CONTROL SYSTEM DESIGN FOR A DOUBLE FEED METHYL ACETATE REACTIVE DISTILLATION

A thesis submitted in partial fulfillment of the requirements for the Degree of Master of Technology
(Refining & petrochemical engineering)

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ABSTRACT

Reactive distillation (RD) represents conjunction of conventional reaction technology and separation process into single unit operation. RD is advantageous for a great number of chemical synthesis, including esters(Methyl Acetate), which is the focus of this work.

This work deals with configuring a Methyl Acetate Reactive Distillation column to meet purity specifications. Methyl Acetate is synthesized by reversible esterification of methanol and acetic acid. This system uses pure methanol and acetic acid as feed. In this project work, steady state model of Methyl acetate reactive distillation column is created using HYSYS. The process objective of RD is to maintain the distillate and bottoms purity. As the column exhibits multiple steady states for methyl acetate purity, inferential variables are selected. The LV(reflux rate and reboiler heat input) configuration is found to be the most appropriate configuration for this column. A control structure that controls a sensitive methanol feed tray temperature using the reboiler duty and maintains the acetic acid feed tray temperature using the reflux flow is found suitable.

The starting point for any dynamic simulation study is a sound steady state simulation. Within HYSYS, steady state simulation can be cast easily into dynamic simulations by specifying additional engineering details, including pressure/ flow specifications and equipment dimensions. A process modeling and simulation using HYSYS is undertaken to assess the feasibility of using decentralized proportional integral (PI) controllers for this multivariable process. Various set point changes and load changes are given to the column and the satisfactory performance of the controllers are ensured.

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CERTIFICATE

This is to certify that the work contained in this thesis titled "CONTROL SYSTEM DESIGN FOR A DOUBLE FEED METHYL ACETATE REACTIVE DISTILLATION" has been carried out by K. Durai Rajan under our supervision and has not been submitted elsewhere for a degree.

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ABBREVATIONS

RD	Reactive Distillation
L	Reflux rate
V	Vapor boil up
D	Distillate flow rate
B	Bottoms flow rate
ETBE	Ethyl Tertiary Butyl Ether
MTBE	Methyl Tertiary Butyl Ether
SISO	Single Input Single Output
MIMO	Multiple Input Multiple Output
PI	Proportional Controller
MPC	Model Predictive Controller

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO SIMULATION

In industry, distillation constitutes one of the most important and widely used unit operation and well studied by many chemical engineers. In spite of this, there are still many aspects of this process which are still not fully understood. One of the important aspects that still need attention is the operation and control of the process.

The chemical processes are dynamic, namely external disturbances, changes in ambient conditions, and degrading equipment performance continually affect the smooth running of a process operation. Through dynamic simulation analyses users are able to effectively study the impacts that changing operating conditions and design modifications have on the operation of a process. Such analyses are value-added. Process configurations and control system designs can be evaluated to ensure that they will meet corporate manufacturing objectives regardless of changing process and market conditions.

Today however, dynamic simulation technology, like most simulation technology is greatly improved – it is now available to the non-experts. First-principle chemical engineering unit operations, thermodynamic property packages, component databanks, and simulation solvers (steady state and dynamic) have been integrated into commercial simulation platforms. Moreover commercial simulation platforms that emphasize intuitive and interactive user-interface designs accelerate the model and project development process.

A HYSYS modeling package is aimed at the process design activity where users need to specify only an appropriate level of equipment and performance detail to capture the major aspects of the process operation.

CHAPTER 2

LITERATURE REVIEW

Barbosa and Doherty (1987) studied the influence of equilibrium chemical reactions on vapor-liquid phase diagrams. The conditions for formation of reactive-azeotropes in constant-volatility systems are derived.

Modeling of reactive distillation systems was proposed by Grosser et al. (1987). Here, the reactive distillation column accompanies a continuous polycondensation reactor system in Nylon 6,6 production.

Agreda et al. (1990) describes the commercial process for the production of high-purity methyl acetate via reactive distillation. The development and scale-up steps described include concept inception, laboratory testing, pilot plant development, modeling and design, full-scale construction and operation, and final troubleshooting and optimization.

A procedure for advanced process controllers utilizing first principles steady state and dynamic models as an alternative to empirical models identified from plant tests is presented (Alsop and Ferrer, 1994). The procedure is illustrated on a challenging control problem posed by the propylene/propane splitter at Scan raff refinery in Lysekil, Sweden. In this unit, a classical control design procedure based on plant step tests is not feasible. It is demonstrated that a workable control strategy that satisfied the control objectives for the splitter could be developed, without the need for any step tests on the live plant whatsoever. This is a highly illustrative example of how dynamic simulation has progressed from an academic discipline to an industrial setting in which economic benefits can be justifiably claimed.

A dynamic mathematical model of reactive distillation in case of kinetically controlled chemical reaction is formulated by Alejski and Duprat (1996) using four basic assumptions: negligible vapor holdup compared to the molar liquid holdup, perfect mixing of phases, corrections of equilibrium values by plate efficiency, corrections of conversion for mixing effects by 'conversion efficiency'. The accuracy of the dynamic simulation results of reactive distillation obtained under different assumptions is verified by comparing with results of actual experiments on a pilot-scale distillation column.

Sneesby et al. (1997, a) studied steady state simulation of ETBE column and design aspects. In this work, column simulation is performed using Speedup and effects of different design parameters is studied. They also worked on dynamic simulation and control aspects (1997, b). They recognized that both ether purity and isobutylene conversion as process objectives and suggested to use only control configuration that manipulate the reboiler. As the one point control scheme suffer from the disadvantage of a low process gain between the temperature controller set point and the ether purity, they also studied two point control of ETBE column (1999). The combined composition and conversion control scheme is implemented on the ETBE column using the inferential conversion model and the LV control configuration. They found that two point control is effective in feed disturbance rejection and in optimizing the isobutylene conversion compared to one point control.

Song et al. (1998) studied the influence of heterogeneous catalysis on the transition from the nonreactive to the equilibrium reactive limits for the esterification of acetic acid with methanol. A Langmuir-Hinshelwood/Hougen-Watson rate model was developed to represent the reaction kinetics.

Two point control of reactive distillation column for composition and conversion was studied by Sneesby et al. (1998).

The output and input multiplicities due to change in various parameters is discussed in simulation and control of reactive distillation column by Sneesby (1998). Pseudo multiplicity and the various reasons for these multiplicities are discussed.

Taylor and Krishna (2000) reviewed about different types of modeling and designing the reactive distillation.

Al-Arfaj and Luyben (2000) reviewed on control of RD. They explored the closed-loop control of an ideal two product RD. Six alternative control structures are evaluated via rigorous dynamic simulation. The interaction between design and control is illustrated by the impact of holdup in the reactive zone. Also stoichiometric amounts of fresh feeds are desired for double feed column. They studied real two product system, the production of methyl acetate (2002, a). Based on the studies on three different control structures, the tray temperature control avoids non-linearity which normally occurs for composition control. They demonstrated that adding additional trays in a RD does not degrade performance, provided the specified degrees of freedom are appropriately chosen (2002, b). Three chemical systems (hypothetical, ETBE and methyl acetate) are chosen for their studies. They showed (2002, c) that a simple single-temperature PI structure provides effective control for ethylene glycol rather than using an advanced nonlinear inverse-based controller. Three different designs for the pentene metathesis are studied (2002, d). They demonstrated that effective dynamic control is provided by a control structure that uses two temperatures to maintain the purities of both product streams. They also studied control of ETBE reactive distillation (2002, e). Sneesby's single feed configuration is optimized and control structures for both double feed and single feed are studied. They found that tray temperature control provides better control over composition for single feed. They used only single end control in order to maintain ETBE purity. The synthesis and plant wide control in production of tert-amyl methyl ether is reported by Al-Arfaj and Luyben (2004). The crucial unit of flow sheet, RD is controlled by using tray temperature at bottom and methanol composition in the reaction zone.

Rivera and Grievink (2002) systematically defines the conditions under which multiple steady states may occur and to determine the effects of their presence upon spatial design of reactive distillation column.

Doherty et al. (2003) describes a hierarchy of methods, models and calculation techniques that support the design of reactive distillation column. The existence of both a minimum and a maximum reflux ratio, a narrow range of reflux ratio that will produce high conversions and high purity methyl acetate and the existence of multiple steady states throughout the entire range of feasible reflux ratios are shown.

Wang et al. (2003) studied the effect of interaction multiplicity on control system design for a MTBE reactive distillation column. Though the column exhibits steady state multiplicities, they explained that a linear control still is possible by selecting appropriate controlled and manipulated variable pairing.

Luyben et al. (2004) compared control of conventional with Reactive Distillation processes for the production of Butyl Acetate. For selected plant wide control structure, both processes are effectively controlled using conventional PI controllers that manage the addition of fresh feeds and stabilize recycle flow rates.

CHAPTER 3

HYSYS SIMULATION SOFTWARE

3.1 INTRODUCTION

A simulation flow sheet is a collection of simulation units to represent computer programs (subroutines or models) that simulate the process units. Computing packages that are used to model the process units are referred to as process simulator, most of which are used to simulate potential processes in the steady state. Nowadays, these packages are being extended to permit the dynamic simulation of processes and their control systems as they respond to disturbances and changes in operating points. HYSYS is one such process simulation software package for Windows. It is the evolution of HYSIM, a DOS-based simulation package. HYSYS is a powerful tool for the simulation of refinery processes.

HYSYS offers a high degree of flexibility because there are multiple ways to accomplish specific tasks. This flexibility combined with a consistent and logical approach to how these capabilities are delivered makes HYSYS an extremely versatile process simulation tool.

3.2 TECHNICAL SPECIFICATION

3.2.1 System Specifications

The usability of HYSYS is attributed to the following four key aspects of it design:

- Object Oriented Design - HYSYS has been developed in C++.
- Operating System - Windows, Windows NT, Windows 95
- Operating Environment - Event Driven Graphical Environment
- Calculation Methodology Steady State - non-sequential modular. Flow sheet calculations are performed automatically whenever the user supplies information. Results of any calculation are passed automatically to any other stream or

operation affected by the calculation, propagating the results throughout the flow sheet. Partial information is also passed bi-directionally throughout the flow sheet.

- Calculation Methodology Dynamic - individual unit operations contain the necessary information to calculate their dynamic response, either integrating their hold-ups, or in the case of operations without hold-ups, algebraically. A variable step-size Euler integration scheme is used, with all streams and operations simultaneously calculated in a time step.

3.2.2 Program Architecture

- Multi-Flow sheet - an unlimited number of flow sheets can be installed in a simulation
- Column Sub-Flow sheets - Column operations reside in their own sub-flow sheet (meaning they posses their own fluid package, PFD and Workbook. Within the Sub-Flow sheet, additional pieces of equipment, either as side equipment to a tray section as new columns or as pieces of equipment can be installed. The entire sub-flow sheet is solved simultaneously, allowing linked towers to be solved without recycles.

3.3 DYNAMIC MODELLING CAPABILITIES

HYSYS uses a flow sheet approach to dynamic modeling, where the individual unit operations can calculate their dynamic response without any user coding. For operations with hold-up, the response is integrated; pieces of equipment without hold-up are solved algebraically.

Highlights of dynamic modeling capabilities include:

- A Pressure/Flow Solver permitting users to accurately simulate "real world" dynamic behavior
- A fully Implicit Euler integration method which has the characteristics of being stable and fast

- Dynamics Extensibility capabilities which allow users to integrate proprietary and custom unit operations
- PID Controllers, MPC Controllers, & Strip Charts for process monitoring and control.

- Speed - set up your model and obtain meaningful results quickly
- Initialization - the steady state solution can be used to initialize the model, rather than having to begin from a dry condition. The flow sheet can be returned quickly to its initial starting point by going back into steady-state and resolving the flow sheet.
- Consistency - since the dynamic application is using the same thermodynamic package as for steady state calculations, consistent results between applications is assured.

CHAPTER 4

REACTIVE DISTILLATION

4.1 INTRODUCTION

Process intensification is an area of growing interest that is defined as any chemical engineering development that leads to a substantially smaller, cleaner, and more energy efficient technology. An excellent example of process intensification is reactive distillation (RD), which provides an alternative to conventional processing schemes that include for instance a reactor followed by a distillation column in chemical production by combining reaction and separation.

4.2 WHY REACTIVE DISTILLATION?

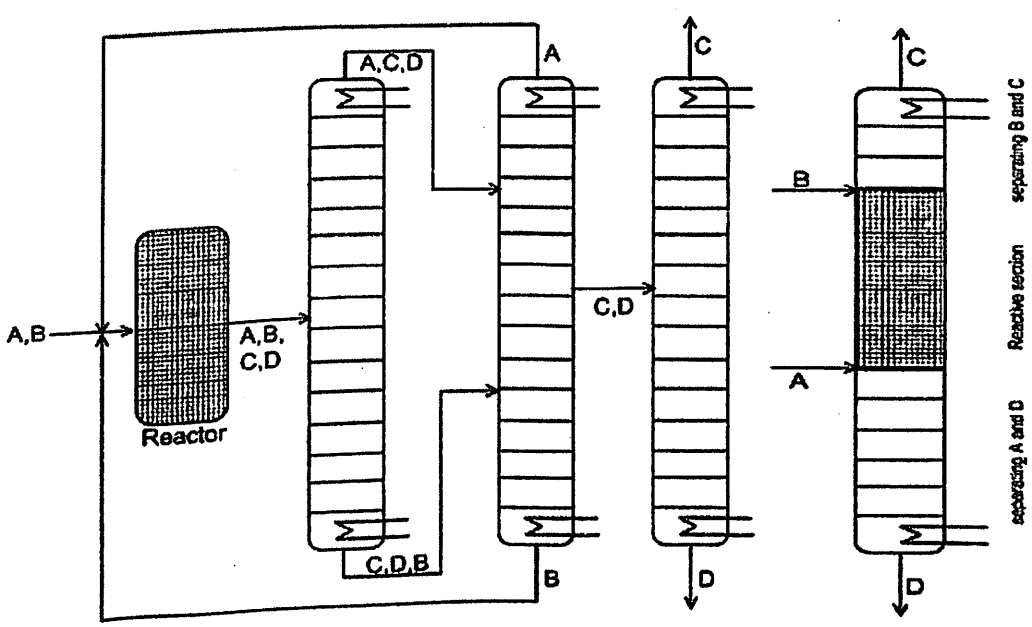
Reactive distillation combines both separation and reaction in one unit. It has been used in a small number of industrial applications for many years, but the last decade has shown an increase in both research and applications. It can offer significant economic advantages in some systems, particularly for reversible reactions

Considering a reversible reaction scheme: $A+B \Leftrightarrow C+D$, where the boiling points of the components follow the sequence A, C, D and B. The traditional flow-sheet for this process consists of a reactor followed by a sequence of distillation columns; see Fig. 4.1(a). The mixture of A and B is fed to the reactor, where the reaction takes place in the presence of a catalyst and reaches equilibrium. A distillation train is required to produce pure products C and D. The unreacted components, A and B, are recycled back to the reactor. In practice the distillation train could be much more complex if one or more azeotropes are formed in the mixture. The alternative RD configuration is shown in Fig. 4.1(b). The RD column consists of a reactive section in the middle with non reactive rectifying and stripping sections at the top and bottom. The task of the rectifying section is to recover reactant B from the product stream C. In the stripping section, the reactant A

is stripped from the product stream D. In the reactive section the products are separated in situ, driving the equilibrium to the right and preventing any undesired side reactions between the reactants A (or B) with the product C (or D). The reduction in the number of processing units and the direct heat integration between reaction and separation can reduce capital investment as well as utility costs.

Applying RD-technology in industrial scale, three constraints have to be full filled:

1. The use of RD technology is only possible, if the temperature window of the vapor- liquid equilibrium is equivalent to the reaction temperature. By changing the column operating pressure, this temperature window can be altered. However, the thermal stability of the catalyst can limit the upper operation temperature of the distillation column.
2. Because of the necessity of wet catalyst pellets the chemical reaction has to take place entirely in the liquid phase.
3. As it is very expensive to change the catalyst in a structured catalytic packing catalysts with a long lifetime are strongly required.



a) Conventional process

b) Reactive distillation

Fig.4.1 Process schemes

Increased overall conversion, as well as improved selectivity in competing reactions, can be achieved in reactive distillation. Of course, the reaction temperatures must be suitable for vapor and liquid phases to exist, and the volatilities of the reactants and products must be such that the products can be removed while containing the reactants in the column.

4.2.1 Advantage of RD and Its Constraint

Reactive distillation (RD) has many advantages over sequential processing, such as a "fixed-bed-reactor followed by a fractionating column, in which the distillate or bottom of the reaction mixture is recycled to the reactor inlet. The most important advantage in use of RD for equilibrium-controlled reactions is the elimination of conversion limitations by continuous removal of products from the reaction zone. Apart from increased conversion, the following benefits can be obtained:

1. An important benefit of RD technology is a reduction in capital investment, because two process steps can be carried out in the same device. Such integration leads to lower costs in pumps, piping and instrumentation.
2. If RD is applied to exothermic reaction; the reaction heat can be used for vaporization of liquid. This leads to savings of energy costs by the reduction of reboiler duties.
3. The maximum temperature in the reaction zone is limited to the boiling point of the reaction mixture, so that the danger of hot spot formation on the catalyst is reduced significantly. A simple and reliable temperature control can be achieved.
4. Product selectivity can be improved due to a fast removal reactants or products from the reaction zone. By this, the probability of consecutive reactions, which may occur in the sequential operation mode, is lowered.
5. If the reaction zone in the RD-column is placed above the feed point, poisoning of the catalyst can be avoided. This leads to longer catalyst lifetime compared to conventional systems.

4.3 MOTIVATION FOR THIS WORK

Methyl acetate reactive distillation is an important system used in a process industry. It has a wide range of industrial applications. Methyl acetate, also known as acetic acid methyl ester or methyl ethanoate, is a clear, flammable liquid with a characteristic, not unpleasant smell like certain glues or nail polish removers. Methyl acetate is used as a solvent in glues and nail polish removers, in chemical reactions, and for extractions.

Moreover, RD involves considerable uncertainties and displays complex behavior such as high non-linearity, strong interactions, multiplicity, and time delay. Due to the functional integration of reaction and separation and the dynamics complexity, RD is exceptionally difficult to operate and control. This calls for systematic research on RD process dynamics and control aspects.

4.4 METHYL ACETATE REACTIVE DISTILLATION

Reactive distillation has enormous potential for the economic synthesis of esters. The production of methyl acetate is a classic example of successful reactive distillation technology.

In recent years, the focus of research has turned to kinetically controlled reactive distillations and the kinetics of methyl acetate synthesis have been studied extensively for both homogeneously and heterogeneously catalyzed reactions.

Methods have also been developed recently for the design, synthesis, and feasibility analysis of kinetically controlled reactive distillation, and methyl acetate synthesis has commonly been used as a model system.

4.4.1 CONVENTIONAL METHYL ACETATE SYNTHESIS

The conventional method using a reactor and separation section is very complex due to reaction equilibrium limitations and the formation of methyl acetate–methanol and methyl acetate–water minimum-boiling azeotropes. A complex multi-unit separation/ reaction/recycle system is required.

The conventional process involves a reactor and eight distillation columns. This includes a component splitter, an extractive distillation column, an azeotropic column, a methanol recovery unit, a decanter and two flash columns. The process diagram for the conventional process is given below. The energy consumption for the whole unit is high. It has one advantage over reactive distillation column; the deactivated catalyst can be easily replaced whereas in RD column it is difficult. The conventional process in a simplified form is shown in fig 4.2.

4.4.2 METHYL ACETATE SYNTHESIS IN RD COLUMN

In reactive distillation column, both the reaction as well as separation is done in as same column. The entire process can be done in a single column instead of going for the above mentioned conventional setup. The purity of product can also be maintained in the column by using effective control system. The energy consumption for this RD column is comparatively less than the conventional process because the heat liberated by the exothermic reaction is used for separation of the product.

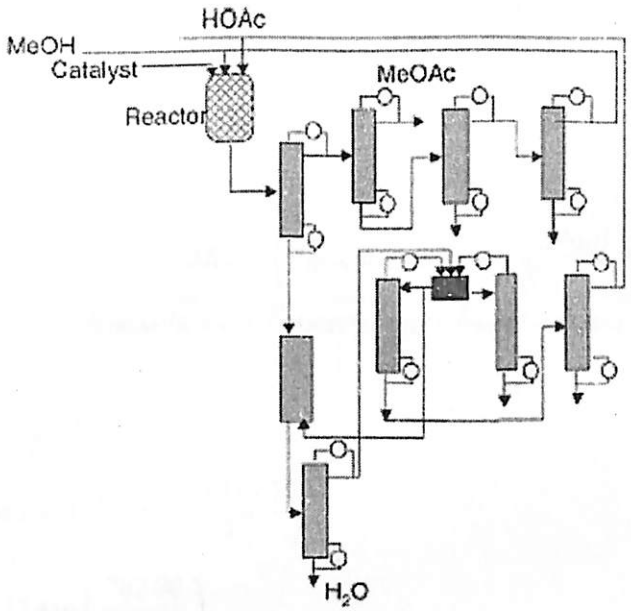


Fig 4.2 Conventional methyl acetate process

4.5 REACTION KINETICS

The production of methyl acetate (MeOAc) via reactive distillation system involves the reaction

$$\text{Methanol} + \text{Acetic acid} \rightleftharpoons \text{Methyl acetate} + \text{Water}.$$

In this system, the heavy reactant is heavier than the heavy product (acidic acid is less volatile than water). This has its impact on both steady state design and dynamic control.

Methyl acetate (MeOAc) can be made by the liquid-phase reaction of acetic acid(HOAc) and methanol (MeOH), catalyzed by sulfuric acid or an ion-exchange resin in the temperature range of 310–325 K and at a pressure of 1 atm. Since the high polarity of water and methanol compared to methyl acetate leads to strongly nonideal solution behavior, the rate expression is given in terms of activities. A new activity-based model,

utilizing the Langmuir– Hinshelwood/Hougen–Watson isotherm, was developed by Song et al. (1998).

$$R_{MeOAc} = \frac{M_{cat} k_1 \left(a_{HOAc} a_{MeOH} - \frac{a_{MeOAc} a_{H_2O}}{K_{eq}} \right)}{(1 + K_{HOAc} a_{HOAc} + K_{MeOH} a_{MeOH} + K_{MeOAc} a_{MeOAc} + K_{H_2O} a_{H_2O})^2}$$

$$k_1 = 6.942 \times 10^9 \exp\left(\frac{-6287.7}{T}\right)$$

$$K_{eq} = 2.32 \exp\left(\frac{782.98}{T}\right)$$

$$K_{HOAc} = 3.18$$

$$K_{MeOH} = 4.95$$

$$K_{MeOAc} = 0.82$$

$$K_{H_2O} = 10.5$$

$$a_i = \gamma_i x_i$$

One of the side reactions in the methyl acetate system is the dehydration of methanol to dimethyl ether (DME) and water.

$$2MeOH \rightleftharpoons DME + H_2O.$$

This side reaction is favored at high pressure; significant amount of DME is formed only at higher liquid holdups, high temperature and pressure. It appears that most studies ignore this side reaction, so we have not considered it.

An increase in pressure leads to an increase in the boiling points of the components and hence the operating temperature of the reactive distillation column. This leads to higher rates of reaction and smaller equipment, which reduces investment costs.

On the other hand, an increase in temperature leads to a decrease in the equilibrium constant (and hence the equilibrium conversion) and could potentially trigger unwanted side reactions such as the methanol dehydration reaction.

Accurate prediction of the VLE of the methyl acetate system is vital to the simulation and design of the process. To correlate the VLE in mixtures containing a vapor-phase associating substance such as acetic acid, Mark's method in combination with a liquid activity coefficient model is usually used. The Wilson equation is recommended in the DECHEMA Vapor Liquid Equilibrium Data Collection. Therefore, the Wilson model is used in our simulation.

CHAPTER 5

STEADY STATE SIMULATION

5.1 ROLE OF STEADY STATE SIMULATION

The starting point for any dynamic simulation study is a sound steady state simulation. Similarly, a sound appreciation of the steady state behavior of a process is required, as this forms the basis for any control study. This is reflected by the observation that a well-tuned PID controller is less sensitive to variations in process dynamics than to gain.

5.2 FUNAMENDAL CONCEPTS

5.2.1 Degree of freedom analysis

A degrees of freedom analysis must be made before unit operations can be successfully modeled with a process simulator.

5.2.2 Fixed Variables: Existing distillation columns have variables that are fixed that cannot be manipulated to alter the output. These variables are for instance: the height of the column, the number of trays, the plate efficiency and so on.

5.2.3 Independent Variables: On the other hand there are a number of variables which can be varied so that the column output meets on the project goals:
Feed condition, Steam flow rate and conditions (thus the reboiler duty in the simulation), Reflux ratio R, Feed plate location. These variables are the ones that are available for planning experiments on the distillation columns.

5.2.4 Dependent Variables: With the fixed and independent variables defined for HYSYS, HYSYS will solve for not only the exit concentrations at the top and the bottom of the column but also all variables in the column. HYSYS will allow the user to adjust

any of these independent variables to either maximize or minimize the product component concentrations.

5.3 SOLVING METHOD

- **Sparse- calculation solver:** This is the solution method used widely for three phase distillation column and reactive distillation column.
- **Acceleration:** The DEM is a numerical solution program, which accelerates convergence of the simple model K values and enthalpy parameters.
- **Damping:** The fixed damping factor controls the step size used in the outer loop when updating the simple thermodynamic models used in the inner loop. For the vast majority of hydrocarbon- oriented towers, the default value of 1 is appropriate, which permits a full adjustment step.

5.4 SIMULATION OF REACTIVE DISTILLATION COLUMN

Steady state models continue to be powerful and efficient tools which form the basis for designing control systems for reactive distillation columns. The methyl acetate system is simulated at 125kpa. The column has 35 trays, a total condenser, a partial reboiler, saturated liquid reflux and theoretical trays. Number of reactive stages is 17. Pure methanol is fed to the column at tray 11 and pure acetic acid is fed at tray 28.

The steady state simulation will be built using these basic steps:

- Choose a property package
- Select the components
- Create and specify the feed streams
- Install and define the column

5.4.1 Selection of property package and components

The selection of property package and components is accomplished by invoking the simulation basis manager. HYSYS uses the concept of the Fluid Package to contain all necessary information for performing flash and physical property calculations. The property packages are Equations of State that are used to describe the P-V-T behavior of the system. For the methyl acetate reactive distillation system Wilson model is widely used. This model is ideal for VLE calculations as well as calculating liquid densities. Equilibrium reaction model is used for the methyl acetate reaction. After selecting the reaction set, the set is attached to the fluid package.

5.4.2 Specification for solution of the material and energy balances

After entering main build simulation environment, the column and streams are installed and column parameters are defined to satisfy the degree of freedom analysis. The column parameters are given as follows:

Pressure profile: The pressure profile in a column is calculated based on the given specification. This can either explicitly enter all stage pressures or entering the top and bottom tray pressures and any intermediate pressures such that HYSYS can interpolate between the specified values to determine the pressure profile. Simple linear interpolation is used to calculate the pressures on stages which are not explicitly specified. The condenser and reboiler pressure drops explicitly within the appropriate operation view. Default pressure drops for the condenser and reboiler are zero, and a non-zero value is not necessary to produce a converged solution.

Number of stages: The number of stages specified for the tray section does not include the condenser and bottom reboiler. HYSYS treats the stages as being ideal. For reactive distillation only ideal stages can be used.

Adding Streams: In HYSYS, there are two types of streams, Material and Energy. Material streams have a composition and parameters such as temperature, pressure and flow rate. They are used to represent Process Streams. Energy streams have only one parameter, Heat Flow term. The feed stream and production stream location, conditions and composition are treated as basic column parameters during convergence.

Column specification: Apart from this, the distillation column has two (for total condensation) or three degree of freedom, depending on the condenser conditions. If reflux flow rate is defined, the degree of freedom reduced to one. For this column, with total condenser, the flow rate of distillate is selected to simplify the convergence of the MESH equations. After convergence of the column with out reaction, the reaction set is made active and then the converged solution to column is obtained. Solver used is sparse-continuation solver.

5.5 METHYL ACETATE SYSTEM DESIGN

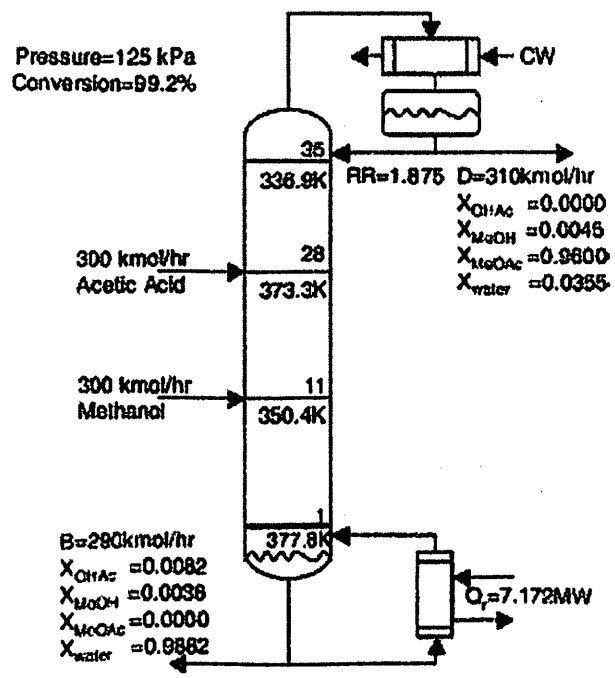
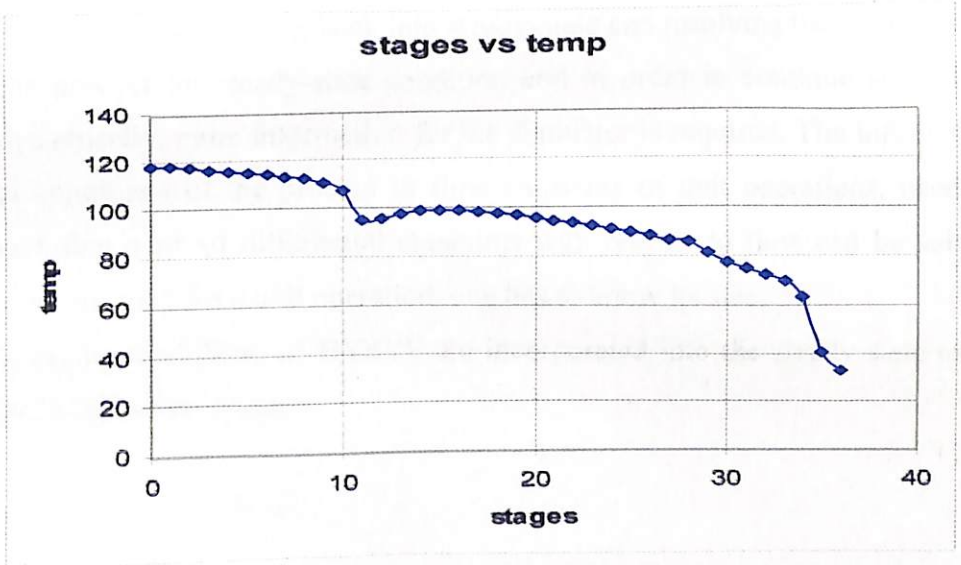


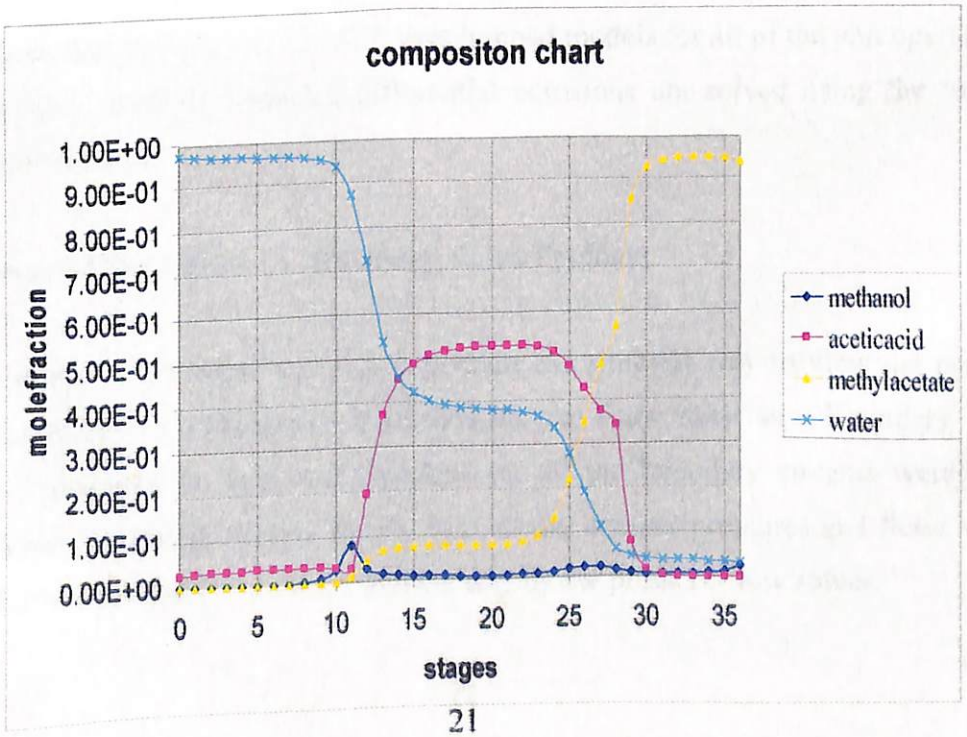
Fig. 5.1 Methyl Acetate System Design

5.6 STEADYSTATE PROFILE FROM ASPEN HYSYS 2004

For the given column data, the steady state simulation is performed using Aspen HYSYS 2004. The fluid package used is Wilson model for liquid phase and ideal gas for gas phase, and also UNIFAC parameter is used by setting binary coefficient. The steady-state simulation is performed by using sparse continuation solver. The equilibrium reaction kinetics based on equilibrium constant is added on each reactive stage. The temperature and composition profile obtained.

(Fig 5.1)





DYNAMIC SIMULATION

6.1 INTRODUCTION TO DYNAMIC SIMULATION

Dynamic simulation is the tool of choice to reproduce the expected behavior of still-to-be built plants, as well as to match the operating conditions of already functioning assets. Within HYSYS, Steady state solution can be used to initialize the model, rather than having to begin from a dry condition. The user can quickly return the flow sheet to its initial starting point by going back into steady-state and resolving the flow sheet. After solving the process for steady-state condition and in order to continue simulating the process dynamically, more information for the simulator is required. The information, on the initial conditions of the process or time constants of unit operations, needs to be known such that a set of differential equations with respect to time can be solved. To obtain a time constant for a unit operation, one has to know its size.

Dynamic capabilities of HYSYS are incorporated into the steady state model of the reactive distillation column.

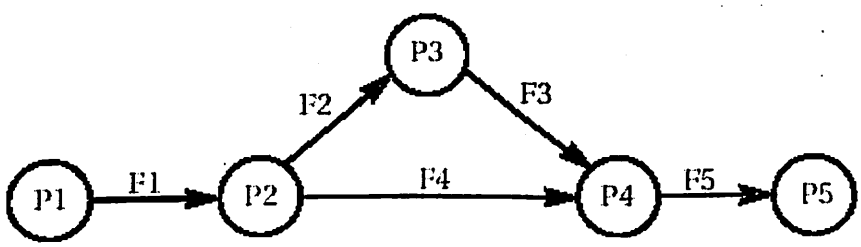
6.2 DYNAMIC CONCEPTS

- **Mathematical model:** HYSYS uses lumped models for all of the unit operations.
- **Solving method:** Ordinary differential equations are solved using the Implicit Euler method.

6.2.1 Pressure-Flow Solver: A Boundary Value Problem

In terms of pressures and flows, perhaps the simplest way to view the pressure flow solver in HYSYS Dynamics is to consider the Flow sheet as a Boundary Value Problem. If pressure or flow specifications on all the boundary streams were made (feeds/product streams in a Flow sheet), then all the internal pressures and flows would be solved simultaneously at each integration step by the pressure-flow solver.

6.2.2 Simultaneous Solution Approach to Pressure Flow Balances



6.1 Pressure Flow relationship

- P1, P2, P3 etc. represent Pressure Nodes (Vessels with hold up)
- F1, F2, F3 etc. represent streams with flow rates

Since pressures at nodes are a function of the flow rates into and out of the nodes and the flow rates through equipment are functions of the upstream and downstream pressures, the relationships between pressure and Flow rate equations in HYSYS Dynamics are significantly coupled. To find a solution to the pressure-flow relationships in HYSYS Dynamics, a simultaneous solution of the Flow sheet is performed. Solving for the flows and pressures requires the simultaneous solution of a set of linear and non-linear equations. Moreover, in order to epitomize computational effort, HYSYS Dynamics partitions the equations describing any unit operation into three classes:

- Pressure/flow relationships
- Energy relationships
- Compositional relationships

These groups of equations can then be integrated/ solved with different frequencies. Typically, the pressure flow relationships will have the smallest step size and the composition relationships the largest. The grouping of the equations also permits a different solution strategy to be applied to each group. In particular, it is possible to solve the pressure/flow relationships simultaneously across the entire Flow sheet. While the other equations (composition, enthalpy) are solved on a module by module basis.

6.3 TRANSITION FROM STEADY STATE TO DYNAMIC SIMULATION

The following areas should be examined when setting up a simulation in steady State and transitioning to Dynamics:

1. Adding Unit Operations
2. Equipment Sizing
3. Adding Control Operations
4. Entering the HYSYS Dynamic Environment
5. Adding Pressure-Flow Specifications

6.3.1 Adding Unit Operations

Material streams which are connected to two unit operations with no pressure flow relation are identified and corresponding flow must be specified in Dynamic mode.

6.3.2 Equipment Sizing

In dynamic simulation, the material and energy holdups are integrated over time, and hence accurate estimates of the vessel capacities are required to ensure reliable results. All unit operations in the simulation need to be sized using actual plant equipment or pre-defined sizing techniques. Vessels should be sized to accommodate actual plant flow rates and pressures while maintaining acceptable residence times.

Tray sizing: The tray sizing utility uses the vapor and liquid flow rates at steady state. Sizes are computed using default specifications, which can be modified by the user. Tray is sized for 2.1 m diameter, 1.61m weir length, and 900mm of tray spacing. In steady state, the pressure profile of the column is user specified. In dynamics, it is calculated using dynamic hydraulic calculations. If the steady state pressure profile is very different form the calculated pressure drop, there can be large upsets in flow in the column when the integrator is run. In this column, the steady state pressure drop and dynamic pressure profile are not varying much.

Reboiler and condenser vessel volumes: Five to fifteen min residence times of liquid are typical; with the nominal flow rates taken from the appropriate column property views. A holdup time of 5 min and a nominal vessel liquid vessel liquid level of 50% of capacity are assumed. To compute the vessel volumes, the flow rates of their feed streams are accessed. Thus, the reboiler volume is computed as

Reboiler volume = holdup time * flow rate/ 0.5

For the condenser, the liquid flow rate is required, which is computed as the sum of the liquid distillate and reflux flow rates.

6.3.3 Strip Charts and Controllers

Strip charts: While the Flow sheet is running dynamically, it is difficult to observe the simulation variables. All variables are updated constantly as the dynamic simulation is running. Using a strip chart allows the user to observe several variables in real time as the dynamic simulation runs.

Controllers: To ensure proper liquid level in condenser and reboiler, level control are configured using distillate and bottom flow rates respectively, flow specification is used for both reflux and distillate, a vessel pressure controller be setup with the condenser duty as the operating variable. After performing these above steps, the steady state mode is transferred to dynamic mode.

CHAPTER 7

CONTROL STRUCTURE SYNTHESIS

Systematic steady state analyses are conducted to synthesize effective control structures for methyl acetate reactive distillation column. A control structure refers to the number of control loops and the specific input-output pairing used in the loops. Potential input variables in a reactive distillation are reflux rate, reflux ratio, reboiler duty, reboil ratio, distillate rate, bottoms rate and the fresh feeds. Potential output variables are easily measurable variables such as tray / stream temperatures and compositions. There are thus several possible input (manipulated) variables and output (controlled) variables even in a simple RD column. Usually, control structure is synthesized based on the process objectives of the RD column.

Reactive distillation combines the functionality of both the reaction and purification stages of a process, and the main operating objective for a reactive distillation column should reflect both roles. In a reactor, the principal process objective which maximizes profitability is conversion of the limiting reactant, while in distillation it is separation which is normally measured by the product purity.

Control of reactive distillation is challenging because of its complex dynamics resulting from its integrated functionality of reaction and separation. In the design of such a control system, the selection of the control structure is the most crucial decision. The approach taken is to study the effect of varying the input handles about their base case values on the column outputs to identify potential input-output pairings. Pairings that are sensitive avoid multiplicities and give nearly linear input output relationships are short listed. This simple philosophy for control structure synthesis is performed on a double feed methyl acetate RD system in this work.

7.1 SELECTION OF MANIPULATED VARIABLE

Distillation control configurations are often described with reference to the two manipulated variables which are not used to control the column inventory. The LV, LB, DV schemes are the most practical combinations since they provide one manipulated variable at each end of the column thereby minimizing lags. The most widely used control configuration in industrial practice is **LV configuration** and is selected here although the LB scheme could have been used equally as well.

7.2 SELECTION OF CONTROLLED VARIABLE

The controlled variable which is used to ensure that the column consistently meets the process objectives will have several characteristics: linearity, sensitivity and responsiveness. Linearity refers to the relationship between the selected controlled variable and the manipulated variable. Sensitivity refers how much the manipulated variable must be changed to change controlled variable to a desired value. Responsiveness again refers to the relationship between the controlled variable and the manipulated variable which is used to provide that control and is a measure of the dead time and dynamic lags between the two variables.

7.2.1 Steady State Multiplicities

Reactive distillation columns are highly nonlinear and multiple steady-state solutions have been reported by many researchers [Doherty et. al. (2001), Wang et. al. (2003)]. Column with multiple steady states is difficult to control than the linear systems. Change in any process conditions may drift the output of these systems from one steady state to another one. Input multiplicity occurs when two or more sets of input variables produce the same output condition. Output multiplicity occurs when one set of process input variables results in two or more sets of process output variables. With reference to control structures, input variables are those that can be manipulated by control valves or other actuating devices. Output variables are those that are either controlled or measured

to describe the conditions of the process. The presence of input and output multiplicities may cause both operation and control problems. The control structure chosen must avoid output multiplicities to ensure that the column does not drift from say a high conversion steady state to a low conversion steady state. However, we shall show that even though the states of the column exhibit multiplicities, simple linear control is still feasible if controlled and manipulated variables with one-to-one relationship can be identified. The presence of multiplicities is common in reaction distillation and reported for many RD columns.

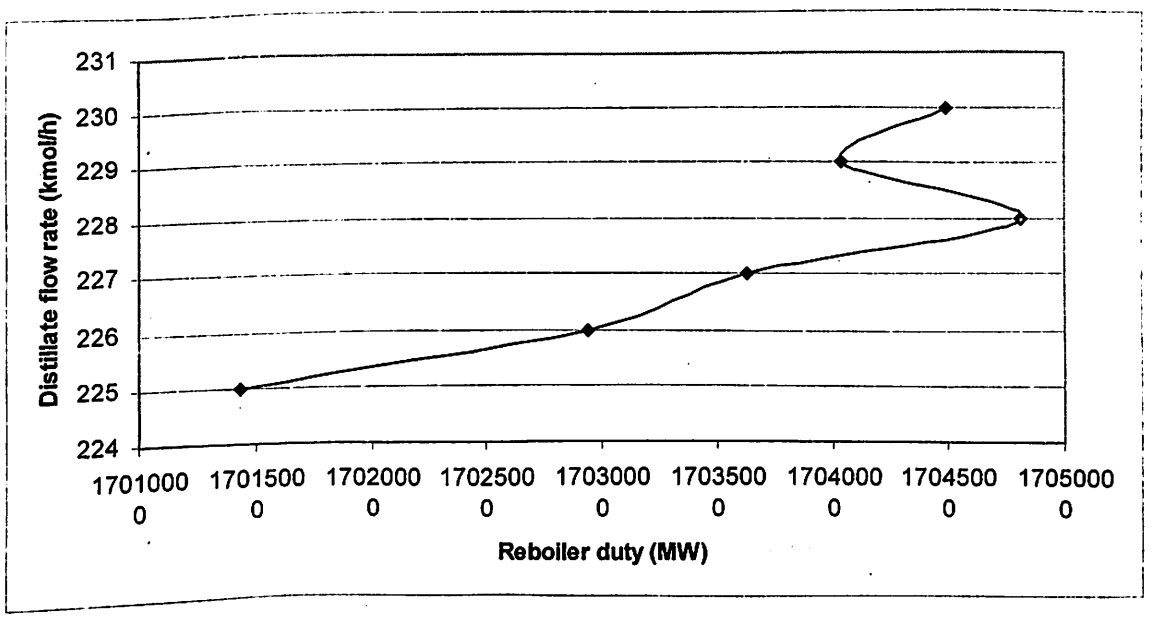


Fig 7.1 Output multiplicity

The consequences of input multiplicity are not as severe as output multiplicity. However, input multiplicity results in the change in the sign of process gain around the nominal operating condition leading to control instability. Directionality of a chemical process means that a vector of inputs is differently amplified according to the direction. Directionality of the process gain has been known to create a considerable complex design of the control system for multivariable process.

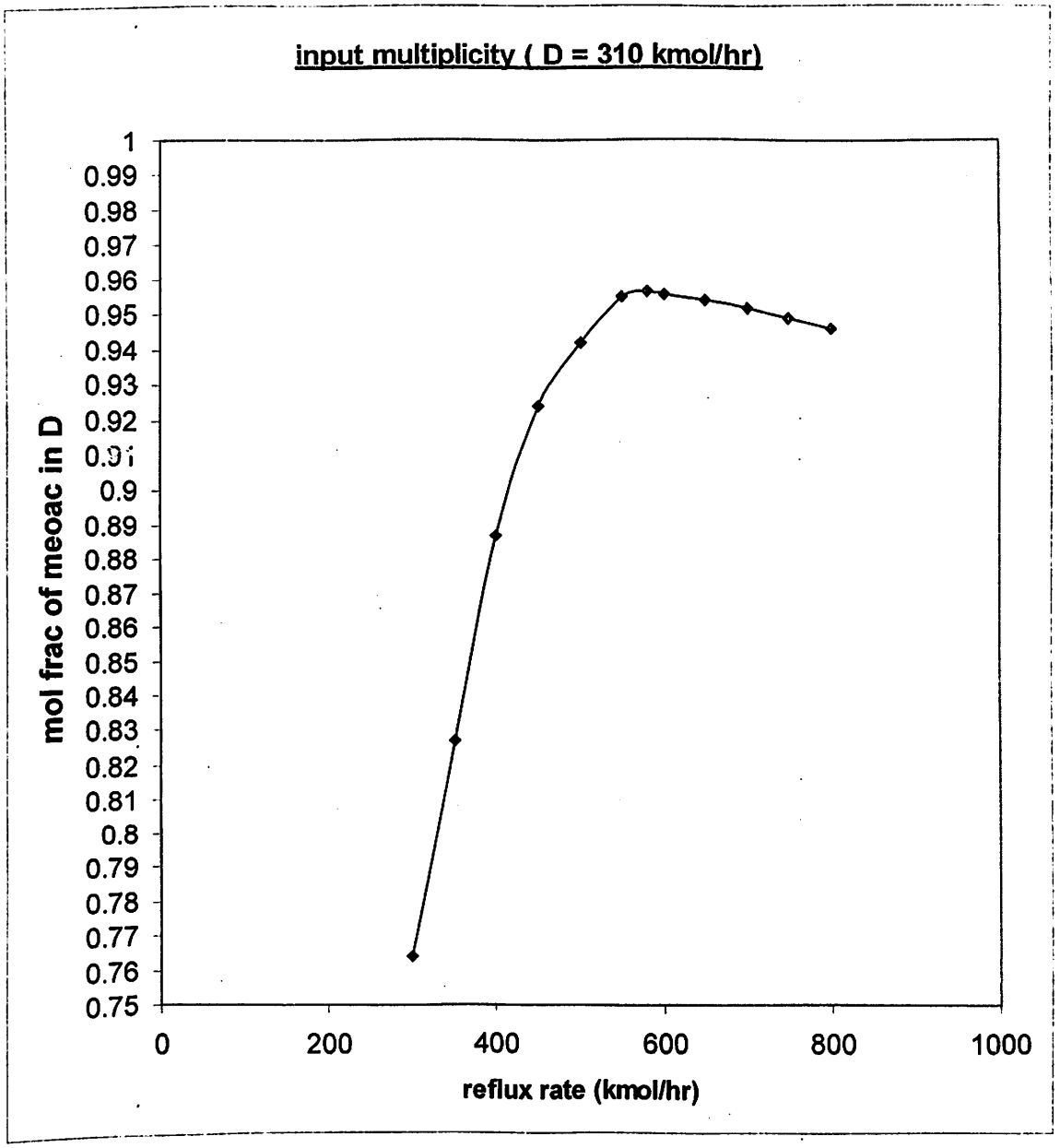


Fig 7.2 Input multiplicity

7.2.2 Selection of inferential variable for methyl acetate purity

Since the methyl acetate composition exhibits multiplicity the 28th tray temperature is selected as inferential variable to control the product purity by manipulating the reflux flow rate.

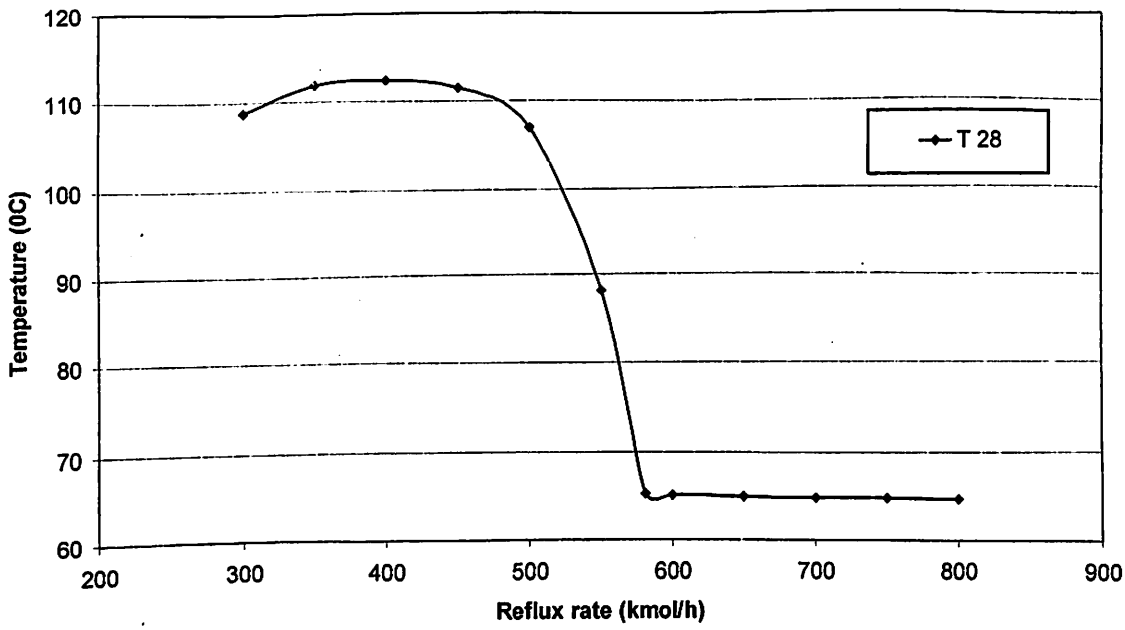


Fig 7.3 Change in 28th stage temperature with reflux rate

7.3 SENSITIVITY ANALYSYS

In the above RD process, the purity of methyl acetate has to be controlled. For this the composition controllers may be used to control the column, but the composition controllers have measuring lags and also are costly and needs maintenance. So in our control structure temperature controllers are used instead of composition controllers.

The trays which are more sensitive for reflux rate and reboiler heat duty are found out from the steady state analysis. These trays are used for controlling the top and bottom purity instead of composition controllers. The control of column temperature avoids the

output multiplicity exhibited by the column so control using temperature controllers avoids bidirectionality of the system.

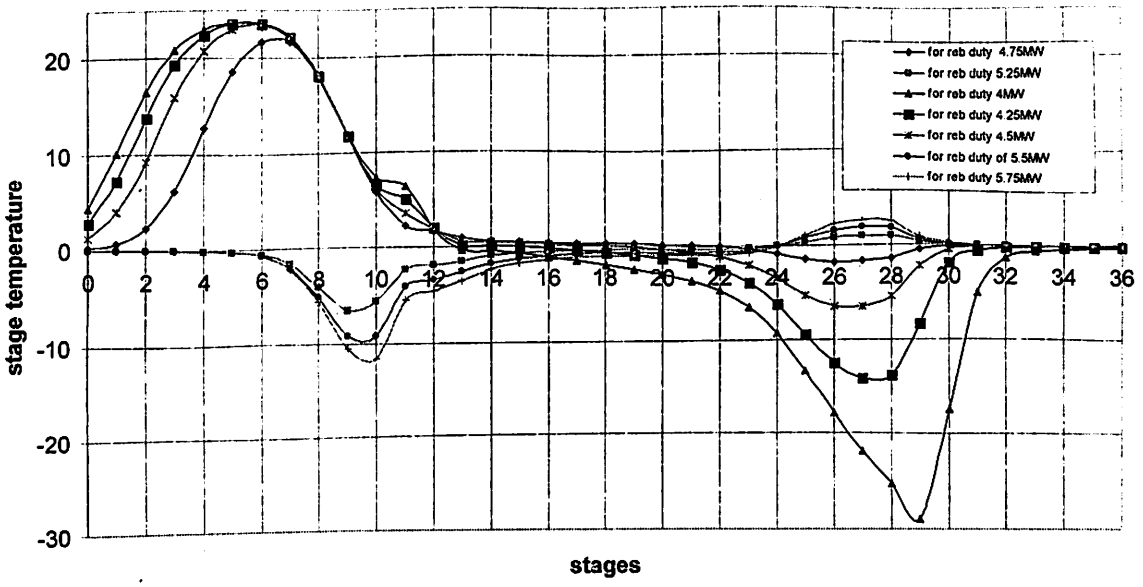


Fig 7.4 Stage temperatures for various reboiler heat duties

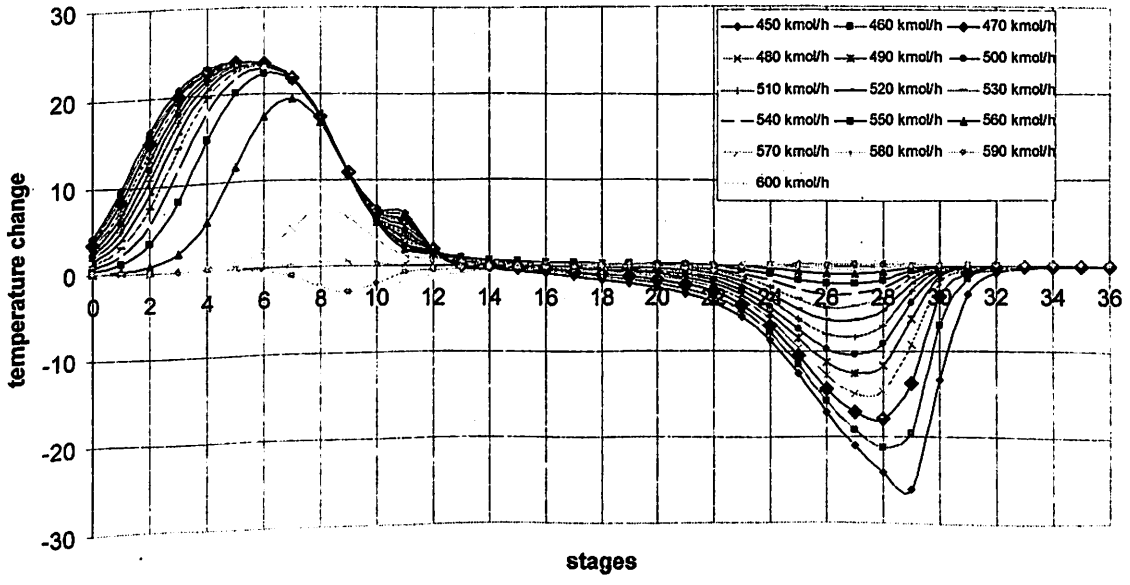


Fig 7.5 Stage temperature for various reflux flow rates

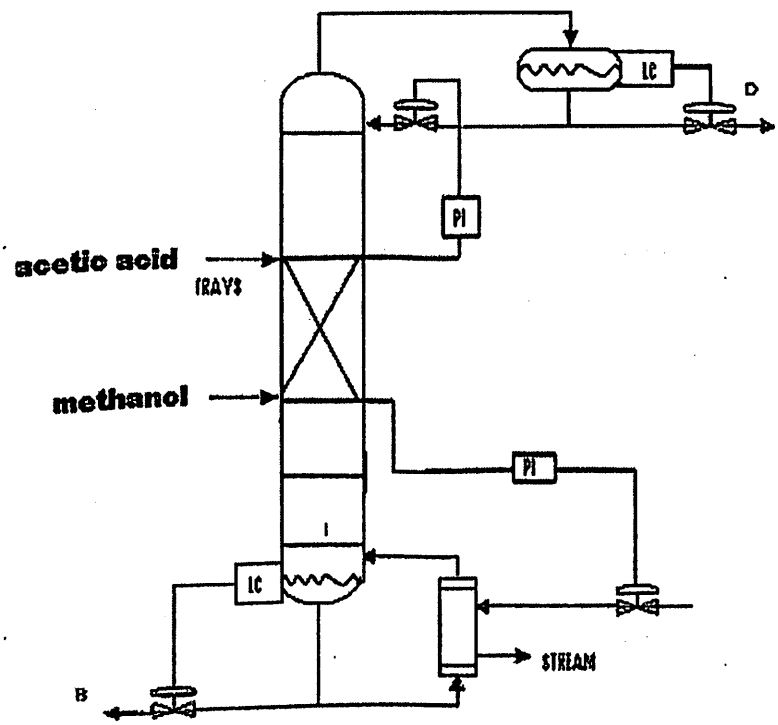
7.4 FINAL CONTROL STRUCTURE

- Methyl acetate purity in the top is maintained by controlling 28th stage temperature in rectifying zone by manipulating reflux flow rate.
- Bottom purity and conversion is maintained by controlling 11th stage temperature in stripping zone by manipulating reboiler heat flow.

CHAPTER 8

DECENTRALIZED PI CONTROLLER

Most industrial control systems use the multiloop SISO diagonal control structure. It is the most simple and understandable structure. Operators and plant engineers can use it and modify it when necessary. It does not require an expert in applied mathematics to design and maintain it. In addition, the performance of these diagonal controller structures is usually quite adequate for process control applications. Decentralized PI control is a desirable controller structure for multivariable systems because of its corresponding hardware and design simplicity. Decentralized control systems can also be designed to achieve levels of fault tolerance that may be difficult to obtain in a centralized multivariable control system. The decentralized PI controller for the methyl acetate column is synthesized by using relay feed back method.



8.1 Control structure

8.1 RELAY AUTO TUNING

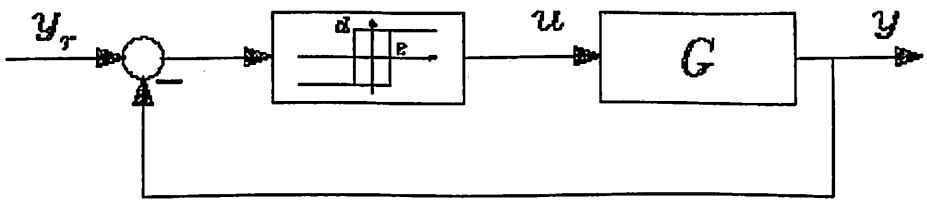


Fig. 8.2 Relay Feedback

The majority of the controllers used in industry are of the PID type. A large industrial process may have hundreds of these controllers. They have to be tuned individually to match the process dynamics in order to provide good and robust control performance. The tuning procedure, if done manually, is very tedious and time consuming; the resultant system performance mainly depends on the experience and the process knowledge the engineers have. It is recognized that in practice, many industrial control loops are poorly tuned. Automatic tuning techniques thus draw more and more attention of the researchers and practicing engineers.

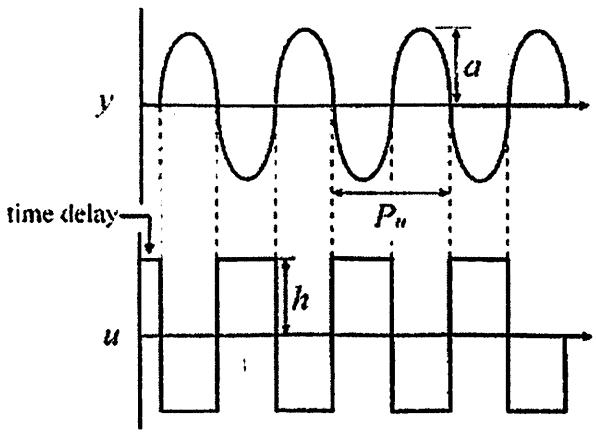


Fig. 8.3 Limit cycle in controller variable

The Astrom-Hagglund relay feedback system is a simple means to identify the critical process information, the ultimate gain and ultimate frequency. A relay of height h is inserted as a feedback controller. The manipulated variable m is increased by h above the steady state value. When the controlled variable y crosses the set point, the relay reduces m to a value h below the steady state value. The system responds to this 'bang

bang' control by producing a limit cycle, provided the system phase angle drops below -180 degree, which is true for all real process.

The period of the limit cycle is the ultimate period (P_u) for the transfer function relating the controlled variable y and the manipulated variable m. So the ultimate gain frequency is

$$\omega_u = \frac{2\pi}{P_u}$$

The ultimate gain is given by

$$K_u = \frac{4h}{a\pi}$$

Where h = height of the relay

a= amplitude of the primary harmonic of the output y

8.1.1 Features of Relay tuning

Relay is mainly used as an amplifier in the fifties and the relay feedback was applied to adaptive control in the sixties. Astrom and co-workers successfully applied the relay feedback technique to the auto-tuning of PID and PI controllers for a class of common industrial processes. The relay feedback auto-tuning technique has several attractive features. Firstly, it facilitates simple push-button tuning since the scheme automatically extracts the process frequency response at an important frequency and the information is usually sufficient to tune the PID controller for many processes. The method is time-saving and easy to use. Secondly, the relay feedback auto-tuning test is carried out under closed-loop control so that with an appropriate choice of the relay parameters, the process can be kept close to the set point. This keeps the process in the linear region where the frequency response is of interest, which is precisely why the method works well on highly nonlinear processes. Thirdly, unlike other auto-tuning methods, the technique eliminates the need for a careful choice of the sampling rate from the a priori knowledge of the process. This is very useful in initializing a more sophisticated adaptive controller. Fourthly, the relay feedback auto-tuning can be modified to cope electively with disturbances and perturbations to the process.

CHAPTER 9

RESULTS AND DISCUSSION

Reactive distillation of methyl acetate is a non-conventional and complex process with high non-linearity, bidirectionality, strong interactions, and multiplicity. As reactive distillation combines the functionality of both the reaction and purification stages of a process, the main process objectives of methyl acetate RD column are methyl acetate purity and conversion.

A steady state simulation of methyl acetate RD column was performed in HYSYS. Dynamic capabilities of HYSYS were incorporated into the steady state model of the reactive distillation column. The steady state simulation was used to initialize the model rather than starting from the dry condition. The control objective was to maintain the purity of the distillate and bottoms product streams. The column pressure and reboiler and condenser levels were controlled to maintain stable operation. Here LV configuration was used to maintain product purity, where the reflux flow rate L was used to control the 28th stage temperature, and reboiler heat was used to control the 11th stage temperature.

Due to the presence of input multiplicities, inferential variables are selected for control of the column. For the selected control structure, decentralized PI controller is implemented. Decentralized PI controller is tuned using relay feedback method.

9.1 DISTURBANCES

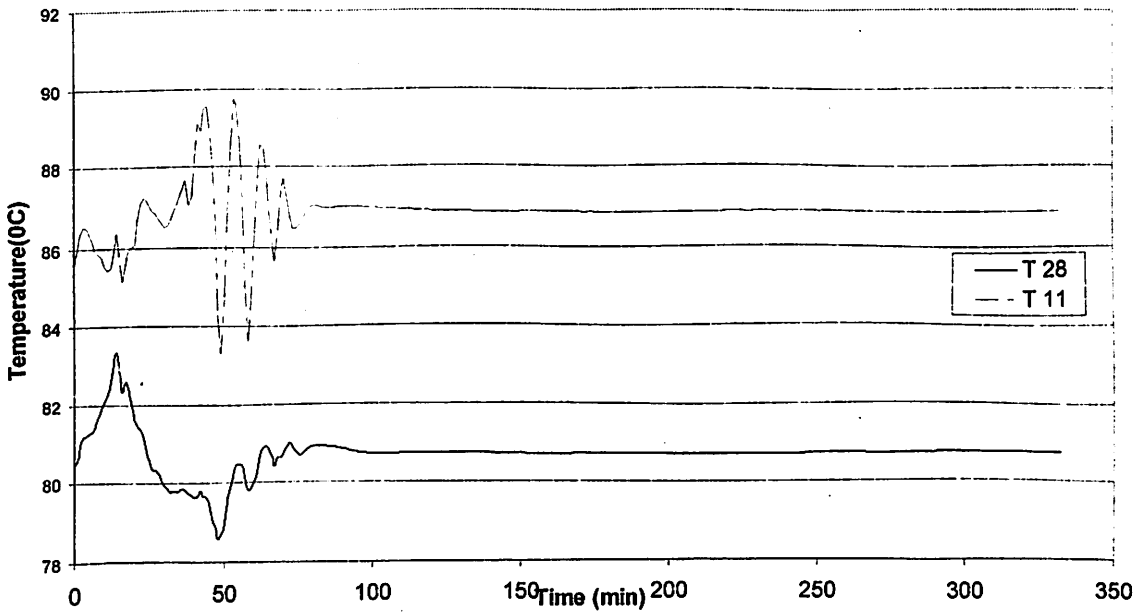
The response of controlled variables for six different disturbances, setpoint change in 11th stage temperature, setpoint change in 28th stage temperature, 10% change in methanol feed rate, 10% change in acetic acid feed rate, change in methanol feed temperature and change in acetic acid feed temperature are given below.

9.1.1 Integral square of errors

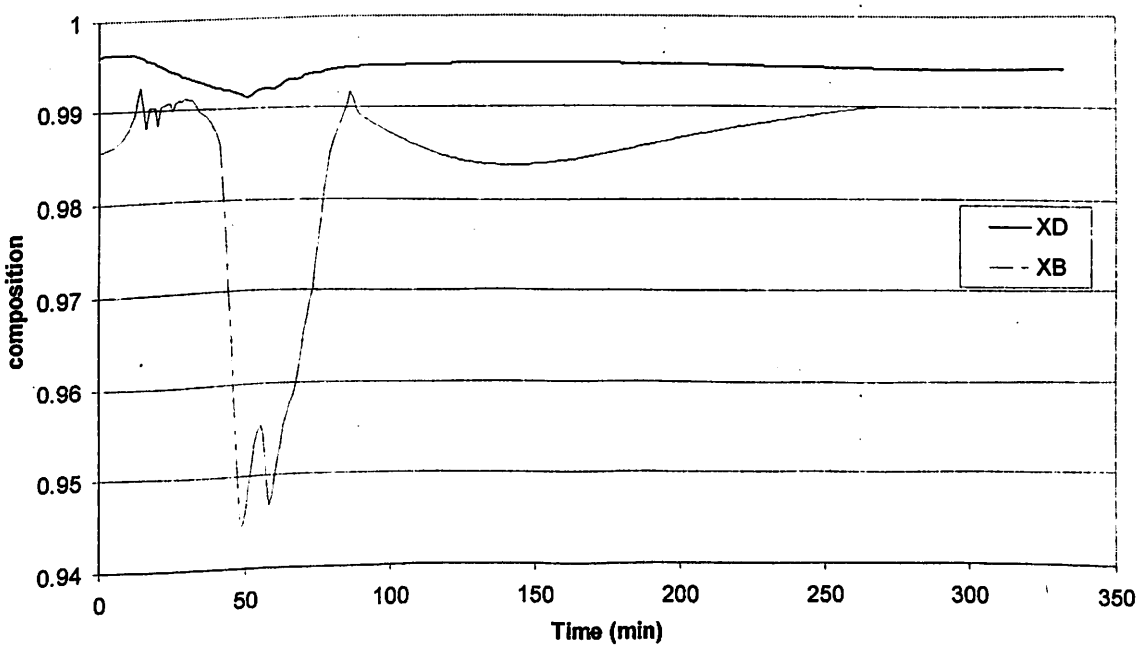
The ISE for different set point and load disturbances T28 and T11 are calculated and tabulated in Table 9.1.

Table 9.1 ISE Values

Disturbances	ISE for top loop	ISE for Bottom loop	Sum of ISE
Positive set point change in T11	80.5402	130.6587	211.1989
Negative set point change in T11	32.0817	299.5366	331.6184
Positive set point change in T28	119.9478	5.9828	125.9306
Negative set point change in T28	247.4905	8.2840	255.7745
Positive change in acetic acid flow rate	36.5574	0.94178	37.4992
Negative change in acetic acid flow rate	2.9568	2.4437	5.4006
Positive change in methanol flow rate	1.1628	0.28106	1.4439
Negative change in methanol flow rate	2.2329	0.3617	2.5946
Negative change in acetic acid feed temperature	0.8349	0.3029	1.1379
Negative change in methanol feed temperature.	0.2030	0.2451	0.4481

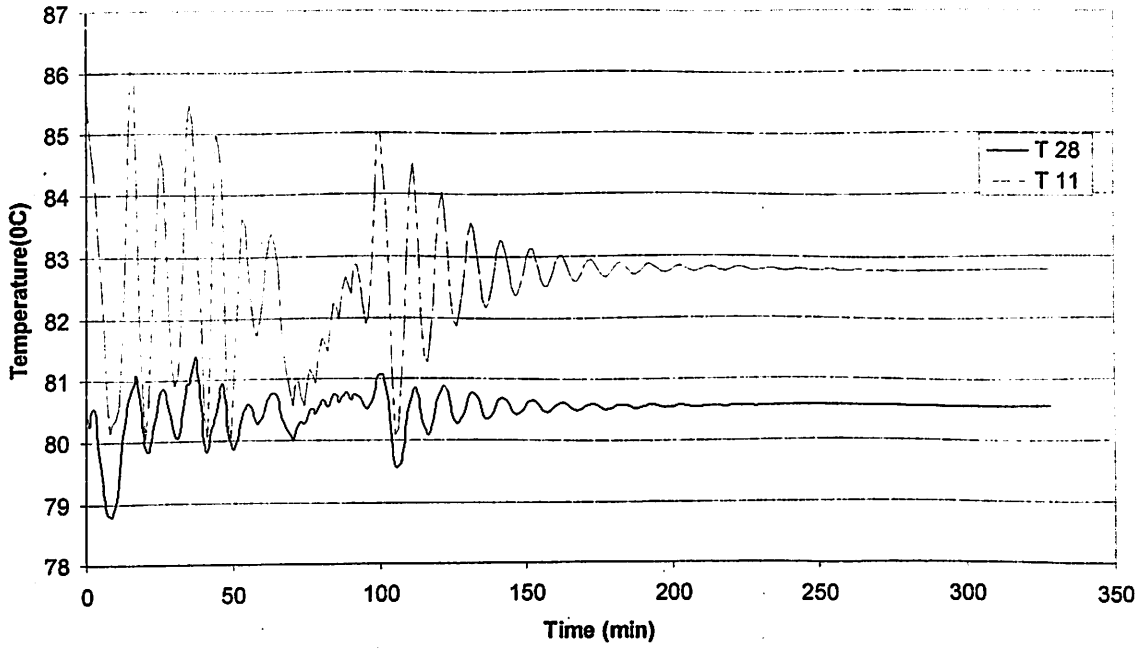


a) 11th and 28th tray temperatures

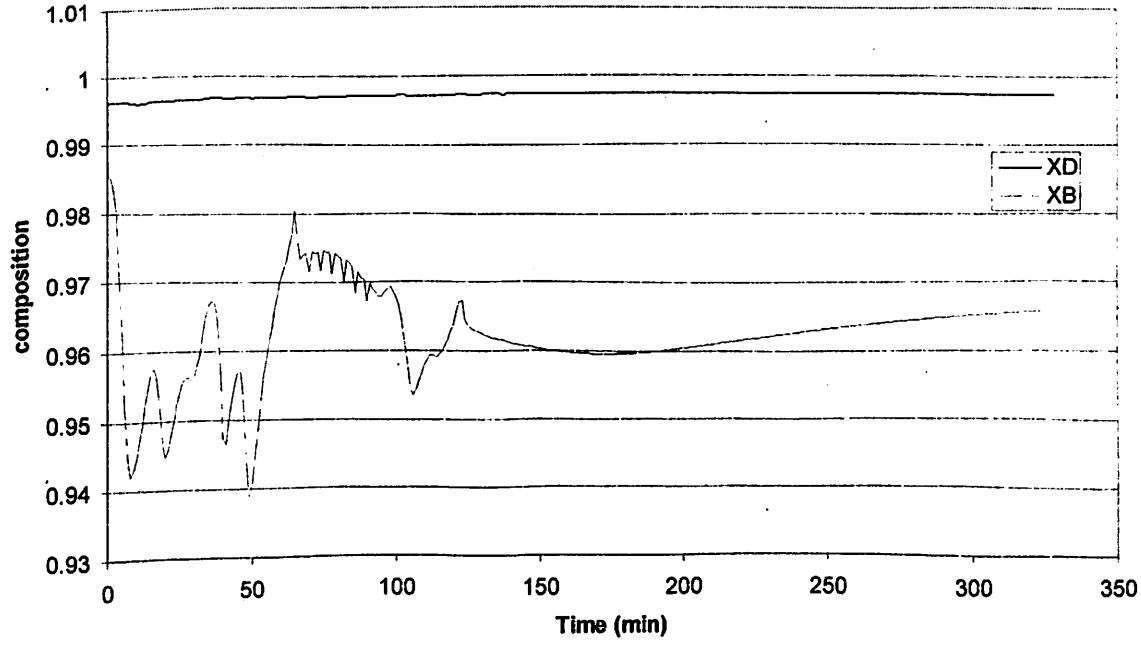


b) Distillate and bottoms composition

Fig 9.1 Response for positive set point change in 11th stage temperature

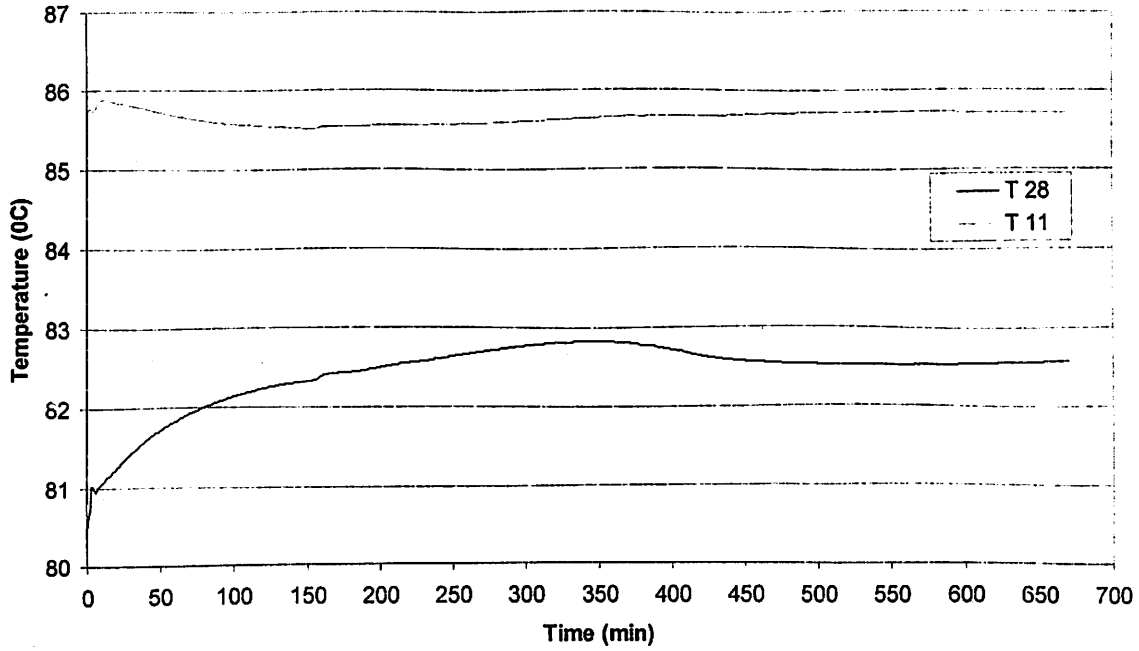


a) 11th and 28th tray temperatures

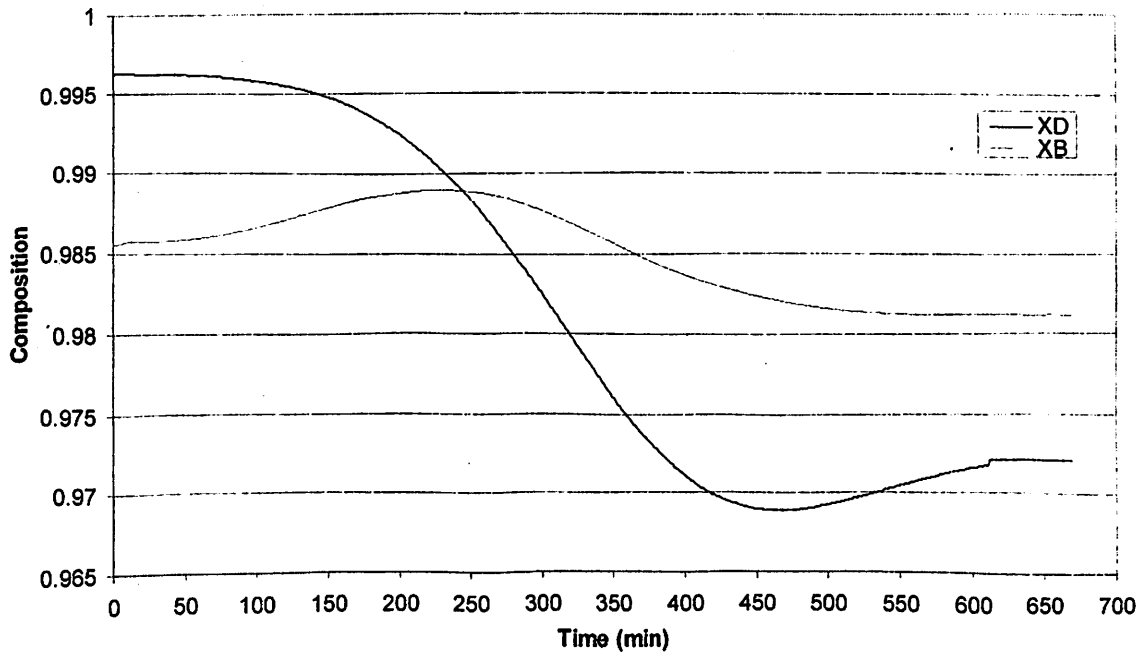


b) Distillate and bottoms composition

Fig 9.2 Response for negative set point change in 11th stage temperature

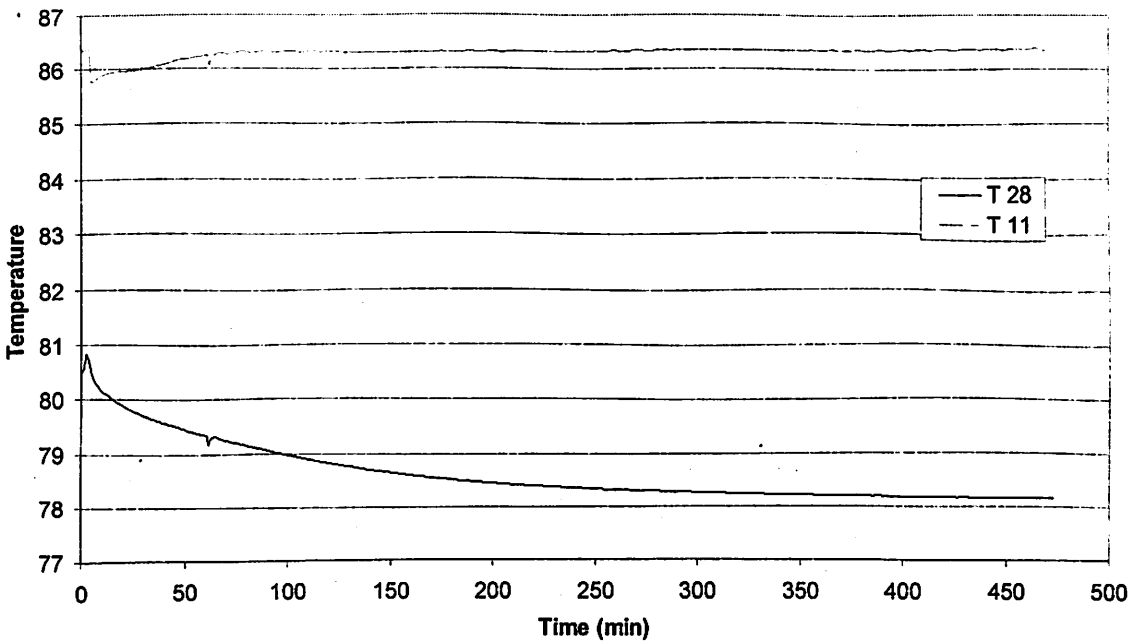


a) 11th and 28th tray temperatures

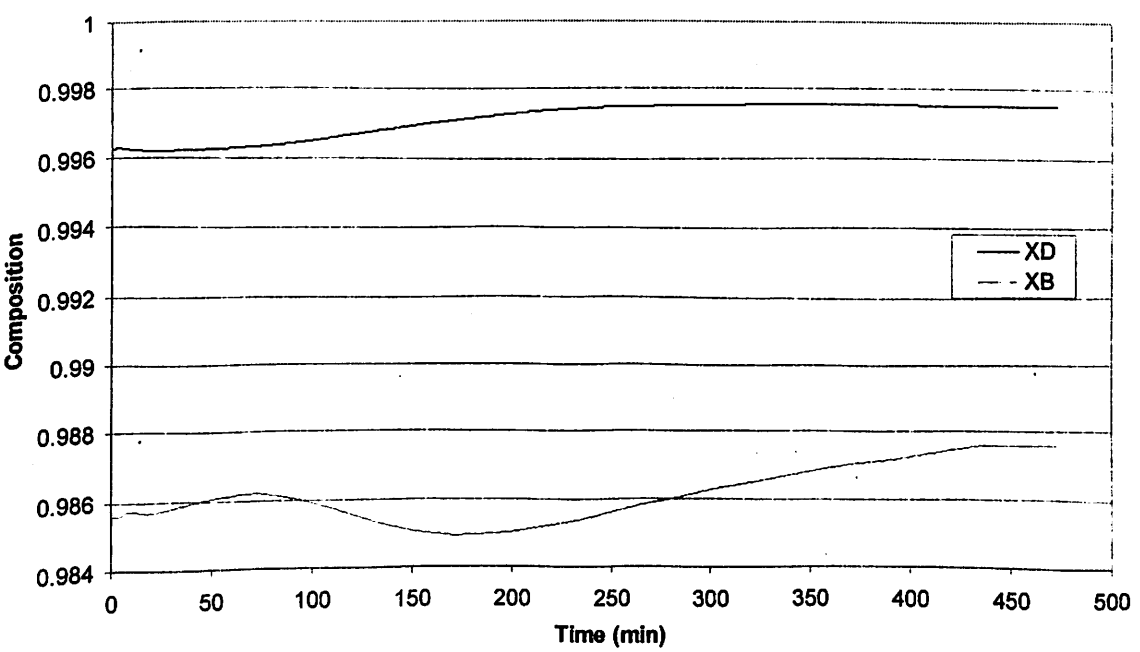


b) Distillate and bottoms composition

Fig 9.3 Response for positive set point change in 28th stage temperature

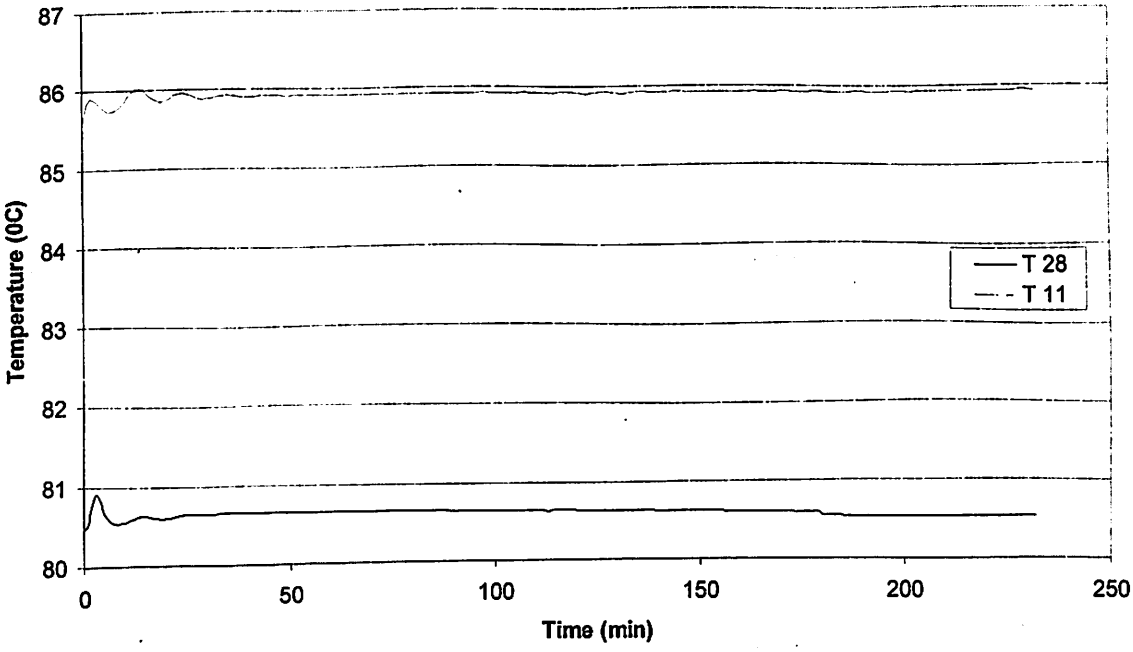


a) 11th and 28th tray temperatures

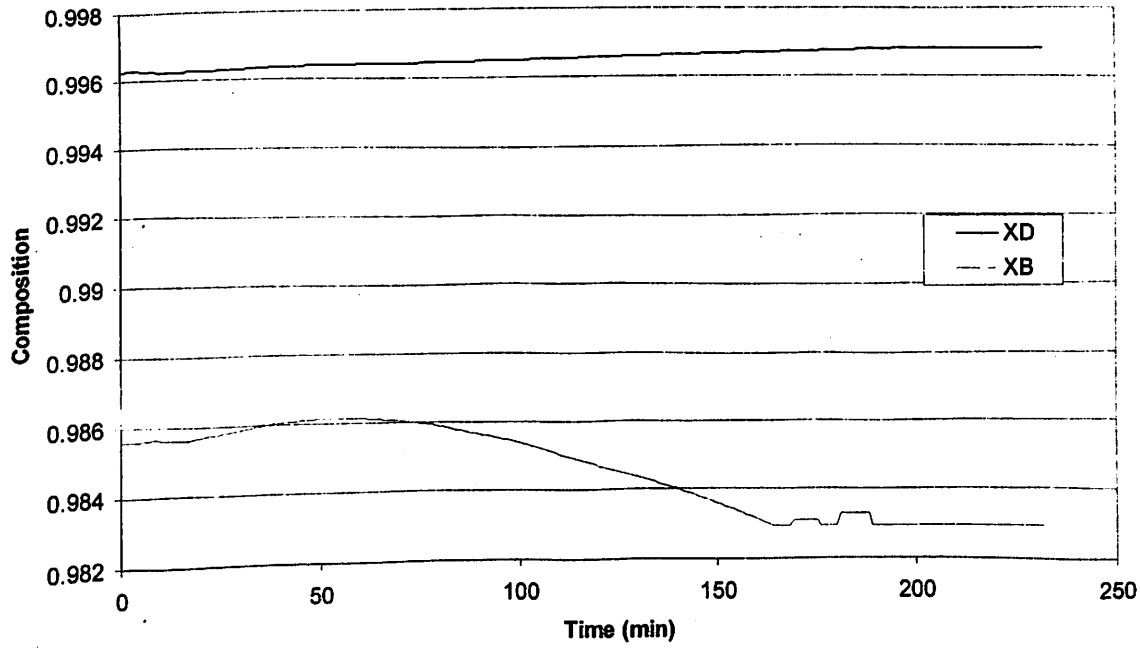


b) Distillate and bottoms composition

Fig 9.4 Response for negative set point change in 28th stage temperature

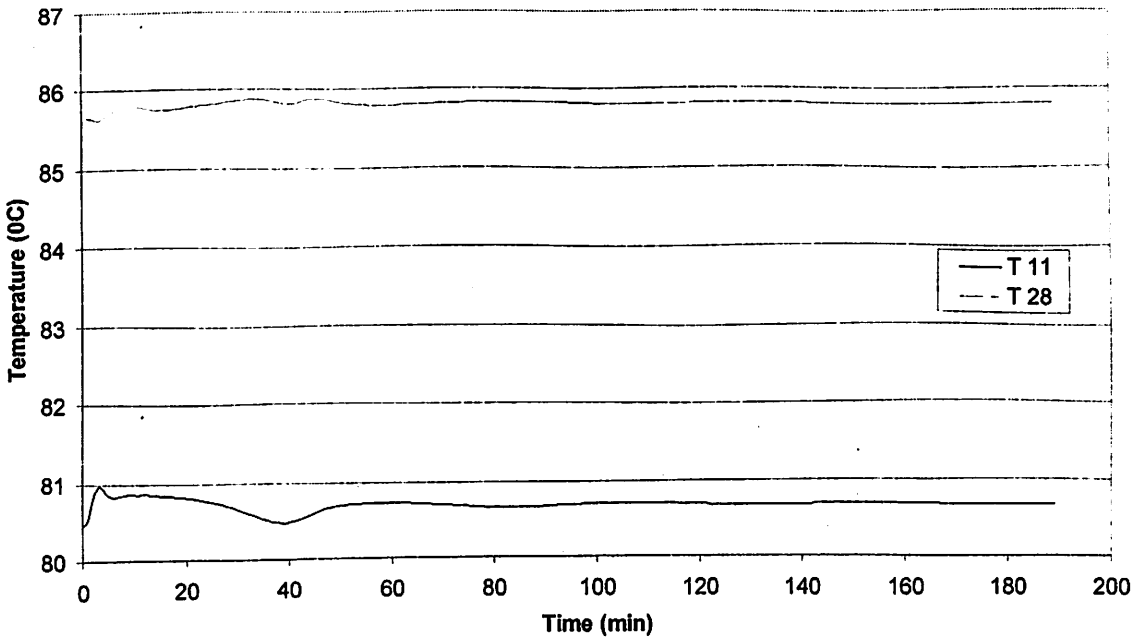


a) 11th and 28th tray temperatures

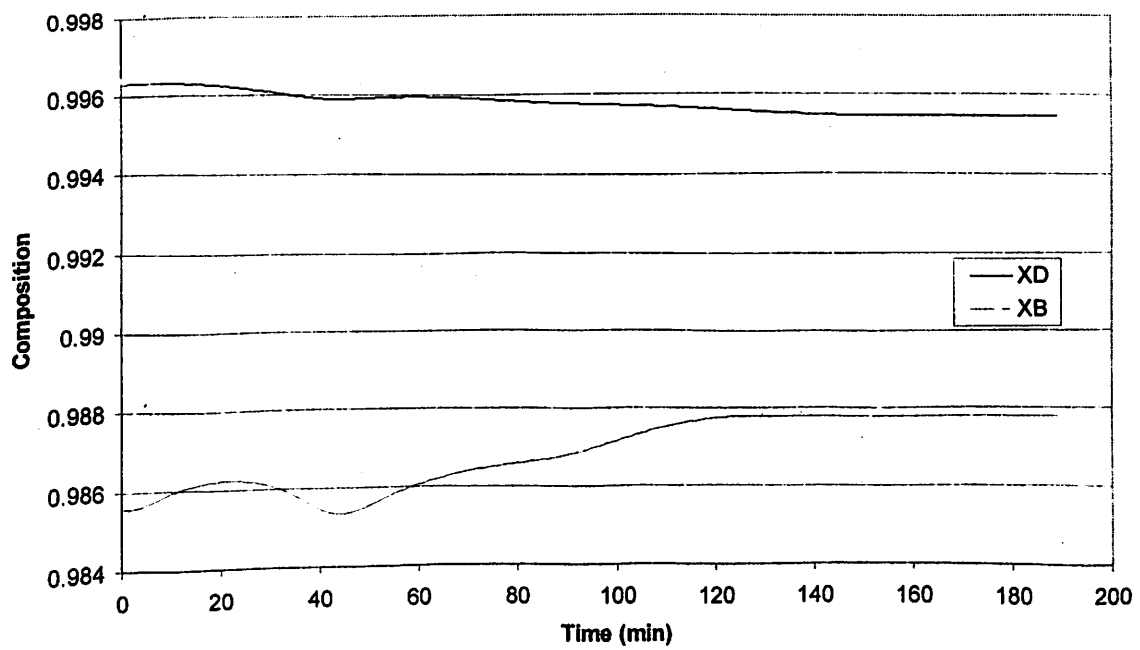


b) Distillate and bottoms composition

Fig 9.5 Response for 10% negative change in methanol feed rate

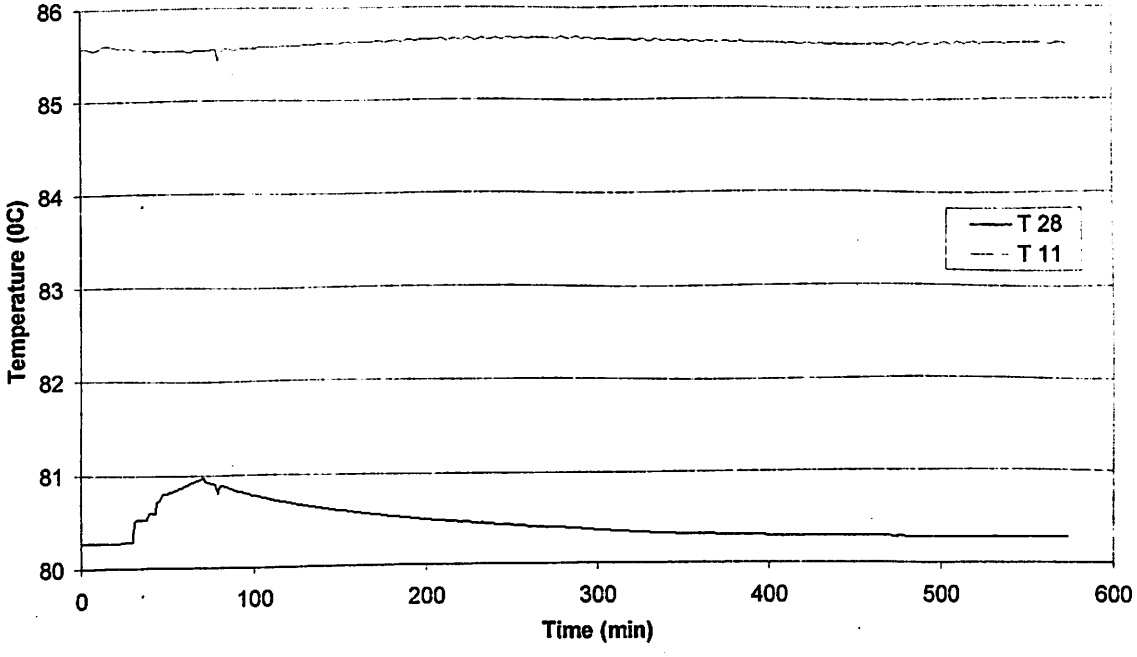


a) 11th and 28th tray temperatures

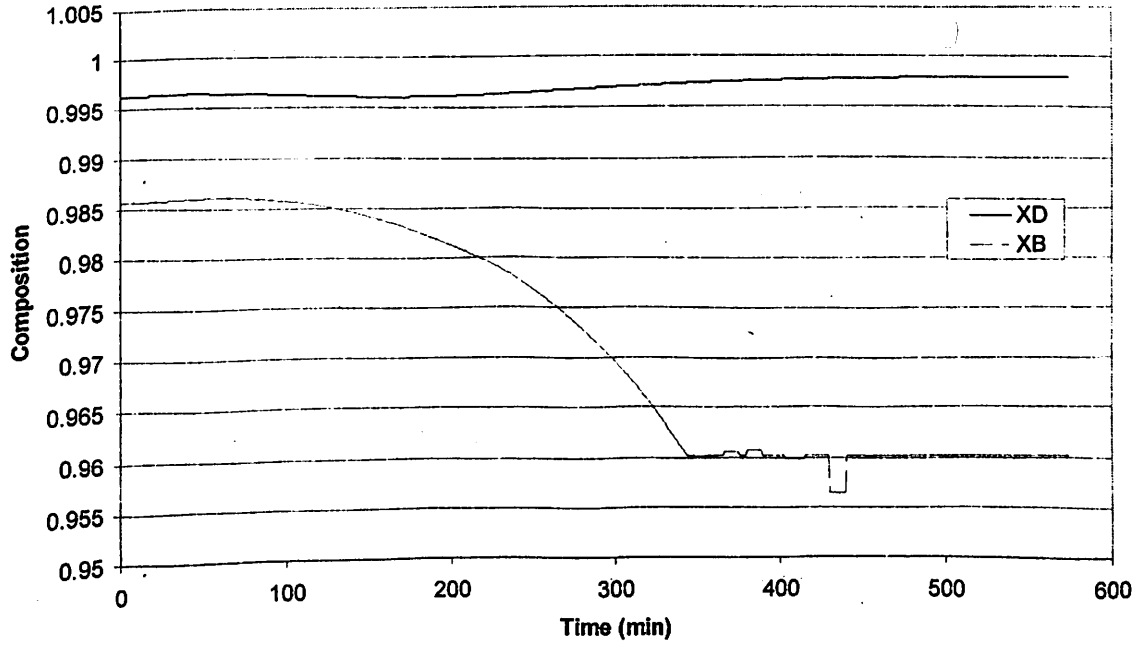


b) Distillate and bottoms composition

Fig 9.6 Response for 10% positive change in methanol feed rate

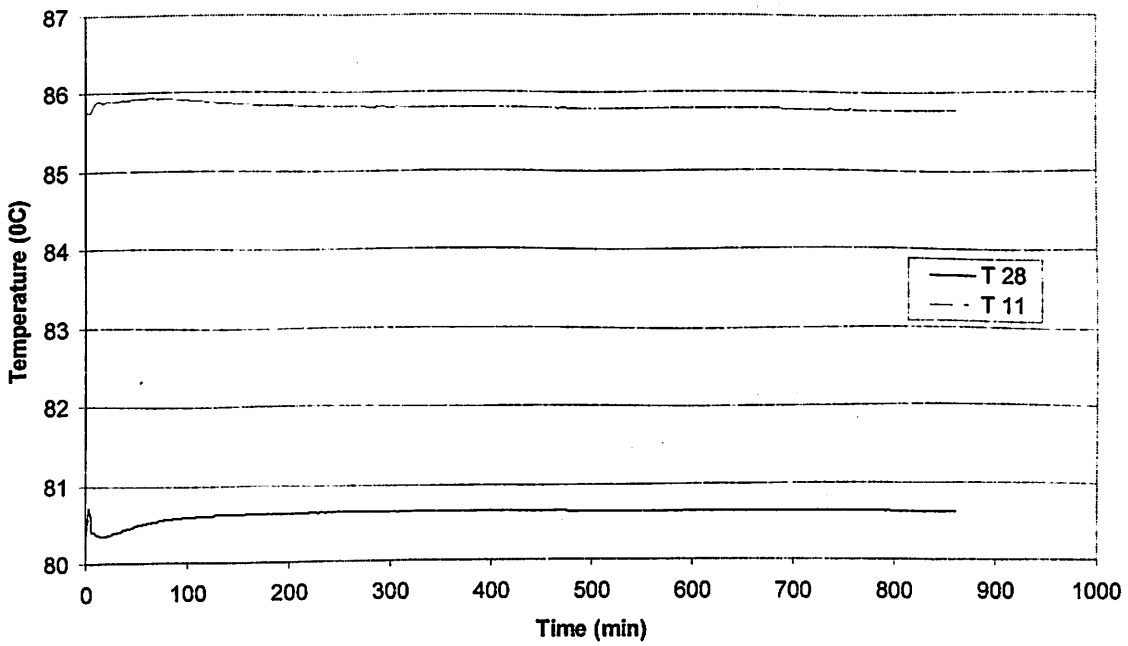


a) 11th and 28th tray temperatures

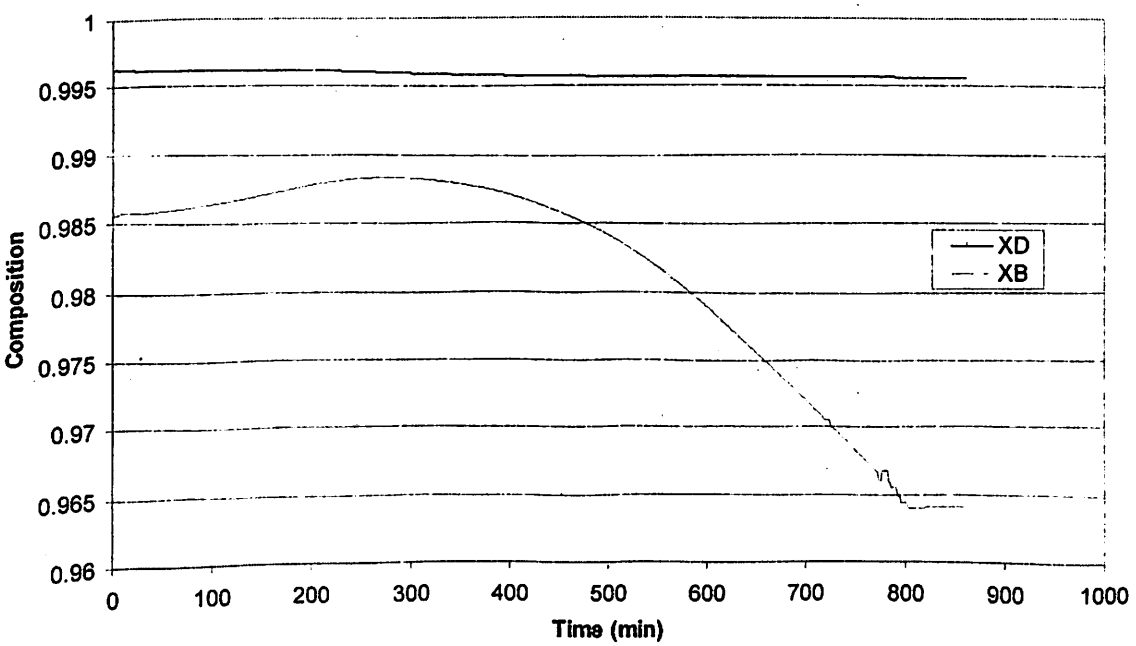


b) Distillate and bottoms composition

Fig 9.7 Response for 10% positive change in acetic acid feed rate

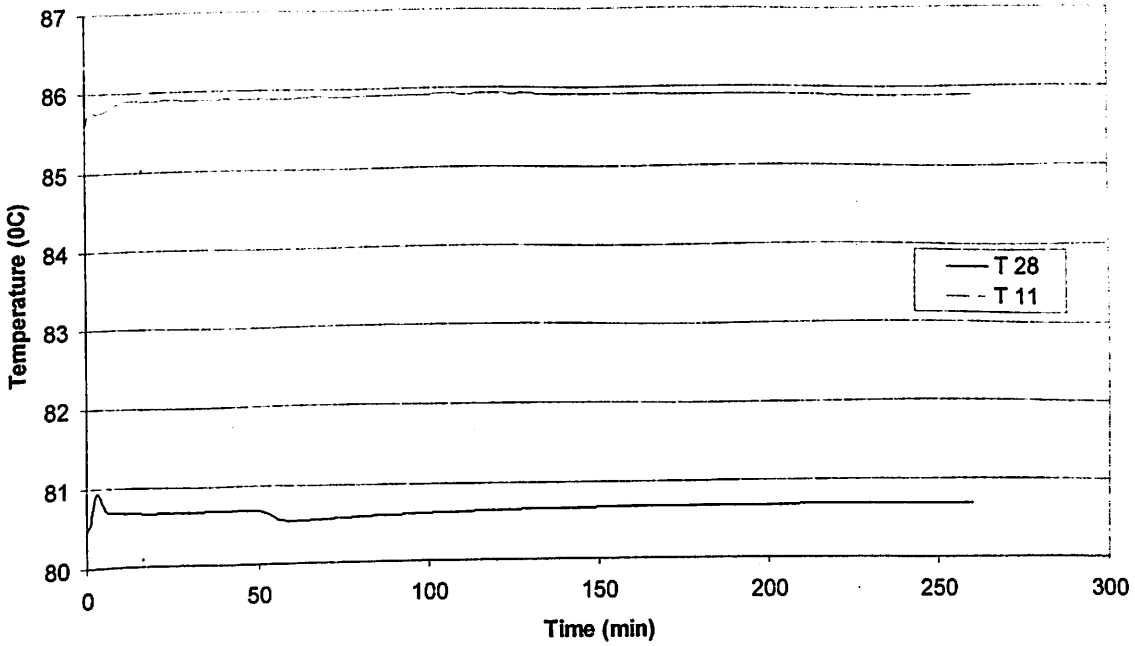


a) 11th and 28th tray temperatures

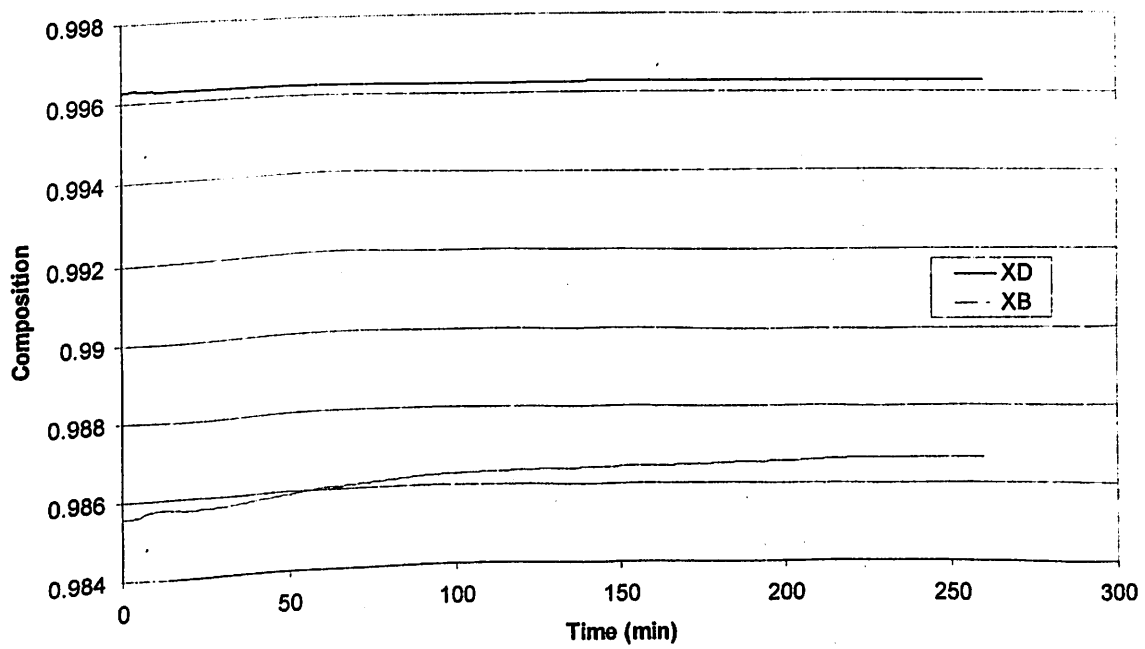


b) Distillate and bottoms composition

Fig 9.8 Response for 3.5% negative change in acetic acid feed rate

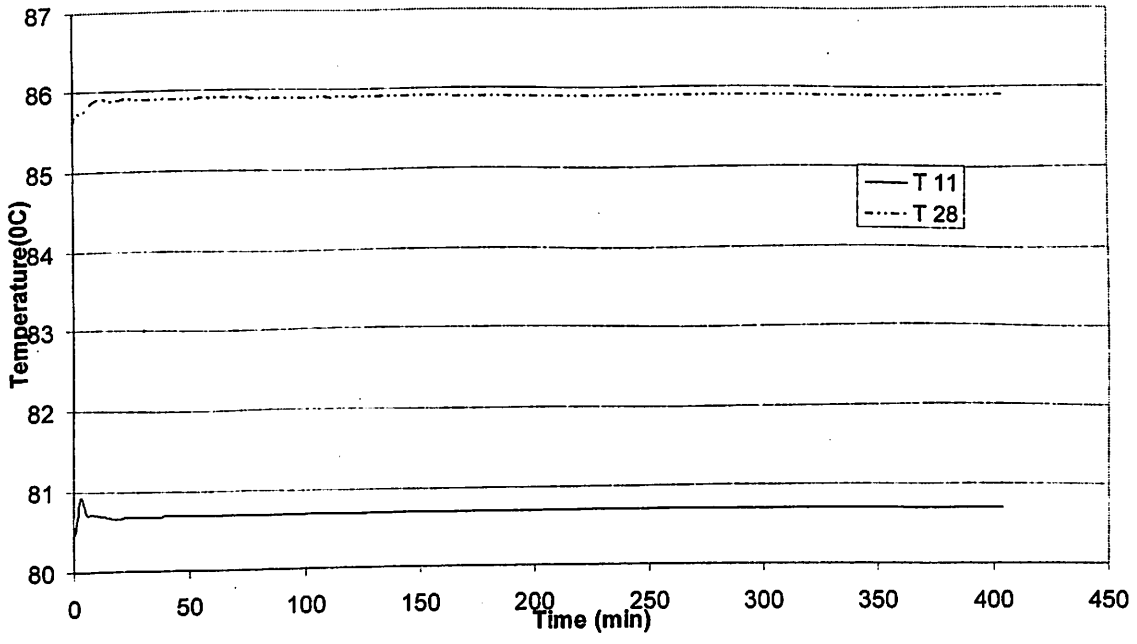


a) 11th and 28th tray temperatures

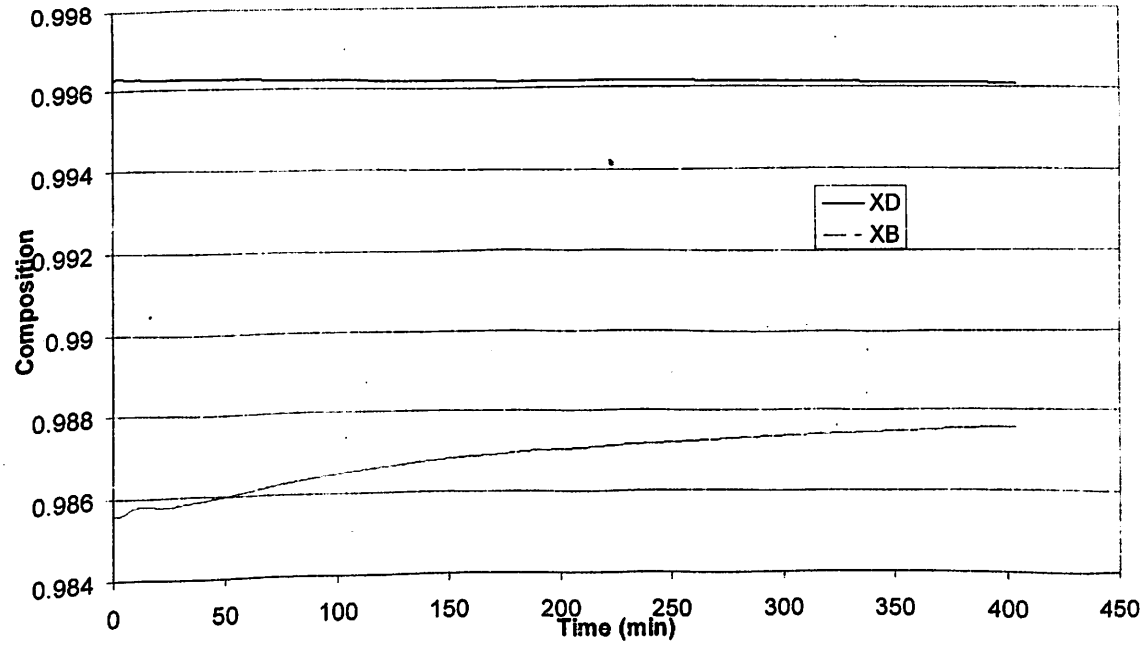


b) Distillate and bottoms composition

Fig 9.9 Response for -7^{0}C change in acetic acid feed temperature



a) 11th and 28th tray temperatures



b) Distillate and bottoms composition

Fig 9.10 Response for -7^{0}C change in methanol feed temperature

CHAPTER 10

CONCLUSION

10.1 CONCLUSION

The design and control of a methyl acetate reactive distillation column have been studied. Several steady-state multiplicities are found. The impact of these multiplicities on the open loop stabilities is discussed.

Decentralized PI controllers are chosen for its hardware and design simplicity. The responses of the controllers for various setpoint and load changes are studied and the satisfactory performance of the controllers is ensured. The column has been designed for higher-than-required purity levels.

The proposed control structure uses only temperature measurements and provides efficient control. It is observed that the stoichiometric feed ratio is necessary for neat operation of the column. Any imbalance in the inflow of the two reactants will result in a gradual buildup of the reactant that is in excess. This will lead to an unavoidable drop in product purity.

10.2 RECOMMENDATIONS

In this project work a LV control structure was configured for Methyl acetate RD column using decentralized proportional-integral (PI) controllers. The controllers used were inbuilt in HYSYS. This work can be extended by creating user defined Model Predictive Controllers (MPC) using Matlab and Visual Basic codings.

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