$$\left(h^{\mathrm{L}}_{\mathrm{tot,1}}\sum_{\mathrm{x}=1}^{\mathrm{NC}} x_{1,\mathrm{j}}H^{\mathrm{L}}_{1,\mathrm{j}}\frac{dH^{\mathrm{L}}_{1,\mathrm{j}}}{dT}\right)\frac{dT}{dt}$$

$$= DR_{\mathrm{D}}x_{\mathrm{D,j}}H^{\mathrm{L}}_{\mathrm{D,j}} + V_2y_{2,\mathrm{j}}H^{\mathrm{V}}_{2,\mathrm{j}} - L_1x_{i,\mathrm{j}}H^{\mathrm{L}}_{1,\mathrm{j}}$$

$$- V_1y_{1,\mathrm{j}}H^{\mathrm{V}}_{1,\mathrm{j}} + Q_1 \qquad [10]$$

For the feed drum (reboiler) the following equations are modified.

Total material balance

$$\frac{dh^{\mathrm{L}}_{\mathrm{tot,R}}}{dt} = L_{\mathrm{N\ stage}} - V_{\mathrm{R}} \qquad [11]$$

Component material balances

$$h^{\mathrm{L}}_{\mathrm{tot,R}}\frac{dx_{\mathrm{R,j}}}{dt} = L_{\mathrm{N\ stage}}x_{\mathrm{N\ stage,j}} - V_{\mathrm{R}}y_{\mathrm{R,j}} \qquad [12]$$

Energy balance

$$\left(h^{\mathrm{L}}_{\mathrm{tot,R}}\sum_{\mathrm{x}=1}^{\mathrm{NC}} x_{\mathrm{R,j}}H^{\mathrm{L}}_{\mathrm{R,j}}\frac{dH^{\mathrm{L}}_{\mathrm{R,j}}}{dT}\right)\frac{dT}{dt}$$

$$= L_{\mathrm{N\ stage}}x_{\mathrm{N\ stage,j}}H^{\mathrm{L}}_{\mathrm{N\ stage,j}} - V_{\mathrm{R}}y_{\mathrm{R,j}}H^{\mathrm{V}}_{\mathrm{R,j}} + Q_{\mathrm{R}} \qquad [13]$$

The set of equations written for all the stages forms a system of nonlinear differential algebraic equations, with initial conditions given by the original charge in the feed drum, tray hold-ups and tray composition profiles and internal flow rates. The vector of initial conditions represents a pseudo steady-state solution for an initial feed whose composition is equal to the vapour in equilibrium with the liquid charge of the feed vessel. The transient behaviour is obtained by the simultaneous solution of eqns [1]–[13], which requires linearization and a combination of matrix inversion and integration techniques.

Despite the large range of computational complexity, simulations of batch distillation show that, in most cases, short-cut and rigorous models agree very well. A distinct advantage of the simplified models is they can be implemented in a spreadsheet. In these models the stage hold-up is considered negligible, except for the feed drum (reboiler) where the following equations hold for the total and volatile component material balances in a column operating at constant distillate composition and variable reflux.

Total cumulative material balance

$$\bar{D} = \bar{V} - \bar{L} \qquad [14]$$

$$dW = -d\bar{D} = \left(1 - \frac{\bar{L}}{\bar{V}}\right)d\bar{V} = \left(1 - \frac{R}{R+1}\right)d\bar{V}$$

$$= (1 - S)\,d\bar{V} \qquad [15]$$

Cumulative component balance

$$W_{\mathrm{i}}x_{\mathrm{wi}} = Wx_{\mathrm{w}} + (W_{\mathrm{i}} - W)\,x_{\bar{\mathrm{D}}} \qquad [16]$$

By differentiating and rearranging one gets:

$$W = \frac{W_{\mathrm{i}}(x_{\mathrm{wi}} - x_{\bar{\mathrm{D}}})}{(x_{\mathrm{w}} - x_{\bar{\mathrm{D}}})} \qquad [17]$$

$$-dW = \frac{W_{\mathrm{i}}(x_{\bar{\mathrm{D}}} - x_{\mathrm{wi}})\,dx_{\mathrm{w}}}{(x_{\bar{\mathrm{D}}} - x_{\mathrm{w}})^2} = d\bar{D} \qquad [18]$$

If eqn [18] is substituted in [15] one gets:

$$(1 - S)\, d\bar{V} = \frac{W_i(x_{\bar{D}} - x_{wi})\, dx_w}{(x_{\bar{D}} - x_w)^2} \qquad [19]$$

The total amount of vapour produced will then be:

$$\bar{V} = \int_{x_{wi}}^{x_{wf}} \left[\frac{W_i(x_{\bar{D}} - x_{wi})}{(1 - S)}\right] \frac{dx_w}{(x_{\bar{D}} - x_w)^2} \qquad [20]$$

Since the cumulative vapour produced is $\bar{V} = \theta V$, the time θ necessary for a run is calculated from the above equation as:

$$\theta = \int_{x_{wi}}^{x_{wf}} \left[\frac{W_i(x_{\bar{D}} - x_{wi})}{V}\right] \frac{dx_w}{(1 - S)\,(x_{\bar{D}} - x_w)^2} \qquad [21]$$

The total amount of distillate produced can be found by integration of eqn [18]:

$$\int_0^{\bar{D}_f} d\bar{D} = \int_{x_{wi}}^{x_{wf}} \frac{W_i(x_{\bar{D}} - x_{wi})\, dx_w}{(x_{\bar{D}} - x_w)^2} \qquad [22]$$

Finally, rearrangement of eqn [16] yields:

$$W_i x_{wi} - (W_i - W)x_{\bar{D}} = W x_w \qquad [23]$$

$$W_i x_{wi} - \bar{D} x_{\bar{D}} = W x_w \qquad [24]$$

The above can be differentiated to give the following result:

$$d(W_i x_{wi} - \bar{D} x_{\bar{D}}) = d(W x_w) \qquad [25]$$

$$-\, d(\bar{D} x_{\bar{D}}) = d(W x_w) \qquad [26]$$

$$-\, x_{\bar{D}}\, d\bar{D} = x_w\, dW + W\, dx_w \qquad [27]$$

The remaining amount of charge in the still is then calculated by combining the above equation with the total differential balance $dW = -\,d\bar{D}$ and subsequently integrating the resultant expression:

$$\frac{dW}{W} = \frac{dx_w}{x_{\bar{D}} - x_w} \qquad [28]$$

$$\ln \frac{W_f}{W_i} = \int_{x_{wi}}^{x_{wf}} \frac{dx_w}{x_{\bar{D}} - x_w} \qquad [29]$$

Eqns [20]–[22] provide an efficient way of calculating the total amounts of vapour and distillate produced and the time necessary for the separation without having to solve the system of equations comprised by eqns [1]–[13]. This calculation provides an economic benchmark since it defines the optimum time for a run, based on the recovered product value and the operating costs. As the run time increases, the cumulative revenues given by the total amount of recovered product multiplied by its value will first increase but then approach an asymptotic value. The decreased economic benefit results either because the amount of distillate decreases (as in the case of constant composition distillate) or because the product stream becomes progressively less pure (as in the case of constant reflux ratio operation). The operating costs on the other hand increase steadily with time and the profit function, which combines these two costs, undergoes a maximum, after which the profit will decrease, as illustrated by **Figure 2**.

An analytical solution can be found for a limiting case which assumes an infinite number of stages (corresponding to minimum reflux) and constant relative volatility. At minimum reflux the operating line ends at a pinch zone and x_w is located in the equilibrium

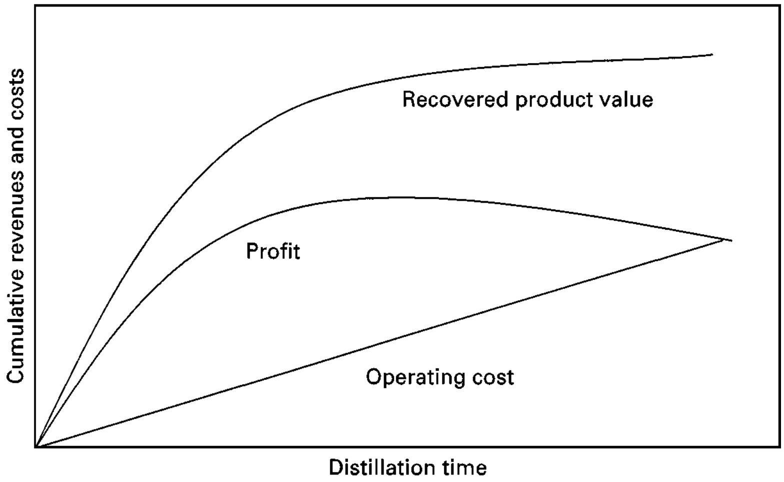

Figure 2 Optimum profit profile: operating costs versus length of time. Recovered product increases rapidly at first but then levels off.

line. The slope of the operating line is then given by:

$$S = \frac{d\bar{L}}{d\bar{V}} = \frac{x_{\bar{D}} - y_w}{x_{\bar{D}} - x_w} = \frac{R}{R+1} \qquad [30]$$

Under the constraint of constant relative volatility the equilibrium relation becomes:

$$y_w = \frac{\alpha x_w}{1 - x_w(\alpha + 1)} \qquad [31]$$

If one takes advantage of eqns [30] and [31], analytical forms for the cumulative distillate production and remaining charge left in the feed still can be derived for the cases of either constant reflux ratio or constant distillate composition operation.

For constant reflux ratio, eqn [15] can be integrated to the expression for the total vapour requirement:

$$\bar{V} = (R+1)\bar{D} = (R+1)\,(W_i - W_f) \qquad [32]$$

Combination of eqns [15], [30] and [31] yields the functional dependence of distillate composition, $x_{\bar{D}}$ on recycle ratio, R, composition of the remaining feed, x_w in the reboiler and relative volatility, α:

$$x_{\bar{D}} = \frac{(R+1)\alpha x_w - R x_w - R x_w^2(\alpha - 1)}{1 + x_w(\alpha - 1)} \qquad [33]$$

Substitution of eqn [33] into the general mass balance expression, eqn [29] and subsequent integration produces an analytical form for the mass balance given by:

$$\ln\frac{W_f}{W_i} = \frac{1}{(R+1)\,(\alpha - 1)} \ln\left[\left(\frac{1 - x_{wi}}{1 - x_{wf}}\right)\left(\frac{x_{wf}}{x_{wi}}\right)\right] + \left(\frac{1}{R+1}\right)\ln\left(\frac{1 - x_{wf}}{1 - x_{wi}}\right) \qquad [34]$$

If the column is operated at constant distillate composition, direct integration of eqn [29] produces the expression for the mass balance:

$$\frac{W_f}{W_i} = \left(\frac{x_{\bar{D}} - x_{wi}}{x_{\bar{D}} - x_{wf}}\right) \qquad [35]$$

The integration of eqn [20], however, requires the development of an expression for the time-dependent operating line, which is accomplished by substitution of eqn [31] into [30] to yield:

$$\frac{d\bar{L}}{d\bar{V}} = \frac{x_{\bar{D}} + x_{\bar{D}}x_w(\alpha - 1) - \alpha x_w}{(x_{\bar{D}} - x_w)\,[1 + x_w(\alpha - 1)]} \qquad [36]$$

Substitution of [36] into the general expression for the vapour requirement (eqn [20]) and integration leads to the vapour requirement equation when the column is operated at constant distillate composition and variable reflux:

$$\bar{V} = \frac{W_i(x_{\bar{D}} - x_{wi})}{(1 - x_{\bar{D}})\,(x_{\bar{D}})\,(\alpha - 1)} \times \left\{(1 - x_{\bar{D}})\ln\left[\left(\frac{x_{\bar{D}} - x_{wf}}{x_{\bar{D}} - x_{wi}}\right) + \left(\frac{x_{wi}}{x_{wf}}\right)\right] + x_{\bar{D}}\alpha \ln\left[\left(\frac{x_{\bar{D}} - x_{wf}}{x_{\bar{D}} - x_{wi}}\right)\left(\frac{1 - x_{wi}}{1 - x_{wf}}\right)\right]\right\} \qquad [37]$$

Eqns [34] and [37] were developed by Bauerle and Sandall, assuming the ideal pinched columns operating at minimum reflux. None the less, their application to real columns yields good approximated results if the equipment operates in a near-pinched zone at the bottom. This is often the case for columns with five or more theoretical stages.

Design

The operation of a batch distillation column, even pilot-scale equipment, is often as technically involved as operation of an industrial-scale column, and the same amount of care in start-up and safety procedures should be taken. Whether designing a new column or revamping an existing one, the necessary safety and physical properties data such as flash and ignition points, flammability and toxicity must be compiled for each component in the mixture. Predictive equations or experimental values for the vapour pressures of all components and binary equilibrium data should be compiled together with parameters of equations of state or activity coefficient models whenever available. Other physical properties to be included are liquid and vapour heat capacities, heats of vaporization and viscosities.

Once the physical property data bank has been put together, preliminary design calculations can be performed. For a multicomponent distillation column a light-key and a heavy-key component should be chosen in order to reduce the preliminary design to a pseudo-binary system. At this point it is possible to use graphical methods like McCabe–Thiele or even something more involved like Ponchon–Savarit to carry our a case study to find out the system response in terms of required number of theoretical stages for a specified purity at different reflux ratios. To accomplish this, the optimization techniques described later can be useful, but since they are also hard to implement. The alternative approach of using a simplified calculation method such as presented in the section on column operation might be more desirable. This initial set (reflux ratio – number of theoretical stages) will permit the preliminary design.

Depending on the intended purpose of the laboratory-scale column, these initial calculations are likely to be sufficient for specifying the details of column design. Reboiler and condenser heat loads permit sizing of steam and condensation coils. Environmental concerns have introduced complexities in design which were not previously an issue for pilot-scale distillation. Current regulations at our site require condensate return to steam generation facilities to recover waste heat. Even a moderate condenser heat load can require prohibitively large quantities of cold tap water and the condenser heat load for even a small distillation column will typically be substantially larger than can be handled by laboratory-scale recirculated chillers. Much of the final decisions on absolute sizing will be dependent upon available facilities and the anticipated intensity of column use. It is important to get to a reasonably accurate preliminary design early in the design process, so that such practical constraints can be considered.

In many situations, a laboratory-scale distillation column will be used for multiple separations, or as a testing ground for additional full-scale design data. Under these circumstances, design for flexibility is a primary concern. Instead of focusing on detailed physical property information, the data collection should focus on obtaining ranges of anticipated physical properties as well as ranges in batch size. The actual design should then reflect the appropriate bounds of properties and separations that may be encountered. It should be kept in mind that there is a practical minimum volume that can be handled, due to tray hold-up, while larger volumes can be handled with multiple batches. Undersizing either reboiler or condenser heat transfer capacity may render the column useless for a specific separation.

In most batch distillation operations, the lighter component is the desired product and the actual column is the rectifying section of a continuous tower. The preceding discussion in this section as well as in the next section implicitly assume this situation. Nevertheless, there might arise design situations where the economical interest lies in the heavier compounds. In more complex operations the designer might even be faced with the task of devising a separation sequence involving two or more columns. For the case where it is desired to recover the heavy component, the calculations for the number of stages should be performed as a stripping column instead.

Since the principles and computational basis of distillation are quite advanced, additional assumptions allow the derivation of simple expressions for the distillate composition and flow rate and the amount of material left in the feed drum. These assumptions render the evaluation of columns with recycle amenable to straightforward solutions.

The remainder of this section includes a description of a versatile laboratory distillation column and its instrumentation and safety systems.

Equipment

Batch distillation equipment can be custom-made to meet particular design specifications or be directly purchased by catalogue selection if no stringent construction features or materials are required. Ordering can be greatly facilitated by a previous search of the manufacturers or suppliers in the worldwide web. Equipment intended to be used for research or educational purposes should be made of glass whenever possible, given the easy observation of the internal flow regimes and their change with the internal flow rates. An existing batch glass column is described here as an example.

Figure 3 shows a distillation column which has a simple conceptual design but is versatile enough to be used for research or teaching applications. The column is atmospheric and functions as the rectifying section of a regular distillation column. The feed drum doubles as a kettle vessel where the feed is vaporized by a coil heater having steam as the heating medium. Instrumentation is reduced to the essentials: the distillate and reflux flow rates are controlled by varying the rotation speed of the distillate and reflex pumps, and the feed flow rate can be controlled by varying the steam pressure in the coil. The safety system consists of a relay actuated by the occurrence of any of the failure conditions in the column, which are pressurization within the equipment, zero flow of condenser cooling water or loss of power to the ventilation system. When any of these conditions occurs, steam admission to the feed drum is switched off.

The pumps are actuated in the remote mode by a driver board that receives signals in the range between 4 and 20 mA from an analog output board installed in a PC. The connection between the pump driver board and the analog output board consists of a screw terminal connector. The variation of the output signal to the pumps is accomplished via

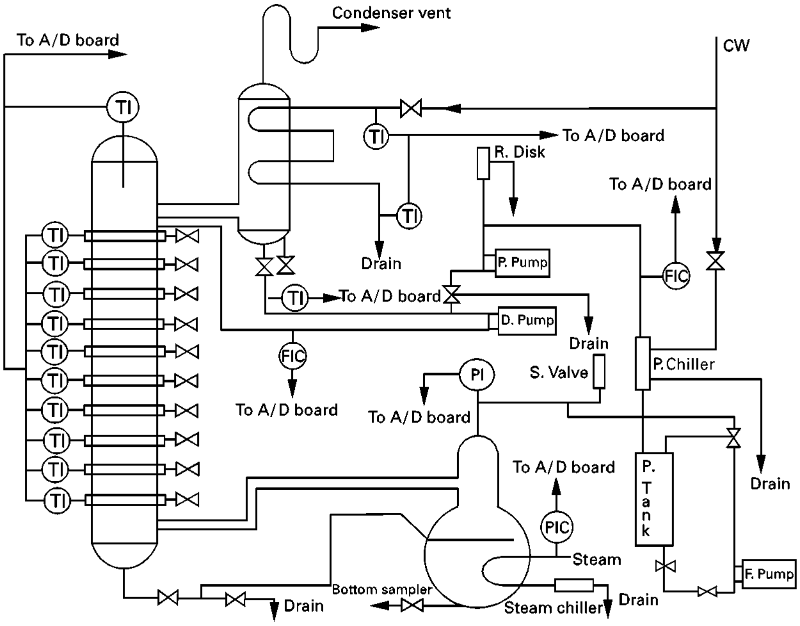

Figure 3 Rectifying batch distillation column. The abbreviations are as follows: A/D board = analog to digital interface board, CW = cooling water, D. Pump = distillate pump, F. Pump = feed pump, FIC = flow indicator control, P. chiller = product chiller, P. Tank = product tank, PI = pressure indicator, PIC = pressure indicator control, R. Disk = rupture disk, S. Valve = safety valve and TI = temperature indicator.

a software utility provided with the board that emulates a control panel, where each of the instruments hooked to the board is assigned a channel number displayed in the panel screen. The user varies the pump flow rate by changing the output current at the computer screen. Manual local control of each pump is also provided in case of failure of the computer-interfaced control. The stepper motor of the steam valve for the feed drum steam coil is also interfaced in a comparable manner.

The column is also provided with thermocouples for each stage, including condenser and reboiler. The thermocouples are wired to a screw terminal connector, that provides the interface to an analog/digital I/O board installed in the PC. When there is a significant difference between the boiling points of the two components of a binary system, the stage temperature is an efficient and straightforward way of evaluating compositions. Under these circumstances, the real-time composition profile within the column can be updated to the computer screen. Sample ports for the liquid phase are installed in every stage, including the condenser and reboiler to corroborate thermal measurements under circumstances where thermal gradients are not sufficiently steep to provide accurate composition correlation. The composition analysis can be performed by a variety of methods. If there is a significant density difference between components being separated, composition can be deduced from a density–concentration curve. Density can be determined gravimetrically, or equipment is available for online density measurement. A particularly versatile online implementation of density measurement is in the condensate stream of an off-set condenser as described in more detail below. If one of the components is an organic acid, sample analysis can be carried out either by titration or by the measurement of any other property related to the dissociation state (such as pH), provided the metering apparatus is sufficiently accurate to discriminate stage-to-stage differences. For organic mixtures, other properties such as refractive index may also be used as analytical method.

The feed drum in the described pilot-scale column is a large glass bulb equipped with a steam heating coil to vaporize the feed. A pressure relief rupture disk provides a mechanical fail-safe against reboiler pressurization. Another pressure gauge is installed at the steam inlet to the coil. The steam outlet is provided with a trap to ensure the total condensation of the steam, and therefore the use of its latent heat. A useful energy balance is achieved by cooling the condensate as it is discharged to the drain. The heat load to the column can be crudely calculated by measuring the discharge flow rate and multiplying this valve by the heat of vaporization of the steam at the inlet pressure.

The distillate is collected in a separate vessel whose volume equals approximately half that of the feed drum. The product collection vessel is fitted to permit charging of material to the feed drum. The remaining material in the drum after a batch processing can be discharged by a valve in the bottom. The subsequent batch charge can also be combined with the remaining heavy ends of the previous operation.

The off-set condenser depicted in Figure 3 provides for direct measurement of condensate flow rate. This eliminates the need to calculate condensate from the condenser energy balance. This is particularly important for pilot-scale units where complete condensation may not be achieved at high boil-up rates. The condensed top vapours drip down and accumulate in the bottom part of the vessel, from which they are removed either to the distillate tank or back to the column as reflux. A match between the condensation rate and sum of product and liquid flow rate returned to the column can be assured by visual monitoring of the condenser liquid level or computer monitoring of the liquid head in the bottom of the condenser with a pressure transducer. The gas entrance to the condenser doubles as a liquid overflow in the event of excessive condensate accumulation.

Instrumentation and Safety Circuits

Although a batch distillation column can be run manually by an attentive and experienced technician, the dynamic nature of operation requires extensive instrumentation for all but the simplest mode of operation. To gain the flexibility necessary for the operation at constant distillate composition, flow rates of the reflux and distillate must be independently controlled. In small units devoted to research, flow control can be easily accomplished by varying the speed of a gear pump through a control panel displayed on a computer screen. The connection of the pump to the computer consists of a driver board wired to a screw terminal connector. The latter is attached to an analog output board. The output signal to the driver board can be varied based on the results of calculations performed by external application programs. If the top composition is to be kept constant, the update on the reflux rate can be calculated by a user routine with the aid of operating charts such as those described later. The value of the reflux rate translated to flow rates (typically current values) controls the distillate and reflux pumps. The product and reflux flow rates must be constrained to balance the rate of condensation. This is conveniently accomplished by monitoring the condenser level as an indicator of the difference between boil-up and distillate and product flow rates. The direct use of the heat load output to control the condenser level is not recommended due to the large dead-time between a change in the reboiler conditions and the resulting effect in the liquid level. The result of the reflux calculation is stored in a data buffer from which it can be retrieved by another application and used to update the corresponding analog output channel.

Analog and digital I/O boards can also be installed to retrieve information such as cooling water temperature and flow rate, steam pressure, flow rate to the reboiler and the temperature profile of the column. The stage temperature is a direct indicator of stage composition; however, it is only useful as a control variable when the temperature variation between successive stages is significant. The greatest variation in temperature during the batch run will take place in the reboiler which is an excellent means of monitoring overall progress of the separation.

Variation of the heat load to the column can be actuated remotely by fitting the steam valve with a stepper motor. A variable heat load adds operation flexibility and can be used in conjunction with other strategies to maximize recovery and purity of a desired component at a lower energy cost. For example, the feed drum contains the highest fraction of the volatile component at the beginning of the process. Therefore, the column can be started up at a lower boil-up rate, which will be gradually increased to match the enrichment of the charge in the heavier component. Figure 3 shows typical column instrumentation, and data acquisition and control.

Three operating conditions are monitored constantly and may independently activate the safety system, stopping steam delivery to the reboiler by closing a steam safety valve that precedes the steam controller valve. These monitored conditions are the column pressure, cooling water flow and ventilation fans. The pressure transducers, flow transmitter and power to the fans are set up as a logic relay where loss of any one of the direct current voltages is sufficient to actuate the steam safety valve. It is important to choose the logic of these circuits such that electrical and mechanical failures will default to termination of the batch run. The safety system circuitry is depicted in **Figure 4**.

Column Operation

While dedicated laboratory-scale distillation can be used for solvent recovery, experimental laboratory-scale columns are used for collection of design data. The operational objective is usually to maximize the recovery of a component under the constraint of a desired purity level. The feature of the batch process which distinguishes it from the more familiar continuous counterpart is its inherently transient nature. The continuously changing feed composition must be

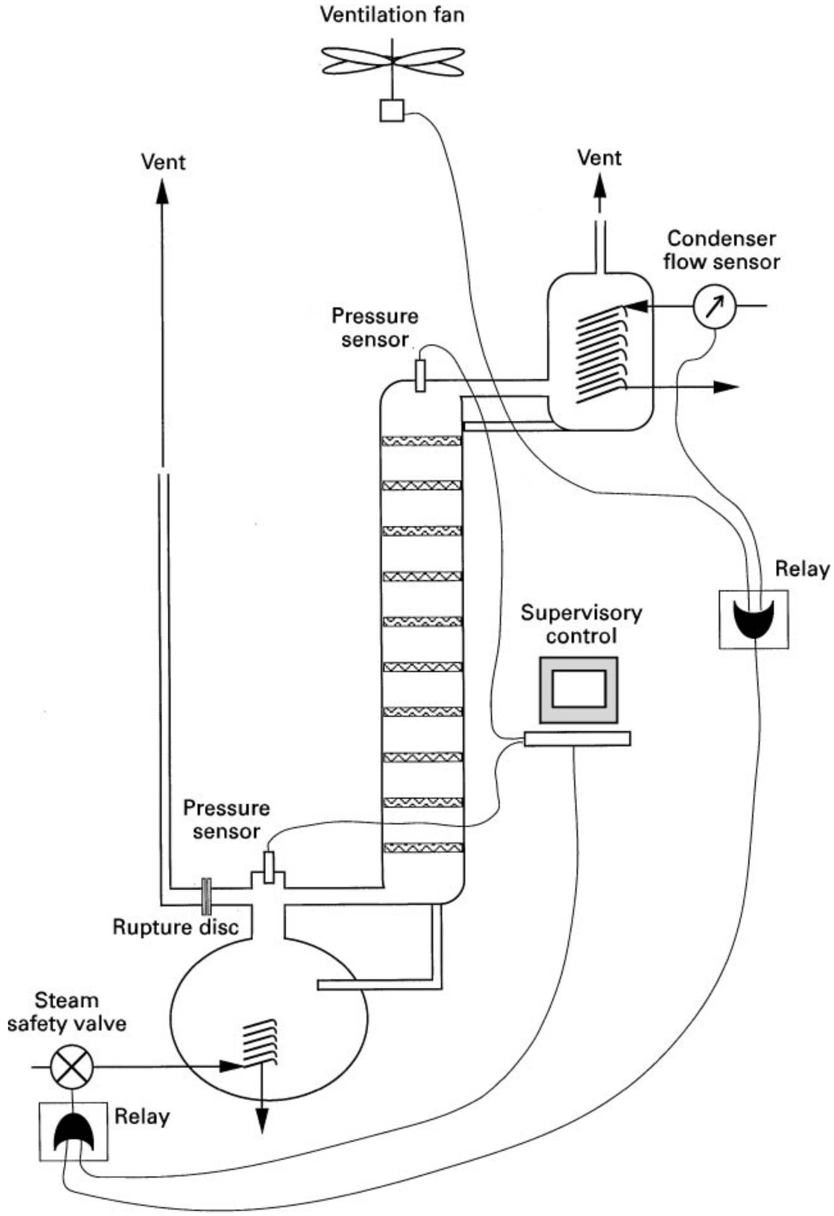

Figure 4 Safety system circuitry.

accounted for in the calculation theory. A variety of operation and completion criteria may be used depending on the process economics, equipment characteristics and product value. Several different basic operational modes are possible:

1. total reflux, with periodic dumping of the accumulated material from the condenser to the distillate tank;
2. constant reflux, with continuous variation of the instantaneous distillate composition, starting above and finishing below the desired product specification;
3. constant composition, with variable reflux ratio in order to keep the instantaneous distillate composition constant.

Operation strategies can take advantage of all three of these operational modes.

Initially the column is operated at total reflux with subsequent product collection at a purity higher than the final product specification. After this initial cut is withdrawn to the product tank, operation is switched to the constant composition mode and the equipment is run until the reflux ratio becomes so high that product collection is minimal. At this point the operation is switched to the constant reflux mode and continued until the average composition of the distillate drops to the desired level, when the equipment is shut down. Variations on this approach are often required due to equipment limitations. If the column is to be operated manually, then it might be difficult to maintain constant distillate composition. Also, if the column consists of less than five ideal stages, it is more advantageous to operate at constant reflux.

Prior to the initiation of any operational procedure, it is necessary to elaborate an operation schedule that can be used as a guide throughout the run. Although the procedures discussed here can be implemented for columns with a very low level of automation, they can also be used in application programs that run as a part of an automated control loop. One can use simplified calculation methods (e.g. McCabe–Thiele) or resort to more extensive numerical computations if the effect of some variables such as the hold-up is to be taken into account. Independent of the calculational basis, better predictions of the composition profiles can be obtained if the stage efficiencies or at least the overall efficiency is known. Efficiencies depend on the physical properties of the system, particularly the viscosity and the relative volatility, but also on the geometric characteristics of the equipment. Determination of the overall and stage efficiencies can be easily accomplished by running the column at total reflux. When the column has reached steady state, the composition profiles within the column must be determined. The overall efficiency is easily calculated by stepping off theoretical stages in the McCabe–Thiele diagram between the equilibrium and the operating line, which at total reflux coincides with $y = x$. The number of theoretical stages is determined when the bottom composition is crossed. The Murphree efficiency for stage n receiving liquid from stage $n - 1$ and vapour from stage $n + 1$ is defined as:

$$\eta_{\mathrm{M}} = \frac{y_{\mathrm{n}} - y_{\mathrm{n}-1}}{y_{\mathrm{n}}^{\mathrm{eq}} - y_{\mathrm{n}-1}} \qquad [38]$$

Eqn [38] is a measure of the degree of separation achieved in the vapour going from stage $n + 1$ to stage n and can be visualized in the McCabe–Thiele diagram as a segment ratio, as shown in **Figure 5**. The maximum degree of separation is represented by the difference in the denominator, where the vapour leaving the stage is in equilibrium with the liquid phase of the same stage.

Determination of the vapour-phase composition is often more difficult than liquid and sample ports are generally only provided for the liquid phase. It is therefore useful to define Murphree efficiency of the liquid compositions as:

$$\eta_{\mathrm{M}} = \frac{x_{\mathrm{n}+1} - x_{\mathrm{n}}}{x_{\mathrm{n}+1} - x_{\mathrm{n}}^{\mathrm{eq}}} \qquad [39]$$

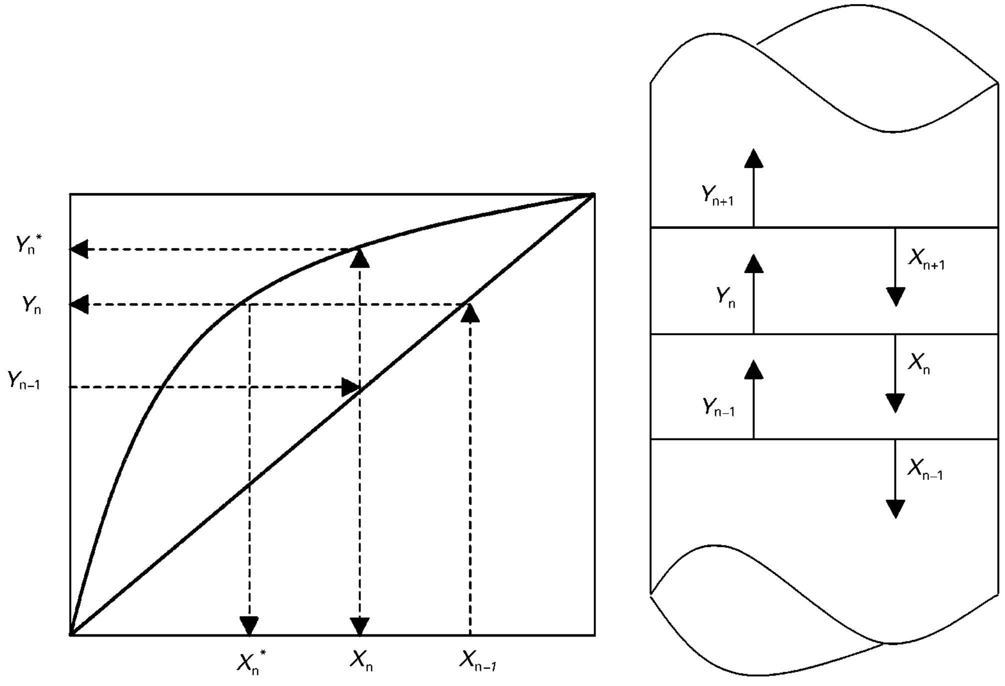

Figure 5 Representation of stage efficiencies.

Once the efficiencies are determined, an operation schedule at constant reflux should be prepared. The operation schedule consists of a family of curves where the reflux ratio is plotted as a function of reboiler composition, holding the distillate composition constant as depicted in **Figure 6**. The curves can easily be generated in a spreadsheet if the equilibrium curve for the system can be regressed as an analytical form, $x = f(y)$. A distillate composition (x_D) is fixed as the fulcrum, around which all the operating lines pivot, as defined for different reflux ratios (R_D), as shown in **Figure** 7. Since the number of ideal stages is known, the bottoms composition (x_B) is found for each operating line by stepping off these stages between the equilibrium curve and the operating lines. Once x_B is found for a particular operating line, the reflux ratio is changed, thereby defining another operating line, and the procedure is repeated to find the corresponding x_B. In this way, a set of data points (R_D, x_B) corresponding to a fixed distillate composition x_D is determined. The next set is determined by the same procedure, changing the value of x_D. These plots of R_D versus x_B represent the reflux ratio required to achieve a specified distillate composition at a given composition within the reboiler.

The R_D versus x_B curves can either be used in manual operation or integrated into an automated control strategy, where information about the feed drum composition is used to calculate the new required reflux ratio to keep x_D constant. The choice of x_D will depend on the minimum acceptable purity for the product. Sometimes, even when a higher purity is desired, the operating x_D may be imposed by equipment restrictions. The flow rate range of the pumps, for example, might restrict operation to a certain range of the reflux ratio. In this case, switching to a lower distillate composition will allow longer runs, thus increasing the total amount of product.

Stopping criteria for an industrial distillation is generally dictated by economics. Operating costs accumulate continuously with time, because of energy and labour costs, as discussed above.

Optimization Techniques

Optimization of batch distillation operations is not addressed with the same frequency as the continuous-case counterpart. The likely reason for the scarcity of publications in this area lies in the transient nature of the problem, which introduces a system of differential equations to describe the dynamics. The optimization problem therefore consists of a target functional (see below) to be minimized and a set of constraints embodied by the differential equations for the time-dependent behaviour of material and energy balances and algebraic equations for phase equilibrium and column hydraulics plus additional constraints such as bounds on certain variables. Optimization problems with nonlinear algebraic model equations and constraints can be solved in a straightforward way by nonlinear programming strategies. On the other hand, unconstrained problems with differential equation models can be handled through the calculus of variations. Models that combine both of these features are currently optimized by imposing some level of approximation to the problem. The problems usually reported in the literature for batch distillation can be classified as:

1. Maximum distillate problem: to maximize the amount of distillate of a specified purity for a specified time.

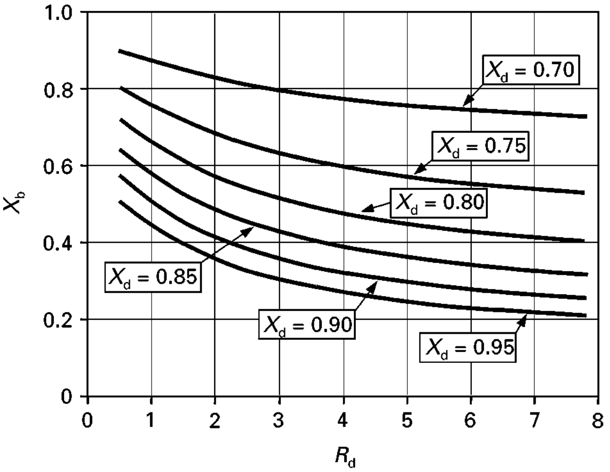

Figure 6 Operation schedule at constant composition. Reflux schedule (based on 45% η overall). X_b is the reboiler composition, X_d is the distillate composition and R_d is the reflex ratio.

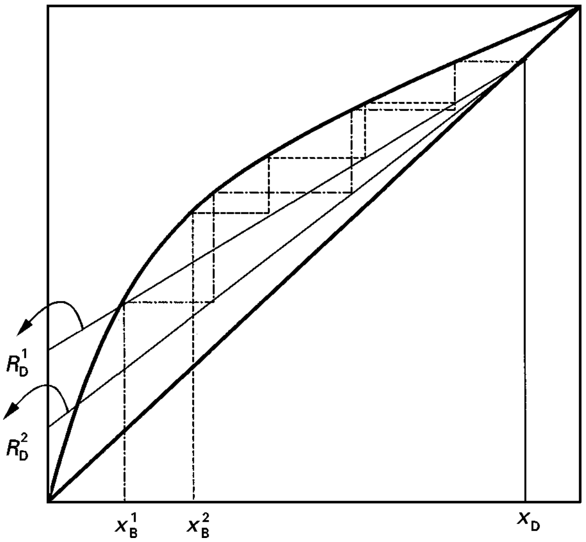

Figure 7 Construction of the operation schedule.

2. Minimum time problem: to minimize the batch time needed to produce a prescribed amount of distillate of a specified purity.
3. Maximum profit problem: to maximize a profit function for a specified purity of distillate.

The maximum profit problem for a column operated at constant distillate composition involves the evaluation of the net profit of the column along its batch run time. The net profit function behaviour has already been discussed. The profit curve displays an extrema and the profit optimization problem therefore seeks the value of the batch run time (a number) that will maximize the net profit function. It is amenable to a simple graphic solution that can be obtained from a spreadsheet as long as a simple zero hold-up model is employed to describe the column operation. On the other hand, the solution of the maximum distillate problem is given by a time-dependent function (the distillate flow rate) that will maximize the cumulative distillate production, a function of the distillate flow rate. This latter function of another function is called a functional.

In this section some of the recently developed techniques to extremize functionals are briefly reviewed. The objective is to offer the reader an introduction to the theme, and provide useful references for further information. The optimization problem belonging to one of the above categories can be posed in terms of an objective function subjected to constraints such as:

$$\min_{\mathbf{u}(\mathbf{t}),\mathbf{z}(\mathbf{t}),\mathbf{p}} \Phi = \Psi(\mathbf{z}(\mathbf{b}),\mathbf{p}) + \int_{\mathrm{a}}^{\mathrm{b}} \mathrm{G}(\mathbf{z}(\mathbf{t}),\mathbf{u}(\mathbf{t}),\mathbf{p})\mathbf{dt} \quad [40]$$

subject to:

$$\dot{z}(t) = F(\mathbf{z}(\mathbf{t}),\mathbf{u}(\mathbf{t}),\mathbf{p}) \quad [41]$$

$$\mathbf{g}(\mathbf{u}(\mathbf{t}),\mathbf{z}(\mathbf{t})) \leq 0 \quad [42]$$

$$\mathbf{g}_{\mathrm{f}}(\mathbf{z}(\mathbf{b})) \leq 0 \quad [43]$$

$$\mathbf{z}(\mathbf{a}) = \mathbf{z}_0 \quad [44]$$

$$\mathbf{z}(\mathbf{t})^{\mathrm{L}} \leq \mathbf{z}(\mathbf{t}) \leq \mathbf{z}(\mathbf{t})^{\mathrm{U}} \quad [45]$$

$$\mathbf{u}(\mathbf{t})^{\mathrm{L}} \leq \mathbf{u}(\mathbf{t}) \leq \mathbf{u}(\mathbf{t})^{\mathrm{U}} \quad [46]$$

In the above set of equations the integral part of the objective function to be minimized can be viewed as the total amount of distillate, withdrawn as top product, whereas the function $\psi(\mathbf{z}(\mathbf{b}), \mathbf{p})$ may account for the final hold-up within the equipment, which can be incorporated into the product at the end of a batch run. The vector $\mathbf{z}(\mathrm{t})$ represents the state variables of the system, such as composition, internal flow rates and temperatures, and the vector $\mathbf{p}$ represents constant parameters. The vector $\mathbf{u}(\mathrm{t})$ carries the control profiles, i.e. the variables used to manipulate eqn [40] and achieve the minimization goal. Distillate of a specified purity can be maximized for instance by changing the reflux ratio. The time-dependent reflux ratio would be then the control variable $u(t)$ for such an optimization problem. The constraints represented by eqn [41] embody the material and energy balances, which are written in their transient form for the batch problem. Algebraic constraints included in eqn [42] may represent the equilibrium relations and the summation of the liquid mole fractions. Inequality constraints with lower and upper bounds (eqns [45] and [46]) may represent either purity requirements in the product or physical constraints in the maximum and minimum attainable values of the control variables. Initial and final states of the system are also written as constraints, as represented by eqns [44] and [43] respectively.

The optimal control problem posed above seeks the time-dependent control profile (control function) that minimizes the objective functional (i.e. a function of functions represented by eqn [40]). It can be solved in a variety of ways, depending on how one chooses to handle the differential equation constraints. Methods based on the calculus of variations use Lagrange multipliers and slack variables to restate the constrained problem of eqns [40]–[46] as an unconstrained one. Since the minimum of the constrained problem is equivalent to the minimum of the unconstrained one, the augmented problem is represented by:

$$\begin{aligned}\min_{\mathbf{u(t),z(t),p}} \Phi^1 &= \psi(\mathbf{z(b)}, \mathbf{p}) + v^T \mathbf{g}_f(\mathbf{z(b)}) \\ &+ \int_a^b [G(\mathbf{z(t)}, \mathbf{u(t)}, \mathbf{p}) \\ &+ \lambda^T(\mathbf{t})(\mathbf{F}(\mathbf{z(t)}, \mathbf{u(t)}, \mathbf{p}) - \dot{\mathbf{z}}(\mathbf{t})) \\ &+ \mathbf{M}^T(\mathbf{t})(\mathbf{g}(\mathbf{u(t)}, \mathbf{z(t)}) + \mathbf{s}^2)]dt \end{aligned} \qquad [47]$$

By analogy to Hamilton's equation of motion, one can define a Hamiltonian as:

$$\begin{aligned} H(\mathbf{z(t)}, \mathbf{u(t)}, \mathbf{p}) &= \mathbf{G}(\mathbf{z(t)}, \mathbf{u(t)}, \mathbf{p}) + \lambda^T \mathbf{F}(\mathbf{z(t)}, \mathbf{u(t)}, \mathbf{p}) \\ &+ \mathbf{M}^T(\mathbf{g}(\mathbf{u(t)}, \mathbf{z(t)}) + \mathrm{s}^2) \end{aligned} \qquad [48]$$

And therefore the problem in [47] becomes:

$$\begin{aligned}\min_{\mathbf{u(t),z(t),p}} \Phi^1 &= \psi(\mathbf{z(b)}, \mathbf{p}) + v^T \mathbf{g}_f(\mathbf{z(b)}) \\ &+ \int_a^b [\mathbf{H}(\mathbf{z(t)}, \mathbf{u(t)}, \mathbf{p}) - \lambda(\mathbf{t})\dot{\mathbf{z}}(\mathbf{t})]\mathbf{dt} \end{aligned} \qquad [49]$$

The minimum of the latter is found in the usual way by taking the derivatives of the augmented problem with respect to all the independent variables ($\mathbf{z}$, v, λ, s, $\mathbf{u}$, $\mathbf{t}$). Setting those to zero and taking into account the conditions for a fixed initial condition problem ($dt|_{t_0} = 0$, $d\mathbf{z}(\mathrm{t}_0 = \mathbf{0})$), one obtains the following variational formulation.

State equations

$$\dot{z} = \frac{\partial H}{\partial \lambda} \qquad [50]$$

Co-state equations

$$-\dot{\lambda} = \frac{\partial H}{\partial z} \qquad [51]$$

Stationary condition

$$\frac{\partial H}{\partial u} = 0 \qquad [52]$$

$$\frac{\partial H}{\partial M} = 0 \qquad [53]$$

$$\frac{\partial H}{\partial s} = 0 \qquad [54]$$

Pontryagin's maximum principle

$$H(x^*, u^*, \lambda^*, t) \leq H(x^*, u^* + \delta u, \lambda^*, t) \qquad [55]$$

Boundary condition

$$(\phi_z + \psi_z^T v - \lambda)^T|_b dz(b) + (\phi_t + \psi_t^T v + H)|_b dt(b) = 0 \qquad [56]$$

For problems with constraints in the control variables like those given by eqn [46], the stationary condition must be modified to include Pontryagin's maximum principle which establishes that the solution values for the constrained control variables must lie along an optimal path. That is, any variation in the optimal control profile $u^*(t)$ at time t, while keeping the state and co-state variables $z(t)$, $\lambda(t)$ and $M(t)$ at their optimal values, will force an increase in the value of the Hamiltonian. This replaces the unconstrained minimum condition of eqn [52] and is stated mathematically in eqn [55]. Also, the second term of the boundary condition in eqn [56] vanishes for fixed-time problems.

Solution of the optimization problem of eqns [40]–[46] in its variational formulation requires integration of two sets of differential equations given by [50] and [51] to get the state variables $\mathbf{z}$ and adjoint variables λ for the ordinary differential equation (ODE). Since these equations are also a function of the control profile $u(t)$, their integration is first performed with guessed values of this vector. Eqns [53] and [54] are used to find the second set of adjoint variables ($\mathbf{M}$) and the slack variables ($\mathbf{s}^2$) associated with the constraint on $\mathbf{g}(\mathbf{u(t)}, \mathbf{z(t)})$. Finally, eqn [52] or [55] provides the updated values for $u(t)$, the control profile, whereas the adjoint variables for the boundary conditions are calculated from eqn [56]. The whole procedure involves successive iterations of the control vector and can be computationally intensive, especially for problems with many constraints.

An alternative solution can be formulated to overcome the difficulty posed by the differential constraints. Eqns [40]–[46] are discretized using finite elements. Within each element, function approximation is expressed in terms of orthogonal polynomials and the resulting problem is amenable to a mathematical treatment intended to minimization problems involving only algebraic equations.

Discretization of the optimal control problem leads to the nonlinear problem model given below. This formulation consists of the discretized objective function of the original problem, the continuity equations for state variables and inequality constraints in the original formulation.

$$\underset{u_{ij},z_{ij},p,\Delta\zeta_i}{\text{Min}} \quad \Phi = \psi(\mathbf{z}_f, \mathbf{p}) + \sum_{i=1}^{NE} \sum_{j=1}^{K} \mathbf{w}_{ij}\mathbf{G}(\mathbf{z}_{ij}, \mathbf{u}_{ij}, \mathbf{p}, \Delta\zeta_i) \qquad [57]$$

subject to:

$$\Delta\zeta_i r_{ij} = \dot{z}_{K+1}\tau_{ij} - \Delta\zeta_i F(z_{ij}, u_i, p) = 0 \qquad [58]$$

$$\mathbf{g}(\mathbf{u}_{ij}, \mathbf{z}_{ij}, \Delta\zeta_i) \leq \mathbf{0} \qquad [59]$$

$$\mathbf{g}_f(\mathbf{z}_f) \leq \mathbf{0} \qquad [60]$$

$$z_{10} - z_0 = 0 \qquad [61]$$

$$z_{i0} - z_{K+1}^{i-1}(\zeta_i) = 0 \quad i = 2, \ldots, NE \qquad [62]$$

$$z_f - z_{K+1}^{NE}(\zeta_{NE+1}) = 0 \qquad [63]$$

$$z_{ij}^L \leq z_{ij} \leq z_{ij}^U \qquad [64]$$

$$u_{ij}^L \leq u_{ij} \leq u_{ij}^U \qquad [65]$$

$$\sum_{i=1}^{NE} \Delta\zeta_i = \zeta_{\text{Total}} \qquad [66]$$

Problem discretization introduces the time element lengths ($\Delta\zeta_i$) as additional variables. Thus, variables in [57]–[66] include: $\Delta\zeta_i$, the finite element lengths for $i = 1, \ldots, NE$; z_f, the value of the state at the final time; z_{ij} and u_{ij}, the collocation coefficients for the state and control profiles where *i* refers to the element and *j* to the collocation point within each element; and *p*, any additional design parameters (such as boil-up rate and final time). In addition, w_{ij} are quadrature weights from the integral in [40]. Lagrange polynomials are applied for the orthogonal collocation within the finite elements. The order of the collocation method should be equal to the index of the system of the state variable differential constraints and algebraic equations. The index is equal to the number of times the algebraic equations must be derived in order to recover the standard form of a first-order ODE.

The solution of eqns [57]–[66] looks for the values of the coefficients z_{ij} and u_{ij} of the polynomial approximation for the state variables and control profiles respectively. In addition, the discretized problem also includes the length of the discretization interval $\Delta\zeta_i$. The problem variables are partitioned into a set of state variables (z_{ij}) and optimization variables (u_{ij} and $\Delta\zeta_i$), which provides a solution strategy where the state variables are calculated separately using the state equations, whereas the control profile and element lengths are obtained via the solution of a quadratic programming problem as follows (see Logsdon and Biegler, in the Further Reading section):

Equation [58] is solved in each element for the values of z_{ij} in the interior collocation points, starting with the first element, from the initial values of the state variables and guessed element lengths ($\Delta\zeta_i$) and control profiles (u_{ij}). The rightmost (exterior) collocation point for the state and control profiles in eqn [58] is calculated from the values at the interior collocation points by:

$$z_{i,k+1} = \sum_{j=0}^{k} z_{ij}\phi_j \qquad [67]$$

$$u_{i,k+1} = \sum_{j=1}^{k} z_{ij}\theta_j \qquad [68]$$

where ϕ_j and θ_j in the above equation are Lagendre's orthogonal polynomials.

Continuity for the state variables is ensured by eqn [62] which establishes the equality between the state variables of the rightmost collocation point of element $i - 1$ and their initial value in element *i*. The initial value problem presented in eqn [58] is thus integrated element-by-element using a marching technique with collocation within each element.

After a new set of state variables is generated by the technique described above, the control profiles (u_{ij}) and element lengths ($\Delta\zeta_i$) are updated using a successive quadratic programming algorithm that solves the following:

$$\underset{\Delta\xi}{\text{Min}} \; \nabla\Phi^T\mathbf{Z}\Delta\xi + \tfrac{1}{2}\Delta\xi^T(\mathbf{Z}^T\mathbf{B}\mathbf{Z})\Delta\xi \qquad [69]$$

subject to:

$$\mathbf{g} + \nabla\mathbf{g}^T\mathbf{Z}\Delta\xi \leq \mathbf{0} \qquad [70]$$

In the above problem, the variables *u* and $\Delta\zeta$ were included in the vector $\Delta\xi$ and the inequality constraint is the same as that of the original problem formulation. ($\mathbf{Z}^T\mathbf{B}\mathbf{Z}$ is the Hessian matrix of the objective function Φ and it is also updated during the quadratic programming step using the BFGS (Broyden–Fletcher–Goldfarb–Shanno) formula). The reduced gradients for the objective and constraint functions appearing in eqns [69] and [70] above are calculated in the iteration *t* during the integration step according to the formula:

$$\{\mathbf{Z}^T\nabla\Phi\}_j = \frac{\partial \mathbf{z}_{f,k+1}}{\partial \xi_j}\frac{\partial \Phi}{\partial \mathbf{z}_f} \qquad \{\mathbf{Z}^T\nabla\mathbf{g}_n\}_j = \frac{\partial \mathbf{z}_{c,k+1}}{\partial \xi_j}\frac{\partial \mathbf{g}_n}{\partial \mathbf{z}_c} \qquad [71]$$

In the equation above, the partial derivatives of the state variables at the rightmost exterior collocation point (z_{k+1}), in relation to the optimized vector ξ, is calculated, via chainruling, by the formula:

$$\frac{\partial z_{i,k+1}}{\partial \xi_j} = \frac{\partial z_{i,k+1}}{\partial z_{i-1,k+1}} \frac{\partial z_{i-1,k+1}}{\partial z_{i-2,k+1}} \cdots \frac{\partial z_{j,k+1}}{\partial \xi_j} \qquad [72]$$

The new set of control variables and element lengths calculated in the optimization step replaces the old one and the integration step is performed once again. The Kuhn–Tucker conditions, which determine the attainment of constrained minimum, are then checked and the calculations are stopped if these conditions have been reached. Otherwise, the optimization step is performed again and the whole procedure is repeated.

The preceding development typifies the complexity involved in rigorous optimization of batch distillation. The gains of reduced costs or shorter process times that can be achieved by such an optimization would not probably be worth the effort for routine operation. None the less, it is possible to utilize sophisticated laboratory-scale distillation units to test alternative control strategies indicated by computational approaches.

List of Variables

Section 2 – Theory

Variables
h = tray hold-up
H = molar enthalpy
$\bar{D}$ = cumulative distillate production, moles
L = liquid molar internal flow rate
$\bar{L}$ = cumulative amount of reflux, moles
MW = molecular weight
Q = heat load
R = reflux ratio
S = $R/(R+1)$
T = temperature
t = time
V = vapour molar internal flow rate
v = liquid molar volume
Vol = volume of the stage
$\bar{V}$ = cumulative vapour production, moles
W = moles of material left in the still
x = liquid molar fraction
y = vapour molar fraction

Superscripts
L, V = liquid and vapour phases

Subscripts
i, j = tray number, component
i = initial
f = final
R = reboiler
w = material in the still
tot = total

Section 5 – Optimization Techniques

Variables
a = initial condition for the optimization problem
b = final condition for the optimization problem
G = component of the objective function due to the integral state
H = Hamiltonian function
M = Lagrange multipliers for the algebriac inequality constraints
p = vector of design parameters
t = time
s^2 = vector of slack variables for the inequality constraints
u = vector of control variables
z = vector of state variables

Superscripts
U, L = upper and lower limits of the constrained variables

Subscripts
z = derivative with respect to z
b = evaluate at point b

Greek alphabet
$\Delta\xi$ = vector of time-finite element lengths
θ = Lagrange polynomial approximation for the control variables
λ = Lagrange multipliers for the differential equality constraints
ν = Lagrange multipliers for the inequality constraints at final conditions
ϕ = Lagrange polynomial approximation for the state variables
Φ = objective function
Ψ = term of the objective function evaluated at final conditions

See also: **II/Distillation:** Historical Development; Instrumentation and Control Systems; Theory of Distillation.

Further Reading

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Sublimation

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Introduction

Sublimation is not a procedure that is generally regarded as an analytical technique. It is a process, however, by which compounds can be purified or mixtures separated and as such can be of value as a single step or as an integral part of a more complex analytical method. It is applicable to a range of solids of inorganic or organic origin in a variety of different matrices and can be particularly useful when heat-labile materials are involved.

As a method of sample purification sublimation has been used to produce high-purity materials as analytical standards. A specific and common example of sublimation used as a means of purification is the removal of water from heat-labile materials in the process known as freeze-drying. The technique is described more fully below.

As a separation technique fractional sublimation has been used either to purify samples for analysis by removing undesirable components of the matrix or to remove the analyte from the matrix for subsequent analysis.

Principles

Sublimation is the direct conversion of a solid to a gas or vapour:

$$\text{solid} + \text{heat} \Rightarrow \text{gas or vapour} \quad (\text{heat} = \Delta H_{\text{subl}})$$

The heat supplied in this endothermic process is termed the heat of sublimation (ΔH_{subl}). The conditions under which sublimation occurs may be predicted for a given substance from its phase diagram, but in practice it is more common to use typical experimental parameters to determine the optimized procedure.

The heat of sublimation is a crucial parameter in deciding upon the applicability of sublimation to a particular substance, or indeed on the possibility of separating two components in a mixture.

An empirical approach to determining the appropriate temperature and pressure for sublimation can be used based upon previously determined data. The temperature (T, °K) and pressure (P) of sublimation can be related by an expression of the form:

$$\log_{10} P\,(\text{mmHg}) = A - (B/T)$$

in which the constants A and B for compounds of interest are available from published tables. The