THEORETICAL & EXPERIMENTAL STUDIES ON A HIGH PRESSURE COLUMN FOR THE SEPARATION OF AN AZEOTROPIC MIXTURE

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of

MASTER OF TECHNOLOGY

in

CHEMICAL ENGINEERING

(With Specialization in Industrial Safety and Hazards Management)

By

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the project entitled "**Theoretical & experimental studies on a high pressure column for the separation of an azeotropic mixture** ", in partial fulfillment of the award of degree of Master of technology in Chemical Engineering with specialization in "**Industrial Safety and Hazard Management**", submitted in Department of Chemical Engineering, Indian Institute of Technology, Roorkee, is an authentic record of my own work carried out during the period from September 2006 to June 2007, under the guidance of **Prof. Dr.-Ing. Günter Wozny**, Department of Process Dynamic and Operation, Technical University, Berlin, Germany and **Dr. Nidhi Bhandari**, Department of Chemical Engineering, Indian Institute of Technology, Roorkee, India

     The matter embodied in this project work has not been submitted for the award of any other degree.

Date: 29 - Jun - 2007

Place: ROORKEE

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CERTIFICATE

This is to certify that the thesis entitled **"Theoretical & experimental studies on a high pressure column for the separation of an azeotropic mixture"** submitted by **Shivom Sharma** to the **Indian Institute of Technology, Roorkee** for the award of the degree of **Master of Technology** is a bonafide record of research work carried out by him during the academic period 2006 - 2007 under our supervision. The contents of this thesis, in full or in parts, have not been submitted to any other Institute or University for the award of any degree.

The research work was carried out at Indian Institute of Technology, Roorkee and Technical University Berlin under DAAD Student Exchange Program.

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ABSTRACT

Distillation is widely used in various chemical industries. The area of study in this work is related to the separation of azeotropic mixture. For the separation of homogeneous azeotropic mixtures pressure swing distillation columns are widely being used. But until now, only a limited number of experimentally validated studies have been published.

The study used a distillation column with total 28 trays with multiple feeding facilities at different trays. We did total 6 experiments and total number of measured variables was 150, which contains measurement of different flows, temperatures and pressures. The experimental work comprised of the investigation of feasible operating conditions of high pressure distillation column and collection of various steady states data for further investigation.

In the theoretical work, we estimated the parameters, which are generally changed from column to column or depend upon the operating condition of the column. This estimation was based upon our steady state experimental results and simulation results from a rigorous model of the column. For the estimation of parameter, we used maximum likelihood method and kept the objective function as minimization of the difference between simulated results and experimental results. The column model is based upon the mass balance, energy balance, equilibrium relations etc. for each stage of the column. We also considered the affect of uncertainty and disturbances in that estimation.

Column's Piping and Instrumentation Diagram (P & ID) and standard operation procedure of working is also discussed in detail. To found out the mixture composition with out the use of gas chromatography, a relation between mixture density and mixture composition based upon excess volume of mixing is also established.

Pressure at the top of the column was controlled by cooling water flow in the condenser For this control, a MATLAB program based upon nonlinear model predictive control was used which changed the cooling water requirement in the condenser according to column's top pressure.

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INTRODUCTION

Distillation is a process in which a liquid or vapour mixture of two or more substances is separated into its component fractions of desired purity, by the application and removal of heat. Distillation is a complete process of separation; this means that no other process is required after or before distillation to find the almost complete separation of two or more components. This process is based on the fact that the vapour of a boiling mixture will be richer in the components that have lower boiling points. Therefore, when this vapour is cooled and condensed, the condensate will contain more volatile components.

Distillation is a very important part of many modern process industries. It consumes a very high amount of energy that is why it contributes a big amount of total operating cost of the plant. Operating cost can be reduced by increasing the efficiency of the distillation process. And efficiency of column increases by improving the operation with optimization and control.

It is a process of physically separating mixture components with different boiling point. When a liquid mixture of two volatile component heated, the vapor comes off will have a higher concentration of more volatile liquid. Separation of mixture component by distillation depends upon the boiling point difference and concentrations of components in the mixture. Therefore distillation process depends upon the vapor liquid equilibrium for the mixture.

1.1 Vapor Liquid Equilibrium diagram:

Vapor liquid diagram is the state of coexistence of liquid and vapor phases. The vapor liquid equilibrium diagram for binary mixture can be present in two forms.

(i)T-XY or boiling point diagram:

Boiling point diagram is a plot between temperature and equilibrium component concentration for both phases.
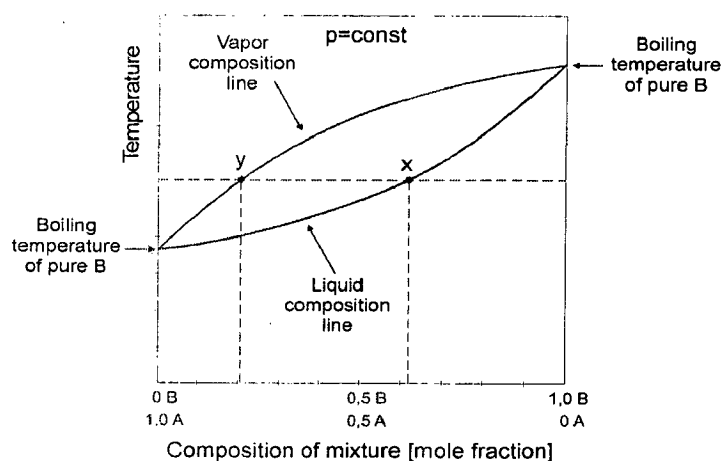
Fig 1.1 T-XY diagram for binary mixture

Where A and B are the two components of the binary mixture and boiling point of pure A is higher than the boiling point of pure B.

(ii) XY diagram:

This is plot between the concentration of component in liquid mixture and equilibrium vapor at a constant temperature.
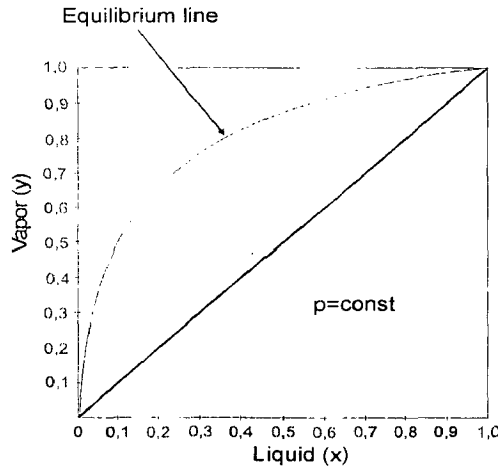
Equilibrium line

Fig 1.2 XY diagram for binary mixture

1. 2 Equilibrium ratio and relative volatility:

Equilibrium ratio is the ratio of mole fraction of component i in vapor phase to mole fraction of component i in liquid phase.

$$K_i = \frac{y_i}{x_i} \qquad\qquad [1.1]$$

The relative volatility of component i and j is defined as:

$$\alpha_{i,j} = \frac{K_i}{K_j} \qquad\qquad [1.2]$$

The relative volatility is a measure of the ease of separation. This is the ratio between the vaporization tendencies of two components. If both components have equal tendency of vaporization, then they can't be separated by distillation.

1.3 McCabe Thiele method:

This is graphical procedure for calculating step by step number of trays either in rectification or in stripping section. This method assumes that the liquid on a tray and the vapour above it are in equilibrium. Both sections have their separate operating lines. If molar flow rate of vapor and liquid in each section is same, then operating lines are straight as shown in picture.

Equation for rectification section:

$$y_{n+1} = \frac{L_n}{L_n + D}.x_n + \frac{D.x_D}{L_n + D} \qquad\qquad [1.3]$$

Equation for stripping section:

$$y_{m+1} = \frac{L_m}{L_m - B} \cdot x_m + \frac{B.x_B}{L_B + B}$$ [1.4]

Where, L_n and L_m is the molar liquid flow in rectification and stripping section.

D and B is the molar flow rate for distillate and bottom product.

x_n and x_m is the concentration in the rectification and stripping section on n^{th} and m^{th} tray.
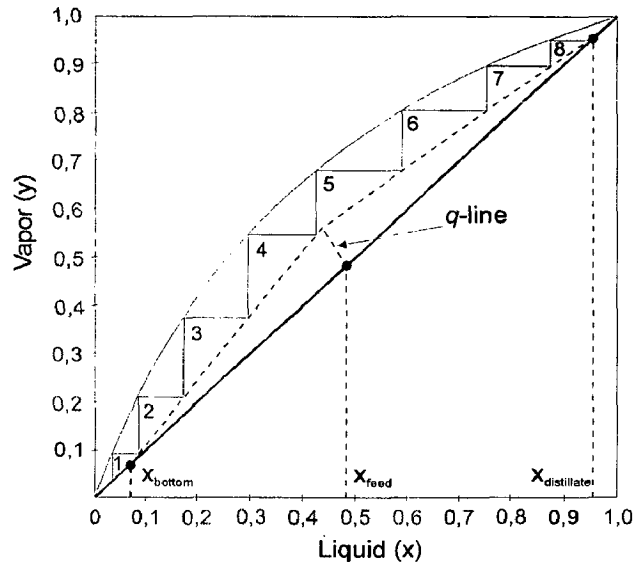
Fig 1.3 Construction of operating line for rectification and stripping section

Reflux ratio for the distillation column is the ratio between reflux flow and distillate flow.

$$R_D = \frac{L}{D}$$ [1.5]

If we insert this value of reflux ratio in the equation of rectification line, then slope and intercept for rectification line are as follows.

Slope of rectification line = $\dfrac{R_D}{R_D + D}$ [1.6]

Intercept of operating line = $\dfrac{x_D}{R + 1}$ [1.7]

At equilibrium, $L_m - B = V_m$, so slope of stripping line is the ration between liquid flow and vapor flow in the stripping section.

Feed should be entered on that tray where feed composition is closed to the tray composition. In McCabe Thiele method feed is entered to that equilibrium stage which is represented by the intersection of two operating lines. If feed composition is such that it doesn't coincide with the intersection of operating lines, this mean feed is not a saturated liquid. Slope of q line (feed line) is used to know about the condition of feed. Slope of the q line can be calculated by this formula.

$$q = \frac{L_s - L_r}{F}$$ [1.8]

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- Saturated vapor: $q = 0$
- Saturated liquid: $q = 1$
- Liquid and vapor: $0 < q < 1$
- Sub-cooled liquid: $q > 1$
- Superheated vapor: $q < 0$

Where, L_s - flow of liquid through the stripping section.

L_r - flow of liquid through the rectifying section.

F - feed flow rate

In this thesis, a rigorous model is used. This model is based on a nonlinear equation system using accurate equations for the decimal properties of the binary mixture and more detailed balances of the effect inside the column.

DISTILLATION COLUMN

A common distillation setup contains a column, a reboiler and a condenser. Performance of the process depends upon

i. Type of column, reboiler and condenser.

ii. Process parameter for whole process and sub processes.
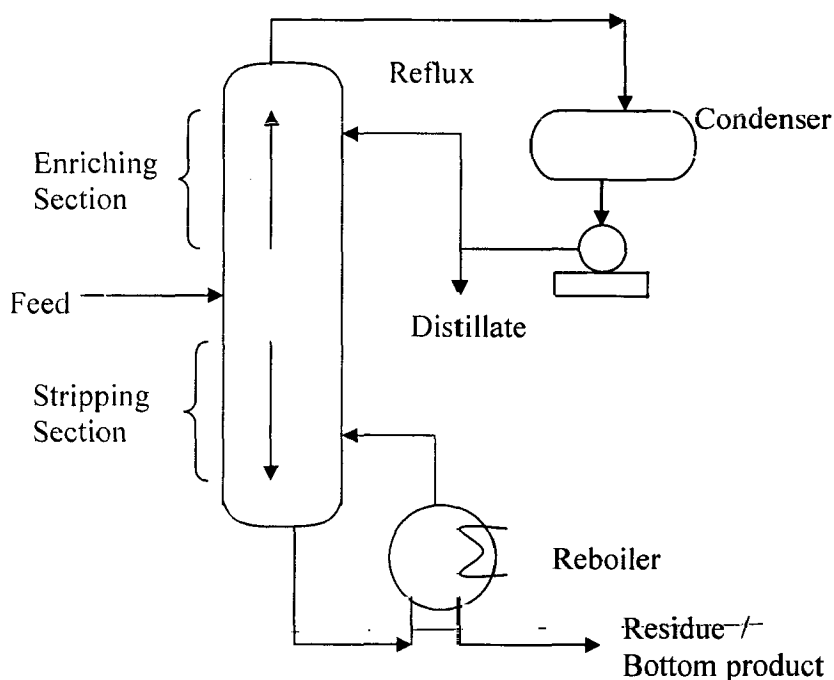
Fig. 2.1 A general diagram of a distillation process

We are using two columns in our laboratory, one is high-pressure column and other is low-pressure column. Parameters for both the column are given below:

Feature	HP column	LP column
Number of trays	28	20
Inside diameter	150 [mm]	210 [mm]
Operating pressure	Max. 5 [bar]	Atmospheric
F - Factor	0,5 - 7,82 [$(N/m^2)^{0,5}$]	0,5 - 6,2 [$(N/m^2)^{0,5}$]
Maximal temperature	150 [^oC]	150 [^oC]
Maximal heat duty	28,37 [kW]	22,76 [kW]

Table 2.1 Parameter for HP Column & LP Colum
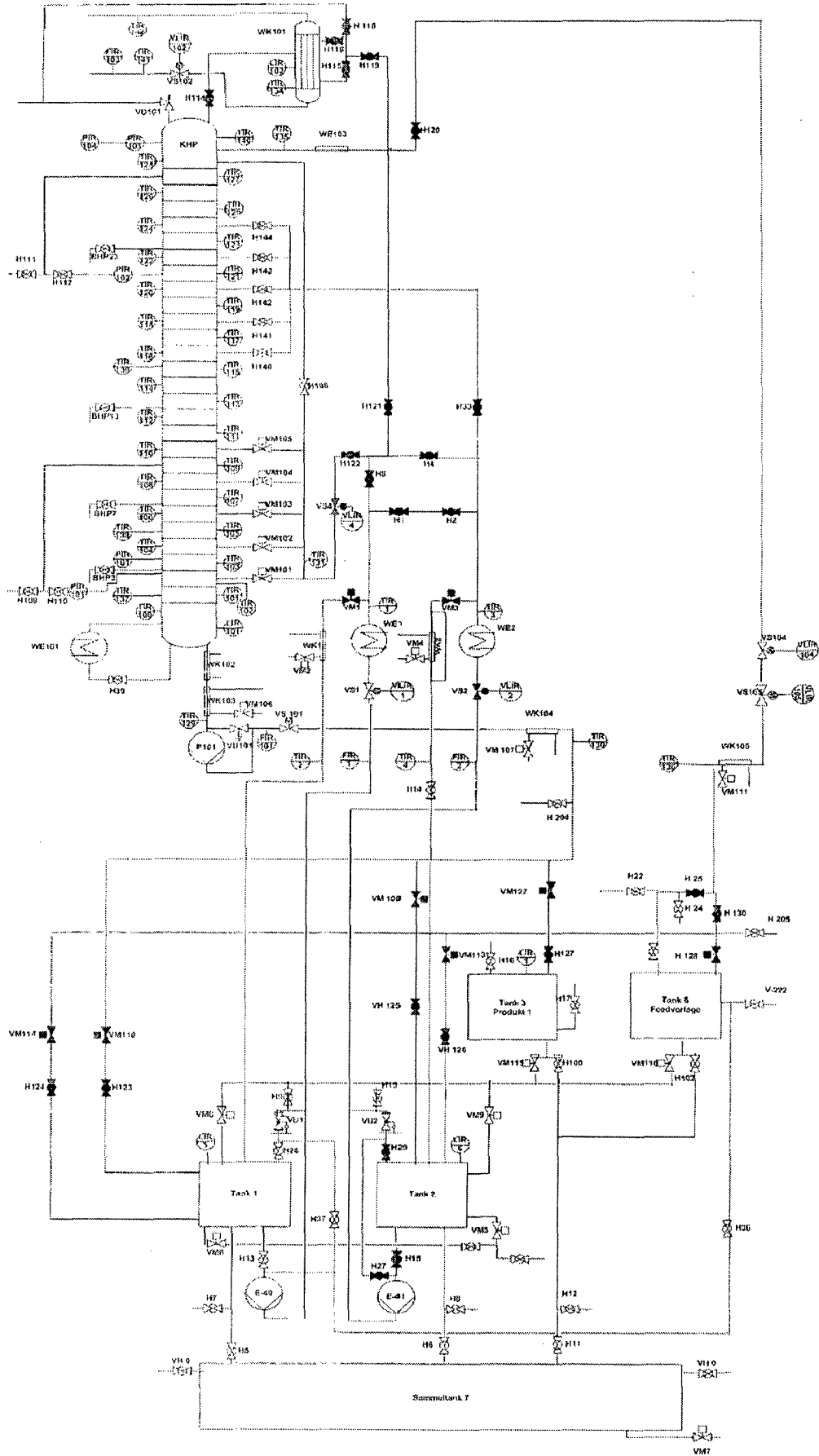
Fig. 2.2 A simple P. I. diagram for high-pressure column

Feed is entered in the column at a fixed temperature and fixed flow rate. Feed for distillation process store in a tank in the basement. A centrifugal pump is used to send feed from tank to preheater. Feed is heated in the preheater before entering to the column. After preheating, feed with a fixed flow rate enters to a plate. Generally, we try to fix all feed parameter during the operation.

As some components are very reactive with air so inerting of the whole column and condenser is necessary before starting the process.

Reboiler section is used to give the necessary energy for separation, so that it can vaporize. In the reboiler section higher boiling point liquid is present, so it is used to remove certain amount of bottom product. Level of the liquid in the reboiler is depends upon the rate of removal of bottom product.

Vapour from the top of the column, highly rich in low boiling point component. Condenser is used to remove the heat from the vapour. Rate of heat removal in the condenser depend upon the heat given in reboiler section and used in column for separation. Vapour after condensation stored in the condenser. Part of this liquid is removed as a distillate from the process and rest liquid is send to the top of the column as reflux, which helps in better separation. Level of condensed liquid in the tank depends upon the rate of removal of top product and reflux.

The whole distillation column plus units can be easily understood by dividing the above figure into **several** parts.

2.1 Condenser with top of column: (second floor)

This is the upper part of column with condenser. At the top of the column a safety valve is used to protect the column from the breakage due excess pressure generation. This valve is directly connected to atmosphere. The value of set pressure (5 bars) for this valve (VD 101) will depends upon the strength of the column.

When we want to inert our column with condenser, then valve H 115 & H 118 are open, so that inert gas can pass through the whole condenser. During normal process H 115 & H 119 are open, as now we are collecting our distillate into the tank 6 or into the feed tank (2). Finally, at the time of shut down, valve H 116 & H 118 should be open, to prevent any vacuum creation inside the column.
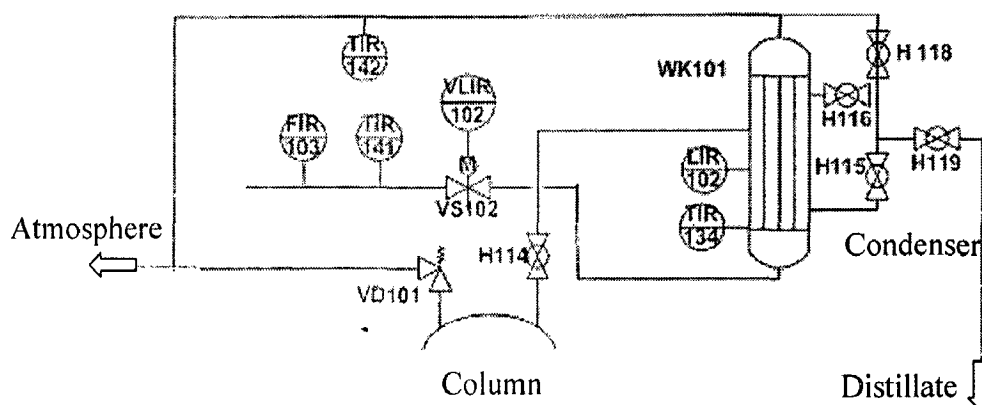
Fig. 2.3 Condenser with top of column

2.2 Condenser cooling system: (second floor):

Water is used to cool the vapour in the condenser. Inlet temperature and exit temperature of water can be easily measured (TIR 141 and TIR 142)
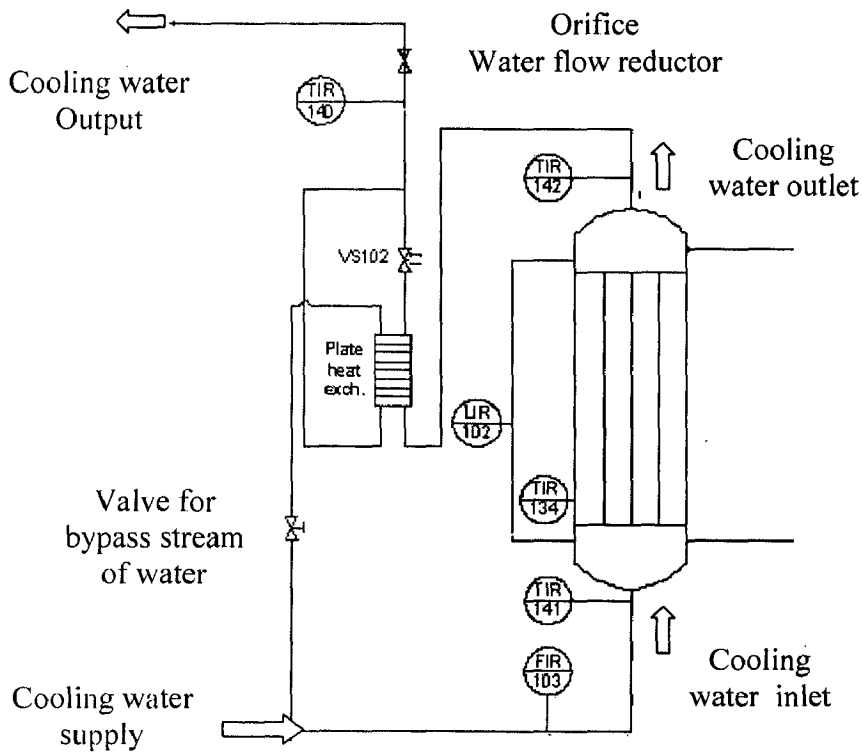
Fig 2.4 Condenser cooling system

Temperature (TIR 134) and level (LIR 102) of liquid inside the liquid can also be measured and controlled by the flow of cooling water. By pass stream of water is used to cool exit water from the condenser, below a certain temperature (T = 70 ^{0}C). A temperature indicator and orifice is also installed after the mixing of bypass stream. The orifice introduces the biggest pressure drop to the cooling water pipeline. It means that temperature of water will also drops to a safe level.

2.3 Reboiler and bottom product removal: (in basement):
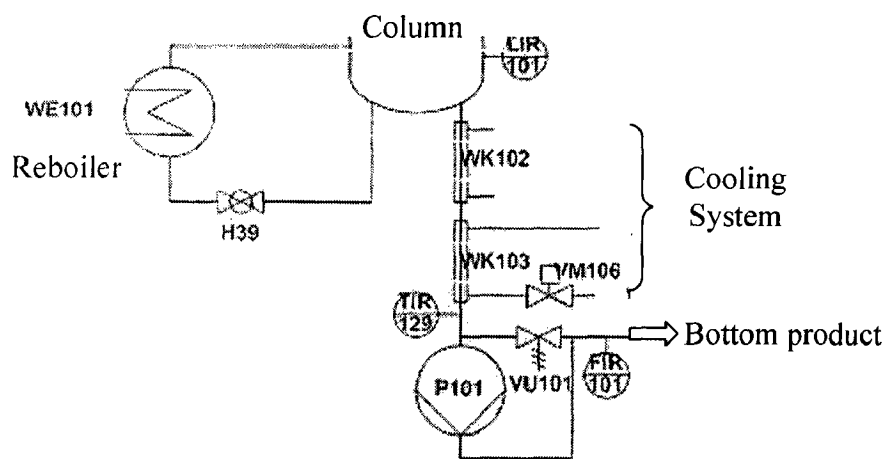
Fig 2.5 Reboiler and bottom product removal

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In the above figure, we show the reboiler section of our distillation plant. Liquid in the lower part of the column is heated by the help of an electric heater. (WE 101) A fixed percent of the bottom product is removed from the bottom of the column. Bottom product is cooled below a certain temperature before sending to bottom product storage tank to prevent any vaporization in the pipeline.

A temperature indicator is also used to check the bottom product temperature before entering to bottom product storage tank. Device for measuring level of liquid in the preheater section and bottom of the column are installed with plant.

2.4 Preheater and feed entrance into the column: (first and second floor):

In this figure, feed from storage tank comes to preheater (WE 2) through valve VS 2. After preheating, feed is send to feed plate by open and closed several valves.
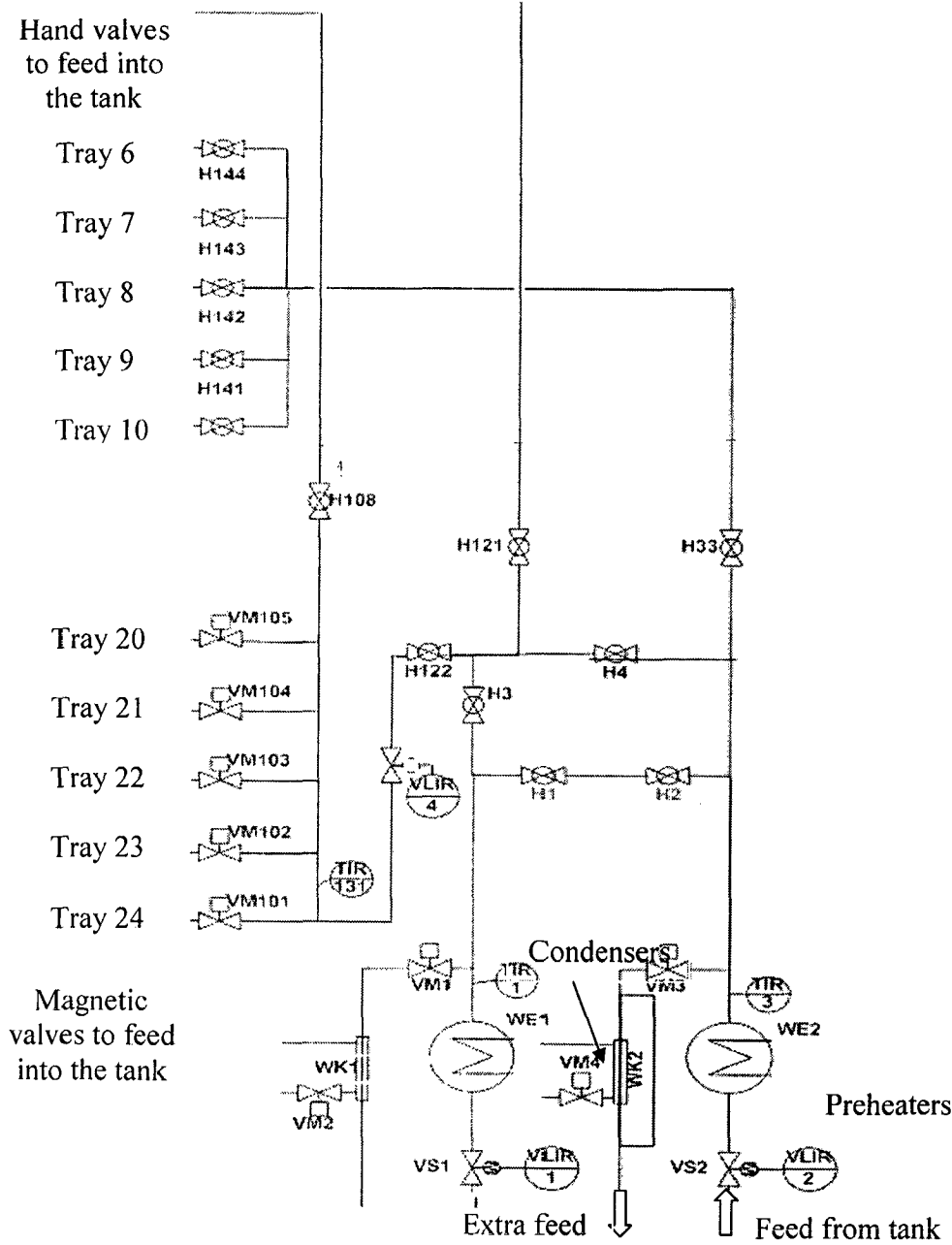
Fig 2.6 Preheater and feed entrance

2.5 Tank system with pumps:

Feed is store in tank 2. Feed sends to the preheater by a pump. (E 41) Bottom product is stored in the tank 3 and distillate stored in the tank 6. We can send our bottom product and distillate into feed tank; this can be also done directly without sending bottom product and distillate to tank 3 and tank 6.

Several other arrangements like level measurement and sample taken facility are also available with each tank. Level indicators are directly connected to the atmosphere with the help of plastic tubes. Sometimes, level indicators are not work properly as they have some restriction in their connection to the environment. Pump rotates at a constant speed and extra feed come back to the tank through valve H 29.
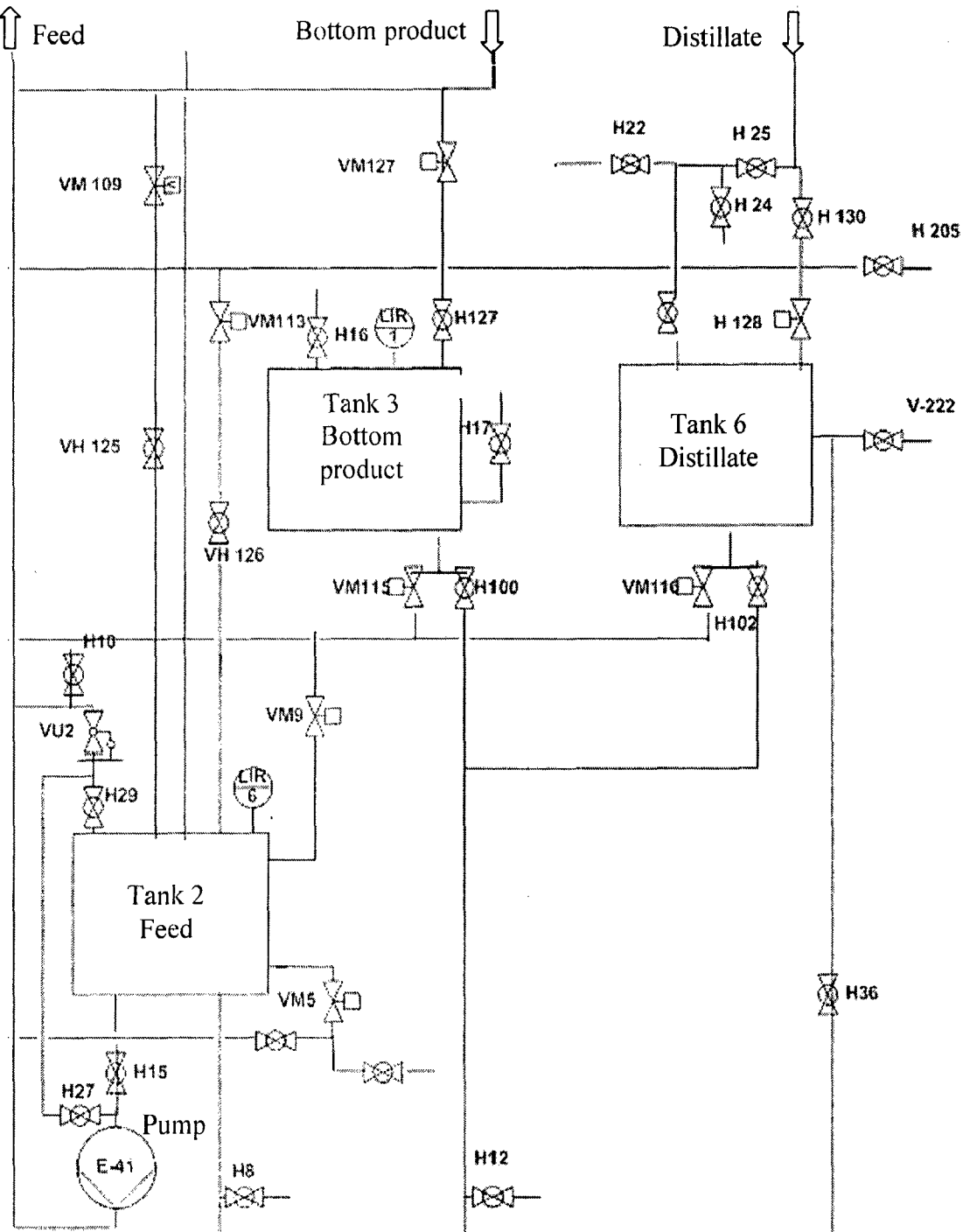
Fig 2.7 Tank system for distillation column

WORKING WITH HIGH PRESSURE DISTILLATION COLUMN

A simple systematic diagram of distillation process with its control mechanism is given below. The distillation column is a tray type column with multiple feed facilities at different tray. Column contains 28 trays and distance between two trays is 21 cm.

Tank system with pump is in the basement. Total six tanks are in the basement. Two big tanks are used for feed and four small tanks are used to collect the bottom and top product from the high pressure and low-pressure column.

Tank 1 - Feed tank with a low concentration ⎫ Not
Tank 2 – Feed tank with a high concentration ⎭ fixed
Tank 3 – Residue from high-pressure column (KHP)
Tank 4 – Distillate from low-pressure column (KLP)
Tank 5 – Residue from low-pressure column
Tank 6 - Distillate from high-pressure column

Nitrogen supply cylinder for the inertization of column is also on ground floor at some distance. Black box for pressure measurement in the upper part of column is installed at the ground floor.

Freelance 51 ABB is using to control the column. It has several features:
- Field unit processor (Analog to Digital)
- Feed flow rate controller.
- Temperature and Pressure measurement for each tray.
- Heat and level control of reboiler section
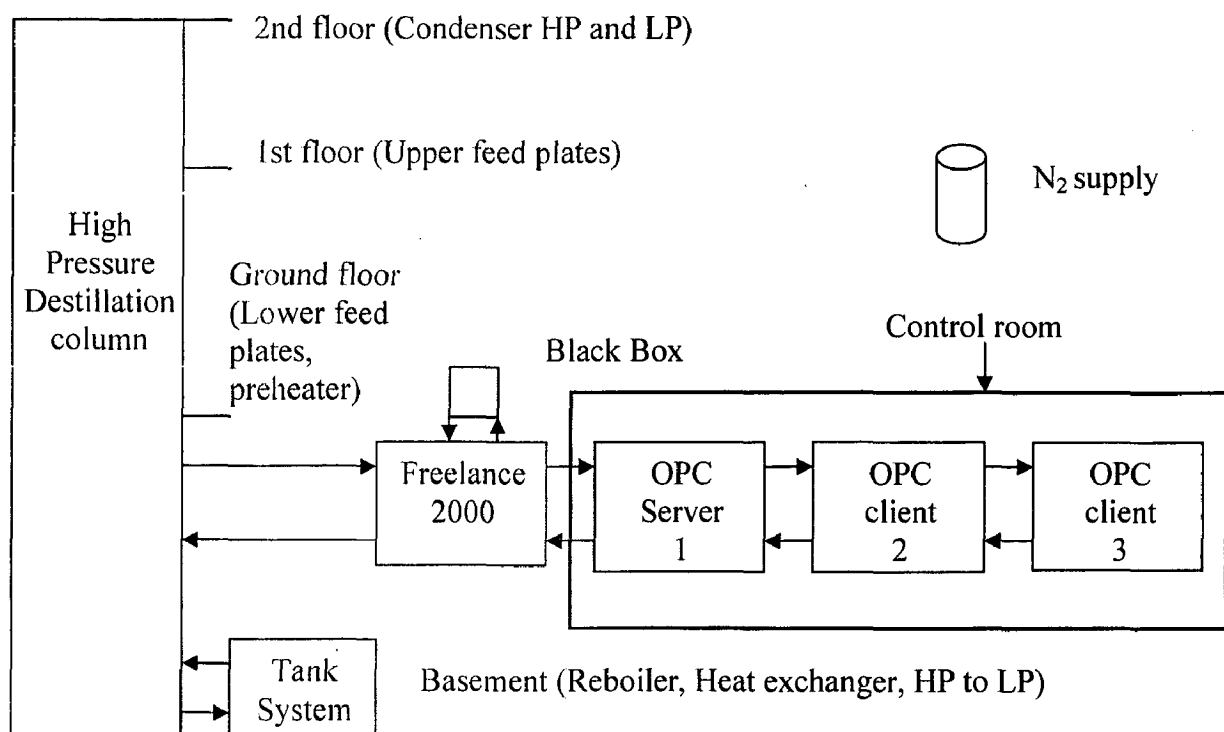
Fig. 3.1 A simple diagram of whole process

3.1 Brief description of control room:

It contains 3 computers system with different use.

Computer System 1: OPC SERVER
- DIGIVIS / Visualization of control by freelance 51.
- Sending data for simulation and optimization to other computers.

Computer System 2: OPC CLIENT
- DIGIVIS / Visualization of control by freelance 51.
- Recording process data in a excel file. (By MATLAB)

Computer System 3: OPC CLIENT
- Simulation and Optimization by the use of MATLAB.

Start all computer systems (with same user name, as OPC connection is between them, so with different user name they will not recognise)
1. Freelance 51 ABB digivis
2. F:\barz\barz\06_stefan_excel_flash\02_excel_schreiben in MATLAB
   Main _Program →Run
3. Do all actions of standard operation procedure

3.2 Start up:

- Set all magnetic or process valves
- Open two blue valve for nitrogen and closed PIR 101; To prevent any pressure difference in KLP
- Set the direction of Nitrogen flow for the distillation column, (other for membrane process), On the ground floor, just back side of the column
- Pass Nitrogen at a pressure difference 0.025 bars for 5 minute, Check that tube is connected to HP, if not change its direction
- Start excel
- Close blue valve at the ground floor (Nitrogen supply) and open PIR 101
- Start all three pumps.
- Start preheating (Set temperature = 70 ^{0}C)
- Set feed flow rate (e.g. 25 l/h)
- Set level in the reboiler section (e.g. 85 %)
- Set heating percentage in the reboiler section (e.g. 20 %)
- Set reflux ratio (e.g. 4)
- Set top pressure (e.g. 2 atmosphere); this is controlled by cooling water flow
- Set level in condenser (e.g. 25 %), this is controlled by total out flow (reflux + distillate) from the condenser
- When all Nitrogen form column is pushed out, the open the valve H 116 and close the valve 115
- Cut the column connection to atmosphere when some level in the condenser

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(Close valve 116)

3.3 Shut down:

- Stop heating in reboiler
- Reflux → 0 ; D → 100 % hand;
- Cooling water → 100 % open, hand.
- Preheating of feed off and feed flow rate → 100 % hand.
- Bottom flow rate → 100 % hand.
- When top pressure → 1.05 bars then open H 116 (Open one black valve after H116 before atmosphere)
- Put feed direct to the reflux, open H 121 & closed H 120,
- Below temperature 60 ^{0}C in reboiler, plant can be shut down.
- Switched 3 pumps off
- Cooling water off in the basement
- Closed the bottle on the basement
- All sample valve are closed
- Save excel data.
- Switch off energy and light.

(i) High boiling point azeotropic mixture: They have boiling point more than the boiling point of any mixture component. They show a positive deviation from the Raoult's law because they always have vapour pressure more the vapor pressure of ideal mixture.

(ii) Low boiling point azeotropic mixture: They have boiling point less than the boiling point of any mixture component. They show a negative deviation from the Raoult's law because they always have vapour pressure less the vapor pressure of ideal mixture.

Acetonitrile make low boiling point azeotropic mixture with water.

4.3 Pressure's influence on azeotropic mixture:

For a binary mixture, relative volatility is the ratio of their equilibrium ratio.

$$\alpha_{AB} = \frac{y_A/x_A}{y_B/x_B}$$ [4.1]

If $p_A^0(T)$ and $p_B^0(T)$ is the vapor pressure of pure components A and B at temperature T and p(T) is the total pressure of mixture at same temperature T. Then

$$y_i = \frac{p_i^0(T)}{p(T)}$$ [4.2]

As concentration of component in liquid phase is not vary with temperature so relative volatility for a mixture can also be written in this form.

$$\alpha_{AB} \propto \frac{p_A^0(T)}{p_B^0(T)}$$ [4.3]

If we increase the pressure of the mixture then boiling point for components will also increase, but change in the partial pressure for component A is more than the change in the partial pressure for component B for this increase in the temperature. So relative volatility will be decrease with increase in the pressure.
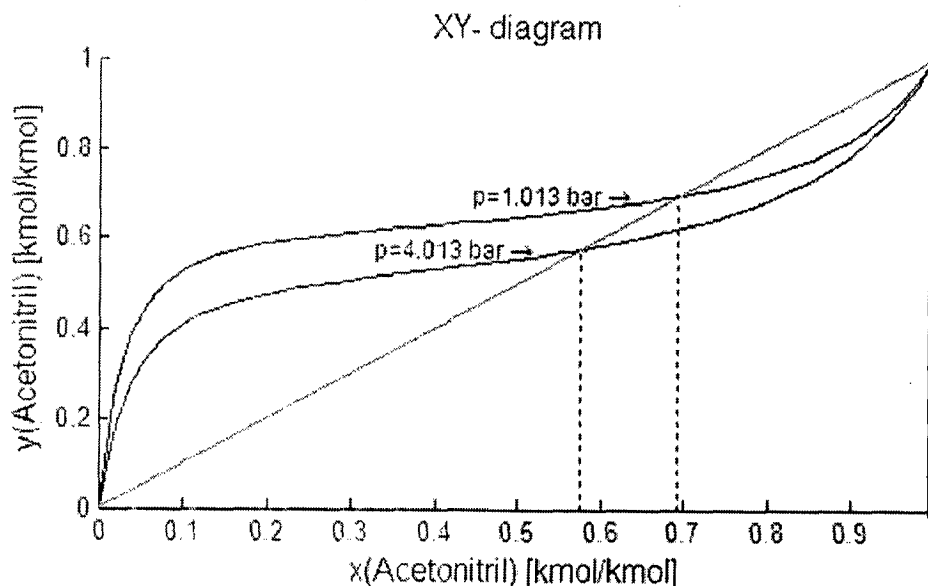
Fig 4.2 XY diagram for water & acetonitrile mixture

Pressure also affects the vapor liquid equilibrium for the separation mixtures. Azeotropic point is shifted with change in the pressure. Separation of azeotropic mixture at different pressure can be used to pass the azeotropic concentration.

XY diagram for acetonitrile and water mixture is given in the above figure. We can see that azeotropic concentration is different at different pressure.

Azeotropic concentration at 1 atm. = 0.68
Azeotropic concentration at 4 atm. = 0.58

Separation at 4 bars is also safety limit of our column system. If we want to separate a mixture with a concentration below than their azeotropic concentration, then first we should separate it in low-pressure column just below the azeotropic concentration. After that we can separate it in a high-pressure distillation column because now we have a mixture, which has concentration more than azeotropic concentration at higher pressure.

4.4 Literature review:

The separation of homogenous and heterogeneous azeotropic mixtures is a common task in the chemical industry. For homogenous azeotropic distillation, the pressure swing distillation is often used as an alternative to the widely used processes azeotropic distillation and extractive distillation, while heterogeneous azeotropic column are widely used to separate the mixture of close relative volatility and breaking of azetropes. But until now, only very few experimentally validated knowledge of this process has been published, which seems to be the reason for its rare application in the industry.

Stanislaw et. al. (2000) shows graphical representation of azeotropes, residue curves and distillation boundaries, which provides about the entire composition space. They used these representations in the optimal design of complex azeotropic distillation columns. Ulas and diwekar (2006) deal with the uncertainties with in data and with efficient sampling techniques. Barz et. al. shows that the controller performance based on the minimum variance control can be regarded as a random input, and thus is also included in the chance-constrained formulation of the model-based stochastic optimization problem.

A novel approach to the design of a model predictive control (MPC) algorithm for a complex plant is given by Fissore et. al. (2006). Sensitivity analysis and steady-state optimization are used to determine the manipulated variables that have the strongest influence on the objective function of the operation. This allows a reduction of the number of variables that are optimized on-line, as well as the use of detailed, first-principle– based models in the MPC algorithm, thus resulting in more reliable predictions.

Generally, measured variables are controlled by a closed loop mechanism while unmeasured variables are controlled by open loop mechanism. In his work, Barz et. al. give a new concept of control, to control open-loop processes by closed-loop control. Unlike the definition where controls are decision variables, in the proposed closed framework the set-points of the measurable outputs are defined as decision variables.

In his work, Forner mention that the main advantages of this process are the saving of energy and that there are no additional substances (entrainers) needed, but it is very complex

and difficult to handle. The dynamic behaviour of the coupled pressure swing system is marked by a highly non-linear and asymmetric performance, which leads to difficulties in the controlling. The disturbance performance of the system is analyzed by simulating a feed disturbance which sets the feed concentration on the other side of the azeotropic point. In his work Larson shows that overall control of the plant require structural decision like selection of manipulated and measured variables and overall decomposition of problem.

In his work, piotr give the conclusion about the restriction of the cooling water flow rate in the plant effects in implementation of the higher operating conditions to the process. According him sensitive cooling water flow can change the behaviour of the high pressure distillation column, shortens the start-up phases for steady operation, allowed to reach long lasting and robust steady states and also provides the possibility of stable operation of the column at a constant pressure.

Azeotropic mixtures show a shift in the azeotropic concentration as pressure changes. Figure 4.2 shows the shift in azeotropic concentration for pressure 1 bar and 4 bars. Pressure swing distillation is based on operating the two columns between different ranges of concentration, so distillate concentrations should be at their set points for the transition between the regions below and above the azeotrope. But until now, only very few experimentally validated knowledge of this process has been published, which seems to be the reason for its rare application in the industry. And according to Perry (1965) the manner in which azeotrope composition is influenced by pressure will vary, depending upon the slopes of the vapor-pressure curves of the individual components of the mixture.

Pressure is a parameter which has a very strong influence on distillation processes in columns as well as on the construction of columns. Considering the operating pressure of a distillation column is necessary from the very beginning of its design phase. According to Hengstebeck, (1963) operational pressure of a particular column effects on the cost of the column, the cost of heat-exchange equipment and heat requirements. In the effectively control column pressure published by The Distillation Group, Inc, (The American Institute of Chemical Engineers), they mention that constant pressure inside the column can play an important and crucial role in the stable operation of distillation column. In this report they also show the common methods of pressure control like direct control of vapor production rate and control recycle vapor rate of compressor etc.

Concentration measurement by gas chromatography is always a very time consuming process. But it can be closely estimated if we know the specific density of mixture and some relation for its conversion into mixture composition. Meurs and Somsen (1993) derived a relation between the excess volume of mixing for water & acetonitrile mixture and mixture of composition.

S.NO.	PAPER AUTHOR & TITLE	MAIN METHODOLOGY	ADVANTAGE	LIMITATION	APPLICATION
1	Ashley, M. J. et al. (1970) The calculation of plate efficiency under conditions of finite mixing in both phases in multi-plate columns, and the potential advantage of parallel flow	Mixed-pool and mixed-cell approaches and dynamic response of a series of n perfectly-mixed pools to an instantaneous injection of tracer material	Obtaining of mixed pools over a tray and establish a relationship between tray efficiency and point efficiency	Only parallel flows were considered in the estimation	In the estimation of trays efficiencies
2	Fileti, A. M. F. et al. (1997) Adaptive and predictive control strategies for batch distillation: Development and experimental testing	Adaptive and non-linear model predictive control	Distillation column more efficient and easy to operate and the process control more accurate.	Need knowledge of neural network	Uses as a methodologies of control in distillation column
3	Chien, I. L. et al. (2000) Experimental investigation of conventional control strategies for a heterogeneous azeotropic distillation column	An inverse double loop control strategy is recommended	Steady state process analysis showed that the optimal operation point should be located at a critical reflux,	The steady state is extremely sensitive to feed disturbances.	Sieve plate distillation column & Investigation of the conventional control strategies

			System less	Control system design
4	**Fileti, A. M. F. et. al. (2000)** Control strategies analysis for a batch distillation column with experimental testing	A programmable adaptive controller (PAC), a self-tuning regulator (STR) and a non-linear model predictive control (MPC).	The developed control systems made the conventional batch distillation column more efficient and easy to operate	System less sensitive to poor initial guesses	Control system design when products of constant purity
5	**Rao, D. P. et.al. (2001)** A direct method for incorporation of tray-efficiency matrix in simulation of multi-component separation processes	Naphtali–Sandholm method	Direct use of tray-efficiency matrix in simulation	Divergence may encounter	The tray-efficiency matrix for well-mixed, dispersed and plug flow of liquid has been obtained
6	**G. Wozny et. al. (2002)** Simulation and experimental analysis of operational failure in a distillation column	Dynamic model based on mass balance, energy balance and equilibrium relations	Effect of different kind of disturbances can be systematically characterized	Pressure is used as a state variable	In safety and potential hazard analysis of columns
7	**Noeres, C. et. al. (2004)** Model-based design, control and optimization of catalytic distillation processes	Dynamic rate based models of different complexity and size with linear controller	Description of process behavior accurately & offline and online optimization and control, reduced order and simplified models	Linear controllers are not able to drive the process in arbitrary regions of operation	Hydrodynamic effects as liquid holdup, liquid back-mixing and pressure drop as well as reaction kinetics

8	**Terelak, K. et. al. (2005)** Pilot plant formaldehyde distillation: experiments and modeling	In this experimental studies Both the overall feed composition and the fluid dynamic loads were varied systematically	The distillation process model is able to describe the experimental data accurately.	Column operated at total reflux in batch mode	The experimental data were successfully modeled with a stage based physico-chemical model for thermal separations
9	**Cheng, Y. C. et al (2005)** Effects of feed tray locations to the design of reactive distillation and its implication to control	Ideal reactive distillation systems	Substantial energy can be saved by feed rearrangement	Combined effect of process parameter is not given	A control structure is proposed to rearrange the feeds as the disturbance comes into the system
10	**Rigs, G. B. et. al. (2006)** Nonlinear model predictive control of a reactive distillation column	Nonlinear model predictive control with orthogonal collocation	Comparison of overhead and bottoms composition control performance	Disturbance terms should remain constant over the prediction	The effect of process /model mismatch on the performance of the NLMPC controller

DILUTION OF MIXTURE

5.1 Determination of concentration:

To calculate the concentration of acetonitrile, it requires a standard plot between mole fraction of acetonitrile and density of mixture. We find density data for various concentrations by two methods.

i. Gas chromatography

ii. Density data from literature

(i) Gas chromatography:

Gas chromatography is calibrated to take a reading at a temperature 25 ^{0}C. So we try to take our reading close to 25 ^{0}C, however correction factor is available to correct the reading at other temperature.

Coefficient of volumetric expansion = 2.5* 10^{-4}

Correct density = (1 - coefficient of volumetric expansion$\times$(T - T$_0$))$\times$Density by GC $\qquad$ [5.1]

Where; T = Measurement temperature

$\qquad$ T$_0$ = Reference temperature (25 ^{0}C)

We mixed water and acetonitrile in various combination of concentration. Concentration of water and acetonitrile is taken in mole fraction.

$\qquad$ Concentration of acetonitrile = X1

$\qquad$ Concentration of water, X2 = 1   X1

Then we find density for all these combination of concentration by gas chromatography and correct these values of density by using equation [4.1].

Con. of acetonitrile [mol/mol]	Con. of water [mol/mol]	Temperature [^{0}C]	Volume of sample [ml]	Density by G. C. [mg/ml]	Correct density [mg/ml]
0	1.0	25.07	500	998	996.735
0.1	0.9	25.05	470	965	963.782
0.2	0.8	25.01	490	924	922.843
0.3	0.7	25.00	430	-	-
0.4	0.6	25.00	440	866	864.918
0.5	0.5	25.00	450	-	-
0.6	0.4	25.01	455	-	-
0.7	0.3	25.00	470	811	809.984
0.8	0.2	25.00	475	797	796.004
0.9	0.1	25.00	480	786	785.018
1.0	0.0	25.01	485	776	·775.030

Table 5.1 Data from Gas chromatography

Density of pure water at 25 ^{0}C = 997.04
Density of pure acetonitrile at 25 ^{0}C = 779

(ii) Data from literature:

Moreau C. and Douheret G. [Thermodynamic behaviour of water acetonitrile mixture, Excess volume and viscosity] give value of density for different combination of water and acetonitrile concentration. These data at four different temperatures are given the table 2. Below curves between mixture density and acetonitrile molar concentration obtain by gas chromatography (corrected) and literature data are compared at a temperature 25 ^{0}C.

Plot between mixture density and acetonitrile conc.
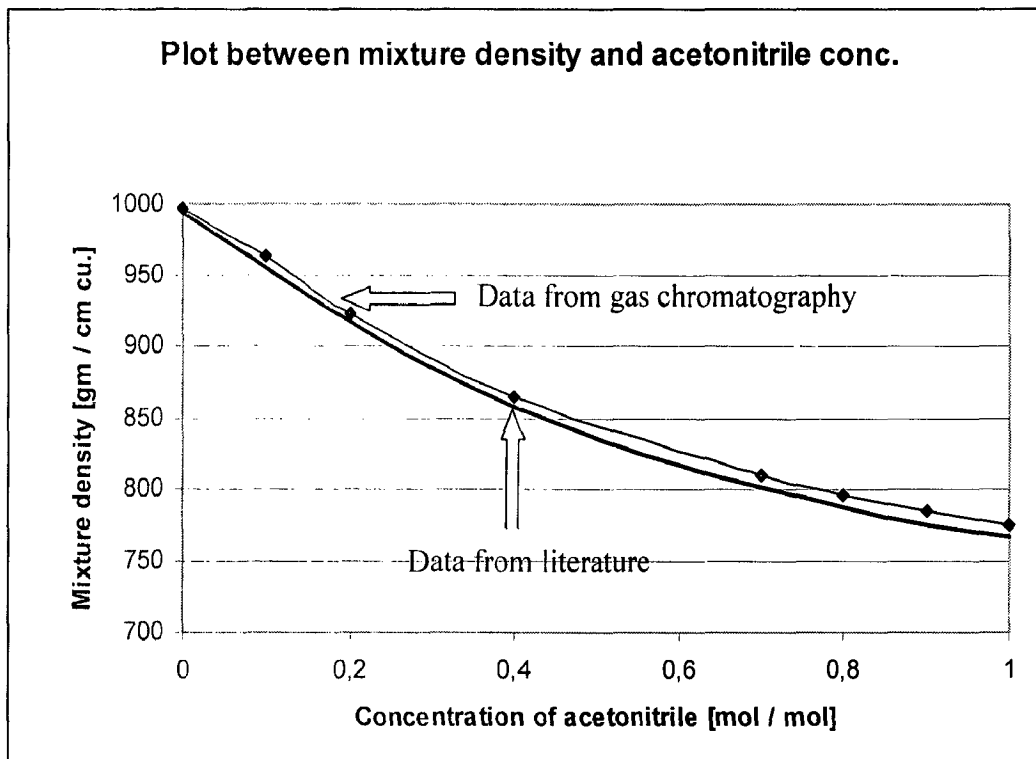
Fig 5.1 Mixture density vs acetonitrile concentration

From the above plot, we can say that variation in mixture density is not linear with change in molar concentration. As both plot are very close to each other, this mean that our density measurement from gas chromatography is correct. Concentration for any value of density can be determined by using reference plot at that temperature.

5.2 Variation in the density of water and acetonitrile mixture:

Below data from above table at four different temperatures is plotted. From the plot, it is clear that value of density is vary with temperature and also nonlinear with change in concentration.

(i) Variation due to temperature change:

As temperature of a liquid is increased, its density decreases due to volumetric thermal expansion. The value of volumetric expansion coefficient is different for different liquids. This value generally depends upon the intermolecular bond strength between liquid molecules.
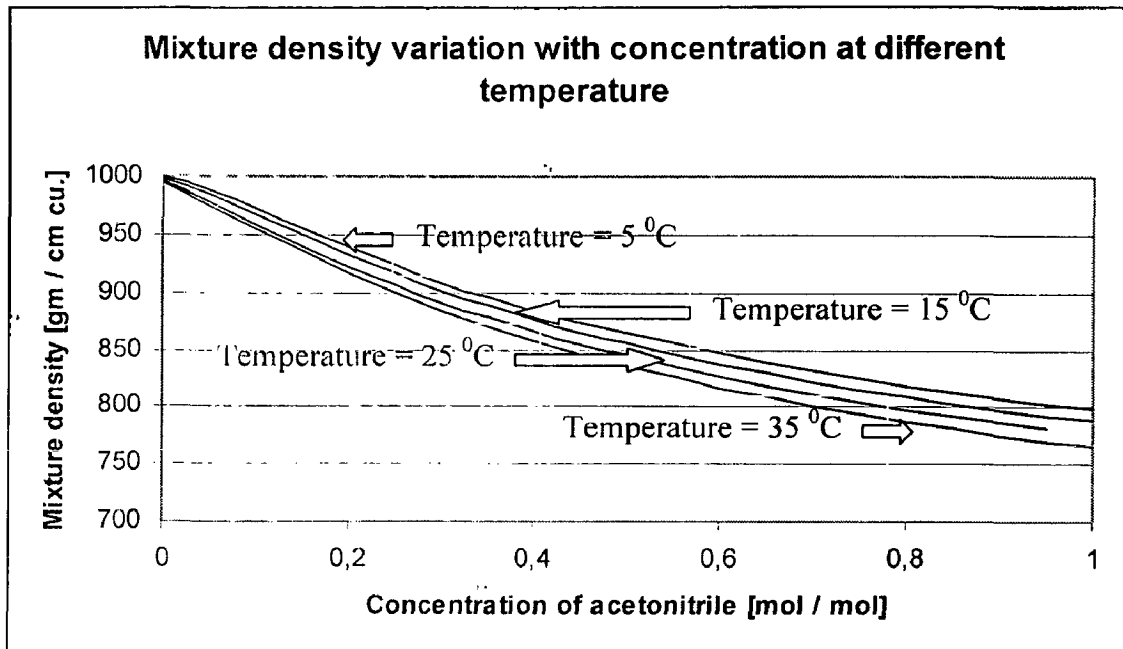
Fig 5.2 Effect of temperature on mixture density

In the above figure, variation in the density of pure water (x = 0) with temperature is less than the variation in the density of pure acetonitrile (x = 1). This is due to that both water and acetonitrile has different coefficient of thermal expansion.

(ii) Nonlinear behaviour of curve:

In the above plot, each line is showing variation in the density with molar conc. of acetonitrile at different temperature. This variation is nonlinear with molar fraction, while for mass fraction this is linear as shown in the plot below.
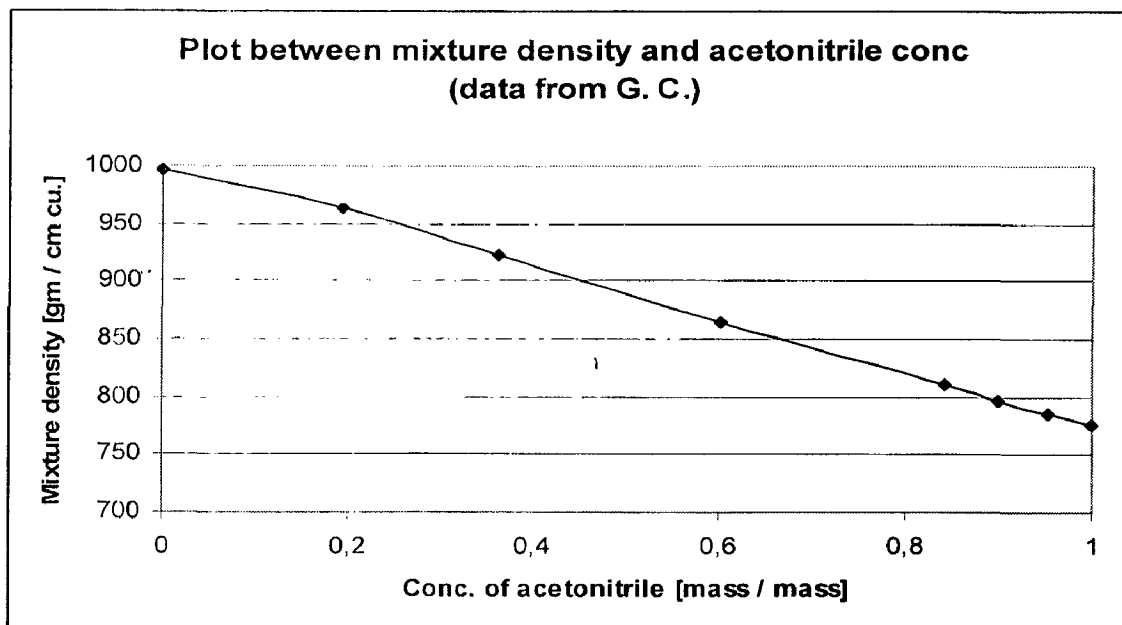
Fig 5.3 Nonlinear variation of mixture density with acetonitrile concentration

The behaviour of the binary mixtures can be explained by the occupation of the free volumes or cavities of water network, by the molecules of acetonitrile. It is still difficult to

attribute the magnitude of cavity volume and the asymmetry of the volume contractions to structural effects rather than to specific interactions between unlike molecules.

Consequently, such evidences support previous assumptions about the existence of three interaction regions in water-acetonitrile mixtures. It is now possible to propose some structural description of these mixed solvents.

i. In the water-rich region ($0 < X < 0.2$), the voids of the aqueous structure are progressively filled by the organic molecules, without enhancement of this structure. Methyl and cyanide groups are not easily engaged in hydrogen bonding processes. However, the geometry of the acetonitrile molecules cannot fit exactly to the aqueous network; it is likely that, independent of the number of available voids, the network will break beyond a given percentage in organic solvent.

ii. In an intermediate region ($0.15 - 0.2 < x < 0.75 - 0.80$), a progressive break of the precedent structure occurs. This range of concentration will be called "micro heterogeneity region". The size of the remaining aggregates is reduced. It is to emphasize that this range is characterized by extreme near $0.3 - 0.4$ corresponding to excess volumes, enthalpic and entropic salvation parameters, ultrasonic absorption extreme and inflection points of viscosity functions.

iii. The third region ($x = 0.7 - 0.8$ to 1) can be compared to some extent with the water-rich region, since we can consider that the initial structure of organic solvent is progressively disturbed by the addition of water molecules, as demonstrated by a sharp maximum of viscosity excess functions and dielectric properties.

5.3 Mixture density calculation:

(i) Use of property function:

We can use this property function directly at different temperatures. Density of water and acetonitrile can be calculated by using the following formula.

Acetonitrile density: $\quad \rho_1(T) = 1000 . \rho_{L\_B_1} \dfrac{1 + \left(1 + \dfrac{T}{\rho_{L\_C_1}}\right)^{\rho_{L\_D_1}}}{M_{Ac} . 1000 . \rho_{L\_A_1}}$ [5.2]

Water density: $\quad \rho_2(T) = \dfrac{\rho_{L\_C_2} + \rho_{L\_B_2} . T + \rho_{L\_A_2} . T^2}{M_{H_2O} . 1000}$ [5.3]

Density of mixture: $\quad \rho(T) = \dfrac{1}{m_{x1} . \rho_1(T) + (1 - m_{x1}) . \rho_2(T)}$ [5.4]

Here, density of mixture is calculated by assuming a linear relationship for mixing of water and acetonitrile.
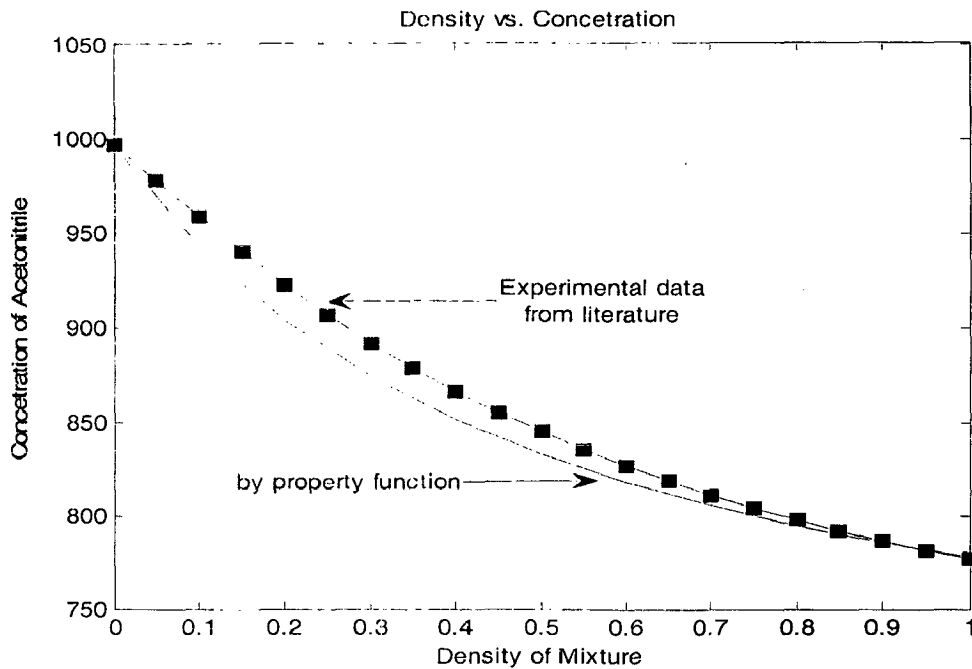
Fig 5.4 Comparison density Vs acetonitrile curve obtained by property function and experimental data

In the above figure, curve obtains by property function is compared with curve obtains by gas chromatography measurement at temperature 25 ^0C. And this is very close to the actual value; roughly $\pm$ 2 - 3 percent.

(ii) Excess volume of mixing: (Redlich Kister equation)

This equation is used to calculate the excess volume of mixing for a binary mixture. Excess volume can be calculated by the following formula. [Meurs N. V. et. al]

$$V_{excess} = X_1.X_2.\sum_{j=0}^{n} A_j.(X_1-X_2)^j \qquad [cm^3] \qquad\qquad [5.5]$$

$$Mass\ of\ mixture = \sum_{i=1}^{2} X_i.M_i \qquad [gm] \qquad\qquad [5.6]$$

$$Volume\ of\ the\ mixture = \sum_{i=1}^{2} \frac{X_i.M_i}{\rho_i} + V_{excess} \qquad [cm^3] \qquad\qquad [5.7]$$

i = 1; for acetonitrile

i = 2; for water

$$And;\ \sum_{i=1}^{2} X_i = 1$$

So, **Density of the mixture = Mass / Volume**

In the next figure, curve obtains by considering excess volume of mixing is compared with curve obtains by literature data of density for various molar concentration of acetonitrile at temperature 25 ^0C. So results are much better.

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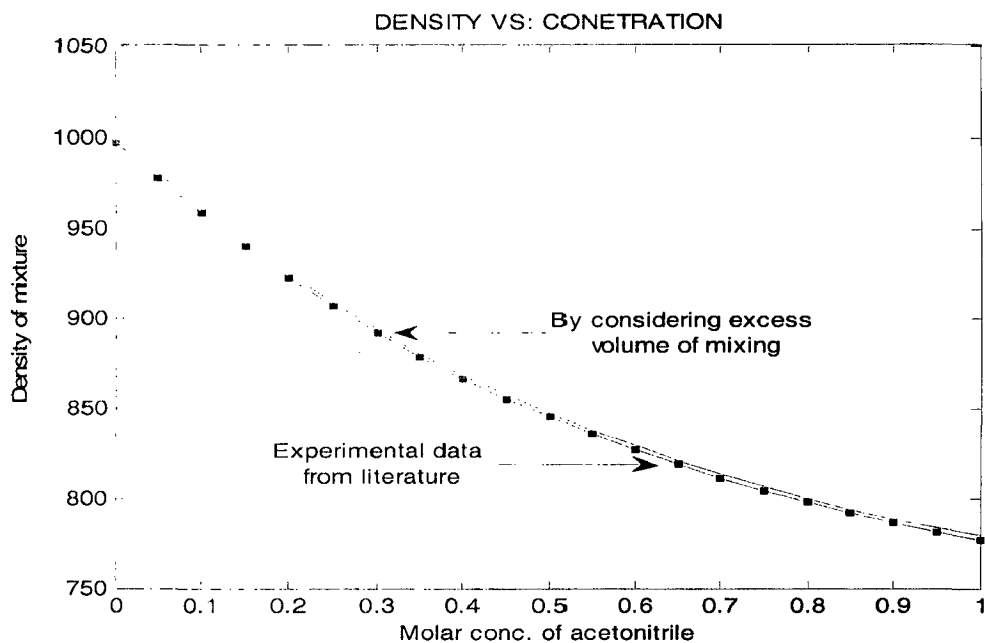
Fig 5.5 Comparison density Vs acetonitrile curve obtained by excess volume calculation and experimental data

5.4 To find a fixed mixture concentration by adding pure water or acetonitrile:

Generally, we work with a constant feed concentration. When, we find a feed of very much different concentration, then we have to make change in the feed concentration to a desired value. And this change either requires addition of water or addition of acetonitrile. This is also used in calibration of chromatograph or density measurement.

X_i^j = Concentration of component

For acetonitrile i = 1 and for water i = 2 & for initial stage j = 1 and for final stage j =2;

So; $\quad \sum_{i=1}^{2} X_i^1 = 1 \quad \& \quad \sum_{i=1}^{2} X_i^2 = 1$

Specific volume of the mixture is calculated by mixture property function by using Matlab programme.

Specific volume of the mixture = v^j	$[m^3/\ kmol]$
Volume of mixture = V^j	$[m^3]$
Moles of mixture $n_J = V^j / v^j$	$[kmol]$

(i) Increase in conc. of acetonitrile:

When given feed has a lower concentration than desire concentration, then we will add acetonitrile to the mixture. For this, first we will calculate moles of acetonitrile require.

Require moles of acetonitrile = $n_2. X_1^2 - n_1. X_1^1$		[5.8]
Total final mole	$n_2 = n_2. X_1^2 - n_2.X_2^2$	[5.9]
Total initial mole	$n_1 = n_1. X_1^1 - n_2.X_1^2$	[5.10]

As; we are adding only acetonitrile, so total moles of water remain unchanged.

$$n_2 - n_1 = n_2.X_1^2 - n_1. X_1^1 \qquad [5.11]$$

$$n_2 = n_1 + \text{require mole of acetonitrile} \qquad [5.12]$$

Require moles of acetonitrile $= (n_1 +$ require mole of acetonitrile)$. X_1^2 - n_1. X_1^1$ [5.13]

Require moles of acetonitrile $= n_T. \dfrac{X_1^2-X_1^1}{1-X_1^2}$ [5.14]

$V_{add} = n_T. \dfrac{X_1^2-X_1^1}{1-X_1^2}$ *(Molar specific volume of pure acetonitrile)   [5.15]

$V^2 = V^1 + V_{add}$ [5.16]

(ii) Decrease in conc. of acetonitrile:

When given feed has a lower concentration than desire concentration, then we will add water to the mixture.

Require moles of water $= n_T. \dfrac{X_2^2-X_2^1}{1-X_2^2}$ [5.17]

$V_{add} = n_T. \dfrac{X_2^2-X_2^1}{1-X_2^2}$ * (Molar specific volume of pure water)   [5.18]

$V^2 = V^1 + V_{add}$ [5.19]

5.5 Gas chromatography:

    Chromatography is a technique for the separation of complex chemical mixtures. It involves passing a mixture dissolved in a mobile phase through a stationary phase, which separates the analyte to be measured from other molecules in the mixture and allows it to be isolated.
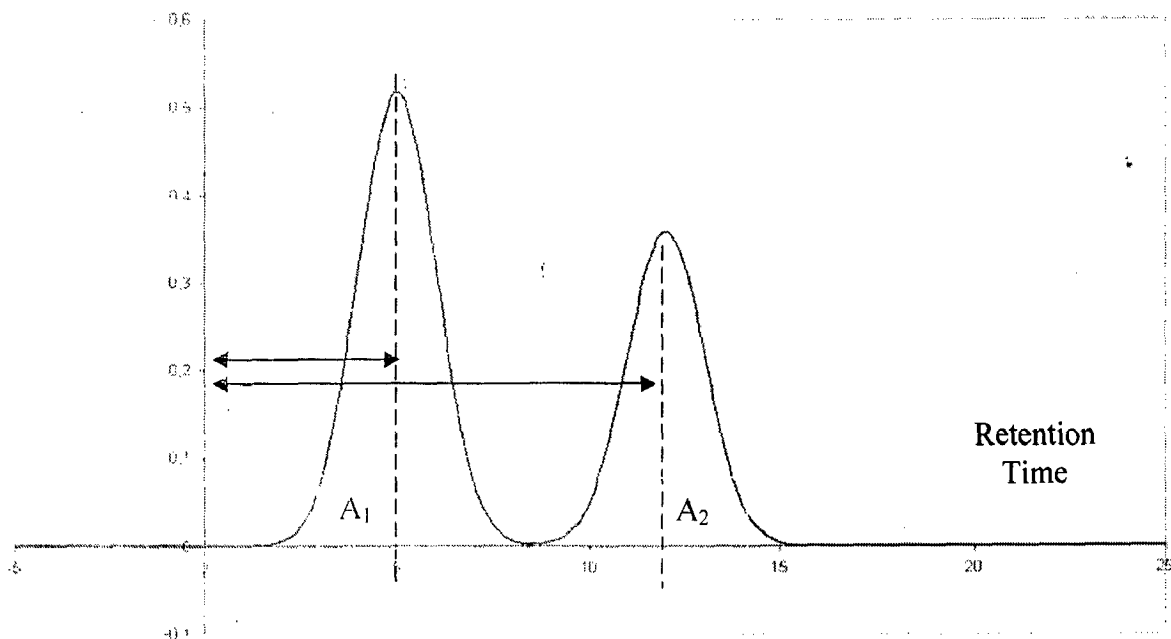
Fig 5.6 Gas chromatography curve

    If mobile phase is a gas (carrier gas, usually inert gases) and stationary phase is a microscopic layer of liquid or polymer, then this type of chromatography is called gas

chromatography. Analytical chromatography is used to identify and determine the concentration of molecules in the mixture. Chromatogram for two components is shown in the above figure.

Retention time is shown on the x axes. Components are identified by their respective position in the chromatogram. Relative concentration of component is obtained by comparing area under the curve.

(i) Use of solvent:

We have total three samples for analysis by gas chromatography. Bottom product contains low amount of acetonitrile; while feed and distillate contains medium range of acetonitrile. We used propanol-2 as a solvent for the analysis of feed and distillate.

(ii) Clarification of samples:

If the samples are not completely clear, then clarification of sample is necessary before their gas chromatographic analysis. Single use syringe filter is used for the clarification of samples. That filter contains PTFE membrane with polypropylene housing. Molcure with size less than 45 micrometer can only pass through this membrane filter.

(iii) Sample preparation:

Sample for feed and distillate is prepared by taking 1 ml of and 5 ml of distillate. We measure their weight individually and mix together.

$$\text{Sample amount} = 100. \frac{M_{Probe}}{M_{Probe} + M_{isopropanol}} \qquad [5.20]$$

Sample name	Sample volume	Sample weight	Propanol-2 volume	Propanol-2 weight	Sample amount
Feed 1 (5)	1 ml	0.8496	5 ml	3.9763	17.60501
Feed 2 (19)	1 ml	0.8380	5 ml	3.9140	17.63468
Feed 3 (19)	1 ml	0.8508	5 ml	3.9339	17.78168
Distillate 1 (5)	1 ml	0.8027	5 ml	3.9786	16.78832
Distillate 2 (19)	1 ml	0.8100	5 ml	3.9324	17.07996
Distillate 3 (19)	1 ml	0.8059	5 ml	3.9202	17.05067

(iv) Experimental parameter:

Oven temperature = 160 ^{0}C

Front inlet temperature = 200 ^{0}C

Back inlet temperature = 76 ^{0}C

Front det temperature = 250 ^{0}C

Back det temperature = 100 ^{0}C

Pressure = 14.6 psig

Sample volume = 0.5 µm

No of measurement per sample = 3

Nitrogern is the carrier gas.

Acetonitrile mass percent	Method	Sample amount
0 – 5 %	Klein 5a	100
5 – 95 %	Acetonil seit 22 – 206	Calculated from equation 1
95 – 100 %	Klein 5w	100

(v) Results:

In this way, we found three peaks for feed and distillate and two peaks for bottom product. We found direct mass concentraion for all the three type of sample.

Sample no	Mass fraction of acetonitrile	Mole fraction of acetonitrile
Feed 1	58.40117	0.3813
Feed 1	59.58693	0.3930
Feed 1	57.47012	0.3734
Feed 2	61.81644	0.4155
Feed 2	60.42860	0.4013
Feed 2	60.43944	0.4015
Feed 3	60.36975	0.4008
Feed 3	59.70447	0.3941
Feed 3	61.12371	0.4084
Distillate 1	79.67567	0.6325
Distillate 1	78.38489	0.6142
Distillate 1	79.67567	0.6325
Distillate 2	74.46170	0.5614
Distillate 2	75.14154	0.5703
Distillate 2	74.22478	0.5584
Distillate 3	76.34109	0.5862
Distillate 3	73.58823	0.5502
Distillate 3	73.58671	0.5502

Gas chromatography calculates concentration in mass fraction independently for each component of sample. So time it shows total component concentration other than 100. We can say from our data that our concentration values are correct with in ± 4 percent.

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Distillation columns are dynamic in behaviour and nonlinear in nature. Here we will see variation in the process variables and their control mechanism.
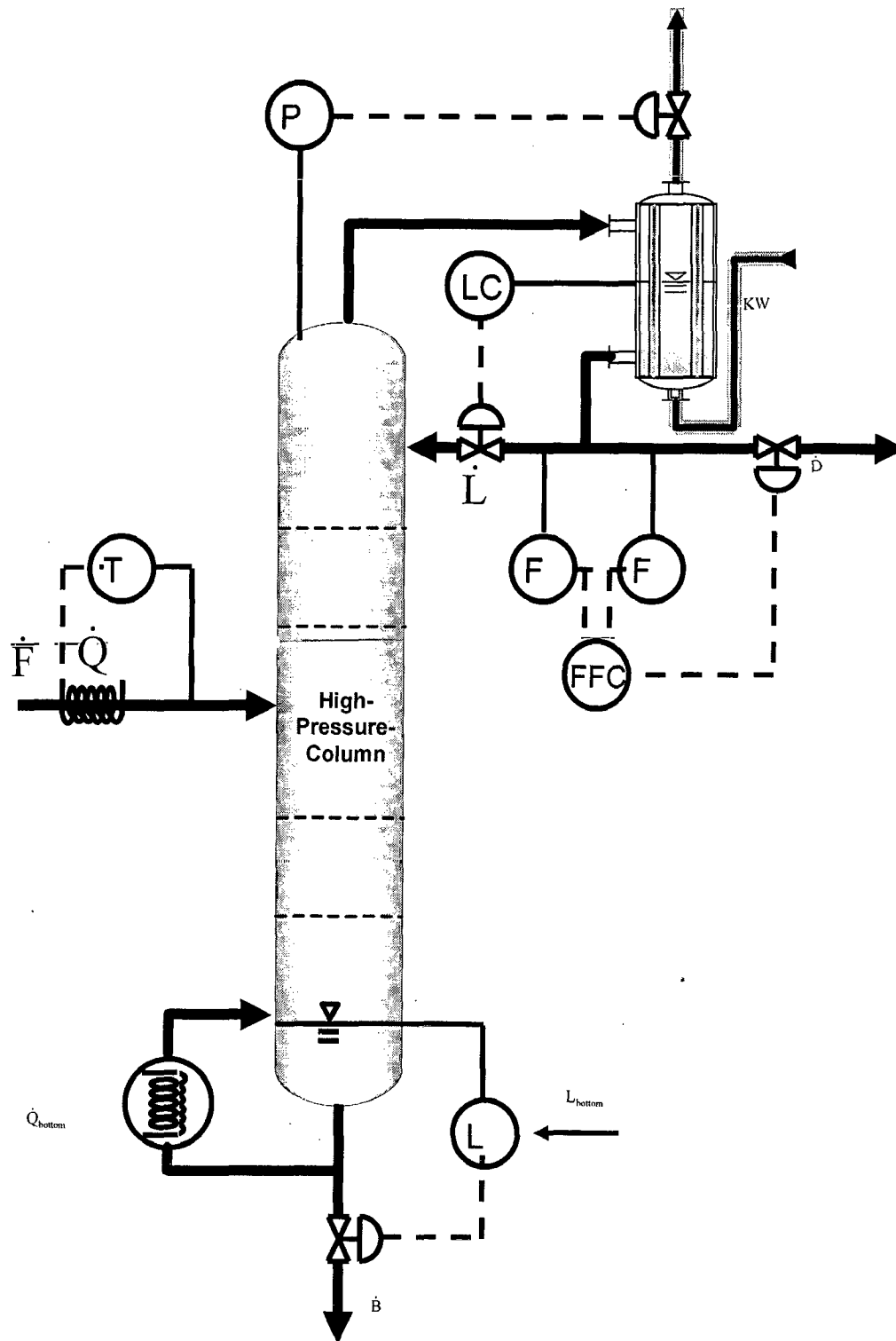
Fig 6.1 Various control mechanism for distillation column

6.1 Tray temperature variation:

Temperature is the maximum in the reboiler section and it decreases continuously from bottom tray to top tray.
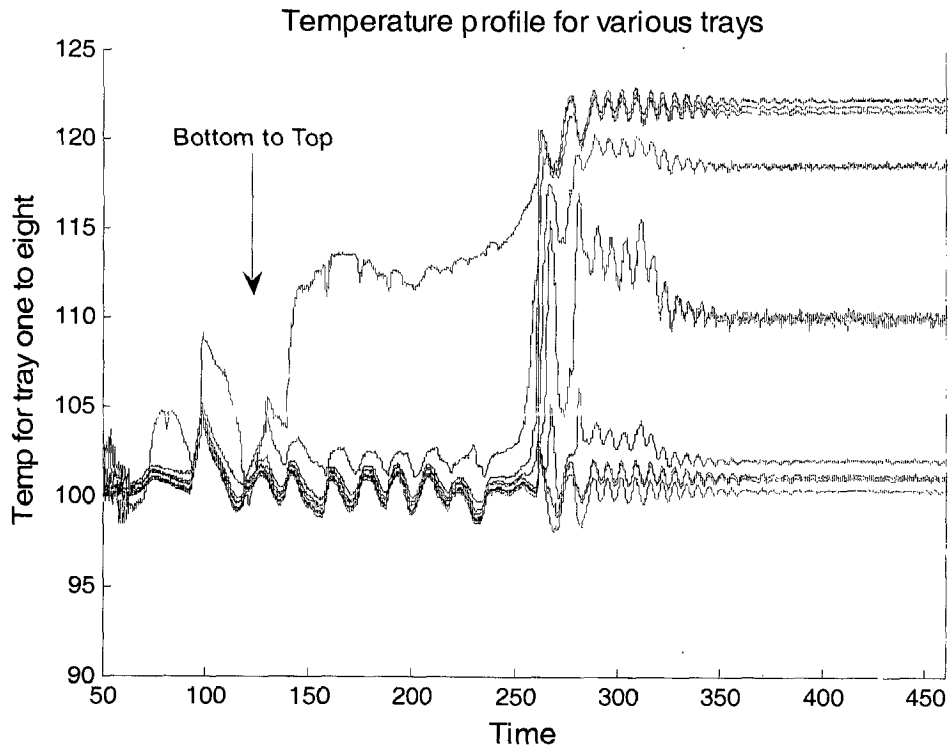
Fig 6.2 Temperature variation inside the column

Decrease in the temperature is higher for first some bottom trays in comparison to top trays, which can be also shown by temperature and concentration curve.
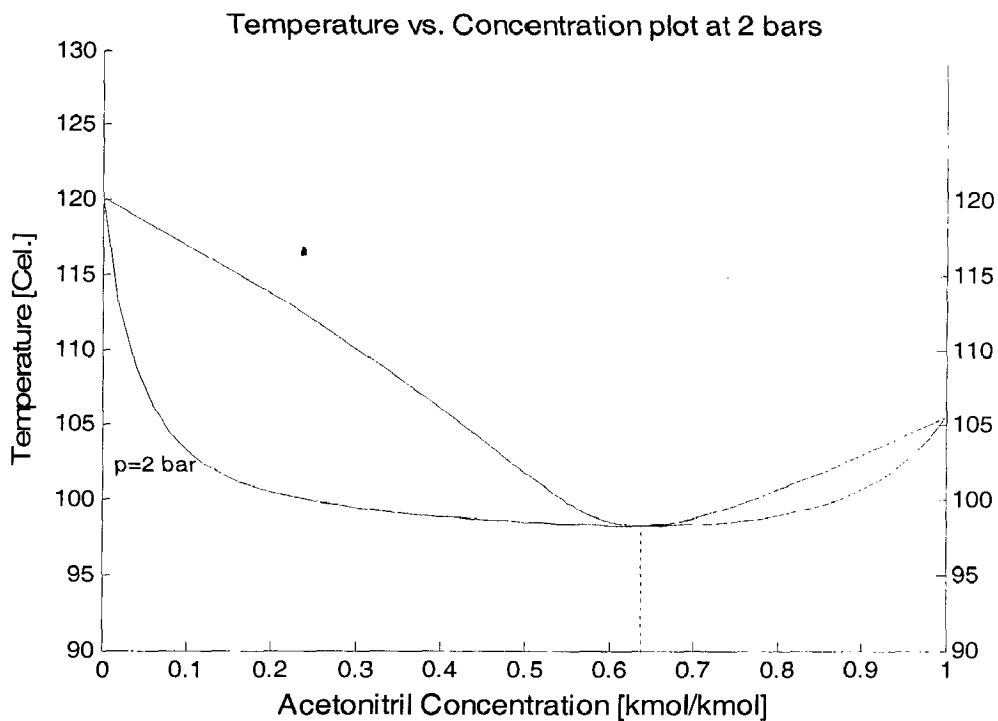
Fig 6.3 Plot for mixture boiling temperature variation with acetonitrile concentration

There is a control loop for the temperature control inside the column. Temperature inside the column is controlled by heating in the reboiler. When heating in the reboiler is increases to fix the temperature of bottom trays, then temperature inside the column increases inside the column and become constant after some times. Temperature inside the column is also affected by feed flow rate, feed temperature, reflux flow rate, reflux temperature and heat losses from the column.

In our experiment, we controlled temperature for the third tray, because in this region we have possibility of maximum variation in temperature or we can say that this region is very sensitive. So, for getting pure liquid at the bottom, we need to minimize the affect of disturbances in the boom of the column.
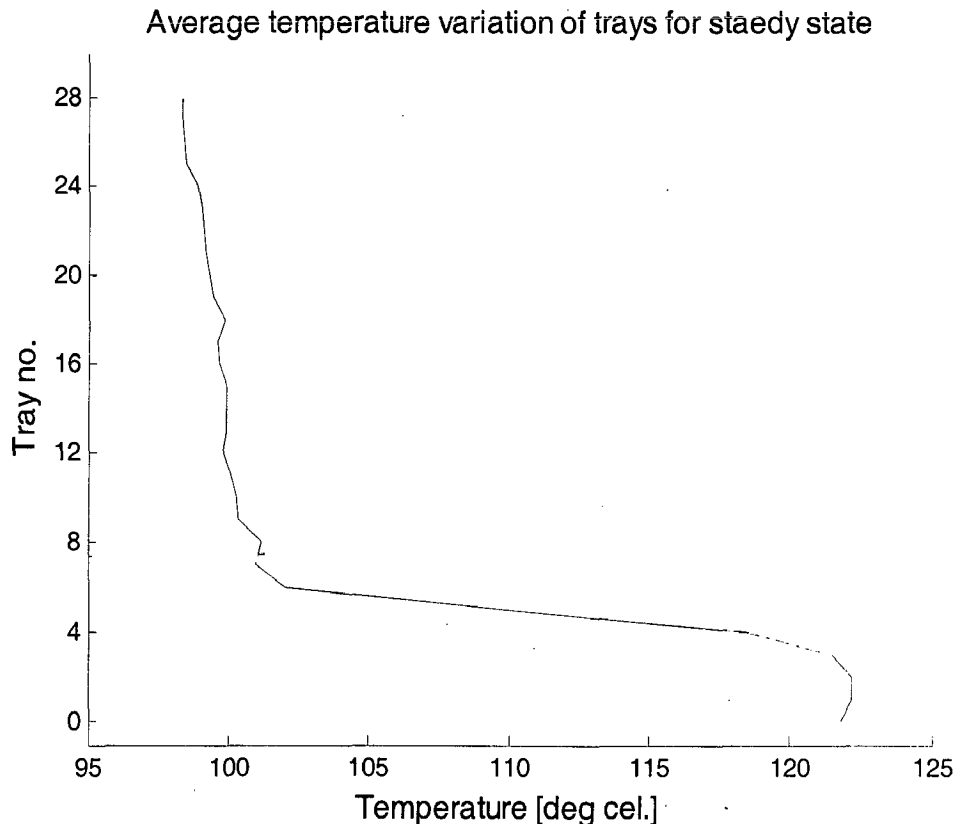
Fig 6.4 Temperature variation inside the column for a short interval

6.2 Pressure variation:

Column can with stand with a fix pressure due to some safety restriction, so pressure control at the top of column is very crucial. Pressure at the top of the column is controlled by cooling water flow inside the condenser. It is a proportional integral (PI) controller.

Pressure at the top of column is less than the pressure at the bottom of column and difference between these two pressures are nearly constant, this mean vapour velocity inside the column is constant.

Pressure at the top of column is varies linearly with top tray temperature. Pressure at the top of column is also a function of vapour composition at the top of column. In the below figure, pressure is varies with temperature. Pressure variation with temperature is shown in the figure.

Pressure differnce inside the column
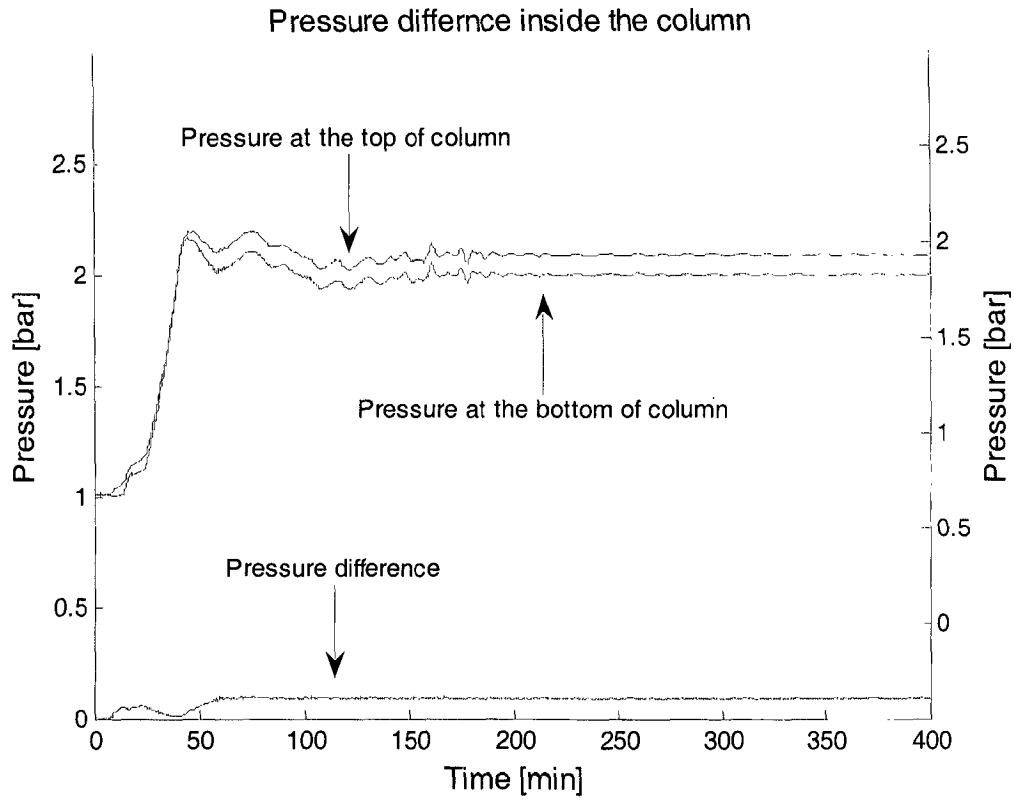
Fig 6.5 Pressure difference inside the column

Column top pressure and Top tray temperature
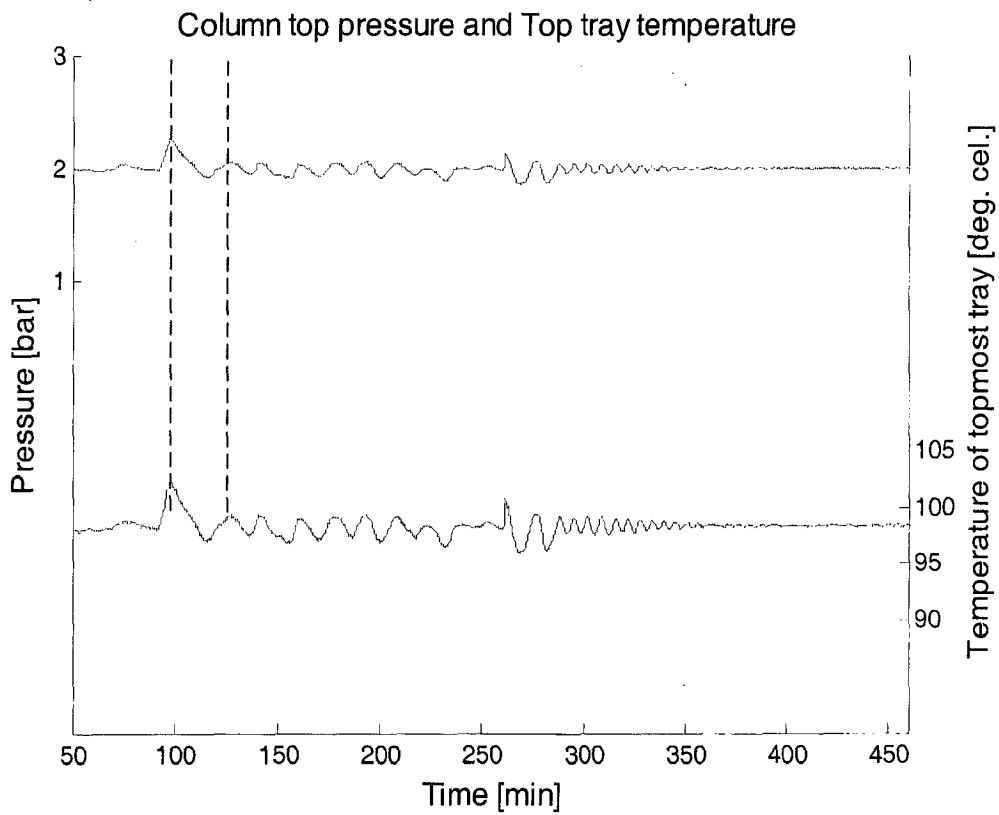
Fig 6.6 Column top pressure variation with top tray temperature

Pressure at the top of column is controlled by the cooling water flow in the condenser. It is also a PI Controller. When top pressure value increases more than set value then cooling water flow in condenser increases very fast, so after some time pressure at the top of column reaches below the set value and at the same time cooling water flows at its minimum. In the figure, we can see some time lag in cooling water flow; it is mainly due to measurement instrument. Control mechanism working good in the final stage of experiment, where very less fluctuation in the top pressure and cooling water flow.
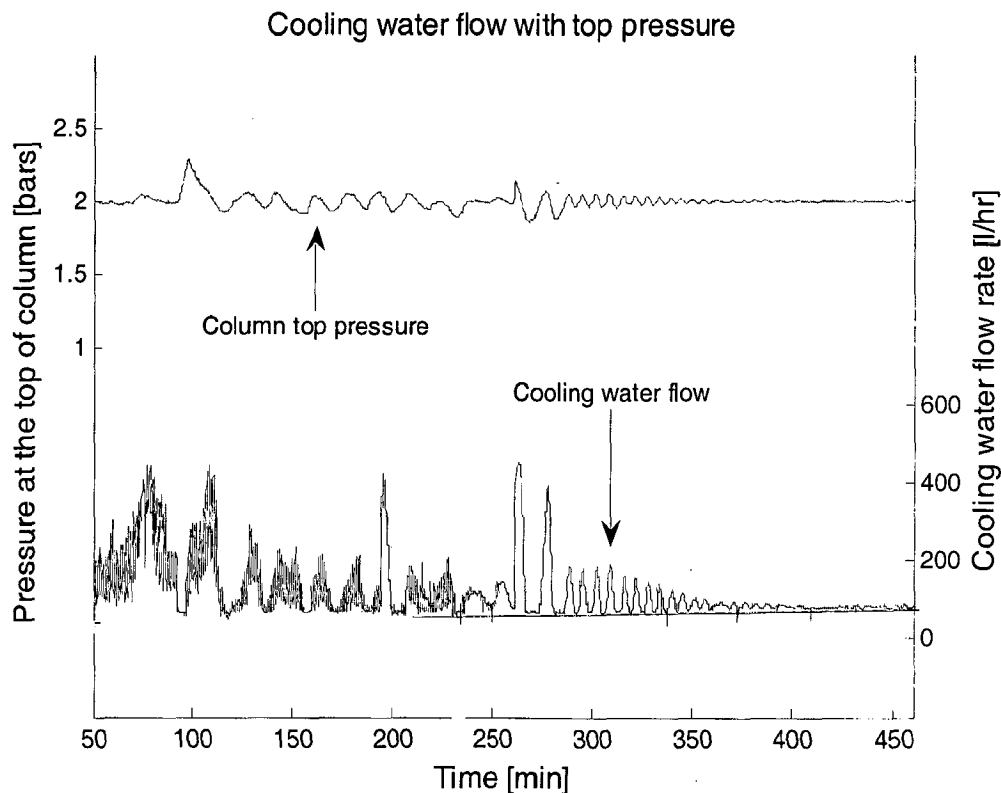
Fig 6.7 Top pressure controlled by cooling water flow

6.3 Level in condenser:

Level in the condenser is controlled by the total flow of distillate and reflux out from the condenser. It is also a PI controller. When level inside the condenser is increased from its set value, flow from the condenser start increases to control the level in the condenser.

In the figure below, level inside the condenser and total outlet flow from the condenser is shown for a short period of time. We can see in the figure, that controller is not functioning well, as level inside the condenser is varying to a much higher level.

6.4 Level in reboiler:

Level in the reboiler is also affected reboiler heating. It is controlled by bottom product removal, which is a PI controller. In the figure below, this controller functioning well as level in the reboiler is almost constant.

Total flow out from Condenser & Level in Condenser
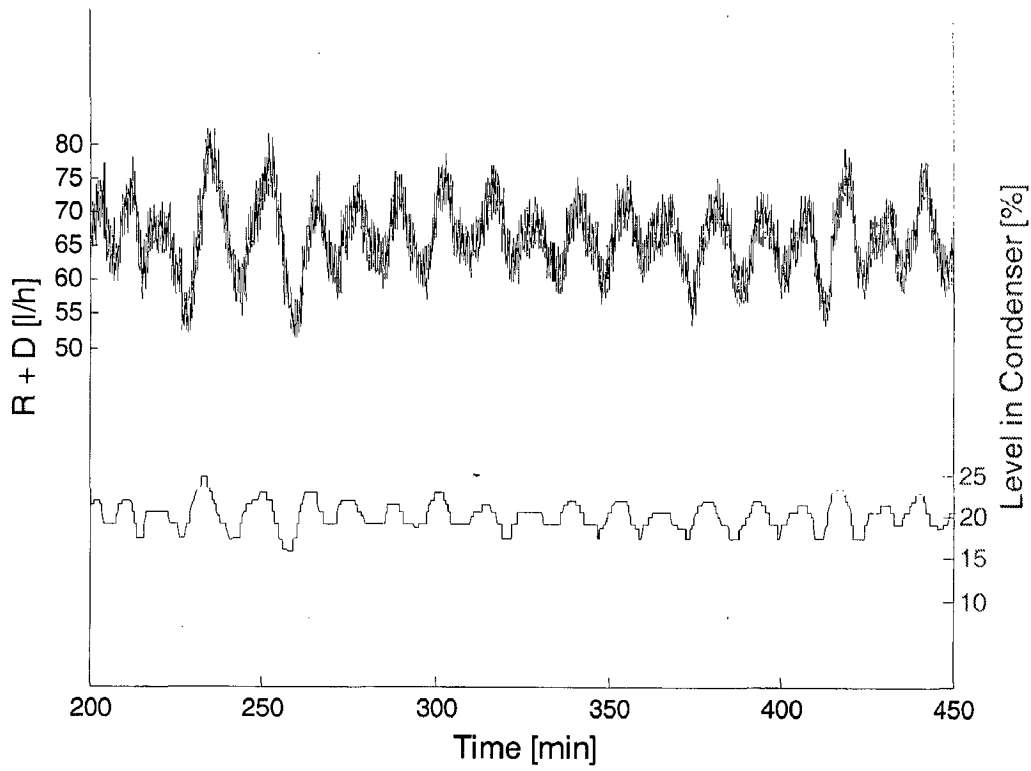
Fig 6.8 Level in condenser controlled by reflux and distillate flow

Bottom product flow & Level in Reboiler
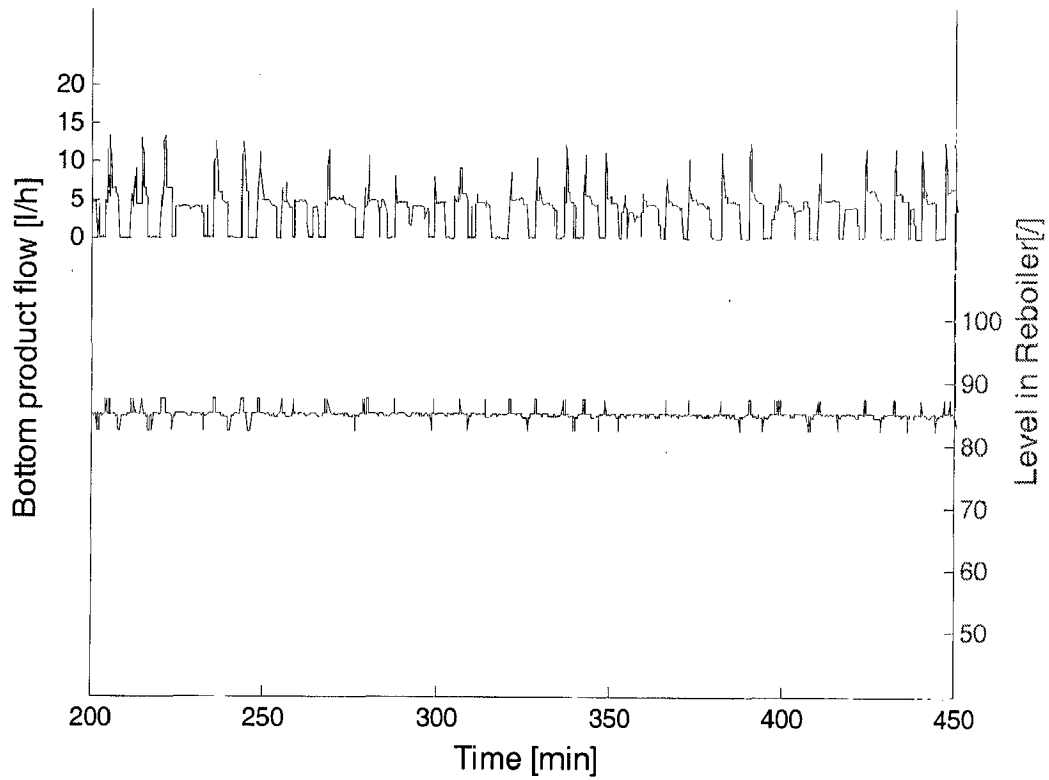
Fig 6.9 Level in reboiler controlled by bottom product removal

6.5 Various streams flow:

Feed flow during the whole process is set at a fix value. Initially, distillate and bottom product flow varies much, but near to steady state distillate flow rate become nearly constant while bottom product flow fluctuate in order to control the level in the reboiler.

Flow rate for "Feed, Bottom product & Distilalte
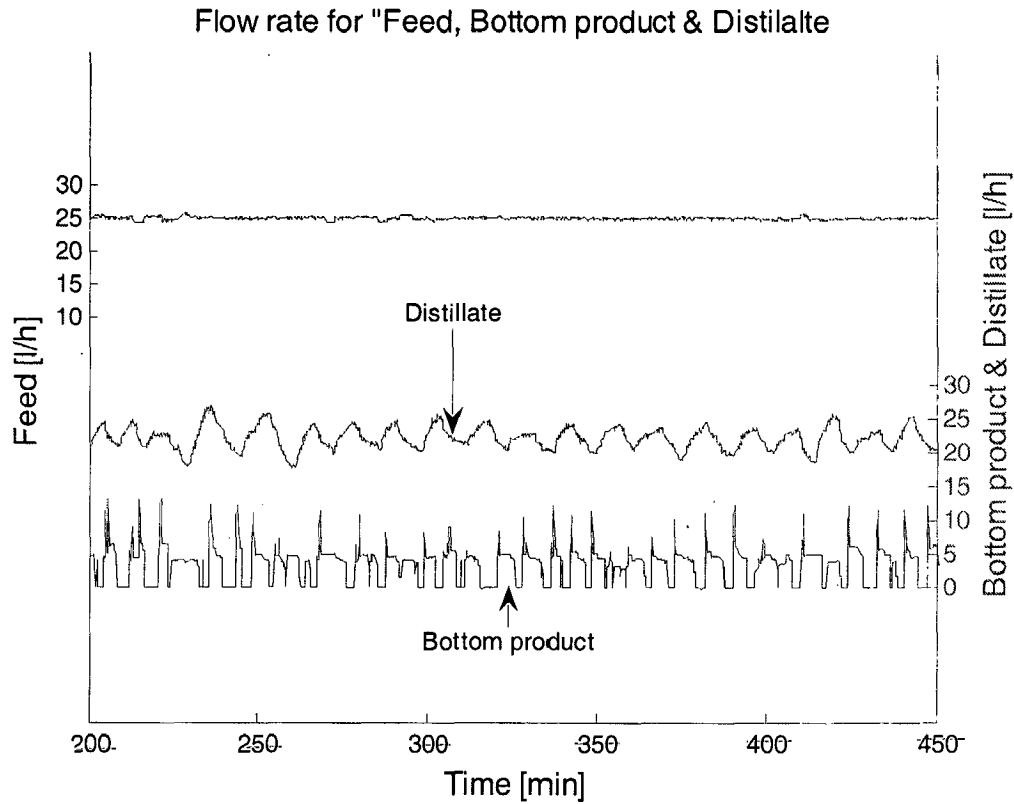
Fig 6.10 Various stream's flow rates

6.6 Energy balance for HP column:

Energy balance over the column can be applied in order to estimate the heat losses from the column.

i. Heat input to feed in preheater:

Feed flow rate = F	[l/hr]
Temperature of feed at preheater inlet = T_i	[^{0}C]
Temperature of feed at preheater outlet = T_o	[^{0}C]
Mole fraction of acetonitrile in feed = X_F^1	
Mole fraction of water in feed $X_F^2 = 1$- X_F^1	

Molar volume and molar enthalpy for this composition of feed can be calculated by assuming a linear mixture of water and acetoniltrile.

$V_F = X_F^1$.Molar volume of acetonitrile + X_F^2.Molar volume of water [l/Kmol]

$H_F(T) = X_F^1$.Molar enthalpy of acetonitrile + X_F^2.Molar enthalpy of water [KJ/Kmol]

$H_F = H_F(T_o) - H_F(T_i)$ [KJ/Kmol]

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Molar flow rate of feed = $\dfrac{F}{V_F}$ [Kmol/hr]

Heat input to feed in preheater = $\dfrac{F}{V_F} \cdot \dfrac{H_F}{3600}$ [KJ/sec]
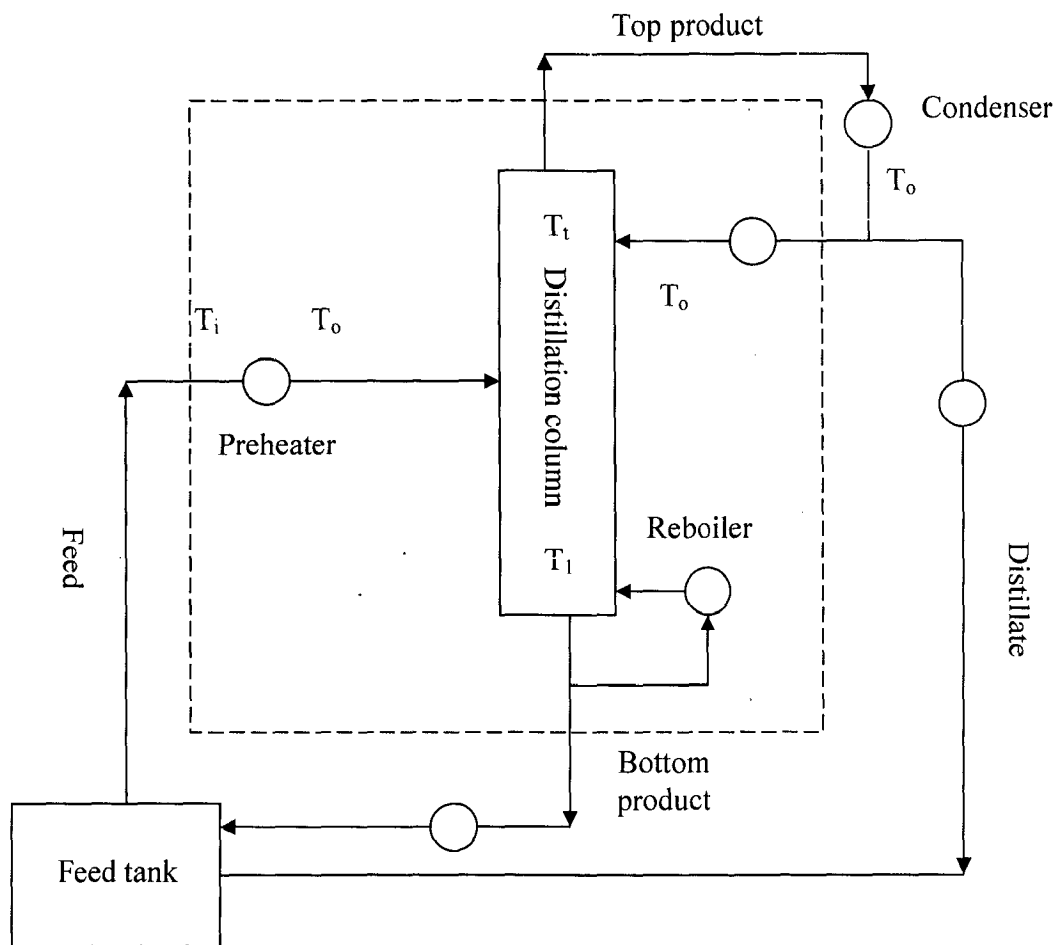
Fig 6.11 Energy balance boundary over the column

ii. Heat removed from bottom product:

Bottom product flow rate = B [l/hr]
Temperature of reboiler = T_i [^{0}C]
Temperature of bottom product after cooling = T_0 [^{0}C]
Mole fraction of acetonitrile in bottom product = X_B^1
Mole fraction of water in bottom product $X_B^2 = 1 - X_B^1$

Molar volume and molar enthalpy for this composition of bottom product can be calculated by assuming a linear mixture of water and acetoniltrile.

$V_B = X_B^1$.Molar volume of acetonitrile + X_B^2.Molar volume of water [l/Kmol]

$H_B(T) = X_B^1$.Molar enthalpy of acetonitrile + X_B^2.Molar enthalpy of water [KJ/Kmol]

$H_B = H_B(T_0) - H_B(T_i)$ [KJ/Kmol]

Molar flow rate of bottom product = $\dfrac{B}{V_B}$ [Kmol/hr]

Heat removed from bottom product = $\dfrac{B}{V_B} \cdot \dfrac{H_B}{3600}$ [KJ/sec]

iii. Heat removed from top product:

Top product flow rate $T = D + L$ [l/hr]

Temperature of topmost tray $= T_i$ [^{0}C]

Temperature of top product after condenser $= T_o$ [^{0}C]

Mole fraction of acetonitrile in bottom product $= X_D^1$

Mole fraction of water in bottom product $X_D^2 = 1 - X_D^1$

Molar volume and molar enthalpy for this composition of top product (distillate + reflux) can be calculated by assuming a linear mixture of water and acetoniltrile.

$V_D = X_D^1$ .Molar volume of acetonitrile $+ X_D^2$ .Molar volume of water   [l/Kmol]

$H_D(T) = X_D^1$ .Molar enthalpy of acetonitrile $+ X_D^2$ .Molar enthalpy of water   [KJ/Kmol]

$H_D = H_D(T_o) - H_D(T_i)$

$HV_D(T) = X_D^1$ .Molar heat of vaporization of acetonitrile $+$

$\qquad\qquad\qquad X_D^2$ .Molar heat of vaporization of water

$HV_D = HV_D(T_o) - HV_D(T_i)$

Molar flow rate of bottom product $= \dfrac{T}{V_D}$

Heat removed from bottom product $= \dfrac{T}{V_D} \cdot \dfrac{(H_D + HV_D)}{3600}$

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Molar volume and molar enthalpy for this composition of reflux can be calculated by assuming a linear mixture of water and acetoniltrile.

$V_D = X_D^1 \cdot$ Molar volume of acetonitrile $+ X_D^2 \cdot$ Molar volume of water $\qquad$ [l/Kmol]

$H_D(T) = X_D^1 \cdot$ Molar enthalpy of acetonitrile $+ X_D^2 \cdot$ Molar enthalpy of water $\qquad$ [KJ/Kmol]

$H_D = H_D(T_o) - H_D(T_i)$ $\qquad$ [KJ/Kmol]

Molar flow rate of bottom product $= \dfrac{L}{V_D}$ $\qquad$ [Kmol/hr]

Heat removed from bottom product $= \dfrac{L}{V_D} \cdot \dfrac{H_D}{3600}$ $\qquad$ [KJ/sec]

vi. Reboiler heating:

Heat given by the reboiler $= Q$ $\qquad$ [KJ/sec]

Heat loss = Feed heat + Reflux heat + Q – Top product heat – Bottom product heat
$\qquad$ = 0.7794 + 0.2363 + 0.5594 + 18.2152 - 17.6191 - 6.0075
$\qquad$ = 1.6986 $\qquad$ [KJ/sec]

MATHEMATICAL MODEL FOR THE COLUMN

7.1 Parameters:

Parameters for distillation process have two categories, one can be adjusted during operation called operation parameters but other can not be change during operation, as they are related to either column design or mixture property, called physical or chemical parameter like tray efficiency, stage area, resistance area etc.

Operation parameter:

Operation parameter can be changed easily according to the requirement of process. Operation parameter are either loaded or controlled.

(i) Feed flow:

Feed flow rate for distillation column can be changed as per requirement. We can also change feed position. Flow control by FIR.

(ii) Feed temperature:

Feed is preheated before entering to the column. We can adjust feed temperature as per our requirement. Generally, we keep it just below the boiling point of the mixture, to prevent any sudden change in temperature on the feed tray and to reduce the reboiler duty. Temperature is controlled by TIR, heating in preheater.

(iii) Column top pressure:

Azeotropic point for the mixture depends upon the operating pressure of column. Distillation at different pressure is used to pass the azeotropic point of the mixture. We can adjust column top pressure as per our process requirement. Pressure is controlled by PIR, cooling water flow.

(iv)Temperature difference between condenser and first tray:

This is the temperature difference between the condenser inlet and condenser outlet. Part of condenser liquid is returned to the column as reflux. Temperature difference between top tray vapor and reflux should be constant for steady state. Sub cooling of condenser liquid is possible due to high flow of liquid, so a preheater is can be heat the reflux to a certain temperature.

(v) Level of the reboiler and condenser:

Liquid level in the reboiler and condenser can be changed by changing the amount of liquid removal from the reboiler and condenser, for a constant reboiler duty.

(vi) Reflux ratio:

Optimum reflux ratio is necessary for the best separation of mixture. This can be easily adjusted during distillation.

(vii) Reboiler duty:

Heat require in the reboiler depends upon the components of the mixture. This can be adjusted by amount of electric heating.

Physical parameter depends upon the design of column, so they can not be changed. Chemical parameters depend on the properties of the mixture components. So they will be different for different kind of mixtures.

Mathematical model for distillation column is based upon the fundamental relation, which is used to show the behaviour of the distillation process. A mathematical model usually describes a system by a set of variables and a set of equations (DAE) that establish relationship between the variables. In a static model, we doesn't consider changes due to time, while in dynamic model, we also consider changes due to time.

We divided our distillation column into three major parts for the purpose of modelling. Each part has different equation in the model.

Part 1	Condenser	Stage 1
Part 2	Trays	Stages 2 – 29
Part 3	Reboiler	Stage 30
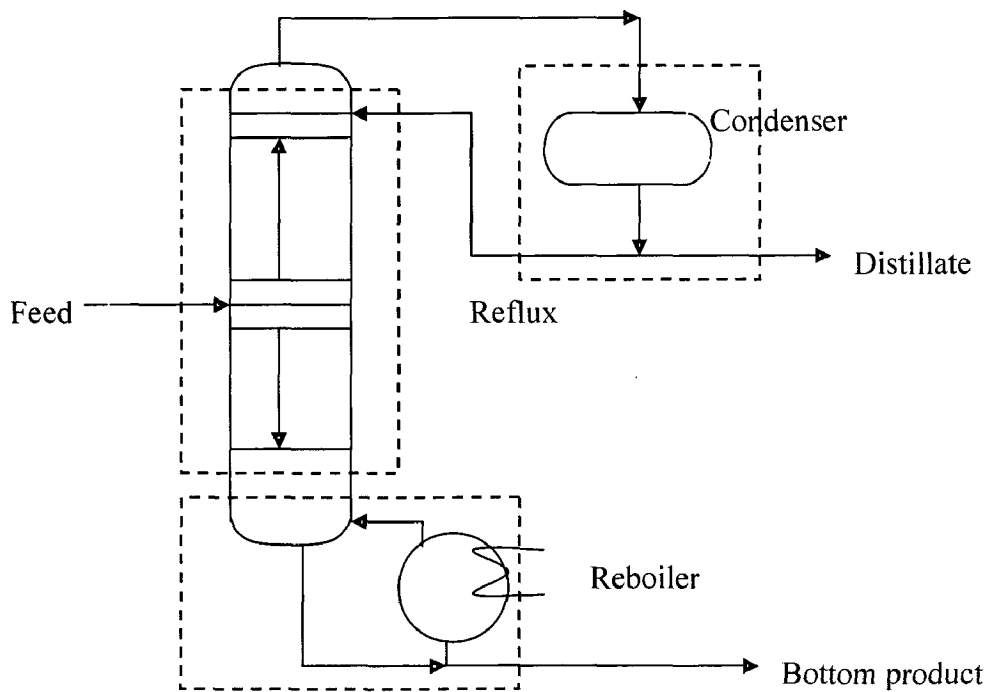
Fig 7.1 Different parts of distillation column

This model is based on maximal nine variables and nine equations for each stage. Nine variables for each stage are given below.

FL – Liquid flow rate [Kmol/hr]

FV – Vapor flow rate [Kmol/hr]

y_1 – Mole fraction of component 1 in vapor phase

y_2 – Mole fraction of component 2 in vapor phase

HU – Hold up

P – Pressure

x_1 – Mole fraction of component 1 in liquid phase

x₂ – Mole fraction of component 2 in liquid phase

x_2 – Mole fraction of component 2 in liquid phase

T – Temperature

7.2 Condenser Modelling: (6 variable and 6 equations)

Condenser is the first stage of our modelling. Various modelling equation for the condenser is given below.

(i) Component balance:

Vapor will come from top of the column and will be condensed in the condenser. So vapor from the first tray is the input for the condenser, while reflux and distillate is the out put from the condenser. Accumulation inside the condenser occurs due to the imbalance between input and output stream for the condenser. Mass balance over the column is shown in the following figure.

$$\frac{\partial}{\partial t}(x_{i,1}.HU_1) = x_{i,1}.\frac{\partial HU_1}{\partial t} + HU_1.\frac{\partial x_{i,1}}{\partial t}$$
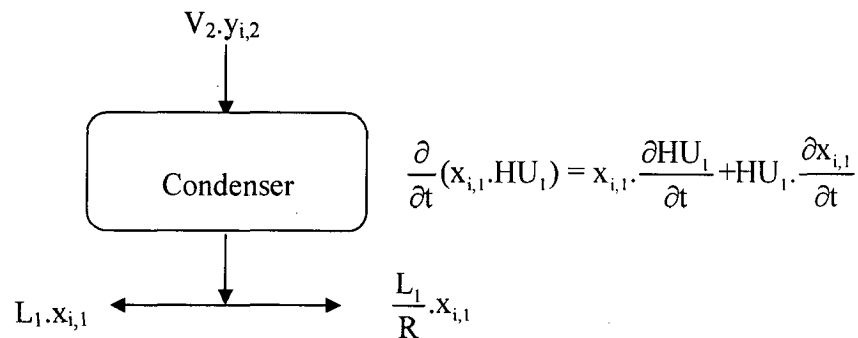
Fig 7.2 Mass balance for the condenser

Applying mass conservation over the condenser,

Mass In + Production = Mass Out + Accumulation

$$x_{i,1}.\frac{\partial HU_1}{\partial t} + HU_1.\frac{\partial x_{i,1}}{\partial t} + L_1.x_{i,1} + \frac{L_1}{R}.x_{i,1} - V_2.y_{i,2} = 0 \qquad [7.1]$$

Where, i is the component 1 and component 2. So, above equation contains total two mass relations, one for component 1 and other for component 2.

(ii) Equilibrium relation:

Our condenser is total condenser, this mean that all vapor condensed inside the condenser. This mean no equilibrium is present between the gas phase and liquid phase as no vapor phase is present.

$$y_1 = 0 \qquad [7.2]$$
$$y_2 = 0 \qquad [7.3]$$

(iii) Hold up balance:

Hold up in the condenser generate only during unsteady state. During steady state entering liquid in the column is equal to outgoing liquid from the column, so liquid level inside the column remains constant.

Liquid inside the condenser = $A_q.l^{Kond}.\rho_1^L$

Hold up = $HU_1.M_1^{avg}$

At steady state, liquid inside the condenser is equal to hold up.

$$A_q.l^{Kond}.\rho_1^L = HU_1.M_1^{0,avg}$$ [7.4]

(iv) Pressure:

Condenser is directly connected to the top of the column and Column top pressure is a fixed variable. So pressure inside the condenser will be equal to the column top pressure.

$$P_1 = P_{Top}$$ [7.5]

(v) Sum balance:

If both liquid and gas phases are completely separated, then sum of molar fraction of all component will be equal to the unity in each phase.

$$\sum_{i=1}^{2} x_{i,1}=1$$ [7.6]

$$\sum_{i=1}^{2} y_{i,1}=1$$ [7.7]

But no vapor is present after cooling, so equation [vii] will be changed into $V_1 = 0$.

(vi) Energy balance:
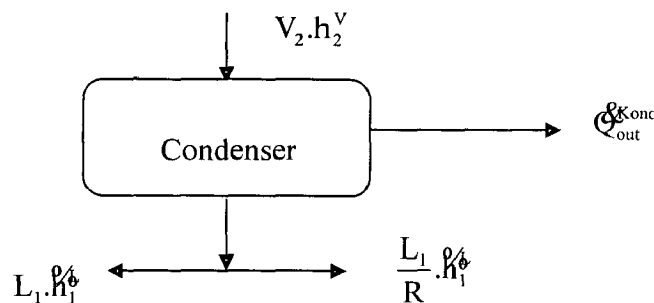
Fig 7.3 Energy balance for column

Here Q_{out}^{Kond} is the heat removed by cooling water. Applying energy conservation over the column,

$$V_2.h_2^V - L_1.h_1^L - \frac{L_1}{R}.h_1^L - Q_{out}^{Kond} = 0$$ [7.8]

But we are interested in keeping a constant temperature difference between condenser inlet and outlet. So we get a new energy relation for the condenser.

$$T_1=T_2-\Delta T$$

Where, T_1 is the temperature at the out let of the condenser.

T_2 is the temperature at the inlet of the condenser or top tray temperature.

ΔT is the temperature difference.

Equations related to variables y_1, y_2 and FL are not using in the design of condenser. HU is also controlled by level in the condenser and pressure inside the condenser is directly related to column top pressure.

7.3 Tray modelling: (9 variables and 9 equations)

In this model each tray modelled independently. But all trays have same type of modelling equation. Only feed tray has one extra flow, but we are not fixing the position of our feed tray before modelling, so we will consider inlet feed flow at each tray. ome common termsthat will used in tray modelling.

Stage area:

Tray area is the total area of tray, which contains liquid. Tray area for each tray and reboiler is same, but area for condenser is different from this area.

Active tray area:

Active tray area is that part of tray area which is used for contact between liquid and gas flow. So this is the sum of different small active area, which is near to the gas flow from different channels or caps.

Tray efficiency:

Point efficiency is the ratio of the change of composition at a point the change that would occur on a theoretical stage. Murphree tray efficiency is similar to the point efficiency, but it covers entire tray.

$$E_{MV} = \left(\frac{y_n - y_{n-1}}{y_n^* - y_{n-1}} \right)_{tray}$$

Efficiency is different in stripping and rectification section. Overall efficiency for a column is the ratio of number of theoretical trays to number of actual trays.

Pressure parameter / resistance coefficient:

This is the total resistance for the flow of vapor due to the tray screen or barriers with out any liquid over it. This resistance depends upon the design of tray.

2.1 Component balance:

Mass balance on the jth tray,

Mass In $(L_{(J-1)} + V_{(J+1)} + F_j)$ + Production = Mass out $(L_j + V_j)$+ Accumulation

$$x_{i,j} \cdot \frac{\partial HU_j}{\partial t} + HU_j \cdot \frac{\partial x_{i,j}}{\partial t} + L_j \cdot x_{i,j} + Vj \cdot y_{i,j} - L_{j-1} \cdot x_{i,j-1} - V_{j+1} \cdot y_{i,j+1} - F_j \cdot x_{i,j}^F = 0 \qquad [7.9]$$

Where i is the number of component and j is the number of stage.

i = 1, 2 & j = 2 ....29 for trays
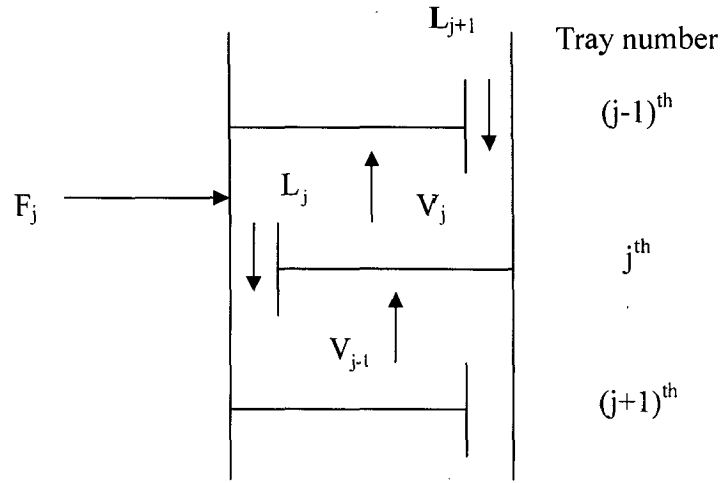
Fig 7.4 Mass balance on j^{th} trays

(ii) Equilibrium equation:

Tray efficiency and equilibrium ratio is used to find the equilibrium relation over the trays.

$$y_{i,j} = \eta.K_{i,j}.x_{i,j} + (1-\eta).y_{i,j+1} \qquad [7.10]$$

(iii) Hold up balance:

Hold up is total level of liquid over the each tray. It contains liquid level up to weir of tray and liquid level over weir necessary for flow of liquid from higher tray to lower tray, which is also necessary for steady operation.

$$HU_j.M_j^{avg} = (V_{j,stat}^L + A_j.L_j^+).\rho_j^L \qquad [7.11]$$

Height of liquid over weir, $L_j^+ = 750.\left[\dfrac{L_j.M_j^{avg}}{\rho_j^L.l_j^{weir}}\right]^{\left(\frac{2}{3}\right)} \qquad [7.12]$

This is Francis weir formula.

(iv) Pressure loss:

Inside the column, liquids vapor flow upward through the tray. It faces resistance due to the design of tray and presence of liquid over the tray. Pressure drop due to liquid is hydrostatic pressure loss, while, pressure loss due to tray design is dry pressure loss.

Hydrostatic pressure loss, $\Delta P_j^{stat} = (h_j^{weir}+L_j^x).g\rho_j^L \qquad [7.13]$

Dry pressure loss, $\Delta P_j^{dry} = \dfrac{1}{2}\rho_j^L C_W (v_j^V)^2 \qquad [7.14]$

Vapor velocity for j^{th} tray, $v_j^V = \dfrac{V_j.M_j^{avg}}{A_j^{aktiv}.\rho_j^V} \qquad [7.15]$

So, total pressure loss, $\Delta P = \Delta P_j^{stat} + \Delta P_j^{dry} \qquad [7.16]$

(v) Sum equations:

If both liquid and gas phases are completely separated, then sum of molar fraction of all component will be equal to the unity in each phase.

$$\sum_{i=1}^{2} x_{i,j} = 1 \tag{7.17}$$

$$\sum_{i=1}^{2} y_{i,j} = 1 \tag{7.18}$$

Where, j = 2, 3…29.

(vi) Energy balance:

If heat loss from each tray is negligible, then total heat input and production will be equal to total heat output and accumulation.
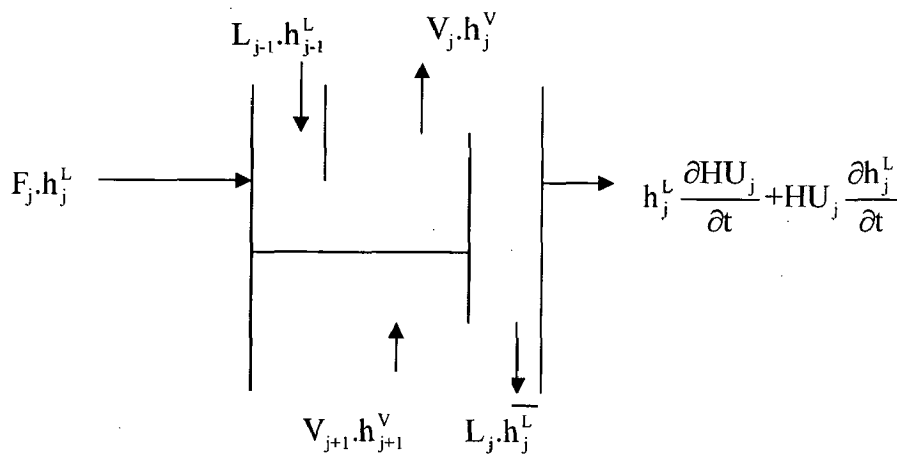
Fig 7.5 Energy balance on the jth tray

Energy In $(L_{(J-1)} + V_{(J+1)} + F_j)$ + Production = energy out $(L_j + V_j)$+ Accumulation

$$h_j \cdot \frac{\partial HU_j}{\partial t} + HU_j \cdot \frac{\partial h_j}{\partial t} + L_j.h_j + Vj.h_j - L_{j-1}.h_{j-1} - V_{j+1}.h_{j+1} - F_j.h_j^F = 0 \tag{7.19}$$

Where i is the number of component and j is the number of stage.

i = 1, 2 & j = 2 ….29 for trays

7.4 Reboiler modelling: (9 variables and 9 equations, HU only for dynamic)

Reboiler is used to supply the necessary energy for the separation. In our laboratory, we have reboiler, which contains electric heater.

(i) Mass balance:

Appling law of mass conservation over the column,

$$x_{i,30} \cdot \frac{\partial HU_{30}}{\partial t} + HU_{30} \cdot \frac{\partial x_{i,30}}{\partial t} + V_{30}.y_{i,30} + L_{30}.x_{i,30} - L_{29}.x_{i,29} = 0 \tag{7.20}$$
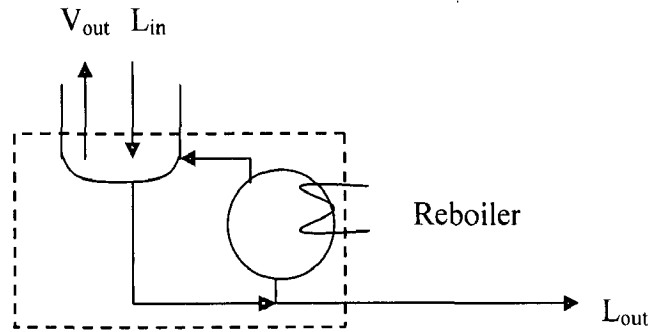
Fig 7.6 Mass balance for reboiler

(ii) Equilibrium relations:

Distillation in this part of the distillation column is flash distillation.

$$y_{i,30} = K_{i,30}.x_{i,30}$$ [7.21]

$$\text{Where, } K_{i,30} = \frac{y_{i,30}}{x_{i,30}}$$

(iii) Hold up balance:

Hold up balance for reboiler will be similar to the condenser. Liquid level in reboiler will be constant during steady state.

$$\text{Liquid inside the condenser} = A_q.L_{30}.\rho_{30}^L$$

$$\text{Hold up} = HU_{30}.M_{30}^{avg}$$

At steady state, liquid inside the condenser is equal to hold up.

$$A_q.L_{30}.\rho_{30}^L = HU_{30}.M_{30}^{avg}$$ [7.22]

(iv) Pressure loss:

Liquid vapor is produced from the reboiler and direct reaches to the bottom tray. So, no hydrostatic or dry pressure loss happens between reboiler and bottom tray.

$$P_{30} = P_{29}$$ [7.23]

(v) Component balance in both phases:

If both liquid and gas phases are completely separated, then sum of molar fraction of all component will be equal to the unity in each phase.

$$\sum_{i=1}^{2} x_{i,30} = 1$$ [7.24]

$$\sum_{i=1}^{2} y_{i,30} = 1$$ [7.25]

(vi) Energy balance:

If reboiler is totally insulated, so that no heat loss from the reboiler. Then, total heat input by liquid flow and electric heating will be equal to the total heat outlet from the condenser.

$$h_{30}.\frac{\partial HU_{30}}{\partial t} + HU_{30}.\frac{\partial h_{30}}{\partial t} + V_{30}.h_{30} + L_{30}.h_{30} - L_{29}.h_{29} + Q_{reb} = 0$$ [7.26]

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NUMERICAL METHOD FOR SOLVING NONLINEAR EQUATION SYSTEM

In equation containing x and y, separating of variables is not always easy. If we do not solve a equation for y, we call y an implicit function of x. Implicit function hard to solve analytically so they are solved by numerical method.

8.1 Newton method for single equation:

Newton method is an efficient method to find the root by finding a zero in function first derivative. It starts with an initial guess near the solution, and then replaces the function by its tangent and compute the zero of this tangent. This zero of tangent is a better approximation to the function's zero.
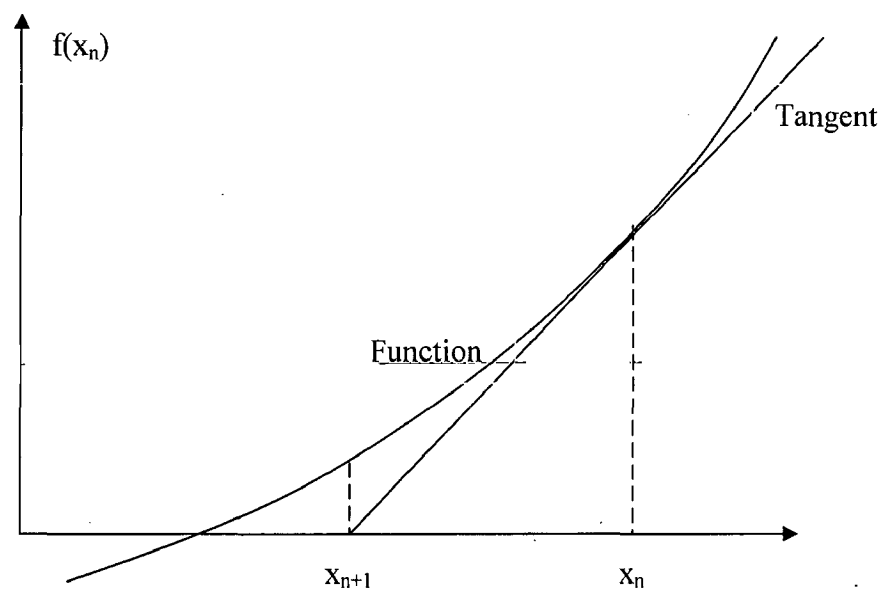
Fig 8.1 Newton method for solving equation with single variables

In the above figure, let we assume that our function has a solution near x_n, then draw a tangent on function from x_n and this tangent cut the axis at x_{n+1}, which is our new solution. If we repeat it in similar fashion, then solution will converge towards real solution. By the defnition of derivative,

$$f'(x_n) = \frac{0 - f(x_n)}{x_n - x_{n+1}}$$ [8.1]

or, $$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$ [8.2]

8.2 Newton Raphson method for equation system:

Newton Raphson method is used to solve the equation system. We applied Newton Raphson method for the solution of our mathematical model. Newton Raphson method for the equation system can be written as:

$$[g_{n+1}] = [g_n] - \frac{F[g_n]}{F'[g_n]}$$ [8.3]

Where, g_n is the initial values vector for the variables. $F[g_n]$ is the vector (F vector) of equation system's value for initial value of variables. $F'[g_n]$ is the value of derivative (Jacobi matrix) of the equation system with respect to variable's vector for initial value of variables.

(i) F vector:

F vector is a vector of all equation's value for the initial variable's values. F vector for a stage can be writing as:

$$F^k_{vector} = \begin{bmatrix} F^k_1 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_2 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_3 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_4 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_5 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_6 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_7 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_8 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \\ F^k_9 \ (FL^k, FV^k, y^k_1, y^k_2, HU^k, P^k, x^k_1, x^k_2, T^k) \end{bmatrix}_{(9\times1)}$$ [8.4]

$$\text{Complete F vector,} \quad F_{vector} = \begin{bmatrix} F^1_{vector} \\ F^2_{vector} \\ \cdots\cdots \\ F^{30}_{vector} \end{bmatrix}_{(270\times1)}$$ [8.5]

(ii) Jacobi matrix:

Jacobi matrix is matrix of partial derivative of system equations with respect to all variables for the initial variable's value. Partial derivative for a stage's equation with respect to stage variables:

$$A^k = \begin{bmatrix} \dfrac{\partial F^k_1}{\partial FL^k} & \dfrac{\partial F^k_1}{\partial FV^k} & \cdots & \cdots & \dfrac{\partial F^k_1}{\partial T^k} \\ \dfrac{\partial F^k_2}{\partial FL^k} & \dfrac{\partial F^k_2}{\partial FV^k} & \cdots & \cdots & \dfrac{\partial F^k_2}{\partial T^k} \\ \vdots & \vdots & \cdots & \cdots & \vdots \\ \vdots & \vdots & \cdots & \cdots & \vdots \\ \dfrac{\partial F^k_9}{\partial FL^k} & \dfrac{\partial F^k_9}{\partial FV^k} & \cdots & \cdots & \dfrac{\partial F^k_9}{\partial T^k} \end{bmatrix}_{(9\times9)}$$ [8.6]

We have to consider, the effects on n^{th} tray due to $(n-1)^{th}$ and $(n+1)^{th}$ trays or separation stage. C^k is the derivative of balance equations between n^{th} and $(n+1)^{th}$ tray with

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respect to $(n+1)^{th}$ stage's variable. Similarly, B^k is the derivative of equilibrium equations between n^{th} and $(n-1)^{th}$ tray with respect to $(n-1)^{th}$ stage's variable. So complete Jacobi matrix:

If A^i, B^i and C^i are submatrix for each stage and between the stages, then Comlete jacobi can be written as:

$$\text{Jacobi} = \begin{bmatrix} A^1 & C^1 & 0 & \cdots & 0 & 0 & 0 \\ B^2 & A^2 & C^2 & \cdots & 0 & 0 & 0 \\ \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots \\ \vdots & \vdots & \vdots & \cdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & \cdots & B^{29} & A^{29} & C^{29} \\ 0 & 0 & 0 & \cdots & 0 & B^{30} & A^{30} \end{bmatrix}_{(270 \times 270)}$$
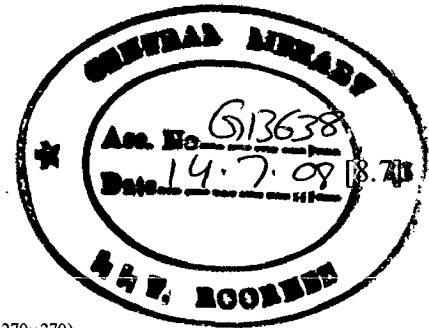
8.3 Checking of derivative (gradient) value:

To check that our calculated partial derivatives are correct our possible solution is to compare their values with numerically calculated gradient's values.

Numerical gradient:

Variable's vector $g = [g_1 \ g_2 \ g_3 \ \ldots \ldots \ g_n]$, with n variables

F vector for this set of variable $= F_{vector}^{old}$, value of all equations for these variables

Now, we make a very small change in any variable: $g_i = g_i + \dfrac{g_i}{C^\Delta}$ for $i = [0 \ldots \ldots n]$

F vector for this change in one parameter $= F_{vector}^{new}$

Numerical gradient of the equation system with respect to variable:

$$dg_i = \frac{F_{vector}^{new} - F_{vector}^{old}}{g_i \ / \ C^\Delta} \qquad [8.8]$$

Checking of gradient is necessary in order to see that our analytical gradient is correct or not. If, the analytical gradient is near to the numerical gradient, this means that derivative value or analytical gradient is correct.

$$\frac{\text{Numerical Gradient - Analytical Gradient}}{\text{Analytical Gradient}} \approx C^{limit} \qquad [8.9]$$

Where,

$C^\Delta = 10^5$

$C^{limit} = 0.01$

It has to be noticed that the selection of C^Δ and C^{limit} depend upon the exactness of the variables in the software used.

$$\frac{FL_1}{R \cdot \rho_D} - FL_1' = 0 \qquad\qquad [9.1]$$

$$FL_{30} \cdot \rho_B - FL_{30}' = 0 \qquad\qquad [9.2]$$

Where, FL_1 and FL_{30} are flow from condenser and reboiler in KMol/hr.

FL_1' and FL_{30}' are flow from condenser and reboiler in lit/hr.

ρ_D and ρ_B are density of distillate and bottom product respectively.

If F is the set of all equation and g is the vector of all variables then we calculate derivatives for all equations with respect to all variables.

$$\frac{dF}{dg} = \begin{bmatrix} \cdots & \cdots & \cdots & \cdot & \dfrac{\partial f_1^1}{\partial FL_1'} & \dfrac{\partial f_1^1}{\partial FL_{30}'} \\[2mm] & \text{Jacobi} & & : & \dfrac{\partial f_2^1}{\partial FL_1'} & \dfrac{\partial f_2^1}{\partial FL_{30}'} \\[2mm] \cdots & \cdots & \cdots & : & : & : \\[2mm] & & & & : & : \\[2mm] \dfrac{\partial f_{271}}{\partial FL_1} & \dfrac{\partial f_{271}}{\partial FV_1} & \cdots & \dfrac{\partial f_{271}}{\partial T_{30}} & \dfrac{\partial f_{271}}{\partial FL_1'} & \dfrac{\partial f_{271}}{\partial FL_{30}'} \\[2mm] \dfrac{\partial f_{272}}{\partial FL_1} & \dfrac{\partial f_{272}}{\partial FV_1} & \cdots & \dfrac{\partial f_{272}}{\partial T_{30}} & \dfrac{\partial f_{272}}{\partial FL_1'} & \dfrac{\partial f_{272}}{\partial FL_{30}'} \end{bmatrix}_{(272 \times 272)} \qquad [9.3]$$

We fixed the value of reflux ratio in our simulation and we want to the estimate reboiler duty, pressure parameter and stripping and rectification efficiencies. We calculate derivative of all equation with respect to four parameters.

$$\text{Parameter vector } U = [\, Q \quad C_W \quad \eta_V \quad \eta_A \,]_{(1 \times 4)} \qquad\qquad [9.4]$$

$$\frac{dF}{dU} = \begin{bmatrix} \dfrac{\partial f_1^1}{\partial Q} & \dfrac{\partial f_1^1}{\partial C_W} & \dfrac{\partial f_1^1}{\partial \eta_V} & \dfrac{\partial f_1^1}{\partial \eta_A} \\[2mm] \dfrac{\partial f_2^1}{\partial Q} & \dfrac{\partial f_2^1}{\partial C_W} & \dfrac{\partial f_2^1}{\partial \eta_V} & \dfrac{\partial f_2^1}{\partial \eta_A} \\[2mm] : & : & : & : \\[2mm] \dfrac{\partial f_9^{30}}{\partial Q} & \dfrac{\partial f_9^{30}}{\partial C_W} & \dfrac{\partial f_9^{30}}{\partial \eta_V} & \dfrac{\partial f_9^{30}}{\partial \eta_A} \\[2mm] \dfrac{\partial f_{271}}{\partial Q} & \dfrac{\partial f_{271}}{\partial C_W} & \dfrac{\partial f_{271}}{\partial \eta_V} & \dfrac{\partial f_{271}}{\partial \eta_A} \\[2mm] \dfrac{\partial f_{272}}{\partial Q} & \dfrac{\partial f_{272}}{\partial C_W} & \dfrac{\partial f_{272}}{\partial \eta_V} & \dfrac{\partial f_{272}}{\partial \eta_A} \end{bmatrix}_{(272 \times 4)} \qquad [9.5]$$

The value of dg/dU can be calculated by using above two Jacobi matrixes.

$$\frac{dg}{dU} = -inv\left(\frac{dF}{dX}\right).\frac{dF}{dU} \qquad [9.6]$$

We calculate parameter by the application of optimization. We use our experimental data and simulation for this parameter estimation. We took total 31 variables in the calculation. These are 29 temperatures for each stage and two flows for distillate and bottom product. Other variables like top pressure, condenser temperature, can be adjusted from outside, so we take only those variable which can be adjusted by simulation. Complete vector for measured value is given below.

$$y^{mess} = \begin{bmatrix} R_T \\ S_T^1 \\ : \\ : \\ S_T^{29} \\ FL_1^{'} \\ FL_{30}^{'} \end{bmatrix}_{(31\times1)} \qquad [9.7]$$

Where R_T is the reboiler temperature and S_T^i is the tray temperature of ith tray. Here tray counting is started from bottom to top.

9.2 Disturbance and uncertainties:

There are some disturbances and uncertainty present in the experimental data. We removed disturbances from the data by taking their average values for steady state. Uncertainty in the data present due to lack of exactness of measurement instrument or due to calibration effect. Uncertainty of data is used for the calculation of covariance matrix. We assume that data from experiment are normally distributed. If that assumption is justified then confidence interval for the data is given below.
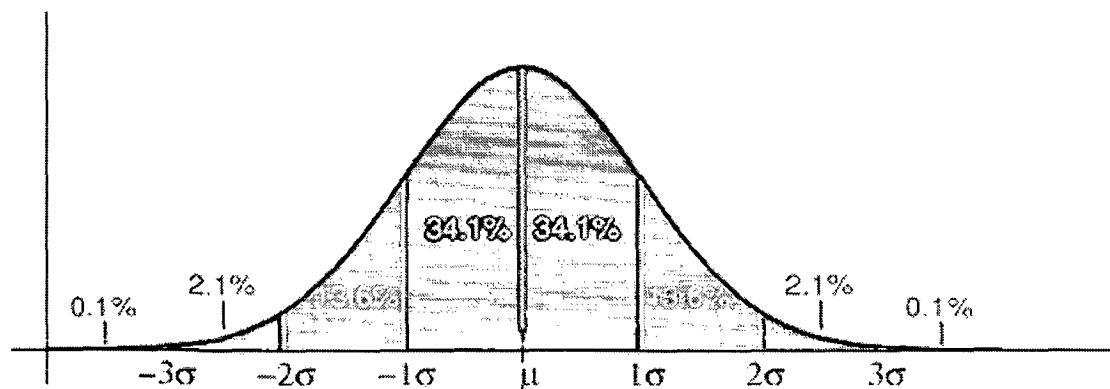

Fig 9.3 Standard deviation diagram

σ	68.26 %
2σ	95.44 %
3σ	99.73 %
4σ	99.99 %

We consider confidence interval 2σ for calculating the variance of all experimental variables, and take appropriate value of that variable so that nearly 95 % variations in that variable come inside the range.

Variable	95 % Uncertainty = 4σ	Standard deviation σ	Variance σ^2
Temperature	0.5 K	0.125	0.015625
Flow	2 l/hr	0.500	0.250000

If μ_T is the variance for all temperatures and μ_F is variance for all flows, then covariance matrix for all variables is given below.

$$cov = \begin{bmatrix} \mu_T & 0 & \dots & \dots & 0 \\ 0 & \mu_T & \dots & \dots & 0 \\ \dots & \dots & \dots & \dots & \dots \\ 0 & \dots & \dots & \mu_F & 0 \\ 0 & \dots & \dots & 0 & \mu_F \end{bmatrix}_{(31 \times 31)} \qquad [9.8]$$

9. 3 Objective function and objective function gradient:

If g (U, θ) is the vector of only those simulated variables, which are also present in the measured value vector y^{mess}, then objective for this optimization is to reduce the difference between variables for their experimental values and simulation values. We can either use least square method or maximum likelihood method. Least square method works well on the data with out uncertainty. Maximum likelihood method is better in the presence of uncertainty. So objective function for our problem is calculated as:

$$Fun = \sum \left[y^{mess} - g\ (U,\ \theta) \right]^T .inv(cov). \left[y^{mess} - g\ (U,\ \theta) \right] \qquad [9.9]$$

Simulated variables are function of parameter vector U and starting parameter set θ. Gradient for the above objective function can be calculated by differentiating the function with respect to parameter vector.

Let $\left[y^{mess} - g(x_0, U, \theta, t) \right] = \underline{x}$ & inv (cov) = A.

Then gradient of objective function:

$$Grad = \frac{d}{dU}(Fun)$$

$$Grad = \frac{d}{dU}(\underline{x}^T .A.\underline{x})$$

$$\text{Grad} = \underline{x}^T(A+A^T).\frac{dx}{dU}$$

$$\text{Grad}=\underline{x}^T(A+A^T).\frac{-dg}{dU} \qquad [9$$

9.4 Optimization by TOMLAB:

Before running the optimization, we require to find out the steady state in our experimental data. So we identify a time region for experimental plot with very little deviation.

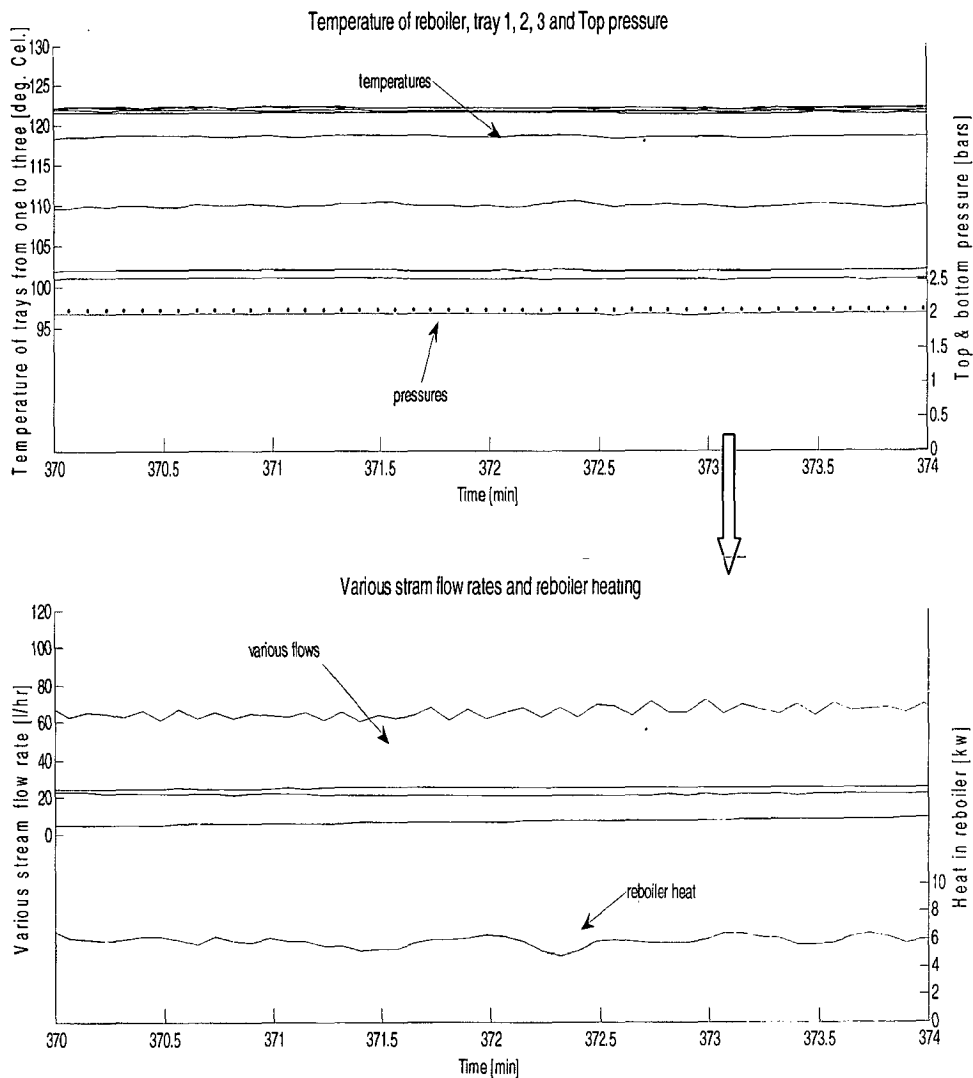Fig 9.4 Steady state for parameter estimation

In the first figure, some variables are plotted with respect to time. We select a time region in the first figure and plot second figure for this time interval and same variable. It is clear from second figure that variables are nearly constant for this time interval. We calculate the value of y^{mess}, which is the average value of variables for this time range.

We provide the function value and function's gradient value to the optimizer and at the same time we also check the error in the objective function gradient. If objective function gradient is not working, that mean our simulation is not converging. Error in the objective function gradient can be check after comparing it with the numerical error in the objective function gradient. Now we provide the initial, upper bound and lower bound value of parameter vector.

Initial value = [14.8 200 0.5 0.4]
Lower bound = [14.7 120 0.4 0.3]
Upper bound = [14.84 210 0.7 0.6]
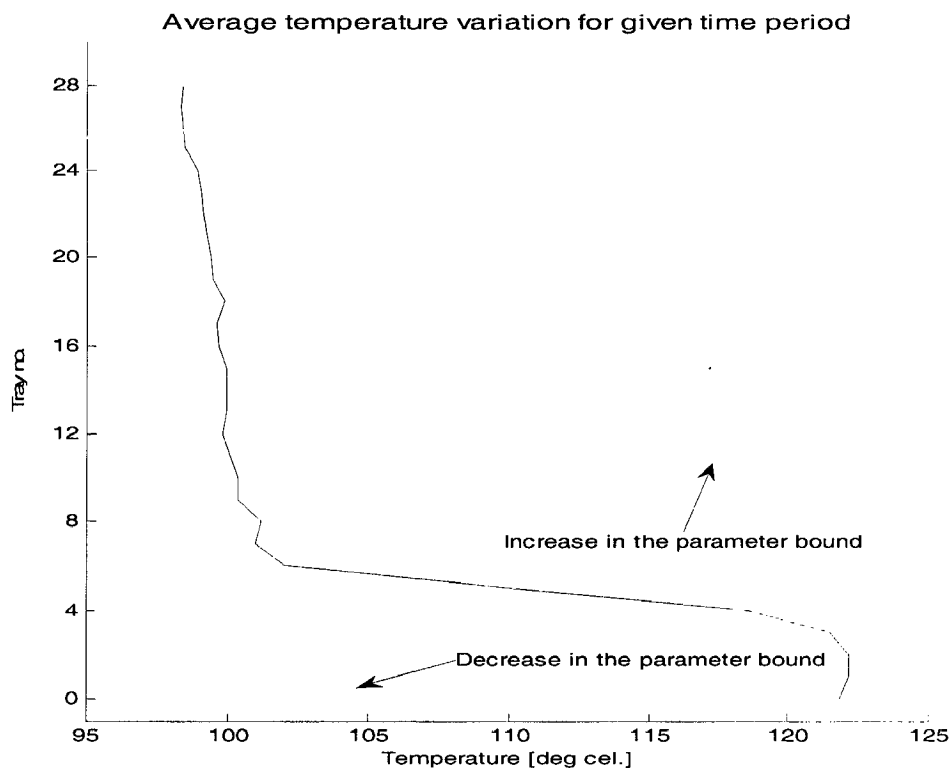
Fig 9.5 Temperature variation with change in parameter bound

Upper figure is showing direction of solution for decrease and increase in the bound value. We do not found any solution after a certain value of.upper and lower bound, because no distillation is possible outside this range. We also gave the maximum value (1000000) and minimum value of objective function (0).

Results:

If temperature profile from simulation is nearly matching with our experimental temperature profile, then new value of the parameters is the estimated value of the parameters.

Estimated parameter = [14.83 200.86 0.64 0.51]

Initial value of objective function = $8.6764814*10^4$

Total major iteration = 83

Final value of objective function = $4.1158122*10^2$

CONCLUSION

In this work, first we discussed about distillation column and standard operation procedure for the safe running of distillation column. After that we have discussed about the relation between the mixture composition and mixture density together with gas chromatography. If we know about the density of mixture, then mixture composition calculation based upon excess volume of mixing can be used for fast measurement of mixture composition without the help of gas chromatography.

Experimental studies on the column are conducted to control the pressure at the top of the column, to see the temperature variation inside the column and liquid level inside the condenser and reboiler section of the column. Pressure at the top of column is controlled by the cooling water flow inside the condenser. During most of the process, process control is working well and pressure difference between the top and bottom of the column is nearly constant with time. Affect on the bottom product, due to the change in feed conditions or column condition, can be reduced by controlling the temperature of a tray near to the bottom. Both levels are controlled by the help of PI controller. PI controller for level control inside the reboiler is working well in comparison to the controller for condenser level control.

A simplification in the mathematical model for the simulation of variables of column is also given in this work. We estimated some column parameter by the help of our steady state experimental results and simulated result based on this mathematical model. We selected four parameters for estimation due to different behavioural regions and applied maximum likelihood method for this estimation of parameter due to presence of uncertainties in experimental data. We minimized the difference between the experimental and simulated variables as the objective of our estimation and found the bound free value of parameters.

Recommendations for future work:

- A mathematical model for pressure control based on selected manipulated variables can be implemented.

- In the case of measurement problem for some variables, value of that particular variable (say feed flow rate) can also be estimated by the help of maximum likelihood method. It will require some changes in model because some measured variables are also an operational parameter.

- Condenser cooling efficiency can also be estimated by the help of experimental studies and heat transfer model for the condenser.

APPENDIX

11.1 Lisit of symbols and indexes

Latin letter:

A		Antoine coefficient
A	m^2	Tray area
A_q	m^2	Condenser area
B		Antoine coefficient
B	Kmol/hr	Bottom product flow rate
C		Antoine coefficient
Cov		Covariance
c_p	KJ/Kmol/K	Heat capacity
c_w		Pressure parameter
D	Kmol/hr	Distillate flow rate
e		Exponential
F	Kmol/hr	Feed flow rate
Fel		Error
F		Function
g	m/s^2	Gravity
HU		Hold up .
h^{weir}		Height of weir
ITZal		Number of iteration
Jac		Jacobi matrix
K		Equilibrium constant
L	Kmol/hr	Liquid flow rate
L^+	m	Extra height of liquid
l^{weir}	m	Longitude of fall
M	kg	Mass
MP	kg/Kmol	Molecular weight
NMAT		Dimension of matrix
n		Number of component
P	bar	Static pressure
$\dot{Q}$	KJ/s	Heat transfer rate
R		Reflux ratio
T	^0C or K	Temperature
T_{uk}	^0C	Temp. between reflux & top tray
t	hr or minute	Time
V	Kmol/hr	Vapor flow rate
V	m^3/kg	Molecular volume
v	m/s	Velocity
x		Molar fraction in liquid phase
x		Variable
y		Molar fraction in vapor phase

Greek letter:

α		Film resistance

η		Murphree tray efficiency
Δ		Difference
ρ	kg/m^2	Density
λ	N/m	Surface tension
$\lambda_{ij} - \lambda_{ii}$		Interaction parameter
ν	$Kg/m/s$	Viscosity
Λ		Wilson parameter

Subscripts:

A	Water
i	Component number
j	Number of tray
k	Column
l	Collocation point
W	Water

Superscripts:

*	Equilibrium value
aktiv	Active
av	Average
dry	Dry pressure
dyn	Dynamic
L	Liquid
stat	Static pressure
V	Vapor
Vek	Vector

11. 2 Computation of mixture characteristics:

(i) Average molecular weight: [kmol/kmol]

$$\tilde{M} = \sum_{i=1}^{n} x_i . \tilde{M}_i$$

(ii) Specific volume: [m³/kmo]

$$V_A = 1000 . \frac{p\_B_1^{1+\left(1-\frac{T}{p\_C_1}\right)^{p\_D_1}}}{p\_A_1}$$

$$V_w = p\_C_2 + p\_B_2 . T + p\_A_2 . T^2$$

(iii) Mixture density: [kmol/m³]

$$\rho_i = \frac{V_i}{\tilde{M}_i}$$

$$\rho^{av} = \frac{\sum_{i=1}^{n} x_i . M_i}{\sum_{i=1}^{n} \frac{x_i . M_i}{\rho_i}}$$

(iv) Antoine equation: [Tor]

$$\log_{10} P_i = A_i - \frac{B_i}{T + C_i}$$

(v) Heat capacity: [KJ/Kmol/K]

$$c_p = c_{p\_}A_i + c_{p\_}B_i . T^2 + c_{p\_}C_i . T^2$$

(vi) Wilson equation:

Total pressure in both liquid and gas phase is not same, due to the different composition in each phase. This is the relation between liquid and vapor phase.

$$x_i . \gamma_i . f_i^0 = y_i^* . j_i . p$$

&
$$f_i^0 = \varphi_{0i}^{LV} . p_{0i}^{LV} . \pi_{0i}$$

For pressure less than 10 bars, $\varphi_{0i}^{LV} / \varphi_i = 1$

$$x_i . \gamma_i . p_{0i}^{LV} = y_i^* . j_i . p$$

So equilibrium constant, $K_i = \dfrac{y_i^*}{x_i} = \dfrac{\gamma_i . p_{0i}^{LV}}{p_n}$

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} . x_2) + x_2 . \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} . x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} . x_1} \right)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} . x_1) + x_1 . \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} . x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21} . x_1} \right)$$

$$\Lambda_{12} = \frac{v_2^L}{v_1^L} . \exp\left(- \frac{\lambda_{12} - \lambda_{21}}{R . T_n} \right)$$

$$\&\quad \Lambda_{21} = \frac{v_1^L}{v_2^L}.\exp\left(-\frac{\lambda_{21}-\lambda_{12}}{R.T_n}\right)$$

(vii) Molar enthalphy: [KJ/Kmol]

Molar enthalpy for acetonitrile (i = 1)/ water (i = 2) :

$$cp\_A_i.T+0.5.cp\_B_i.T^2+\frac{1}{3}.cp\_C_i.T^3 - cp\_A_i.Tref-0.5.cp\_B_i.Tref^2 -\frac{1}{3}.cp\_C_i.Tref^3$$

(viii) Molara heat of vaporiztion: [KJ/Kmol]

Molar heat of vaporization for acetonitrile $= r\_A1.\dfrac{\left(1-\dfrac{T}{Tcrit\_1}\right)^{r\_B1}}{1000}$

Molar heat of vaporization for water $= r\_A_2 + r\_B_2.T + r\_C_2.T^2$

11.3 Geometric explanation of column:

(i) Condenser:
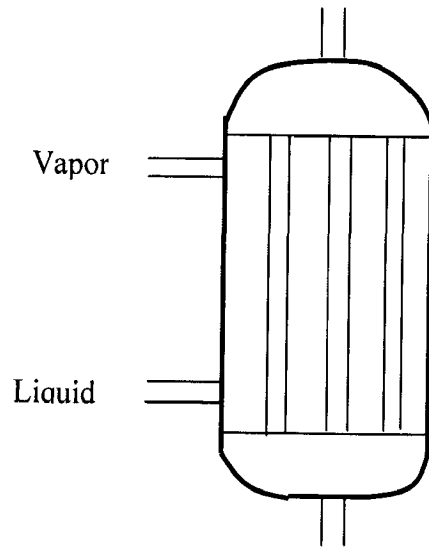
At steady state, liquid inside the condenser is equal to hold up.

Liquid inside the condenser $= A_q.l^{Kond}.\rho_1^L$

$\qquad$ Hold up $= HU_1.M_1^{\%avg}$

$\qquad A_q.l^{Kond}.\rho_1^L = HU_1.M_1^{\%avg}$

Where, Condenser height, $l^{Kond} = 1$ m

$\qquad$ Condenser area, $A_q = \Pi.d.l^{Kond} \times N$

$\qquad$ Outer diameter of tube, d = 0.01

$\qquad$ No of tube = 15,

(ii) Trays:

$\qquad$ Inside column diameter = 0.15 m

$\qquad HU_j.M_j^{\%avg} = (V_{j,stat}^L + A_j.L_j^+).\rho_j^L$

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Height of liquid over weir, $L_j^+ = 750.\left[\dfrac{L_j.M_j^{0avg}}{\rho_j^L.l_j^{weir}}\right]^{\left(\frac{2}{3}\right)}$ **(Francis weir formula)**

Tray area, d = 0.107 m

Area of tray, $A_j = \dfrac{\Pi}{4}.d^2$ m^2

Active tray area = 8. 987465 × 10^{-3}

Longitude of weir, l^{weir} = 0.025 m

Height of weir, h^{weir} = 0.028 m
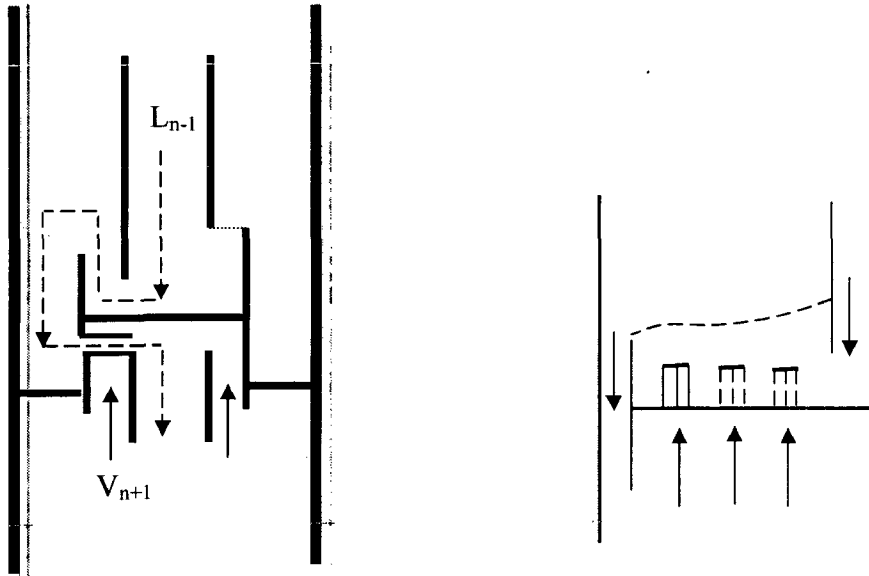
(iii) Reboiler:
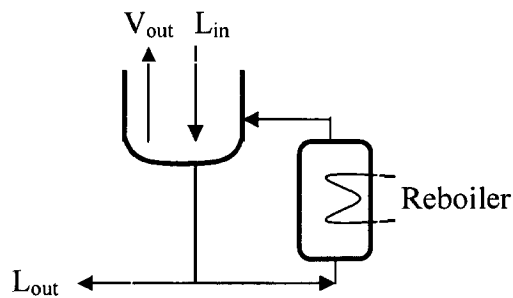
Liquid inside the condenser $= A_q.L_{30}.\rho_{30}^L$

Hold up $= HU_{30}.M_{30}^{0avg}$

At steady state, liquid inside the condenser is equal to hold up.

$A_q.L_{30}.\rho_{30}^L = HU_{30}.M_{30}^{0avg}$

Volume in the bottom of column = 6 liter

Volume in the heating part = 12 liter

11.4 Tables:

(i) Data for computation of mixture characteristics:

Molecular weight

$\tilde{M}_A = 41.053$ $\tilde{M}_w = 18.0153$

Specific volume:

Component	ρ_A_i	ρ_B_i	ρ_C_i	ρ_D_i
Acetonitrile (1)	1.3088	2.2642×10^{-1}	5.455×10^2	2.8128×10^{-1}
Water (2)	6.4031×10^{-5}	-3.36×10^{-2}	2.24035×10^1	

Antoine equation:

Component	A_i	Bi	C_i
Acetonitrile (1)	7.33986	1.48229×10^3	2.50523×10^2
Water (2)	8.07131	1.73063×10^3	2.33426×10^2

Heat capacity:

Component	$c_p\_A_i$	$c_p\_B_i$	$c_p\_C_i$
Acetonitrile (1)	9.7582×10^1	-1.222×10^{-1}	3.4085×10^{-4}
Water (2)	1.06975×10^2	-1.913×10^{-1}	2.8882×10^{-4}

Wilson equation:

$|\lambda_{12}-\lambda_{11}| = 6.439541 \times 10^2$ $|\lambda_{21}-\lambda_{22}| = 1.3880606 \times 10^3$

Component	v_i^L
Acetonitrile (1)	52.86
Water (2)	18.07

Molar enthalpy:

Component	$c_p\_A_i$	$c_p\_B_i$	$c_p\_C_i$
Acetonitrile (1)	97.582	-0.1222	3.4085×10^{-4}
Water (2)	106.9750	-0.1913	2.8882×10^{-4}

Molar heat of vaporization:

Component	r_A_i	r_Bi	r_C_i
Acetonitrile (1)	4.31×10^7	0.3354	-
Water (2)	-0.0908	18.6793	$4.63761 0^4$

(ii) Standard operation procedure:

In Basement:

- Switch on light near steps in basement and light in the basement.
- Cooling water supply to whole column and put bucket below the valve so after shut down the plant any extra liquid drop into the bucket due to back pressure
- Insert tube to the bottle at the tank to collect condense (venting) AN from all tank
- O – Open and C – Closed

(A) BASEMENT:

Feed from tank 1:

		Part of Plant	Process	Description
H 13	Open	Y	Y	Feed from tank 1 to pump 1
H 36	Closed	Y		For pump working and VU_2 for recycle
H 37	Closed	Y		To stops any flow between tank1 and tank 6
H 28	Open	Y		To complete recycling of VU_2
H 9	Closed	Y		To take a sample

Bottom product: (Pump 101→ VS 101→ after cooling, TIR 101→ Tank 1, recycle feed)

VM 109	Closed		Y	To stop HP residue into feed tank 2
VH 125	Closed	Y	Y	To stop HP residue into feed tank 2
VM 210	Open		Y	For HP residue into feed tank 1
H 210	Open	Y	Y	For HP residue to feed tank 1
VM 127	Closed	Y		To stop HP residue into HP residue tank 3
H 127	Closed	Y	Y	To stop HP residue into HP residue tank 3
VM 216	Closed	Y		To stop HP residue into LP residue tank 5
H 216	Closed	Y		To stop HP residue into LP residue tank 5
H 204	Closed	Y		To take a sample from bottom product of low pressure column

Top product: (Pump 102→ VS105→ after cooling, TIR 136→ Tank 1)

VM 113	Closed	Y	Y	To stop HP distillate into feed tank 2
H 126	Closed	Y	Y	To stop HP distillate into feed tank 2
VM 114	Open	Y	Y	For HP distillate to tank 1
H 124	Open	Y	Y	For HP distillate to tank 1
H 128	Closed			To stop HP distillate into HP distillate tank
H 130	Open	Y	Y	For HP distillate to tank 1
H 25	Closed			To stop side stream from HP distillate
H 205	Closed	Y		To take a sample from distillate of HPK

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Others valve:

H 105	Closed	Y		To stop LP distillate into any tank
H 207	Closed	Y		To stop LP distillate into any tank
H 38	Closed	Y		Between HP distillate and LP reboiler
H 201	Closed	Y		Between LP distillate and feed HP

- Valve H 38 and H 201 are below the high-pressure column.
- All sample valves should be closed.
- Sample valve in the bottom of H P column (reboiler) is also closed.

(B) GROUND FLOOR:

H 35	Closed	Y		This is directly connect to pump 2
VM 211	Open		(Y)	Cooling of LP distillate vapour; always open
H 101	Closed	Y		Between HP residue and feed LP; front of the column
VM 101 - 5	Open / Closed		(Y)	Feed into lower portion of HP
VS 4 (100 %)	Open, hand			To enter feed into lower part of KLP (never used to send feed into upper part of column)
VS 1	Open, auto		Y	Valve below the preheater 1 , Feed control
VS 2	Closed,hand		Y	Valve below the preheater 2
H 100	Closed		y	To supply feed to the top of KHP for the shut down of the plant

- Open, 7 red valve for the water supply in various condensers, back of the column
- Both blue valve to supply Nitrogen to the controller should be closed (front of column)
- PIR 101; Pressure difference valve, blue valve

(C) FIRST FLOOR: Valve H 34 – Closed, distillate from KLP, first floor

To give feed to the upper part of column:

H 1 (VH1)	Closed	Y	Y	Feed 1 to KLP
H 2 (VH 2)	Closed	Y	Y	Feed 2 to KLP
H 3 (VH 3)	Open	Y	Y	Feed 1 to KHP
H 4 (VH 4)	Open	Y	Y	Feed 2 to KHP ; (wrong indicate in PLS)
H 122	Closed	Y	Y	Feed to the lower part of KLP
H 121	Closed	Y	Y	Prevent connection between feed line to the reflux of KHP or condenser (H 119 open) for shut down
VM 1	Closed		Y	To stop feed from top of preheater 1 back to the feed tank1
VM 3	Closed		Y	To stop feed from top of preheater 2 back to the feed tank 2.
H 32	Closed			To stop feed from preheater 2 to KLP
H 33	Open	Y		Between preheater 2 and top of KLP

To give feed to the lower part of column:

H 1	Closed	Y	Y	Feed 1 to KLP
H 2	Closed	Y	Y	Feed 2 to KLP
H 3	Open	Y	Y	Feed 1 to KHP
H 4	Closed	Y	Y	Feed 2 to KHP
H 122	Open	Y		Feed to the lower part of KLP
H 121	Closed	Y	Y	Prevent connection between feed line to the reflux KHP or condenser (H 119 open) for shut down
VM 1	Closed		Y	To stop feed from top of preheater 1 back to the feed tank
H 201 (basement)	Closed	Y		Connected to the bottom product of KLP
H 108 (2nd floor)	Closed	Y		To feed to the upper most part of the column

- Bypass cooling water 3 turns open

(D) SECOND FLOOR:

H 117	Open	Y		Between HP distillate condenser and atmosphere
H 118	Open	Y		Between HP distillate condenser and atmosphere.
H 209	Open	Y		Between condenser of KLP and atmosphere
H 119	Closed	Y		Between HP reflux and condenser of KHP
H 114	Open	Y	Y	From top of KHP to condenser
H 113	Closed	Y		To heat exchanger from top of KHP
H 116	Closed	Y		From top of condenser to the atmosphere
H 115	Open	Y		From bottom of condenser to the atmosphere
H 120	Open	Y		Reflux valve by VS 4 feed to the top of KHP (then closed)

- Flow restrictor (black) – open three turns

(iii) List of valves which make connection to LP Column:

Valve	Action	Description
H1, H2, VS3	Closed	To feed into low pressure column
H31, H32	Closed	Connection between preheater 2, HP distillate and feed to the upper part of LP column
H 101	Closed	between HP bottom product and feed HP
H201	Closed	Between LP bottom product and feed Lp
H117	Closed	For inertization of LP column
H209	Closed	Connection of LP condenser to the atmosphere
H 35	Closed	Pump 2 and top of the low pressure column

(iv) Valves to take samples:

Valve	Action	Description
VH 0 (two)	Closed	Sample from upper part of sammel tank
VM 7	Closed	Sample from lower part of sammel tank
VM 5, VM 6	Closed	Sample from feed tank 2 and tank 1
H 104	Closed	Sample from HP bottom product
H 105	Closed	Sample from HP distillate
H 204	Closed	Sample from LP bottom product
H 205	Closed	Sample from LP distillate
H 7	Closed	Sample from tank 1
H 8	Closed	Sample from tank 2
H 12	Closed	sample fro tank 1 or tank 2 or tank 3 or tank 4
H 22	Closed	Samples from HP distillate
H 44	Closed	Samples from the line between tank 1 and tank 6

(v) Important security limits for upper two parts / units:

Sensor	Description	Security level	Security system action
TIR 140	Maximal permissible cooling water temperature after connection of sub pipelines	70 [^{0}C]	Open the valve VS 102 totally
TIR 142	Maximal permissible cooling water temperature on the outlet of condenser	120 [^{0}C]	Open the valve VS 102 totally & disables the reboiler duty
FIR 103	Average minimal permissible flow rate of the cooling water in the condenser cooling section	30 [l/h]	Open the valve VS 102 totally
PIR 103	Maximal permissible pressure at the top of the column	4.5 [bar]	Open the valve VS 102 totally
PIR 103	Extreme pressure at the top of the column	5 [bar]	Disables the reboiler duty & Opens the security valve at the top of the column

(v) Mole fraction Vs density data for different temperature:

Mole fraction of acetonitrile	T = 35 ^{0}C	T = 25 ^{0}C	T = 15 ^{0}C	T = 5 ^{0}C
0	994.06	997.07	999.13	999.99
0.05	974.4	977.9	984.2	988.1
0.10	954.4	958.6	967.3	972.5
0.15	935.0	939.9	949.8	955.7
0.20	916.7	922.3	932.7	939.0
0.25	899.7	906.2	916.6	923.2
0.30	884.2	891.5	901.8	908.7
0.35	870.2	878.2	888.3	895.7
0.40	857.5	866.2	876.2	884.1
0.45	846.0	855.2	865.3	873.7
0.50	835.5	845.1	855.3	864.2
0.55	825.9	835.7	846.1	855.3
0.60	817.0	827.0	837.6	847.1
0.65	808.7	818.7	829.6	839.2
0.70	800.9	811.1	822.0	831.8
0.75	793.7	804.0	815.0	824.8
0.80	787.0	797.5	808.5	818.4
0.85	780.8	791.6	802.6	812.5
0.90	775.2	786.3	797.2	807.4
0.95	770.2	781.3	792.3	802.6

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