Batch Reactor Systems Technology Symposium

Teesside, October 2001

DYNAMIC MODELLING

OF

BATCH REACTORS & BATCH DISTILLATION
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1.0   INTRODUCTION

Batch processes are used extensively in the manufacture of relatively small volume products with relatively high value. These processes are frequently carried out in production facilities intended for multi-purpose use.

The achievement of stable and reproducible operating conditions is important in order to achieve the required product purity, yield and cycle times to satisfy the commercial requirements and relevant regulatory authorities.

Batch processes are inherently transient in nature and the capability to demonstrate dynamically the adequacy of the equipment design and performance provides a powerful design tool. Dynamic modelling can prevent costly mistakes prior to start up. Once a process model signature has been validated against real plant performance the dynamic model can be used as a diagnostic tool to identify operating problems.

This paper reviews the basic techniques for dynamic modelling the process and control of batch reactors and batch distillation systems using the Chemstations integrated range of software which is supported by an extensive component physical property database and thermodynamic options.

The power of this database is demonstrated below where the relative merits of the heat transfer fluids under consideration can be rapidly presented without wasting design time. These plots alert the designer to the benefits and disadvantages of the respective fluids which otherwise could be missed. For example note the difference in liquid specific heats between water and thermal fluids being a ratio factor varying from 2.8 to 1.8, quite significant.
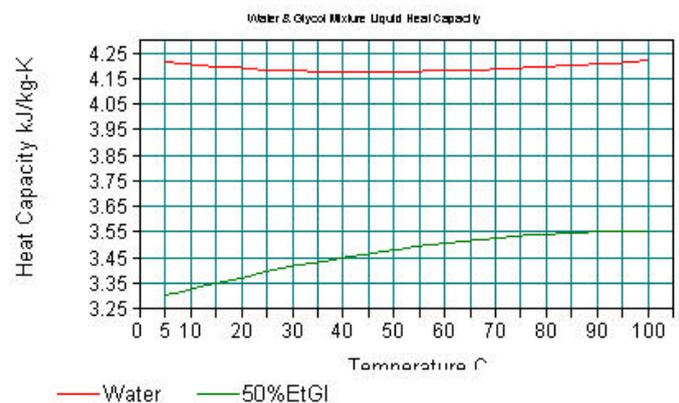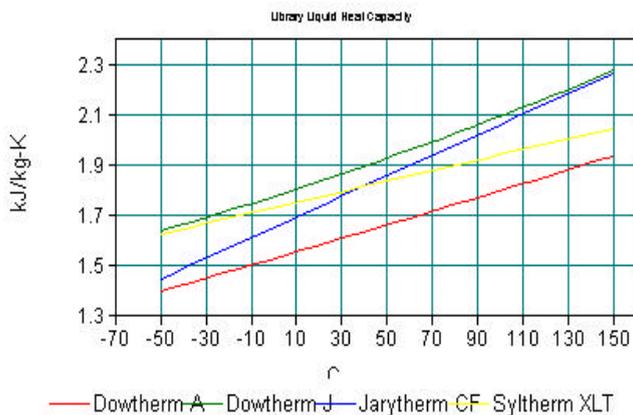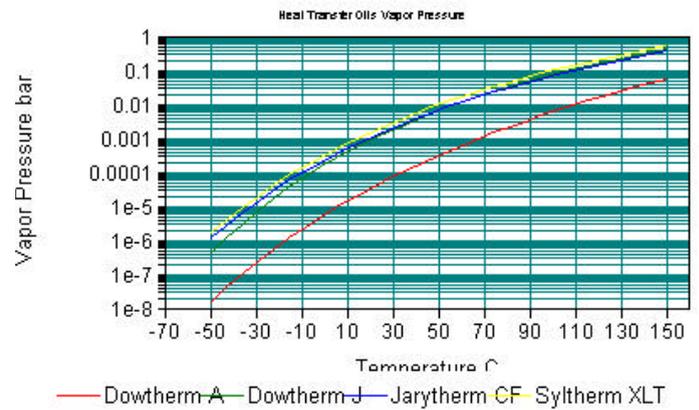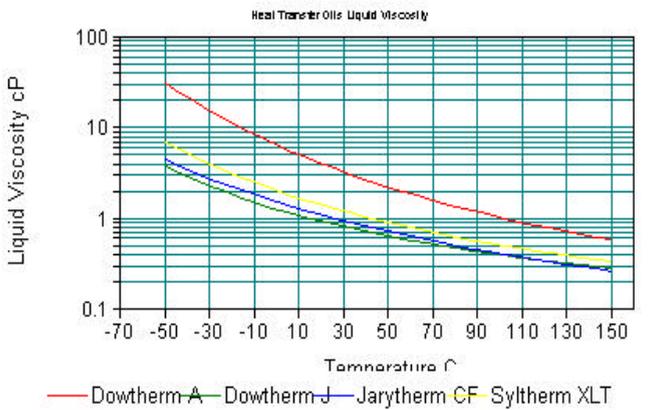
2.0   DYNAMIC MODELLING CONSIDERATIONS

2.1   Heat Transfer

The fundamental equation for heat transfer across a surface is given by:

$$Q = U \; A \; \Delta T_m$$

The mean temperature difference ΔT_m for a batch reactor with contents temperature T and utility inlet and outlet temperatures t_1 and t_2 is approximated by:

$$\Delta T_m = T - \frac{(t_1 + t_2)}{2}$$

The overall heat transfer coefficient U is the sum of individual resistances as follows:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{1}{h_{fi}} + \frac{1}{k \, / x} + \frac{1}{h_o} + \frac{1}{h_{fo}}$$

The agitated batch reactor **inside film coefficient h_i** is predicted using the Seider-Tate equation where C, p, and q are constants derived empirically for the agitation system which are available from manufacturers and is defined as follows:

$$Nu = C \; Re^{0.667} Pr^p \left(\mu_i / \mu_w \right)^q$$

Nu Nusselt number
Re Reynolds number
Pr Prandtl number
μ_i process side viscosity
μ_w process side viscosity at the wall

The reactor **wall thermal conductivity k** when considering glass lined equipment considers the glass thickness x_g and metal wall thickness x_m with the appropriate thermal conductivities for glass k_g and metal wall k_m to give the following expression:

$$k = \frac{x_m + x_g}{x_g / k_g + x_m / k_m} \quad \text{where} \quad x = x_m + x_g$$

The **outside film coefficient h_o** depends on the type of heat transfer surface design namely external jacket(s) with or without mixing nozzles, external half coil(s) or internal coil(s). The film coefficient is a function of the **Nu**, **Re** and **Pr** numbers in the conventional form with the empirical parameter constants depending on the type of arrangement used.

The **inside fouling coefficient h_{fi}** and **outside fouling coefficient h_{fo}** values are determined by practical experience and there is extensive literature available on this subject. The combined fouling coefficient h_f is given by:

$$h_f = \frac{h_{fi} h_{fo}}{h_{fi} + h_{fo}}$$

2.1   *Heat Transfer*

The Chemstations CCReACS software allows data entry of all the essential thermal design parameters discussed above. The program will calculate film coefficients dynamically at the prevailing process conditions or user defined film coefficients may be entered.

A powerful time saving data entry feature allows the user to select the size and type of reactor to be used in the model and the relevant dimensions will be entered into the input table automatically. The data entry screens for the reactor are shown below. It can be seen that these are in Windows format making them very efficient and easy to use.
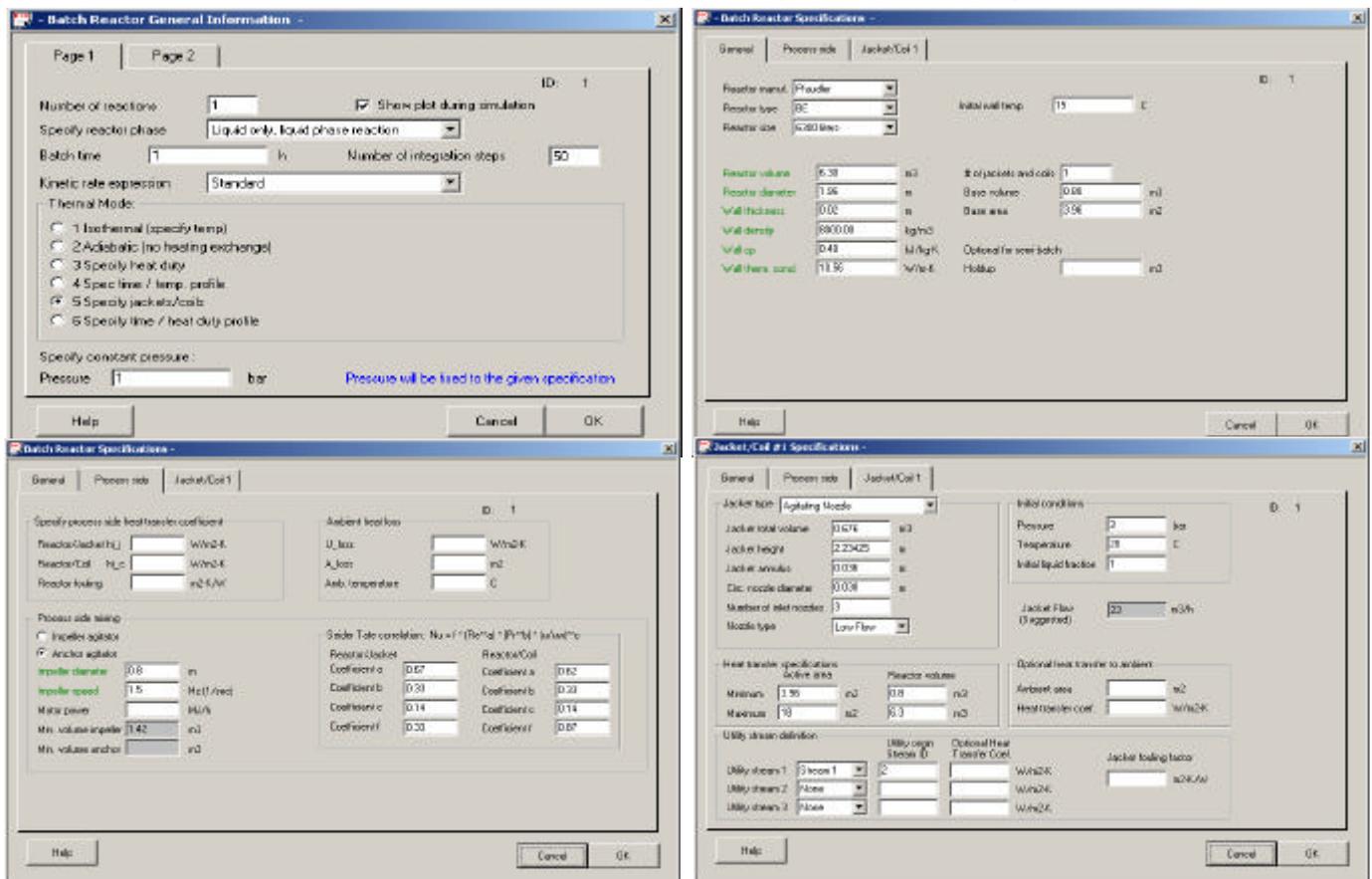
Stirred batch reactors, with coils or external jackets, exhibit thermal lags due to the heat capacities of the reactor, reaction mix, jacket contents and jacket services and circulation system dead time. The utility side film coefficient will become controlling if turbulent conditions are not established by using an adequate circulation rate together with inlet mixing nozzles on jackets. The program provides details of the number of mixing nozzles and the recommended circulation rate.

The thermal conductivity of the reactor materials of construction have a significant effect on the wall temperatures which can limit cycle times. Extreme temperature differences can result in product quality problems on certain processes.

The heat removal capability is a function of the resistances to heat transfer, the temperature difference and the heat transfer area. A thermal runaway (increasing reaction temperature increases rate of reaction) will occur if the heat cannot be removed fast enough further accelerated by a reduction in heat transfer area due to a decrease in reactor contents. It may not always be possible to design for stability where not enough heat transfer area is available for the design temperature difference. However, stability will be assured if heat is removed by boiling one or more of the components since this tends to make the system isothermal.

2.2   Reaction Chemistry

The **molecularity of a reaction** is the number of molecules of reactant(s) which participate in a simple reaction consisting of one elementary step.

Unimolecular
one molecule decomposes into two or more atoms/molecules $A \rightarrow B+C$
one molecule isomerizes into a molecule with a different structure $A \rightarrow B$

Bimolecular
two molecules can associate $A+B \rightarrow AB$
two molecules can exchange $A+B \rightarrow C+D$

Arrhenius rate law states that the rate of a chemical reaction increases exponentially with absolute temperature and is given by

$$k = A \exp\left(\frac{-E_a}{R\ T}\right)$$

Where **R**=universal gas constant   J / °K mol
     E$_a$=activation energy   J / mol
     A=frequency factor or pre-exponential factor   s^{-1}

The values of **E$_a$** and **A** for any reaction can be determined experimentally by measuring **k** the rate of reaction at several temperatures and plotting on logaritmic scales

$$\ln k = \ln A - \left(\frac{E_a}{R\ T}\right) = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$

 Representing a plot of **ln k** vs **1/T** with a slope **E$_a$/R** and intercept of **ln A**

The kinetic data can be entered for single or multiple reactions in the screen shown below:

2.2   Reaction Chemistry

Endothermic reactions exhibit a marked degree of self regulation in regards to thermal stability and do not require further consideration.

Exothermic reactions require a detailed understanding of the reaction kinetics to provide reaction rate and heat of reaction which should be determined by screening tests using the appropriate calorimeter.[2]

The heat removal requirement depends on the type of reaction. Vapour pressure systems with reaction at the reflux temperature are referred to as a tempered reaction system due to heat removal by latent heat reducing the heat removal requirement for the jacket/coil cooling system.

Gassy systems generate a permanent gas and require total heat evolved to be absorbed by the jacket/coil cooling system.

Hybrid systems are a combination of the previous two reaction types and can result in a significant emission of volatile organic compounds from the overhead condensing system due to inerts.

The reaction rate [1] depends on the reaction order where a first order reaction conversion varies with time and a second order reaction conversion varies with square of the reactant concentrations. First order reactions have the highest rate where the conversion is least i.e. at time zero.

The reaction rate can be limited by adding the reactant continuously at a controlled rate to ensure heat of reaction rate does not exceed the heat removal capability of the system.

Some reactions are carried out with all the reactants charged i.e. "all on board". Their reactions are frequently carried out at total reflux which enhances the system heat removal capability.

Predicting the physical properties of the reaction mix during various steps in the process due to composition and temperature changes can have a significant effect on the reactor performance.

When processing flammable solvents it is standard practice to eliminate explosive mixtures by establishing and maintaining an inert atmosphere in the reactor. Inerting systems can be based on pressure balance or continuous flow. However, when carrying out reactions at reflux the inert flow should be reduced/eliminated to minimise volatile organic compounds (VOCs) emission to the environment. Some reactions involve the evolution of non condensable compounds which will become saturated with VOCs in proportion to the component vapour pressures at the condenser exit temperature and pressure.

The presence of non condensables in the condenser results in a significant increase in the thermal resistance which can result in up to half the heat transfer area being required for the last zone alone. Chemstations software module CCTHERM allows the modelling of this process situation.

2.3   Control System Considerations

The conventional control system uses cascade control with the reactor contents temperature (master/primary) controller output being cascaded to the jacket/coil inlet/outlet temperature (slave/secondary) controller set point.

This arrangement ensures disturbances in the jacket/coil loop are corrected by the secondary controller before they can influence the primary controller. The secondary loop thermal time constant must be less than the primary loop thermal time constant.

The secondary controller is normally a Proportional only controller as Integral Action Time will slow the response. A proportional band of $\leq 25\%$ is typical. When carrying out boil up control, where the temperature difference between jacket/coil and reactor contents is set by by controlling jacket/coil inlet temperature, Integral Action is required to eliminate offset. The primary controller is normally three mode (Proportional + Integral + Derivative).

Temperature measurement is invariably by resistance sensor in conjunction with Smart transmitters which allows considerable flexibility when setting ranges. There is hardly any thermal lag associated with the sensor, however, there can be significant thermal lags associated with the thermowell if incorrectly designed or installed which can lead to an uncontrollable system. Designs are available which ensure fast response and should be adopted.

The set up screen for the controller is shown below. The controller UnitOp provides the facility for proving the suitability of a particular control configuration and for optimisation of the controller settings dynamically.

2.3   Control System Considerations (Cont)

The selection of a control valve with the appropriate operating characteristics is essential for satisfactory control loop performance. A valve has two characteristics namely the inherent characteristic (relationship between flow and stroke at constant ΔP) and the operational characteristic where the inherent characteristic is modified by the process pressure conditions. An equal % valve operating characteristic tends towards a linear characteristic as ΔP max/ΔP min increases. A linear valve operating characteristic tends towards a quick opening characteristic as ΔP max/ΔP min increases.

Control valve characteristic used is normally equal % though situations may arise where a linear characteristic provides better control. The operational characteristic of a valve can also be modified by controller output signal characterisation using various techniques.

Control valve actuators should be pneumatic with positioners fitted. The calibration for split range operation of the valves should be achieved at the positioners, not with scaled multiple controller outputs, to ensure loop integrity is maintained.
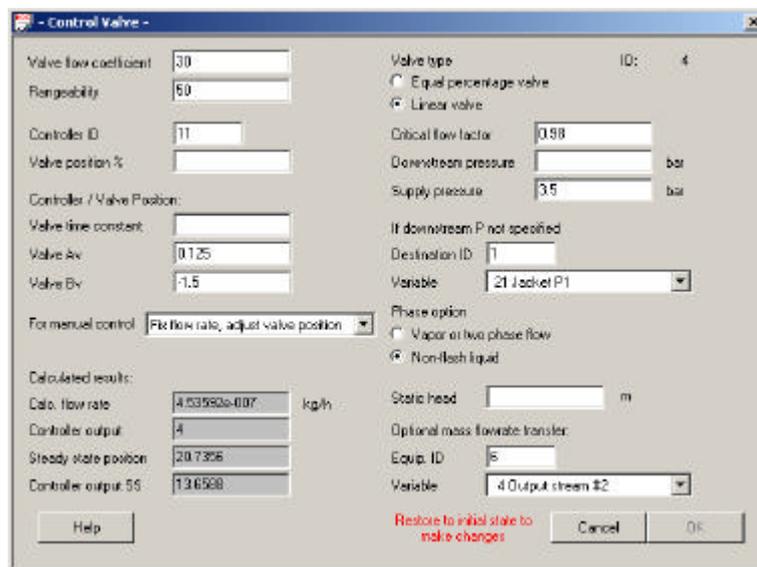
There are several methods available for control loop tuning. The Ziegler and Nichols[3] is commonly used and involves establishing the proportional band at which the process begins to oscillate at constant amplitude as shown below. Control parameters are then set based on these values. Refer Appendix III for details of the method.
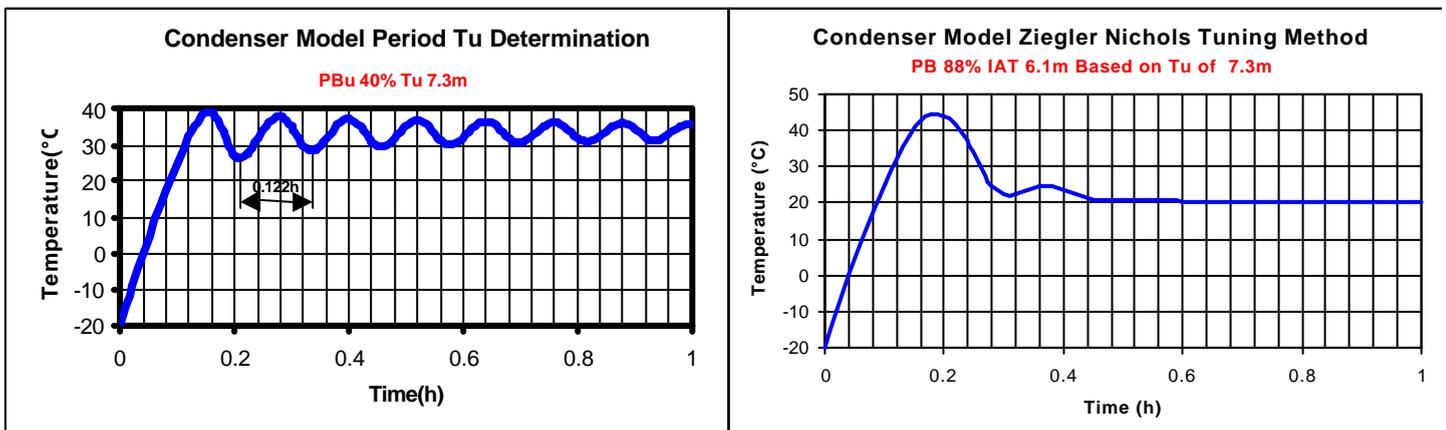
3.0   EQUIPMENT CONFIGURATIONS

3.1   Direct Jacket Heat / Cool

These systems involve the connection of the appropriate supply and return services directly to the reactor jacket/coils. There are many arrangements in use from total manual control to full automatic control involving forced circulation with steam/water mixing facilities.

Systems are in use providing operating ranges from –20°C to 180°C with ethylene/glycol mixes, water and steam as services. Ethylene glycol mixes should not be used above their boiling point.

The scheme below indicates the basic system with automatic control of the steam and cooling water services. The changeover between heating and cooling modes can be done manually or automatically involving a complex sequence of valve switching operations involving time. The changeover is not seamless as with a single fluid system and requires careful consideration if used on exothermic reactions. The heat up and cool down curves demonstrate the fast response of these systems which can lead to thermal shock problems with glass line equipment.

BATCH REACTOR JACKET SERVICES
BASIC HEAT/COOL CONTROL SYSTEM

6.3 M3 GLASS LINED REACTOR
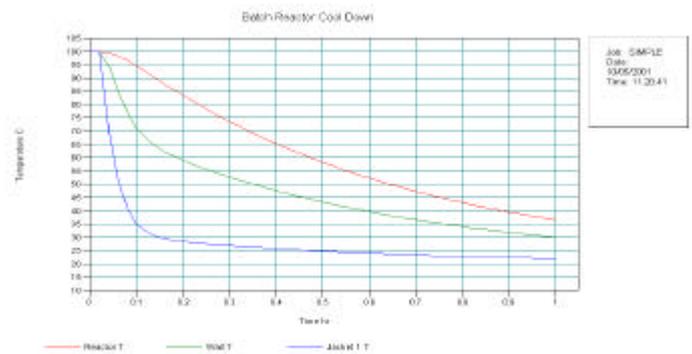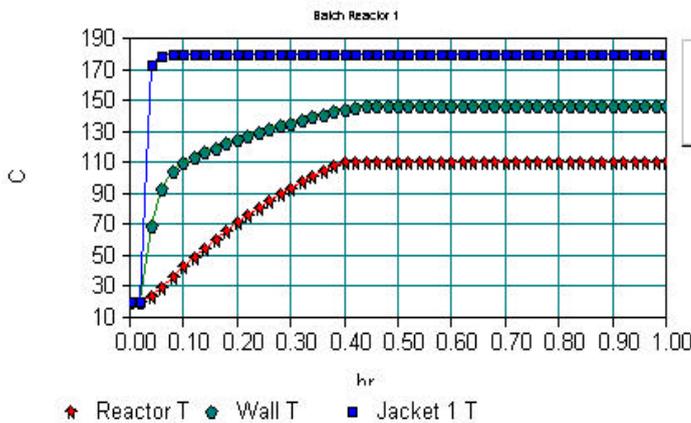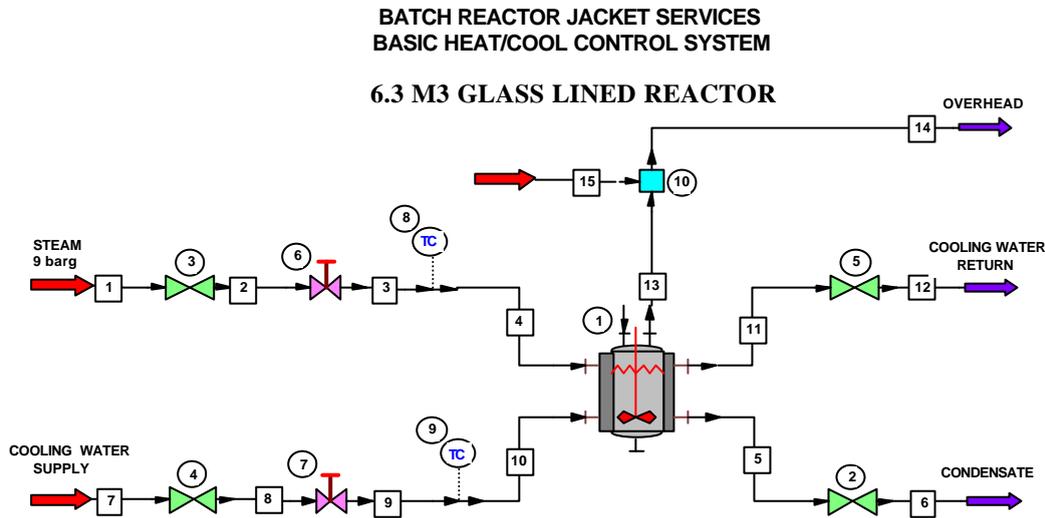
3.1   Direct Jacket Heat / Cool (Cont.)

Ciba Geigy and Wiegand developed a steam jet heater providing a wide range of heating duties with a single phase in the operating range 5°C to 180°C. This arrangement requires careful design in relation to air removal/expansion/pressurisation facilities and service returns from high operating temperatures require special automatic blowdown facilities.
A simplification of this scheme is shown below

BATCH REACTOR JACKET SERVICES
SINGLE FLUID HEAT/COOL SYSTEM
STEAM / WATER MIXING

6.3 M3 GLASS LINED REACTOR
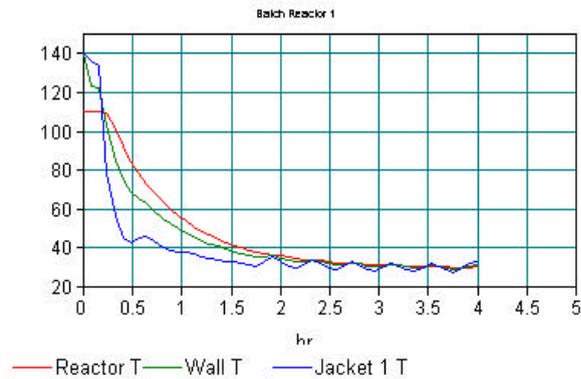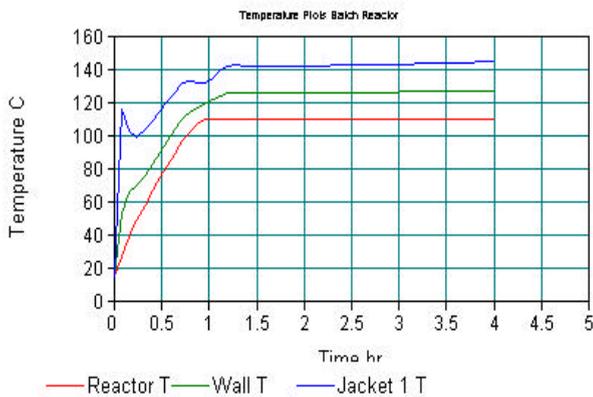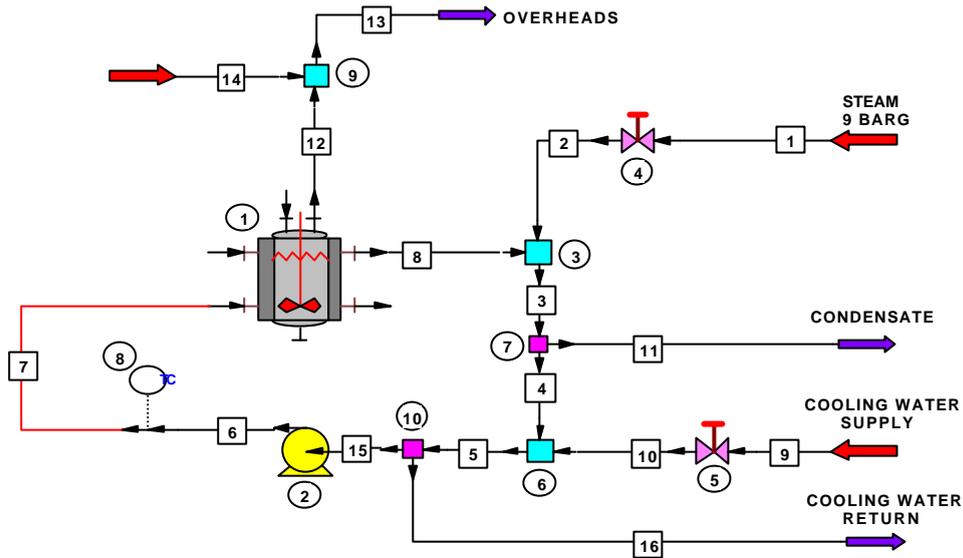
These systems provide excellent thermal response due to the elimination of heat transfer lags associated with heat exchangers. However, to provide combined heating/cooling facilities, with the exception of the Wiegand system, requires involved automatic valve sequencing and jacket/coil blowdown routines when changing services resulting in discontinuous control which can cause serious operational problems when handling exothermic reactions.

Operational problems associated with these systems include cross contamination of services, corrosion and the need for complex control routines when changing services from heat to cool involving time lags. These systems are not always cheaper than other alternatives.
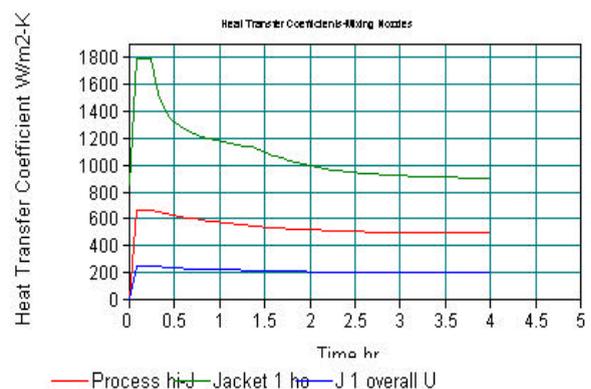
3.2 Direct Jacket Cool/Indirect Heat

This system is based on the use of a single appropriate heat transfer fluid for the desired operating range, typically –20°C to 180°C. The circulation rate is set depending on the number of mixing nozzles and achieving the recommended nozzle pressure drop.

The coolant is directly injected into the reactor jacket/coil circulating loop and a heat exchanger with steam is provided for heating. Changeover between heating and cooling modes is seamless using control valves in split range. The heat transfer fluid is on the plate side of the shell and plate heat exchanger, which provides a high film coefficient. The heat transfer area is selected based on a reasonable LMTD at approach to service supply temperature and is sized to ensure that reactor heat transfer is limiting. Equipment in common use include sealless pumps and gasket free fully welded plate and shell heat exchangers.

Thermal response on cool is excellent due to direct injection and the use of a three way valve on the heat exchanger minimises thermal lags on heating. Adopting a three way valve allows the steam to be applied continuously to the heat exchanger shell at full pressure which eliminates problems associated with condensate lift/return, prevents freezing when operating below 0°C and provides excellent linear control characteristics. These systems require careful consideration to ensure thermal expansion is allowed throughout the loop.

On initial commissioning these systems have to be thoroughly dried out to prevent operational problems and equipment damage. Water breakthrough due to contamination or equipment failure will result in considerable downtime.

INDIRECT HEAT / DIRECT COOL

6.3 M3 GLASS LINED REACTOR
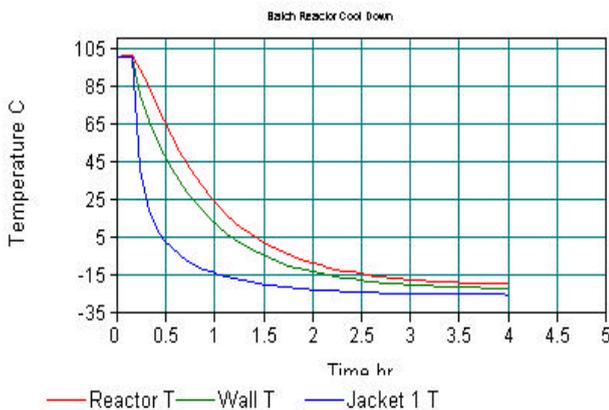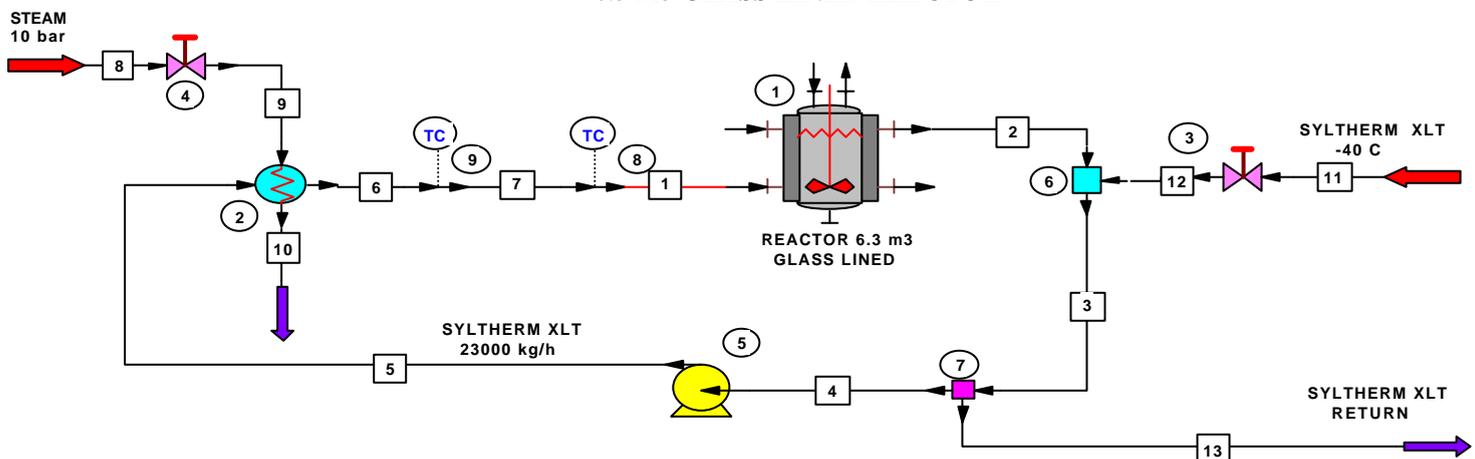
3.3   Indirect Jacket Heat/Cool

The key features of this system are as for the previous system. The use of an additional heat exchanger for cooling allows the selection of a less expensive fluid for the cooling service which may provide cost benefits with a centralised refrigeration facility involving the use of significant volumes of heat transfer fluid.

This system also allows for segregation of the reactor service system from other reactors which enables rapid identification of water breakthrough problems on a facility with several reactors.

BATCH REACTOR WITH EXTERNAL STEAM HEAT EXCHANGER
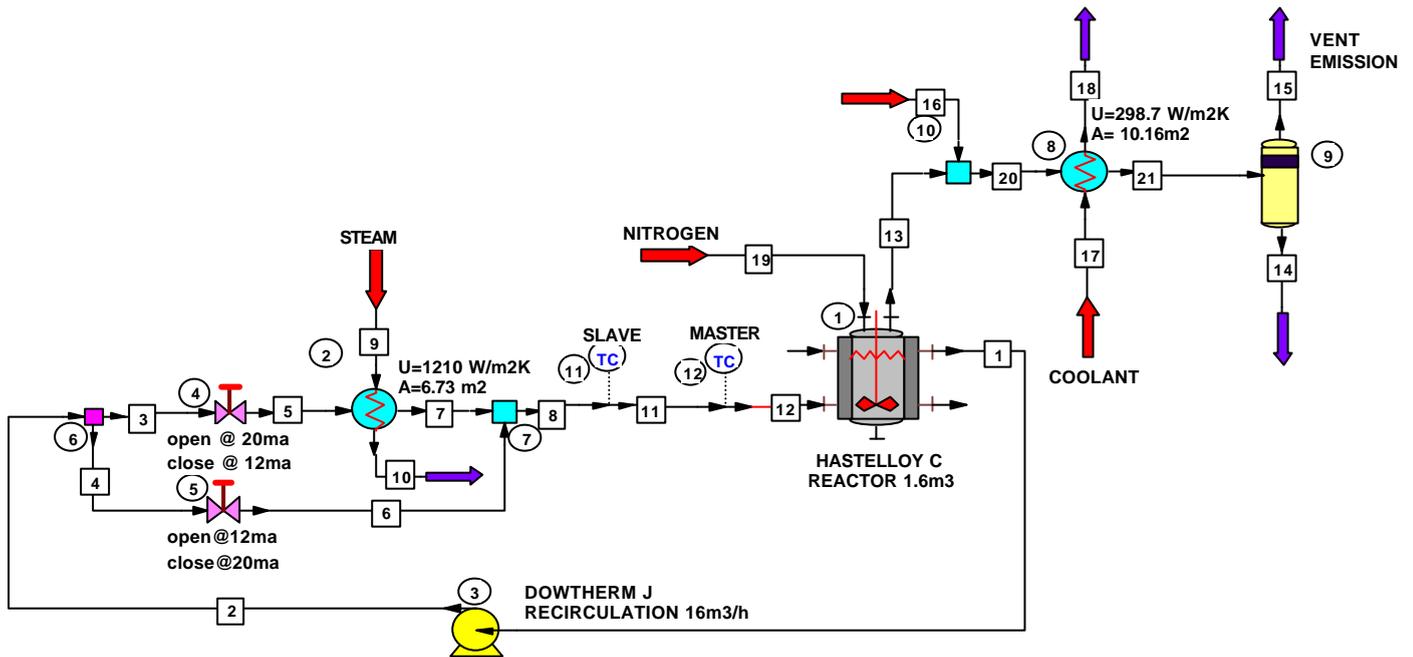
BATCH REACTOR WITH EXTERNAL COOLING HEAT EXCHANGER
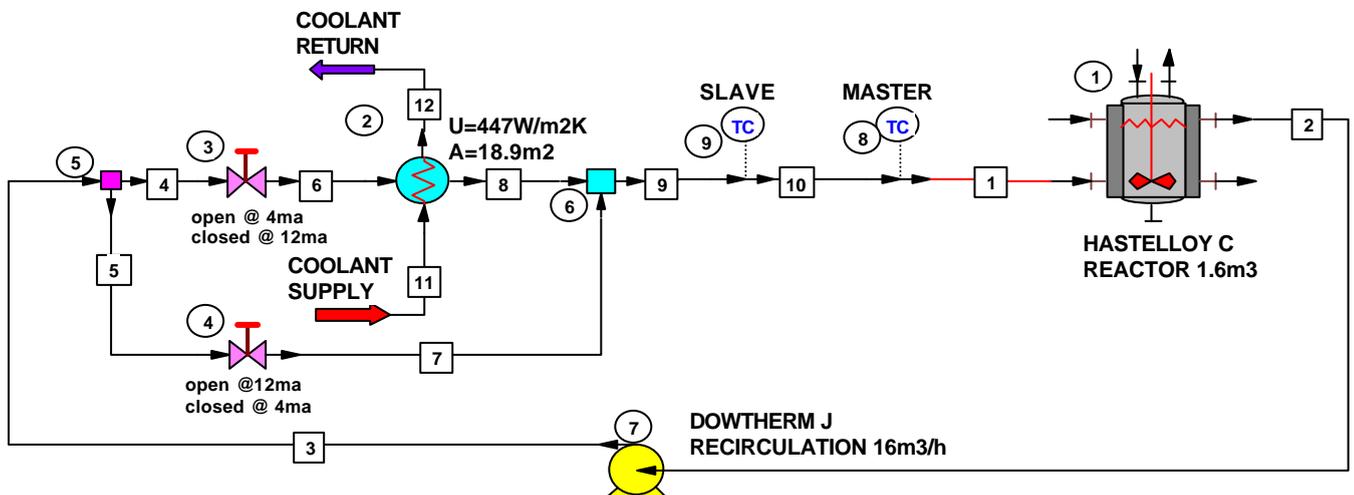
4.0   Performance Characteristics

Dynamic modelling provides the designer and the plant operator with the tools necessary to study the performance characteristics of a variety of process equipment and control system configurations. A study of the results from the dynamic models presented verify the following inherent characteristics

Reactor Parameters

The heat transfer area / reactor volume ratio increases as the reactor size reduces. The use of oversized reactors should be avoided and can lead to heat removal limitations.

Appendix I provides data for Carbon Steel, Stainless Steel, Hastelloy C and Glass.
The density and specific heats differences are not significant for heat transfer but the thermal conductivity differences are. Glass lined carbon steel and Hastelloy C are similar with stainless steel a factor 1.5 higher and carbon steel a factor of 4.7 higher.

Unbaffled jackets result in laminar flow and result in very poor thermal performance which is enhanced by the use of baffles, dimpled jackets and inlet mixing nozzles.
When using heat transfer fluids that may have high viscosities within the operating temperature range, mixing nozzle pressure drops may become limiting and half pipe coil constructions should be considered.

The lags associated with the utility side using thermal fluids are minimised by using forced circulation and plate heat exchangers for fast response.

For a given set of process conditions the reactor **UA** is predetermined and it is important that the external heat exchanger **UA** does not become limiting at approach temperature differences. Dynamic modelling confirms the suitability of the design under all conditions.

Heat up

The maximum heat input is achieved when using steam directly on the jacket/coil side, however this can lead to thermal shock when using glass lined equipment. The changeover to cooling water based fluid systems requires a control sequence.

Direct steam injected circulating liquid systems avoid the thermal lags associated with external heat exchangers and hence have superior heat input characteristics. The reduced heat input associated with single fluid systems can lead to difficulties in achieving required boil up rates when doing batch distillations. The only variable available to increase boil up is the jacket/coil temperature which will be limited on water based systems.

Single fluid systems using heat transfer fluids and external heat exchangers have the lowest heat input capability for a given temperature difference of the systems considered. The heat input is achieved by increasing the temperature difference at a rate consistent with thermal shock considerations.

4.0   Performance Characteristics (Cont.)

Heat Removal

Heat removal is normally achieved using single fluid liquid systems which will determine the **UA** achievable for a given reactor system. The use of partially filled reactors is to be avoided if possible. The heat removal is therefore determined by the operating temperature difference which can be enhanced by operating at higher reaction temperatures or under reflux conditions consistent with reaction kinetics.

The heat removal capability of a facility is limited by the temperature of the utility fluids available. The heat load on any refrigeration system is to be minimised by cooling using the higher temperature medium available such as cooling water and then switching to the lower temperature medium when appropriate.

Heat transfer fluid viscosity effects at low temperatures can become limiting resulting in low jacket/coil side heat transfer coefficients and high prressure drops. Selection of a heat transfer fluid with reasonable viscosity characteristics will allow operation down to -90°C.

Boil up Rate

The boil up rates achievable with the various heating systems considered vary between being excessive with direct steam and being limiting with indirect heat transfer fluid systems.

The overhead condenser heat duty achievable determines the maximum boil up rate allowed and the batch distillation process determines the minimum boil up rate to achieve a satisfactory separation by satisfying the minimum reflux ratio requirements.

To control the boil up and wall temperature, if required, with steam requires pressure control. To achieve the boil up rates required with single fluid systems the temperature difference is controlled; the utility heating medium temperature needs to satisfy this requirement.

Temperature Control

Temperature control of batch reactor systems is inherently difficult due to the thermal lags associated with the heat transfer process. Appendix III provides a method for establishing the thermal time constants for the different interfaces. Typical values are shown below for heating 1000kg toluene in a 1600L Hastelloy C reactor with Dowtherm J fluid.

Reactor contents to reactor wall	15.4 min	Reactor wall	3.1 min
Reactor wall to jacket contents	2.6 min	Overall	21.7 min

In other words the main contribution is the reactor contents to reactor wall which increases as reactor size increase. This is further compounded by the decrease in heat transfer area per reactor volume ratio as the reactor size increases. This emphasises the importance of correctly matching reactor size to the batch size as using partially filled reactors reduces the heat transfer area as well as increasing the potential for minimum stir problems.

5.0   Dynamic Batch Distillation

Batch distillation techniques are used extensively in the Fine Chemicals and Pharmaceutical Industries to achieve a variety of processing objectives. These include:-

- Removal of impurities/unwanted components from reaction mixes.
- Water removal and drying.
- Solvent change between reaction stages on multistage syntheses.
- Concentration prior to crystallisation.
- Heat removal control for reactions at reflux.
- Solvent recovery.

The simplest form of batch distillation involves a single separation stage (represented by the act of evaporation) which is used where a large difference in volatility exists between the components to be separated. Such a distillation does not need a fractionating column between the batch still (normally a stirred jacketed reactor) and the condenser. Simple batch distillation (sometimes referred to as pot to pot) provides only one theoretical plate of separation.

Batch Distillation Unit
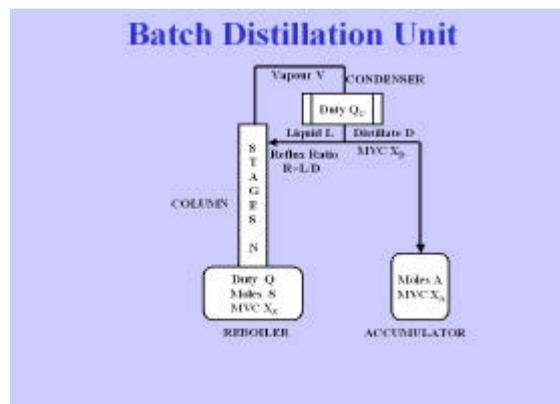
When the difference in volatility between the components to be separated is small or when operating over narrow composition ranges a rectification section is required between the still and the condenser. Overhead facilities are also required to provide control of reflux ratio and layer separation when handling heterogeneous azeotropes.

In operation the system is brought to steady state under total reflux which is taken as the start condition for simulation. Overheads are continuously withdrawn in accordance with the reflux control strategy. Cuts are taken by switching to different receivers, following a time or overhead composition strategy, at which point simulation conditions may be changed whilst starting from the current condition.

Batch distillation with rectification can be operated as follows [8]:-

- **Constant reflux ratio, varying overhead composition.**
  Distillation is continued until the desired composition is achieved in the still or the distillate receiver as required.

- **Constant overhead composition, varying reflux ratio.**
  As the distillation proceeds the still is depleted of the lighter component with the reflux ratio continually increasing. The stage is terminated at a maximum economic reflux ratio or achieving the desired still composition. This technique can be extended to a multi-component mixture.

5.0   Dynamic Batch Distillation (Cont.)

- **Cyclical total reflux.**
  The unit is operated at total reflux until equilibrium is established and then distillate is withdrawn as total draw off for a short period of time before returning to total reflux. This technique is useful when required to separate a light end with a low overhead composition.

- **Minimum time, varying reflux ratio.**
  This provides the most cost effective mode of operation consistent with achieving the desired separation.

The distillation is normally operated at atmospheric pressure, however reduced pressure operation is sometimes required to achieve the desired separation, to reduce operating temperature for economic reasons, or when processing temperature sensitive materials. For multipurpose operation careful consideration is required when selecting column internals to achieve acceptable column loadings and operational turndown.

The boil up rate achievable with stirred jacketed reactors is dependent upon many factors associated with heat transfer and has been discussed previously.

The basic techniques are reviewed for process modelling of batch distillations using Chemstations CC-BATCH simulation package

To achieve a successful simulation an understanding of the relevant thermodynamics as applied to the batch distillation process is essential and is reviewed elsewhere.[11]

5.1   Operational Constraints [9]

To establish the number of theoretical stages **N** required at total reflux to achieve a specified separation of a binary mixture with near ideal behaviour the Fenske equation is used
.

$$N_{min} \ln \alpha = \ln F$$

Separation factor

$$F = \left(\frac{X_D}{1 - X_D} \right) \left(\frac{1 - X_S}{X_S} \right)$$

Where **X** is the mole fraction of the more volatile component and **D** and **S** represent distillate and still compositions respectively.

These relationships can be used to form the basis of establishing performance guarantee criteria or to establish a performance benchmark based on a given test mixture.

5.2   Mass and Energy Balances

The primary objective in batch distillation is to minimise the batch cycle time by maximising the heat input and minimising the reflux ratio to achieve the required separation.

The process variables are interdependent as determined by the mass and energy balances and the mode of operation.

The heat input for a variable top composition achieved by setting a fixed reflux ratio is given by:-

$$Q = l \left(S_O - S_1\right)\left(R + 1\right)$$

The heat input for a fixed top composition is achieved by varying the reflux ratio to maintain a fixed top temperature at constant pressure is given by:-

$$Q = l \left(S_O - S_1\right) \int_{R_O}^{R_1} \left(R\right) d R$$

Both relationships indicate that the reflux ratio must be kept to a minimum, subject to satisfying the requirements for the desired separation specification, to optimise the heat input.

When it has been established that a given column can achieve the required separation at total reflux it remains to determine the minimum reflux ratio R_{min}.

Reflux ratio $R = \dfrac{L}{D}$ $m = \dfrac{L}{V} = \dfrac{R}{\left(R + 1\right)}$ where m is slope of the operating line

Underwood's equation for a binary system is given by:-

$$R_{min} = \frac{1}{\left(a - 1\right)} \left[\frac{X_D}{X_S} - \frac{a\left(1 - X_D\right)}{\left(1 - X_S\right)}\right]$$

When X_D is a high degree of purity > 0.995 mole fraction the above can be simplified to:-

$$R_{min} = \frac{1}{\left(a - 1\right)X_S}$$

For a high separation factor F a minimum relative volatility of 1.5 is considered reasonable setting a top limit of R_{min} at $2 / X_F$.

Batch distillations are started with R_{min} equal to that required for a continuous split and it should be noted that R_{min} increases as the more volatile component in the still reduces.

The overall mass balance at the top of the column yields:-

$$V = L + D \quad \text{which transposes to} \quad \frac{D}{V} = \frac{1}{R + 1}$$

The mass balance demonstrates [1] that the top composition is established by the D/V ratio which is dependant on the reflux ratio.

If the D/V ratio is high, separation will be low, and withdrawal of distillate must be stopped at a relatively high value of X_D, i.e. light ends recovery will be poor.

5.2   *Mass and Energy Balances*

If the **D/V** ratio is reduced to enhance recovery the distillation may consume an uneconomic amount of time and energy. A mass balance [1, 10] on the MVC yields the following relationship, known as the Rayleigh equation:-

$$(dS)\,X_A = d\,(S\,X_S) \qquad \ln\left(\frac{S_0}{S_1}\right) = \int_{X_{S1}}^{X_{S0}}\left(\frac{d\,X_S}{X_A - X_S}\right)$$

The overall mass balance for the system, i.e. still and receiver, yields:-

$$S_0 - S_1 = A$$

A mass balance on the MVC yields the following:-

$$S_0\,X_{S0} - S_1\,X_{S1} = A\,X_A \qquad \text{and transposing gives}$$

$$X_{S1} = \frac{S_0\,X_{S0} - A\,X_A}{S_1} \qquad\qquad \frac{A}{S_0} = \frac{X_{S0} - X_{S1}}{X_A - X_{S1}} \qquad\qquad S_1 = S_0\left(\frac{X_{S0} - X_A}{X_{S1} - X_A}\right)$$

The batch time at constant reflux ratio is given by:-

$$J = \frac{R+1}{V}(S_0 - S_1) = \frac{1}{V} \quad \text{from above for constant reflux}$$

Chemstations CC-BATCH mathematical model is based on rigorous unsteady state mass and enthalpy balances and the phase equilibrium relationships due to those given by Distefano.

5.3   Parameter Specification

The mass and energy balances demonstrate the interdependence of the process parameters. Setting one process parameter (specification mode) results in all dependent parameters being set. The setting of two independent process parameters defines the batch distillation operational state.

First Specification Mode	Second Specification Mode
Reflux ratio	Distillate mass rate
Condenser duty	Distillate mole rate
Distillate temperature	Reboiler duty
Distillate mole fraction	Boil-up mole rate
Distillate mass fraction	Boil-up mass rate

A sound modelling strategy is to define the still condition by specifying the reboiler duty or boil up rate which should be adequate to sustain the overhead condition specified, i.e. fixed or variable composition. As the distillation proceeds, i.e. less MVC in the system, the reboiler duty requirement will increase to sustain the same boil up rate and to satisfy the increasing reflux ratio if operating at constant top composition. The following should be taken into consideration when selecting specification modes.
Distillate temperature (@ constant pressure) sets distillate composition.
For constant boil-up rate reflux ratio sets the distillate withdrawal rate.
Reflux ratio and distillate rate cannot be independently set and neither can reboiler duty and condenser duty.

5.4 Dynamic Model Formats

The flow diagram and data entry screens are shown below and are in the easy to use Windows format. A typical result plot is shown for the distillate composition as the distillation proceeds. Every parameter is available for plotting to allow detailed investigation of the process. Adjustment of operational parameters and end step conditions enable an optimised process to be established readily. Again once a process has been modelled against actual plant operating conditions dynamic modelling provides a powerful diagnostic tool.
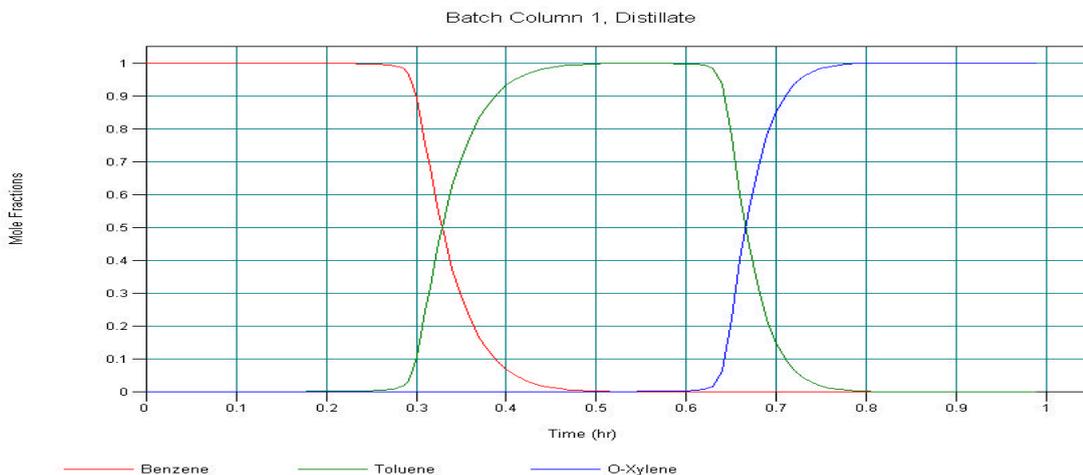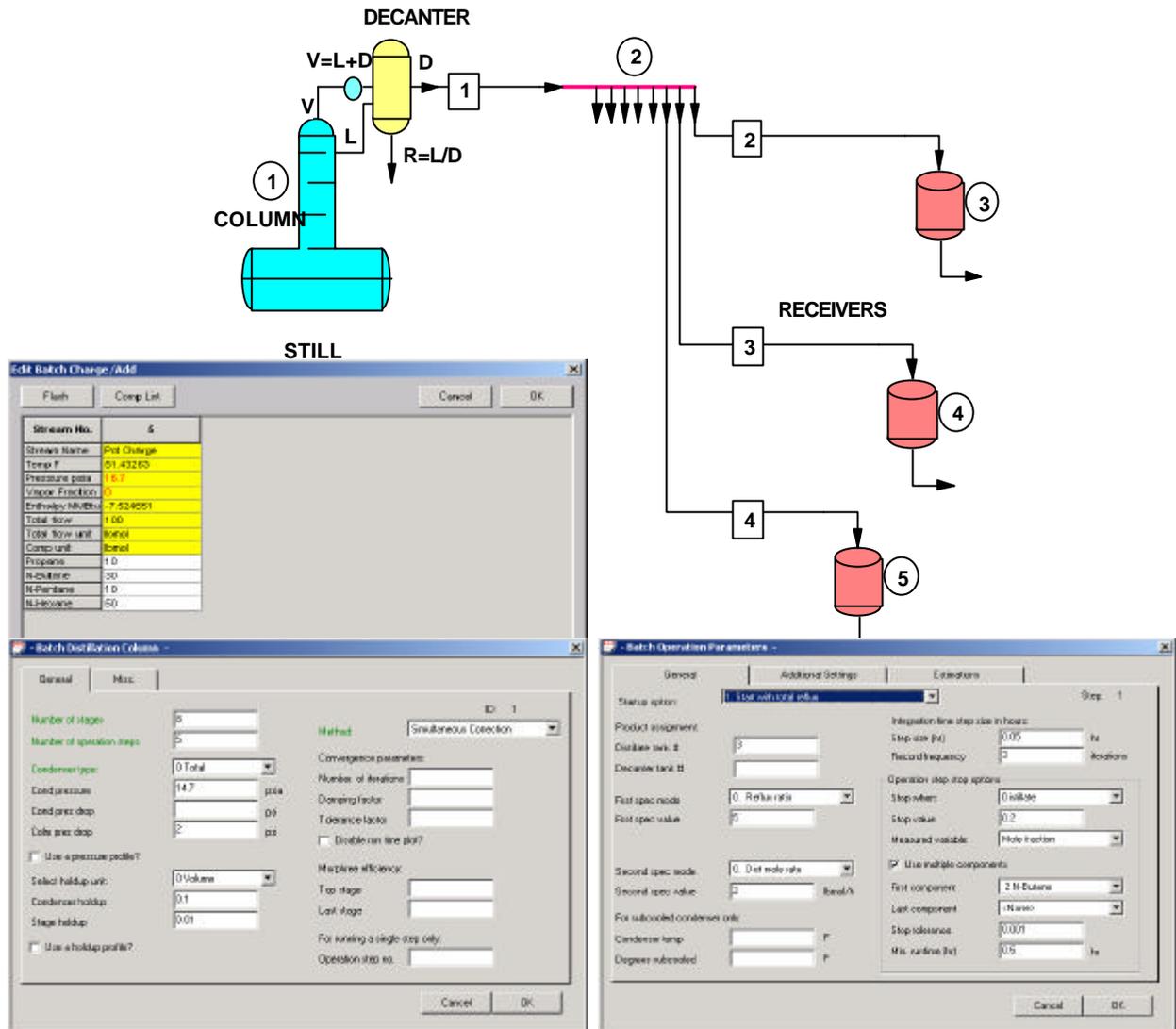
Appendix I

Useful Reference Data

Heat Transfer Data
Acknowledgements to Pfaudler Reactor Systems for permission to reproduce this information

Thermal conductivity of glass $\mathbf{k_g} = 6.9$ Btu/ft^{2}h°F/in

Glass thickness can vary between 1 mm and 2 mm. Use 1.5mm(0.06in) thick as a good average.

Physical properties of common reactor materials are as follows

	Density(kg/m^3)	Specific Heat(kJ/kgK)	Thermal Conductivity(w/mK)
Hastelloy C	8690	0.423	11.1
Stainless steel	8000	0.5	16.2
Carbon steel	8000	0.4	52(360 Btu/ft^{2}h°F/in)

Outside film coefficient

For steam on the jacket side take an outside film coefficient of 8517 w/m^{2}K (1500 Btu/ft^{2}h°F)

For water or other fluid on the jacket side, use the Pfaudler equations or consult the circulating nozzle leaflets.

Fouling coefficients

| Fouling on inner vessel | - | typical value 5678 w/m^{2}K (1000 Btu/ ft^{2}h°F) |
| Fouling on jacket side | - | typical value 5678 w/m^{2}K (1000 Btu/ ft^{2}h°F) |

Typical Agitator Constants

	AGITATOR TYPE	**C**	**p**	**q**	**RANGE**
ONE PIECE	IMPELLOR	0.33	1/3	0.14	$2\times10^4 < \text{Re} < 2\times10^6$
	ANCHOR	0.55	1/4	0.14	$5\times10^3 < \text{Re} < 4\times10^4$
	TURBINE (6 BLADES)	0.44	1/3	0.24	$200 < \text{Re} < 1\times10^3$
	LOOP	0.36	1/3	0.14	$300 < \text{Re} < 4\times10^4$
YRO LOCK	CBT – TURBINE	0.48	1/3	0.14	$2\times10^4 < \text{Re} < 2\times10^6$
	FBT – TURBINE	0.69	1/3	0.14	$400 < \text{Re} < 3\times10^5$
	PBT – TURBINE	0.62	1/3	0.14	$300 < \text{Re} < 3\times10^5$
	TURBOFOIL	0.55	1/3	0.14	$1\times10^3 < \text{Re} < 1\times10^6$

Useful Reference Data

Typical overall heat transfer coefficients U for steam heating

Product	XL 3410(L)	RA60 1360(L)	RA60 2270(L)	RA84 9090(L)	RA96 13640(L)	hi
Water	70	68	68	68	67	659
Toluene	59	55	55	55	56	232
Chloroform	60	57	57	57	57	259
Ethyl alcohol	57	54	54	53	54	213
Methyl alcohol	62	58	58	59	59	302
Acetone	62	59	59	58	58	284

Overall heat transfer coefficients units Btu/h ft^2 ^{0}F

Assumptions:	glass thickness	1.5 mm
	fouling steam side	3333 Btu/h ft^2 ^{0}F
	fouling process water	1000 Btu/h ft^2 ^{0}F
	fouling organic solvents	1000 Btu/h ft^2 ^{0}F
	impellor speed	90 rpm
Jacket side film coefficient	steam	1500 Btu/h ft^2 ^{0}F
	water	500 Btu/h ft^2 ^{0}F
	heat transfer fluid	250 Btu/h ft^2 ^{0}F
	glycol/water mix	30 Btu/h ft^2 ^{0}F

Reaction Kinetics

Reaction Type	What happens?	E_{act} (kj/mol)	A
Isomerization	break π bond	$\cong 234$	$\cong 10^{13}$ (1/s)
Elimination	bend bonds	$\cong 200$	$\cong 10^{13}$ (1/s)
Dissociation	break bond	$\cong 380$	$\cong 10^{14-17}$ (1/s)
Bimolecular	break form bonds	$\cong 5\text{-}30$	$\cong 10^{14}$ (cm^3/mol s)
Recombination	form bond	$\cong 0$	$< 10^{14}$ (cm^3/mol s)

Appendix II

Control Loop Tuning

When tuning control loops it is important to understand the impact the tuning parameters have on the process. The minimum effective values are:-

Proportional Band	(PB%)	highest value (minimum gain)
Integral Action Time	(T_i min)	longest time
Derivative Action Time	(T_d min)	shortest time (or off)

The following ground rules should be considered:-

1. **Proportional Band**
   Wide PB (50 – 500%) on fast and noisy processes such as Flow, Liquid Pressure and Composition.
   Narrow PB (1- 50%) on slow processes such as Gas Pressure, Temperature and Vapour Pressure.

2. **Integral Action Time (T_i)**
   Integral action time changes the controller output at a rate proportional to the magnitude of the error (e) and should never be set so short such that the resulting load change imposed exceeds the load response characteristics of the process. (Consider approaching a corner too fast).
   Short T_i (0.05 – 2 min) on fast and noisy processes such as Flow and Liquid Pressure.
   Long T_i (2 – 120 min) on slow processes such as Temperature, Vapour Pressure and Composition.
   T_i is unnecessary on Gas Pressure and is seldom used on Liquid Level as steady flow is usually the required condition.

3. **Derivative Action Time (T_d)**
   Derivative Action Time changes the controller output at a rate proportional to the rate of change of error $\left(\dfrac{de}{dt} \right)$ and as such should never be used on noisy processes such as Flow, Liquid Pressure and Liquid Level.
   T_d is used on Temperature, Vapour Pressure and Composition and should be set conservatively (short T_d) to protect against control instability resulting from unanticipated load changes. T_d set in the range $\dfrac{T_i}{4} < T_d < \dfrac{T_i}{2}$ is considered reasonable.

4. **Integral Action Time Saturation (Windup)**
   When a sustained error is maintained between set point and measured variable on a controller with T_i the output is driven off scale (valve full open or closed).
   Control action does not commence until the measured variable crosses the set point resulting in overshoot.
   This condition is typical of heating/cooling a batch reactor to a desired temperature and composition endpoint control.
   Controllers incorporating Proportional and Derivative modes overcome this problem.

5. Controller Loop Tuning Method

Ziegler and Nichols [3] developed the Ultimate Sensitivity Method which provides a useful basis for control loop tuning as follows:-

1. Set the control modes to their minimum effective values.
   Maximum **PB** (%)   Maximum T_i (min)   Minimum(or off) T_d (min)

2. Reduce **PB** whilst making small set point changes (both directions) until the measured variable begins to oscillate at constant amplitude.
   The proportional band PB_u and the period T_u are noted.

3. Initial controller settings proposed are:-

   Single mode P only controller $PB = 2\ PB_u$

   Two mode P + I controller $PB = 2.2\ PB_u$ $T_i = T_u\ /\ 1.2$

   Three mode P + I + D controller $PB = 1.6\ PB_u$ $T_i = T_u\ /\ 2$ $T_d = T_u\ /\ 8 = T_i\ /\ 4$

This procedure can be used as a 'starting point' for tuning control systems on batch processes, T_u being established at a stable condition. Typical periods (T_u) for batch reactors vary in the range 15 to 60 minutes.

Fine tuning involves a trade off between the conflicting requirements of heat up/cool down to a set point, control of exothermic reactions at a set point, controlling on jacket temperature to achieve required boil up rates and constraints associated with wall temperature requirements.

Appendix III

Reactor Time Constant Estimation [1] [(pages 75 to 76)]

$$Q = h_1 A \left(T - T_1 \right) + W_1 C_1 \frac{dT}{dt}$$

Q	=	rate of heat evolution	T	=	reactor temperature
h_i	=	inside film coefficient	T_1	=	wall temperature
A	=	heat transfer area	W_1	=	weight of reactants
C_1	=	specific heat of reactants			

Rearranging in the standard form we have

$$T + \frac{W_1 C_1}{h_i A} \frac{dT}{dt} = T_1 + \frac{Q}{h_i A}$$

The thermal time constant for reactor contents to reactor wall is given by

$$\tau_1 = \frac{W_1 C_1}{h_1 A} = \frac{W_1 C_1}{Q} \left(T - T_1 \right)$$

The thermal time constant for reactor outside wall to reactor inside wall is given by

$$\tau_2 = \frac{W_2 C_2 L}{k A} = \frac{W_2 C_2}{Q} \left(T_1 - T_2 \right)$$

W_2	=	weight of wall	L	=	wall thickness
C_2	=	specific heat of wall	T_2	=	outside wall temperature
k	=	thermal conductivity of wall			

The thermal time constant for reactor outside wall to jacket contents is given by

$$\tau_3 = \frac{W_3 C_3}{h_3 A} = \frac{W_3 C_3}{Q} \left(T_2 - T_c \right)$$

W_3	=	weight of jacket contents	h_3	=	outside film coefficient
C_3	=	specific heat of jacket contents	T_c	=	average coolant temperature

The reactor contents time constant based on the overall heat transfer coefficient U is given by

$$\tau_0 = \frac{W_1 C_1}{U A}$$

A study of the heat up and cool down curves the thermal response can be characterised below

Time Constant	% Temperature Change
1	63.2
2	87.0
3	95.0
4	98.0