STUDIES ON DIVIDED WALL DISTILLATION COLUMN

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by

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Dedicated

to my parents

CERTIFICATE

This is to certify that thesis entitled "STUDIES ON DIVIDED WALL DISTILLATION COLUMN", being submitted by Mr. Vikas Kumar Sangal, to the Chemical Engineering Department, Thapar University, Patiala for the award of degree of DOCTOR OF PHILOSOPHY, is a record of bonafide research work carried out by him. Mr. Vikas Kumar Sangal has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results embodied in the thesis have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

Distillation is the most employed, but also the most energy-intensive separation method being used in chemical process industry. Therefore, the efficient design of the distillation process is important so as to reduce the energy requirement without compromising with the product quality. Divided wall column (DWC) is an innovative design in this direction where two or more simple columns are thermally coupled into one column by providing a vertical wall, dividing the core in two parts that work as the pre- or post-fractionator column and the main column. Thermodynamically, a DWC can be considered as an equivalent of Petlyuk column; the only difference being that a DWC is built in only one shell, whereas a Petlyuk column consists of two or more columns.

Simulation of a DWC is a challenging task, as it involves many connecting streams making the problem highly non-linear. Further, simulation of a DWC requires simultaneous solution of material, momentum and energy balance equations. For a simple distillation column, the momentum balance equations are important only at the mechanical design stage for the estimation of effects of pressure drop whereas these are usually neglected during theoretical design (simulation) stage as its impact on vapour-liquid equilibrium is not appreciable.

The optimal design of a DWC is obtained by minimizing the energy duty, as it accounts for the major fraction of the operating cost. The design variables such as reflux ratio and split ratios interact with each other and need to be optimized simultaneously for optimal operation and design. The optimization of the DWC operation cannot be handled with the existing commercial simulation software without coupling them with an external sub-routine/ software for optimization. The structural and process parameters of a DWC are generally optimized separately and there are no reports in the open literature on the simultaneous optimization of the structural and operating parameters of a DWC.

The present thesis reports about the modelling of a DWC, the rationalization of the degree of freedom analysis, the effect of column pressure drop, the effect of feed quality

and the optimization of energy requirement for a ternary system. A mathematical model was developed for a DWC by applying the conventional MESH equations plus the pressure drop (ΔP) equation, taken together as MESHD equations. Rigorous simulation of this DWC was carried out using Multifrac model of ASPEN Plus™ software (for solving MESH equations). For calculating the pressure drop, 'Tray Rating' feature of ASPEN Plus™ was used. Box–Behnken design (BBD) under response surface methodology (RSM) was used for the optimization of the design and operational parameters and to evaluate the effects of these parameters and their interactions on the energy efficiency of a DWC.

The importance of pressure drop in a DWC was analyzed theoretically by attempting to relate the 'natural' or 'feasible' vapour split as a function of pressure drop, reflux ratio and the liquid split ratio of a DWC. Benzene-toluene-para-xylene (BTX) separation was taken as the case study. The results are interesting in that they show virtually no effect of liquid split ratio on the feasible vapour split ratio. Significantly different pressure drops are obtained at the same internal vapour flow rate in the two sides of the DWC, and even a slight variation in the vapour flow rate leads to a large variation in the concentration profile of the components. The tray hydraulics plays an important role in the performance of a DWC. It was concluded that the pressure drop should be taken as one of the key parameters for the optimal design of a DWC.

The effect of feed (thermal) quality on the performance of a DWC was also studied. The feed quality was varied from the superheated vapour to sub-cooled liquid feed. It was observed that the feed quality influences the pressure drop across the feed side of the divided wall which in turn affects feasible vapour split ratio. However, the vapour split ratio is almost independent of liquid split ratio and reflux flow rate for sub-cooled and saturated liquid feed. For saturated vapour and superheated feeds, liquid split ratio has appreciable influence on the feasible vapour split ratio. It was also observed that the equalization of pressure drop leads to nearly equal vapour flow rate on both the sides of the DWC when a sub-cooled or a saturated liquid feed is introduced in the DWC.

The BBD under RSM was used to optimize the parametric values for obtaining the optimum energy efficiency for a specified separation using a DWC for different thermal quality of feed. Optimization of a DWC was carried out to study the product quality and energy efficiency as a function of reflux rate, liquid spilt and vapour split. It was also targeted that the difference between the pressure drops across the two sections of the divided wall remains zero. The reflux rate and vapour split are highly significant for the reboiler duty of a DWC and for the pressure drop across the dividing wall as compared to liquid split.

The structural and process parameters of a DWC were optimized simultaneously for the energy efficiency, for the separation of a specified ternary mixture. The system has nine structural variables and four process variables including the location of the feed tray, the location of the side stream tray, and the number of trays in the main column and in the post-fractionator, location of the divided wall, number of trays in the divided wall section, reflux rate, liquid spilt, vapour split and the feed quality. These variables were used for the optimization of the product purities and the reboiler and condenser duties. The process variables were found to have significant effect on the energy efficiency of a DWC as compared to the effect of structural variables. The predictions from the BBD optimization agreed well with the results of the rigorous simulation. Optimization by BBD under response surface methodology (RSM) vividly underscores the effects of different parameters and their interactions on the energy efficiency of a DWC. This method may prove to be very useful for the industrial operation of a DWC, as it requires a fewer number of simulation runs and can be carried out in a shorter time.

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NOMENCLATURE

A_h	Total cross-sectional area of all the holes on a tray, m^2
ANOVA	Analysis of variance
B	Bottom product
BBD	Box-Behnken design
C	Number of components
C_0	Orifice coefficient
c_p	Replicate number of the central point
CPI	Chemical process industry
DWC	Divided wall distillation column
D	Distillate
D_e	Equivalent diameter, m
D_s	Shell side diameter, m
D_t	Column diameter, m
d_h	Hole diameter, m
DOF	Degree of freedom
f°	Friction factor
F	Feed flow rate, kmol/h
FTCDC	Fully thermally coupled distillation columns
g	Acceleration due to gravity, m/s^2
H	Enthalpy of vapour, kJ/mol
h	Enthalpy of liquid, kJ/mol
h_d	Pressure drop across the dry plate, m
h_{ow}	Height of the liquid crest over the weir, m
h_r	Residual liquid head, m
ht_i	Liquid head equivalent to the pressure drop between i^{th} tray and $(i\text{-}1)^{th}$ tray
h_w	Weir height, m
H_f	Feed enthalpy, kJ/mol
$(H_v - H_f)$	Heat required to make the feed as saturated vapour
$(H_v - H_L)$	Latent heat of vaporization of the feed mixture
HK	Heavy key
K	Equilibrium constants

l	Component flow rates in liquid phase, kmol/h
L_i	Flow rate of liquid leaving from the i^{th} tray, kmol/h
Ls	Liquid side stream flow rate, kmol/h
L_{NS1}	Liquid flow rate to stage number N_{S1}+1 of section 1, kmol/h
L_w	Liquid flow rate, kg/s
L_{23}	Liquid leaving tray number 23
L_{23} - Ls	Liquid entering tray number 24
L_P	Liquid connect stream from column 2 to column 1
LK	Light key
M_L	Average molecular weight (kg/kmol) of the liquid stream
M_V	Average molecular weight (kg/kmol) of the vapour stream
MW_j	Molecular weight of the j^{th} component in the liquid stream
MESH	Material balance, vapour-liquid equilibrium, summation, and enthalpy (H) balance
MESHD	Conventional MESH equation plus the pressure drop equations
MK	Middle key
N	Number of trays (stages) in section 1 including condenser and reboiler
N_{exp}	Number of experiments or simulation runs required
N_{Pass}	Number of tube passes in the reboiler
N_{s1} (L location)	Tray number from where the liquid side stream Ls is withdrawn
N_{s2} (V location)	Tray number from where the vapour side stream Vs is withdrawn
$(N_{s2} - N_{s1})$	Number of trays in the postfractionator section
N_{s3}	Tray number from where the middle product S_3 is withdrawn
N_T	Total number of trays (stages) in section 1 and section 2, including condenser and reboiler
P	Pressure, kPa
P_i	Absolute pressure above i^{th} tray, kPa
ΔP	Pressure drop, kPa
ΔP_{Re}	Pressure drop in the reboiler, kPa
ΔP_1	Pressure drop in section 1, kPa
ΔP_2	Pressure drop in section 2, kPa
q	Feed quality
Q_B	Reboiler duty, kW

Q_C	Condenser duty, kW
r	Reflux rate, kmol/h
R	Reflux ratio
R_1	Liquid split ratio
R_2	Vapour split ratio
RSM	Response surface methodology
S	Side stream
S_3	Middle product flow rate, kmol/h
t_p	Plate thickness, m
T	Absolute temperature, K
TCDS	Thermally coupled distillation sequences
u_h	Vapour velocity through sieve tray holes, m/s
v	Component flow rate in vapour phase, kmol/h
V_i	Flow rate of vapour leaving the i^{th} tray, kmol/h
Vs	Side stream Vapour flow rate, kmol/h
V_{NS2}	Vapour flow rate going to stage N_{S2}-1 of section 1, kmol/h
V_{59} - Vs	Vapour entering the tray number 58
V_{59}	Vapour leaving the tray number 59
V_P	Vapour connect stream from column 2 to column 1
VLE	Vapour-liquid-equilibrium
W_L	Weir length, m
x	Component mole fraction in liquid phase
y	Component mole fraction in vapour phase
Y	Response
Subscripts	
f	Feed plate location
i	Stage number from where the stream is originating
j	Component number
Greek letters	
ϕ_S	Ratio of viscosity of liquid to the viscosity of water
ρ_L	Density of liquid, Kg/m^3
ρ_v	Density of vapour, Kg/m^3
σ_L	Surface tension of liquid, N/m

Chapter –I

INTRODUCTION

1.1 General

Efficient design of separation systems is the key to success in chemical process industry (CPI). Distillation is still the bulwark of the separation technology in CPI, even when important developments have taken place in new separation technologies during the past decades. Distillation is used for about 95% of liquid separations in CPI, and the energy used for this accounts for an estimated 3 % of the world's total energy usage (Hewitt et al., 1999). Therefore energy-efficient distillation design and operation are the major concerns in CPI. Distillation is also one of the most capital- intensive unit operations. Driven by global industrial development, distillation units are growing both in number and size of applications (Olujic et al., 2009).

Distillation is well suited for the separation of high purity products from a liquid mixture since Any degree of separation can be obtained by increasing the number of trays or height of the packings in a single column. For more than two components in the mixtures (or mixtures forming azeotropes) cascading of more than one distillation column is required.

A simple distillation column with a feed and two products, i.e. overhead and bottom products, can be made to perform better, by employing improved operation and control strategies, by using more advanced column internals. The options are particularly interesting because they allow capacity and/or efficiency increase (reduction of specific energy requirement) of existing columns at minimum investment. Considerable energy savings can be expected only from implementing energy saving concepts in new designs.

The implementation of highly efficient energy saving technologies makes the distillation more capital intensive. Typical example is the employment of heat pump assisted distillation, which obviates the use of an external heat source in the reboiler. The use of a compressor, makes it a high- investment proposition. It can, therefore, be a viable proposition only when used in a high throughput column with end of the train (practically binary) separations of close boiling mixtures which account for minimum compressor/compression effort-related costs. This appeared to be the case mainly with separation of rather light hydrocarbons, like C_2, C_3 and C_4 components, where adiabatic compression power exponent of substances is large enough to effect significant temperature rise by a relatively low compression effort. More costly and risk associated options include the implementation of theoretically and experimentally proven, but industrially not yet applied, column configurations that offer potential for energy savings more than that obtained with conventional heat pump- assisted distillations. Typical example is the so-called internally heat integrated column, which, by combining direct vapour recompression with uniform distribution of heat duty along the integrated part of the column allows minimization of energy requirement of a distillation column. However, being a heat pump assisted process requiring a heavy and reliable heat transfer infrastructure, a heat integrated column becomes a complex and highly capital intensive column configuration (Olujic et al., 2006).

In binary distillation, a feed mixture of two components is separated into two products, including and often limited to an overhead distillate and a bottom product, whose compositions differ from that of feed. Most often, the feed is a liquid or a vapor-liquid mixture. The bottom product is almost always a liquid, but the distillate may be liquid or vapor or both.

1.2 Multicomponent Distillation

For the separation of more than two components from a liquid mixture, a sequence of columns needs to be employed. A single distillation column cannot separate more than one component in a reasonably pure form from a multicomponent mixture. For separation of N components from a liquid mixture, (N-1) columns will have to be employed in a sequence.

In the classical direct sequence arrangement for separating ternary mixtures consisting of A, B and C, (Fig. 1.1 a), the feed is introduced to the first column where the lowest-boiling (most volatile) component A is recovered as the top product. The bottom product is fed to the second column where the medium-boiling component B is distilled off as the top product and the high-boiling component C remains as the bottom product (residue). The purity of A, B and C will depend on the column internals, reflux ratio, etc. Alternatively, the indirect sequence (Fig. 1.1 b) may be applied, where the high-boiling component C is obtained as the residue of the first column and the low- and medium-boiling fractions consisting of A and B are obtained as the top and bottom products of the second column.

The optimum column sequence is selected after the consideration of the requirements to be met, e.g. the quantity of the individual fractions, the relative volatility and the thermal stability of the components, the available utilities, etc., so that the investment and operating costs are minimized (Kolbe and Wenzel, 2004). The column sequencing leads to an increase in the energy requirement. Therefore, the heat integrated column arrangements are preferred which entail savings of approximately 30-40% in the energy requirement. The thermal coupling of columns leads to a reduction in the energy requirement.

The thermally coupled distillation column is thermodynamically equivalent to a divided wall distillation column (DWC). The DWC offers an alternative to conventional distillation column, with the possibility of savings in both energy requirement and capital costs.

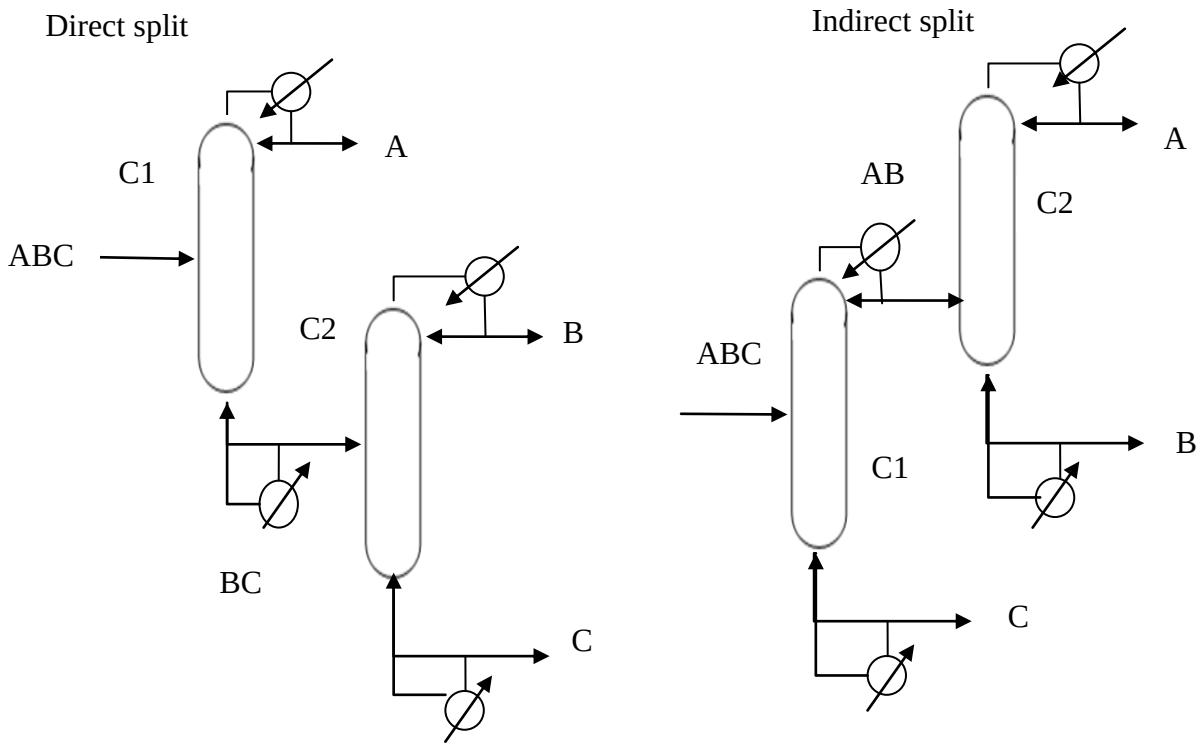

Figure 1.1: Sequencing of two columns for the separation of a ternary mixture, (a) Direct Sequences (b) Indirect sequence.

1.3 Thermally Coupled Columns

In an alternative procedure, ternary mixtures can be separated in thermally coupled columns (Fig. 1.2). The first thermally coupled distillation system was patented by Wright (1949). Detailed theoretical study of thermally coupled column was provided by Petlyuk et al. (1965) who suggested that a thermally coupled column can be a novel alternative to the two-column distillation configuration, as shown in Fig 1.1. They used a ‘prefractionator’ and a ‘main column’ for effective separation of components from a ternary mixture. As shown in Fig.1.2, the ‘prefractionator’ has three feed streams: (i) the ternary mixture containing A, B and C as the main feed to the column, (ii) a liquid stream from the upper

part (rectification section) of the main column, and (iii) a vapour stream from the lower part (stripping section) of the main column. The vapour, containing mainly A and B, goes from the prefractionator to the rectification section of the main column and the liquid, having mainly B and C, flows into the stripping section of the main column.

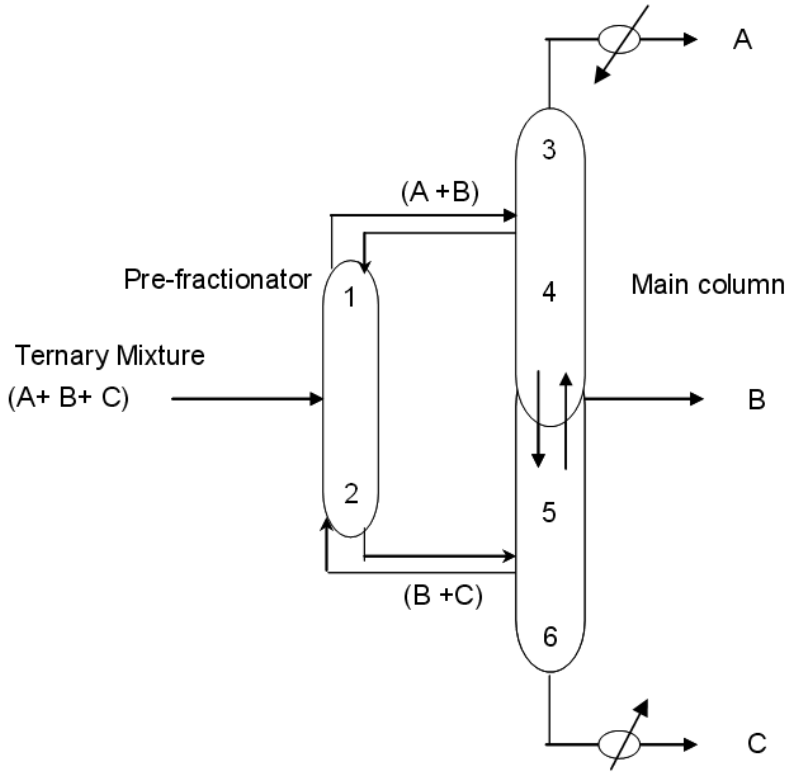

Figure 1.2: The integrated Petlyuk column arrangement for separation of components of a ternary mixture.

With the configuration as shown in Fig. 1.2, the main column separates components A and B more efficiently in the upper part, and B and C in the lower part. The peak concentration of component B attains a much higher value in the middle of the main column than that in column 2 of Fig. 1.2, with the same number of stages as that in the cascaded column.

The medium-boiling fraction consisting of mainly B accumulates in the main column and is taken as a side draw, the purity of which can be varied as desired. Compared to the conventional cascaded columns, the thermally coupled columns require

only one heating or condensing device for both the columns. In addition, the thermodynamic advantages of this kind of arrangement over conventional sequenced fractionation result in lower energy requirements. The reason for this improvement in energy requirement is the avoidance of remixing of internal streams, which in two columns in series arrangements exhibits concentration peaks of middle boiling component either above or below the feed. Additional gain in this respect comes from the fact that the prefractionator arrangement, which distributes the intermediate component between top and bottom, allows greater freedom to match the feed composition with a tray in the column to further reduce mixing losses at the feed tray. This mixing as well as remixing of the streams with different compositions that occurs at feed point and along the column, are accompanied by entropy of mixing formation. This is an intrinsic source of thermodynamic inefficiency of the separation process taking place in a multicomponent distillation column. The Petlyuk system has a first law (of thermodynamics) advantage (low utility requirements) but a second law disadvantage (wide range of operational temperature).

The utilization of a Petlyuk column is not limited only to ternary mixtures. In general, a Petlyuk column is: “A column arrangement, separating three or more components using a single reboiler and a single condenser, in which any degree of separation (purity) can be obtained by increasing the number of stages, provided the reflux is above a certain minimum value and the separation is thermodynamically feasible” (Christiansen et al., 1997).

The original Petlyuk column, having a prefractionator with the main column or a main column with a postfractionator can be considered as a thermally coupled arrangement. Fig. 1.3 shows the thermally coupled column arrangement with a prefractionator and a postfractionator.

Thermally coupled distillation schemes are viewed as a promising alternative to conventional distillation scheme due to the appreciable energy and capital savings of some of these designs as compared to conventional ones (even > 30 % in total annual cost).

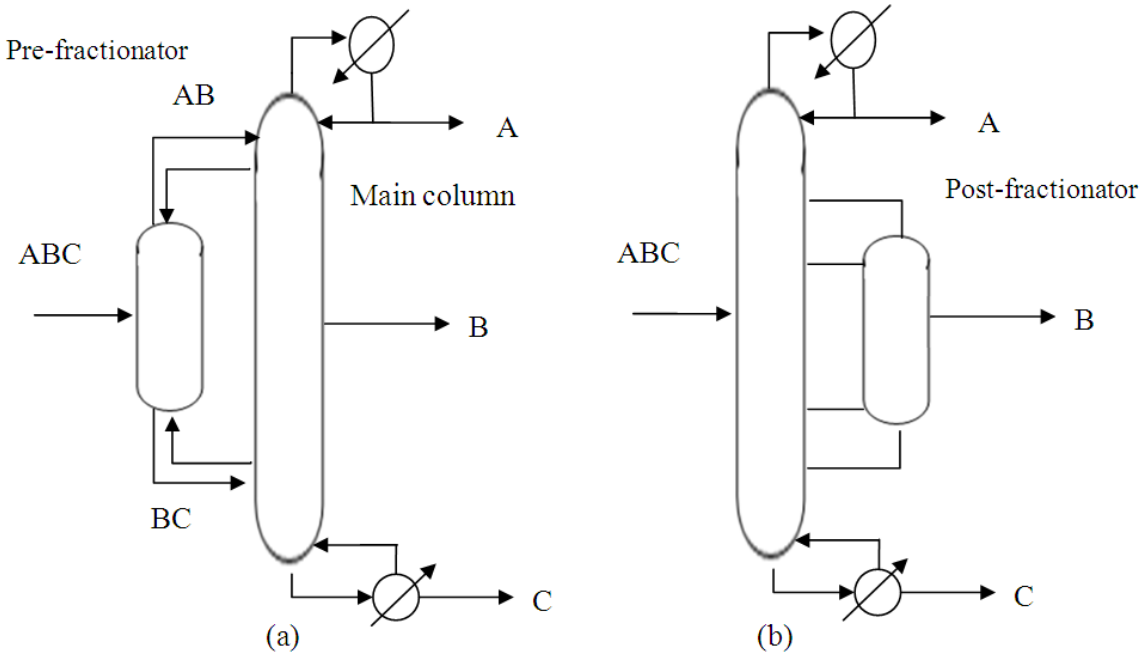

Figure 1.3: Thermally coupled columns (a) with a prefractionator or Petlyuk column (b) with a post fractionator.

1.4 Divided Wall Column (DWC)

If the thermally coupled columns are configured and fabricated to incorporate the side column, i.e. the pre- or post- fractionator in to the main column itself, the configuration will result in considerable saving in the investment costs. This arrangement is generally referred to as the divided (or dividing)-wall column (DWC) (Fig. 1.4). A partition wall in the mid-section of the main column creates two columns internally. The dividing walls are vertical partitions formed by flat metal sheets, which are either welded to the column shell or consist of flexible thin metal sheets which are stacked together. When structured packings are applied, the positioning of the dividing wall and the welding procedure must be carried out carefully. When a multi-component feed is introduced to the

pre-fractionator side of the DWC, the low- (LK) and high-boiling point key (HK) components are separated in the pre-fractionator while the middle boiling component (MK) distributes to the top and the bottom of the wall along with LK and HK, respectively. Further separation of LK and MK occurs in the upper section of the main column while the separation of HK and MK occurs in the lower section of the main column. As the compositions of the MK at the top and the bottom of both the sides of the dividing wall have to be matched, the concentration of the MK reaches a peak value in the middle section on the other side of the wall. A high purity MK can then be withdrawn from the middle section of the main column, as a side draw. Sharp split between LK and HK achieved in the pre-fractionator effectively reduces the contamination of MK drawn at the other side of the wall. This is simply because neither the LK can pass to the bottom section of the main column nor the HK can pass to the upper section of the main column provided there is no azeotropes present in the mixture (Ennenbach et al., 2000). Hence, the MK can be withdrawn at its maximum concentration from the other side of the wall. Simultaneously, the problem of re-mixing in the conventional columns when feedstock contains more than two components is avoided (Triantafyllou and Smith, 1992). In addition, the distribution of MK between the top and the bottom of the pre-fractionator provides greater freedom for the proper selection of the feed stage to ensure better matching between the feed stream composition and the composition of the feed tray. This leads to significant reduction in the mixing losses at the feed tray. Divided wall columns are preferred when the desired purity of middle boiling component (B) is higher than that which can be achieved with a side draw. The energy requirements and the concentration profiles of the thermally coupled columns and the divided-wall columns for the separation of ternary mixture are completely identical (Kolbe and Wenzel, 2004).

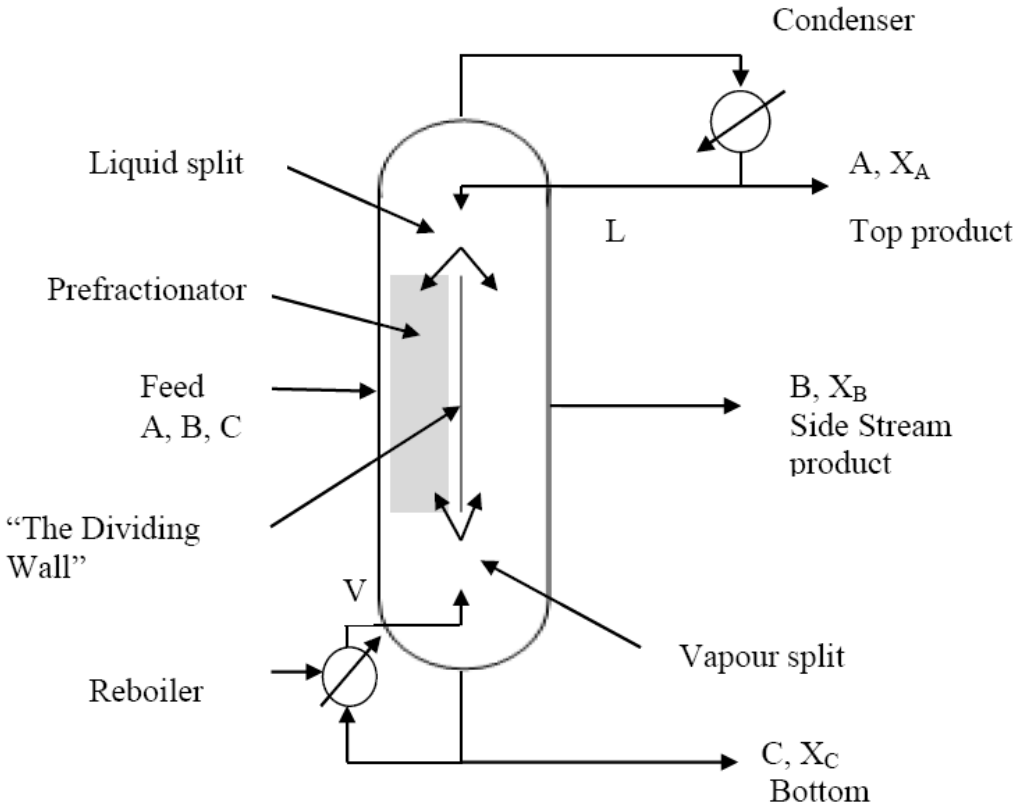

Figure 1.4: Dividing wall column.

The dividing wall prevents the lateral mixing of liquid and vapour streams. In a DWC, the flow along the wall should be avoided since it would deteriorate the purity of the products. This can lead to difficulties especially in cases of poor tolerances of the column shell.

An important motivation for studying integrated distillation column arrangements (either thermally coupled or divided wall column) is to reduce the energy requirement. On a global basis, distillation columns require a large portion of the total industrial heat consumption. Therefore, even a small improvement in the heat efficiency can save huge amount of energy. Savings to the tune of 20-40% reboiler duty can be obtained if a three-product integrated Petlyuk column is operated at its optimum, instead of using a conventional column sequence.

In 1985, the DWC found its first industrial application in BASF. Presently there are more than 100 DWCs in operation. There are a number of relatively well known potential applications for DWCs, including the straight-run naphtha fractionation upstream or downstream of reformers, FCC naphtha fractionation including FCC debutanisers, C4 isomer separation and BTX separation, etc. Table 1.1 shows some industrial applications of DWCs for ternary systems.

Table 1.1 Industrial applications of DWCs for ternary systems.

Company	System	Constructor and year	Features
BASF SE, diverse sites	Mostly undisclosed	Majority of the columns are built by Montz GmbH	More than 70 DWCs Diameter 0.6–4 m
Sasol Johannesburg, South Africa,	Separation of hydrocarbons from, Fischer–Tropsch synthesis unit	Linde AG, in 1999	World's largest DWC Height 107 m Diameter 5 m Tray column
Veba Oel Ag, Münchs münster, Germany	Separation of benzene from pyrolysis gasoline	Uhde in 1999	170,000 MT/year feed capacity
Saudi Chevron Petrochemical Al Jubail, Saudi Arabia	Undisclosed	Uhde in 2000	140,000 MT/year feed capacity
ExxonMobil Rotterdam, Netherland	Benzene-toluene xylene fractionation fractionation	ExxonMobil Was planned for 2008	No data available
Undisclosed	Separation of C7 + aromatics From C7 + olefin/paraffin	UOP	Five DWCs

Source: Yildirim et al. (2011)

The recent study of Premkumar and Rangaiah, (2009) shows that the operating cost can be reduced by more than 30% by using a DWC instead of a conventional 2-column (C2C) system, in addition to a reduction in capital cost for new plants. They also stated

that the retrofitting of a C2C system to a DWC is an attractive proposition with a payback period of less than 3 years for five of the six applications studied by them. It is expected that the DWC has a good prospect in the near future and that it might become a standard distillation configuration in chemical process industries (CPI) in the next 50 years (Schultz et al., 2002). With increasing number of applications, the number of patents has also grown. Today nearly half of all patents in this field are owned by BASF and Montz. Figure 1.5 shows the reported number of industrial DWCs.

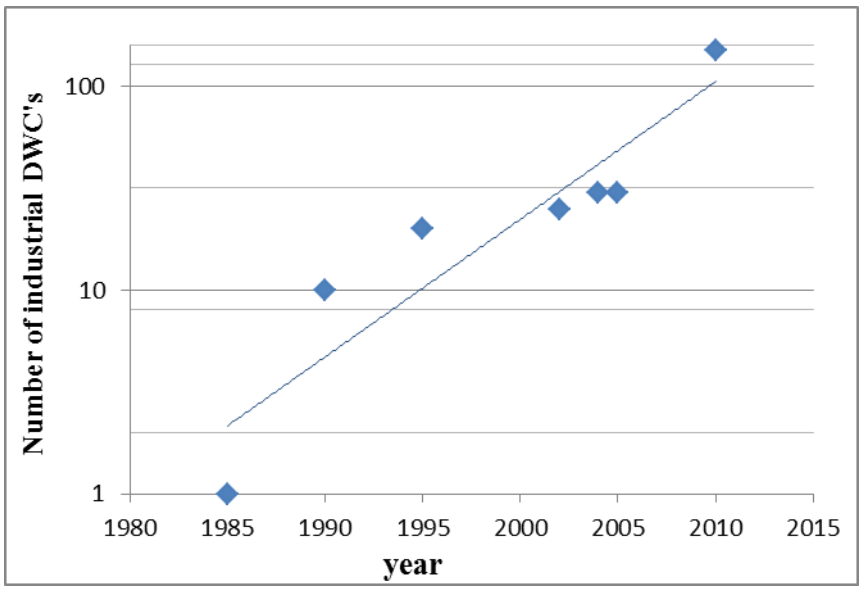

Figure 1.5: Number of reported industrial DWCs over the years.
Source: Yildirim et al. (2011)

An efficient DWC contributes directly in the reduction of CO_2 emission, because CO_2 emissions are directly related to the energy utilization (Halvorsen and Skogestad, 2011). The increasing energy cost and concern on global warming in the recent years have made the DWC an attractive alternative to reduce the energy requirement in CPI. In addition to energy savings, such integrated DWC units have also a potential for reduced capital cost, that add on attraction. There are also indirect benefits: less space, and

therefore, shorter piping and electrical runs (Gomez-Castro et al., 2008). Flare loads also reduced because of lower heat input and smaller and smaller fire-case surface, leading to smaller flare system (Schultz et al., 2002).

The main advantages of DWC include:

1. Two columns combined in one shell i.e. lowering of the overall capital cost.
2. Compact design, lower space requirements.
3. High thermodynamic efficiency due to reduced remixing effects.
4. Increased energy efficiency.
5. High purity for all three or more product streams reached in only one column.
6. Small CO_2 footprint and low investment cost due to the reduced number of equipment units.

Disadvantages of DWC:

1. Limited feedstock flexibility (design for one single feedstock).
2. Additional reflux divider required.
3. Increased operational and maintenance complexity.
4. Increased column diameter.

The industrial use of DWCs has been limited, and the difficulties in design and control have been reported as the main reasons for this limitation. The potential of energy savings that can accrue with the use of DWCs has not been fully exploited by the industry so far. The industry is not confident on the reliability of the design methods and on the operational and control aspects of DWCs. This hesitation stems from the maturity of the distillation technology over the last few decades. Therefore, a better understanding of the characteristics of these systems is required. This motivates further research in this area for better understanding of DWCs.

Chapter – II

LITERATURE REVIEW

This chapter deals with the review of the existing literature on divided wall distillation column (DWC). The review includes open literature and patented information. The chapter has been divided into three parts: the first part deals with review of literature available on the degree of freedom (DOF) analysis, configurations of thermally coupled/divided wall distillation column (DWC) and energy saving aspects of a DWC. In the second part, a comprehensive review of literature on the design, simulation and optimization of a DWC has been reported. The third part is devoted on the control aspects of a DWC, reactive distillation in a DWC and the application of the response surface methodology (RSM) for optimizing a DWC.

2.1 Degree of Freedom (DOF) Analysis

Several investigators have modelled thermally coupled and divided wall columns for design and operation purposes using different model equations or commercial software (Dunnebier and Pantelides, 1999; Serra et al., 1999, 2001; Kim et al., 2002 a-c; Halvorsen and Skogestad, 2004; Kolbe and Wenzel, 2004; Wang et al., 2007; Wang and Wong, 2007; Cho et al., 2009; Malinen and Tanskanen, 2009a, 2009b; Rangaiah et al., 2009). These investigators have reported conflicting and contradicting statements about DOF of thermally coupled and divided wall distillation columns. Many researchers have reported that a Petlyuk column has five degree of freedom in steady state operating condition (Chavez et al., 1986; Wolf and Skogestad, 1995; Halvorsen and Skogestad, 1997). These five DOF are: reflux flow, boil up flow, side draw flow, liquid split ratio and vapour split ratio. The column pressure was not considered as an adjustable parameter, which would have increased the DOF to six. While the vapour and liquid split ratios were used as extra

degrees of freedom to minimize the reboiler duty, the other three were used as design variables to satisfy the product purity specifications. However, Wolf and Skogestad (1995) showed that the prefractionator of a Petlyuk column does not contain any degree of freedom and, thus the energy benefit can be achieved by adjusting the additional two degrees of freedom viz. liquid split and vapour split ratios.

Ponton (1994) reported that for a distillation column, conventional method for DOF analysis (Kwauk, 1956) gives the maximum degrees of freedom, which is higher than the actual DOF for steady state simulation. The standard practice for distillation column involves use of some of the available DOF and leaving aside some of them. The unused DOF are generally associated with column pressure. Mutalib and Smith (1998) did a DOF analysis using conventional approach proposed by Howard (1967), that is based on the fact that the degrees of freedom for a system is equal to the sum of the degrees of freedom of all the units in the system minus the sum of degrees of freedom for all the interconnecting streams and reported that in contrast to the more established side draw column, a divided wall column has two additional degrees of freedom which are the liquid and vapour splits.

In case of unsteady or pseudo steady state conditions, the Petlyuk column or a DWC has relatively large number of controlled variables or degrees of freedom (Dunnebier and Pantelides, 1999). The effect of the degrees of freedom on the operation and control of Petlyuk columns has been the subject of investigation by Lestak and Smith (1993) and Wolff and Skogestad (1995). It was shown that the problem of dealing with the additional degrees of freedom can be solved with a suitable control strategy and that the Petlyuk column is stable and shows a reasonable dynamic behavior.

The number of degree of freedom increases further if the design variables are also included. Kim et al. (2002c) analysed the degrees of freedom at the time of designing and

found ten degree of freedom for a DWC. The ten DOFs are divided into two groups: structural design variables/parameters and operation related variables. The six structural variables are the number of stages of the prefractionator and the main column, feed and side product locations and the two interlinking stages between the prefractionator and the main column. The four operational variables are vapour boil-up rate, reflux flow rate, liquid split ratio and vapour split ratio.

The observations of Ponton (1994) that the conventional method for DOF analysis gives the maximum degrees of freedom were ignored by many investigators, because of which some investigators reported that the complexity of the divided wall distillation columns stems from an extra degree of freedom (Amminudin, 2001; Kim, 2002a) because of connecting streams. Serra et al. (1999, 2001) and Kim et al. (2002a) reported that the complex design of a DWC offers two extra degrees of freedom which can be used for process optimization. Halvorsen and Skogestad (2003b) considered that the two additional degrees of freedom are liquid and vapour split ratios that decide energy efficiency of the column. Wolff and Skogestad (1995) and Rangaiah et al. (2009) reported that the pre-fractionator does not contain any DOF; however, the main column has five DOF including vapour and liquid connecting streams from the main column to the prefractionator. These two extra DOF were used by Malinen and Tanskanen (2009a, 2009b) for energy minimization. Several investigators (Kolbe and Wenzel, 2004; Wang et al., 2007; Wang and Wong, 2007 and Cho et al., 2009) explained the five DOF for a DWC as the reflux flow, boil up flow, side draw flow, liquid split ratio and vapour split ratio. Obviously column pressure was not considered as an adjustable parameter, which would have increased the DOF to six. While the vapour and liquid split ratios were used as extra degrees of freedom to minimize the reboiler duty, the other three were used as design variables to satisfy the product purity specifications.

Many authors have reported DOF of Petlyuk configuration to be less than five. Adrian et al. (2004) reported that the number of manipulated variables (degrees of freedom) for the two column configuration is four. Ling and Luyben (2009) reported that the four DOF that are adjustable during design and operation of a DWC are reflux flow rate, vapour boil-up, side stream flow rate and the liquid split ratio. Although they did not present a DOF analysis, but just reduced the number by one assuming that the vapor split between the two sides is proportional to the cross-sectional area of each side (which is fixed by the physical location of the wall), i.e. the vapour split ratio below the divided wall is assumed to be such that it gives equal pressure drop across the two parallel branches of the DWC.

Ruiz-Marin et al. (2011) have done a degree of freedom analysis for a modified fully thermally coupled distillation system with a postfractionator. The modified structure has been divided into three subsystems, the prefractionator, the main column, and the postfractionator, each one constituted by basic elements (stages, condenser and reboiler). The degrees of freedom of each subsystem were calculated by adding the DOF for its basic elements, and then subtracting the DOF for each redundant stream. Finally, the DOF for the modified system was obtained by adding the DOF for each subsystem and then subtracting the DOF of the corresponding interlinking streams. Kiss and Bildea (2011) carried out a degree of freedom analysis for control purposes and found that a DWC system has seven degrees of freedom. This is one more than that reported for a typical distillation column with a side stream. According to them, an additional degree of freedom arises from the flow of liquid between the two sections of the column, i.e., the liquid coming down from the rectifying section at the top of the divided wall section can be split, in a controlled manner, between the two sides of the wall using a total liquid trap-out tray

and sending part of the total liquid to the prefractionator side and the rest to the side stream side of a DWC.

The degrees of freedom (DOF) analyses of a DWC carried out by various investigators are confusing. They did not consider pressure as a variable parameter in their analysis. The importance of pressure drop in the DWC and the prediction of pressure drop across each tray of a DWC are necessary. Therefore, there is a need for rationalizing the DOF analysis of a DWC using detailed mathematical models.

2.2 Energy Saving Aspects of Thermally Coupled and DWC columns

The fully thermally coupled system of distillation column has been known for more than the last six decades (Wright, 1949). Petlyuk et al. (1965) compared the performance of a thermally coupled distillation system to that of conventional schemes. They compared the amount of liquid to be vaporized in the reboilers and the thermodynamic work required to separate a ternary mixture, and found that the thermally coupled distillation system consume much lower energy in comparison to the conventional schemes for multicomponent distillation at all concentration levels of the middle component.

Most of the energy saving in a Petlyuk column arrangement is attributed to the pre-fractionator. Prefractionator arrangement distributes the intermediate component between the top and bottom and allows greater freedom to match the feed composition with a tray in the column to reduce the mixing losses at the feed tray. The mixing (and remixing) of streams with different compositions along the column and at feed point is a major source of separation inefficiency in conventional multicomponent distillation (Petyluk et al., 1965). Triantayllou and Smith (1992) reported that the reduction in the remixing inefficiency is provided by a non-sharp split in the prefractionator. Further, they added that a prefractionator minimizes the mixing losses at the feed tray.

Several thermally coupled arrangements with conventional, direct and indirect arrangements had been compared by Fidkowski and Krolikowski (1986, 1987). They approximated energy requirements with the sum of vapor flow rates from all reboilers. This approximation can be used only if the cooling and heating medium used in all the condensers and reboilers are of similar type. They found that if the energy consumption is the only criterion, the Petlyuk arrangement is the best. Kaibel (1987) also showed that, the energy consumption and investment cost of a DWC are lower as compared to other column arrangements, because the Petlyuk arrangement is thermodynamically advantageous. The thermodynamic process of separation by distillation consists of the removal of entropy of mixing of the feed stream by exergy (heating in the reboiler at higher temperature and cooling in the condenser at a lower temperature). Therefore, the additional mixing in a distillation process must be avoided as far as possible by an appropriate design of the distillation column. The undesirable additional mixing would result in excess entropy to be removed and would require more exergy or more energy for the separation (Kaibel 1987). For ternary systems, Agrawal and Fidkowski (1998a) found that, the total vapour flow in the fully thermally coupled scheme is lower by 10 to 50% than the conventional direct and indirect split sequences. Flores et al. (2003) also found an energy saving for thermally coupled distillation sequences between 10 and 30% in comparison to the two conventional direct and indirect distillation sequences for ternary mixtures.

A simple way to analyze different column configurations for the separation of multicomponent mixture by the use of network presentations was proposed by Agrawal (1996). They set a rule that the maximum number of separation sections is n (n-1) for a n-component mixture. Agrawal and Fidkowski (1998a, 1998b, 1999) presented the basis for generating feasible alternatives for fully thermally coupled distillation systems in which all

the heat is provided to the system by a single reboiler and all the heat is removed from the system by a single condenser. These basic rules were reviewed and systematized in the form of a minimum set of logic propositions by Caballero and Grossmann (2003, 2004) and translated into a set of linear equations for their use in a mathematical programming environment. A novel superstructure for designing a sequence of distillation columns ranging from conventional to fully thermally coupled systems was given by them. They analyzed several alternative intermediate possibilities also.

A possible modification and improvement to the fully thermally coupled arrangement was given by Agrawal and Fidkowski (1999) and Agrawal (2000 a-c, 2001 and 2003). They included the possibility of decreasing the number of thermal links among columns, schemes for multi-effect heat integration, and the basic rules for generating all the thermodynamically equivalent configurations for a given column configuration. Shah and Agrawal (2010) introduced a simple ‘‘matrix’’ method for obtaining all the basic distillation configurations and additional thermally coupled configurations. The only information needed to generate the configurations was the number of components in the feed. The proposed method can be easily generalized for any number of components in the feed. Rev et al. (2001) compared different distillation arrangements based on exergy analysis and total annualized cost. They showed that the DWC is favoured when relative volatilities of the feed components are balanced and high energy to investment cost ratio is achieved for lower amount of the middle component in the feed. Apart from Petlyuk column, various thermodynamically equivalent arrangements for separation of more than three components can be synthesized (Rong et al., 2003a,2003b, 2004; Rong and Turunen, 2006a, 2006b). Hernandez et al. (2006) gave the six thermodynamically equivalent distillation schemes to the Petlyuk column for ternary mixture. The second law of thermodynamics calculations were performed for the Petlyuk column and six alternative

distillation schemes that show unidirectional flow and found that the alternative distillation systems had very similar values of energy demands in the reboiler and thermodynamic efficiency.

The DWC configurations for the separation of a four component-mixture with five different feed compositions were studied by Errico et al. (2009). After selecting the best simple column (SC) sequence, the hybrid structures obtained by considering a configuration with a DWC replacing the first or the last two SCs of the sequence were considered. To simulate the DWCs, a short-cut method, given by Muralikrishna et al. (2002), was used to get the input data necessary to initialize the rigorous simulations. The results obtained for the hybrid structures were compared with the performance of the best SC sequence from which the energy and capital cost savings were evaluated. The Petlyuk and the DWC structures were considered independently for the capital cost evaluation to select the most economic configuration. Significant energy reduction was achieved with DWC schemes, while the saving in the capital costs was lower than the 30% value reported in most of the specialized literature. Rong (2011) gave a four step procedure, which systematically generates all the possible DWC columns from the simple column sequences.

Most of the researchers have neglected the heat transfer across the divided wall in the DWC analysis. Only Lestak et al. (1994) and Suphanit et al. (2007) investigated the effects of heat transfer across the divided wall on the separation efficiency. The analysis tool proposed by Lestak et al. (1994) to predict stage enthalpy deficit profile or column grand composite curve was used by Suphanit et al. (2007). They reported that the energy consumption can be reduced, if some part of the wall is insulated, i.e. closer to ideal distillation process. To determine the area of the wall, where the heat transfer should be allowed, Suphanit et al. (2007) modified the Lestak concept by combining the exergy loss

analysis for estimating the minimum driving force profile. A quantitative relationships between the degree of remixing and the vapor saving was developed by Ho et al. (2011) to quantify the potential energy saving of DWC.

2.3 Design, Simulation and Optimization of DWC

The design and optimization strategies for conventional distillation sequences are well known. However, the design and optimization of a DWC is more complicated in comparison to conventional distillation sequences because of recycle streams. Simulation of a DWC is a challenging task. Lack of a straightforward and proven design method was the main reason for slow acceptance of DWC by chemical process industry (CPI).

Design, simulation and operation of a DWC require the simultaneous solution of the material, momentum and energy balance equations. A common difficulty associated with the design, simulation and optimization of a DWC is the number of variables. These variables interact with each other and need to be optimized simultaneously for optimal operation. Final design of a DWC should be based on results obtained by rigorous steady state simulations carried out by employing one of the well established 'stage by stage' models to simultaneously provided necessary parameters and a rigorous performance simulation of DWC system. Carrying out DWC performance simulations requires great experience and these are computationally demanding. Optimization of a DWC is a multi-objective problem. Bhaskar et al. (2000) gave a review on the applications of multi-objective optimization in chemical engineering.

Stupin and Lockhart (1971) proposed an initial design method based on Underwood's equations, for the thermally coupled distillation system studied by Petlyuk et al. (1965) and found that thermally coupled scheme is a lower cost alternative to the conventional schemes for the separation of closed boiling components. A similar study was carried out by Tedder and Rudd (1978) to find the optimality region with respect to

the feed compositions. The theory for calculating the minimum reflux conditions and the number of stages and feed tray location for ordinary and thermally coupled distillation by shortcut methods was given by Cerda and Westerberg (1981).

The possibility for multiple steady states in complex column like Petlyuk column was discussed by Chavez et al. (1986) and found that the Petlyuk column has four different steady states and five degrees of freedom at steady state. This work was extended by Faravalli et al. (1989) to find out the most resilient steady state to changing internal flows.

Glinos and Malone (1985a, 1985b, 1986, and 1988) developed a short-cut method for screening different distillation network alternatives based on the Underwood equations. Due to the assumptions of ideal behavior, the Glinos and Malone method is reliable only for nearly ideal and non-azeotropic systems. The minimum reflux ratio and the vapor rate, both of which are critical for the column design, were calculated for a ternary mixture. The method covers conventional columns, side stream columns, and Petlyuk columns. An extension to a four-component mixture is also possible for all alternatives except the Petlyuk column. In certain cases, Glinos and Malone found that the complex column designs led to savings in both capital and operating costs. In particular, a maximum vapor flow reduction of 50% was found to be possible depending on the feed composition and the relative volatilities of the components in the mixture.

There is no information available on the effect of feed quality on the performance of a DWC. Feed thermal condition q (thermal quality) expressed as a manipulative variable can be used for the operation of a DWC. Feed thermal condition can change the pressure drop profile across the divided wall. The pressure drop calculations are extensively used for finding tray spacing at the time of designing a column, but these are rarely performed for the simulation purposes since a minor change in pressure (from

condenser to reboiler) does not have significant effect on the vapour-liquid-equilibrium (VLE). However, pressure difference plays an important role in deciding vapour and liquid flow rates across a tray (or trays), particularly in case of interconnected or a divided wall distillation column (DWC).

The optimal design of a DWC is obtained by minimizing the energy duty, as it accounts for the major fraction of the operating cost. An appropriate solving tool is required for the optimal design of a DWC, as it is a highly nonlinear and multivariable problem (Gomez-Castro, 2011). This can be handled with the coupling of an external sub-routine/ software for optimization with commercial process simulation software. Most of the researchers optimized the structural and process parameters of a DWC separately. There are no reports in the literature on the simultaneous optimization of the structural and operating parameters of a DWC.

2.3.1 Shortcut methods for simulation

Many researchers (Tedder and Rudd, 1978; Cerda and Westerberg, 1981; Triantayllou and Smith, 1992; Finn 1996; Dunnebier and Pantelides, 1999) concentrated their efforts on developing short-cut design procedures that allowed process screening and initialization for rigorous simulation. The methods were restricted in their application by simplifying assumptions such as ternary mixtures, sharp separations, saturated liquid feeds, constant molal overflow and constant relative volatility.

An optimal design of a DWC requires adequate models and computer-based simulations. However, commercial process simulators do not include particular subroutines for DWCs. The so-called decomposition method developed by Triantafyllou and Smith (1992) simplifies the design problem. They proposed a short cut design method for design and optimization of the fully thermally coupled columns. Using a three-column model, they applied the conventional Fenske-Underwood-Gilliland short cut design

technique in each column, not only for process screening, but also to provide a reliable initialization for rigorous simulation. They developed a simple optimization approach by considering both energy (minimizing the reboiler duty) and capital costs (minimizing the number of trays), instead of using the minimum vapour flow criteria (Fidkowski and Krolikowski, 1987). Triantafyllou and Smith (1992) identified several design variables that need to be optimized, such as the reflux ratios and the recoveries of the key components in the pre-fractionator. Finn (1996) showed that the conventional Fenske-Underwood-Gilliland method for short cut distillation design is appropriate for thermally coupled columns and reported a method for the evaluation of heat duties under minimum reflux ratios. This identifies the thermally coupled sequences that minimize heat duties under those extreme conditions, but no initial design would be available. Muralikrishna et al. (2002) also used three column model and proposed a shortcut method similar to Triantafyllou and Smith (1992), which represent all feasible DWC designs on a simple two-dimensional plot. Equi-parameter curves could be placed in the design space for the designer to examine various design options. Using this graphical technique one can easily visualize all the possible designs simultaneously, and at the same time, a search for the optimum design can be made on the plot itself. A graphical design procedure using column profile map for the comprehensive analysis and design of the fully thermally coupled (Petlyuk) distillation column at sharp-split conditions was given by Holland et al. (2010). It is shown that, only a small region of key parameters (vapor and liquid split ratios) result, for set product composition specifications and a set reflux ratio, in feasible separations. A novel short-cut method based on the development of a rational and efficient net flow model and the application of the methods of Fenske, Underwood, and Gilliland, and the Kirkbride equation had been given by Chu et al. (2011). This method can be used to rapidly determine near-optimal values of important design parameters, including the

reflux ratio, number of stages in all sections, and split liquid and vapor ratios for the DWC.

Amminudin et al. (2001) reported that the design of the dividing wall column is more complex than a simple column because of larger number of degrees of freedom that need to be specified. Key variables and parameters such as the distribution and number of plates in each of the column sections, the feed stage location, side-draw locations, reflux ratio, liquid and vapour splits on each side of the dividing wall, must be established before simulation can be performed. All these degrees of freedom interact with each other and need to be optimized simultaneously to obtain the best design. Amminudin et al. (2001) and Amminudin and Smith (2001) improved the earlier design procedure of Triantafyllou and Smith (1992) using a semi-rigorous model based on the equilibrium stage composition concept to define a liquid composition profile by solving the mass balance rigorously on each equilibrium stage, while restricting the procedure to the assumption of constant molal overflow. Due to its semi-rigorous nature, there is no need to assume constant relative volatility. They pointed out that the use of Kirkbride equations, to find thermal coupling locations can lead to error when transferred to rigorous simulation. The procedure follows from the feasible product distribution from the Underwood equations, which must be estimated at minimum reflux conditions prior to the use of the concept for designing the fully thermally coupled column. They claimed that this method is more accurate than the standard Fenske-Underwood-Gilliland based shortcut methods. But their method was computationally more demanding. However the method initially developed by Triantafyllou and Smith (1992) was simpler (Wenzel and Rohm, 2003). For the application to DWC design, Sotudeh and Shahraki (2007) also pointed out that the use of Fenske equation for minimum number of stages is inadequate. Because Fenske equation is based on the assumption of equal compositions of liquid and vapour streams at the top and

bottom of the prefractionator, This may not used for a DWC. Therefore, they used Underwood equation only for the design of a DWC. Halvorsen and Skogestad (2003a-c) also used Underwood equations and analyzed the minimum energy requirement for three and larger number of products using Petlyuk arrangement. It was observed that the energy requirement was equal to that observed for the most difficult of the two separations (top/middle or middle/bottom product) in a conventional single column. They developed their model by assuming constant relative volatility and constant molar overflow for ternary feed and rigorously proved that fully thermally coupled systems always produce the lowest vapor flow rate (at least for systems with constant relative volatilities and constant molar flow in each column section) giving a simple explicit equation for this result. The graphical representation of the $V_{\min}$ versus distillate diagram is found to be a useful tool for obtaining conceptual insights about the process. From V_{min} diagram it is easy to see the vapour and liquid flow needed in every column section, which can directly serve as the basis for column design. Also, the minimum theoretical energy, represented by vapour flow, needed for the separation can trivially be seen, as the highest peak on the diagram. They also provide the designer with a theoretical minimum boil-up ratio, which they claim to be a good indication for optimality of design without using rigorous optimization techniques. But the determination of the optimal trade-off between the reflux ratio and the number of stages is a difficult task, since their work is based on Underwood equations (infinite number of stages). An overview of some energy saving distillation arrangements based on V_{min} diagram was given by Halvorsen and Skogestad (2011). They showed as to how the V_{min} diagram can be used to assess separations and calculate energy requirements and provide a basis for detailed design.

Kim and co-workers have reported on various aspects of a thermally coupled distillation column. A rigorous structural design procedure for fully thermally coupled

distillation columns (FTCDC) was applied by Kim (2001 a, b) for different systems of butanol isomers in order to show the design performance. The procedure gives structural information of the column. Using the outcome of the structural design, several features, such as thermodynamic efficiency, dividing wall column structure and the arrangement of interlinking streams, were investigated.

An approximate design procedure for fully thermally coupled distillation columns (FTCDC) for ternary system was given by Kim et al. (2002c). The procedure gave a fast solution for structural and operational design for a preliminary study of the FTCDC. This procedure also eliminates difficulties encountered in the design of the FTCDC by using conventional design techniques.

A structural design procedure for FTCDC was proposed by Kim (2005), using a semi-rigorous model and tested on three separation systems, viz. isomers of butanol, BTX and hexane/2-methyl hexane/heptane mixtures having different feed compositions. The design procedure employed material balances and equilibrium calculated using UNIQUAC activity model and the Peng–Robinson equation of state (EOS) for the computation of tray compositions. The structural information was utilized in HYSYS simulations to find the operating variables that would meet a given set of product specifications. The outcome of the structural design was used as initial estimate for the rigorous simulation. Kim (2006) also proposed a new system of a FTCDC, and examined its performance on two industrial processes. The system had an extra column called post-fractionator, attached to the main column of an original FTCDC. VLE data were obtained using Peng-Robinison EOS for both processes. The structure of FTCDC system was implemented for the fractionation process of a naphtha reforming plant for BTX production and the gas concentration process to produce gas products from a gas mixture drawn from crude distillation, naphtha reformation and naphtha-cracking processes in a refinery. The outcome of the performance investigation using HYSIS indicated a 29 %

energy saving with fractionation process and a 7 % saving with gas concentration process over the original FTCDC. In addition, he also discussed the new column construction, such as arrangement of distillation column sections and divided wall construction.

Feasibility study of a DWC for fractionation in industrial scale naphtha reforming plant by applying the structural design procedure for FTCDC was discussed by Lee et al. (2004). Because the commercial design software HYSYS requires the structural information in the beginning of the simulation, the procedure yielding the information helps the HYSYS design process of the FTCDC. An energy saving of 13% and a investment cost reduction of 4% were reported.

Rangaiah et al. (2009) developed a procedure for a quick design of DWC for industrial applications. Simulation and optimization results of DWC for six different examples were presented using HYSYS. They used three-column shortcut simulation that is capable of providing reasonable estimates for the initialization of rigorous simulation and design of DWCs. They noted that the vapour and liquid splits in the column have significant impact on the energy requirements and that the locations of the feed tray, side draw and pre-fractionator can affect energy requirements and, therefore, they should be optimized. For different applications of industrial importance, the retrofitting of conventional column systems to DWCs was studied by Premkumar and Rangaiah (2009). They found that the retrofitting conventional two column systems to a DWC can reduce operating cost by more than 30 % for all the six applications which they studied.

Gutiérrez-Antonio and Briones-Ramírez (2009) estimated the set of optimal solutions between minimum reflux (i.e. infinite number of stages) and minimum number of stages (i.e. infinite reflux) using a genetic algorithm. An optimization model in the form of a non-linear programming problem for fully thermally coupled systems using short cut design method was presented by Ramirez- Corona et al. (2010). The model was used to detect Petlyuk and DWC structures that minimize the total cost for a variety of case studies. They observed that the feed composition affected the optimal structure more than

the ease of separability index of the mixture. The energy consumption and the total annual cost of the system, depend directly on the composition of the middle component of the ternary mixture.

A design method for the modified thermally coupled system with post-fractionator was given by Ruiz-Marin et al. (2011). A shortcut method was used to provide the minimum reflux conditions of the system, and the boundary value method was used to complete the design task. To verify the shortcut method applicability for process initialization, they carried out a preliminary design for the same separation task as considered by Gomez-Castro et al. (2008) and compared their results with the final optimized structure obtained with genetic algorithms and found that product purities were quite close.

Dejanovic et al. (2011a-b) carried out a preliminary evaluations using short-cut method (V-min diagram given by Halvorsen and Skogestad (2003 a, b, c) and found that a 15 component aromatics mixture can be separated very efficiently into four fractions according to the specified product compositions employing either a single or a multiple partition wall DWC. These results had been used to initiate rigorous simulations, for the determination of the number of stages required in different sections, as well as to obtain internal flows of vapour and liquid necessary for dimensioning and adequate cost estimation for the two design alternatives as one with a single longitudinal partition wall, with some sections off-centre, and a multiple-partition wall column containing three sections in parallel. They replaced three columns configuration by a single DWC for obtaining four products. The simulation studies showed that a DWC has a large energy saving potential compared to conventional configuration, resulting in 40.1% and 48.2% lower total annualized costs for single- and multiple partition wall DWC, respectively. This means that a complex, multiple-partition wall column is a more attractive option for industrial implementation, but due to its constructional complexity it may appear impractical. Dejanovic et al. (2011c) presented a comprehensive overview of DWCs.

Ghadrdan et al. (2011) optimized the operation of Kaibel distillation columns keeping two different objectives, namely, the minimization of the energy requirement at fixed product purities and maximizing product purities with a fixed boilup. The information from V_{min} diagram was used in UNISIM simulation to obtain initial estimates for the detailed simulation. They found that the operation with fixed product purities is more difficult to be handled for control. However, it is easier to operate, when the product purities are free. A two-step approach for the optimal design of a DWC using short cut sloppy configuration was suggested by Lee et al. (2011). Lee (2012) reported that the utilization of dividing wall columns for the integration of depropanization debutanization during the natural gas liquid recovery process. DWCs were optimized by RSM. They proposed that a compact DWC configuration is economic and could be used in the liquid recovery. They found that the feed splitting could eliminate the demethanizer reboiler and also may reduce the energy for processing. Long and Lee (2012 a) also showed that the use of a DWC improves the performance of deethanizer and depropanizer in NGL processing. They reported that the use of the DWC enhances the purity and recovery rate of ethane.

A strategy for the simulation of thermally coupled distillation sequences using process simulators was presented by Navarro et al. (2011). They substituted the two side stream connections involved in a 'thermal couple' by a combination of a material stream and heat flow; enabling a sequence of thermally coupled distillation columns to be simulated without recycle streams. Simulation without recycle streams for a sequence of thermally coupled distillation columns may be difficult to converge than other distillation systems without recycles. They verified this approach with several case studies and found that this approach introduced negligible errors, and provided excellent starting points for rigorous simulations of actual thermally coupled systems with recycle streams.

2.3.2 Dynamics and rigorous methods for simulation

Short-cut design methods have proven their suitability for ideal mixtures. Except for simple cases, such as binary distillation, short-cut design methods are suitable only for preliminary design studies. However, in any case for the final designs are required, rigorous methods required, for which shortcut methods can provide good initialization values.

Hernandez and Jimenez (1996) gave rigorous dynamic model for the design of both direct and indirect thermally coupled distillation sequences for ternary system, with the aim of minimizing the total heat duty. The complexity of DWC operation and control was assessed by Mulalib and Smith (1998). They investigated the impact of liquid and vapour split ratio on the operation and control of a DWC, based on dynamic simulation. A pilot plant study for the operation and control of a DWC was conducted by Mutalib et al. (1998) by using temperature control. Pilot plant and simulation studies using temperature controls showed that there is an offset in one of the product purities.

Kim (2000) also gave a rigorous design procedure of a fully thermally coupled distillation column, which is applied to find initial information of operation variables, used in dynamic simulation and examined the performance with a case study of butanol isomer ternary system.

The optimal design of thermally coupled distillation columns and divided wall column using rigorous model with mathematical programming was considered by Dunnebier and Pantelides (1999). They assumed constant relative volatility, constant molar overflow and neglected heat transfer across the dividing wall. However, this problem is computationally more involved than the short-cut design procedure. This model is able to simulate both conventional (direct sequence) and thermally coupled columns, which allowed the comparisons of different structural alternatives. They used

two case studies, one for the separation of close boiling C4's and the other for the separation of alkane mixtures and showed up to 30% possible saving in both operating and capital costs. Design and optimization of fully thermally coupled distillation column was also studied by Amminudin et al. (2001), wherein the degree of freedom was optimized simultaneously and an optimized initial design was established for rigorous simulation.

The implementation of the divided-wall column technology for processing petrochemical cuts (morphylane extractive distillation) was studied by Kolbe and Wenzel (2004). Special proprietary estimation tools were developed for the design of the overall column configuration and an evolutionary algorithm was used to find the optimum column design based on the total annual costs. Uhde (Kolbe and Wenzel, 2004) designed and constructed commercial plants while continuing laboratory investigations. Practical operation was verified on a laboratory scale with a special set of divided-wall column elements designed as a variable unit construction kit. Using the process simulator, utility and investment costs was estimated. The data was taken from an industrial divided wall column for the processing of pyrolysis gasoline. Thermodynamic behavior was calculated using UNIFAC model and energy saving was estimated to be 19.8% in the divided wall column in comparison to conventional direct sequence columns.

Caballero and Grossmann (2004) proposed a method based on a two-stage decomposition procedure. In the first stage, only the best sequence of separation tasks was obtained, in which each separation task was considered like a pseudo-column. Once the structure of separation tasks was established, the sequence of actual columns was extracted among all the thermodynamically equivalent alternatives. The model used the Underwood–Fenske–Gilliland approximation and was formulated as a generalized disjunctive programming problem. The model was solved as an MINLP. The model was

claimed to be very robust, reliable and flexible. Rigorous simulations in HYSYS for the separation of a mixture of aromatics had shown good agreement with this shortcut model.

Rigorous simulations of Petyluk distillation column were conducted by Abad-Zarate (2006) using Aspen Plus™ RATEFRAC Module for the separation of ternary mixtures. They found that the heat duties predicted by the equilibrium model are significantly lower than those obtained by using the non-equilibrium model, which is consistent with the results reported previously.

Malinen and Tanskanen (2007) used a rigorous minimum energy calculation method for the FTCDC, which is based on column simulation with a large number of equilibrium stages to mimic infinitely high columns. A modified bounded Newton homotopy method was used to detect the optimum point of the operation of the column system, which is described with a full set of MESH equations (material balance, vapour-liquid equilibrium, summation, and enthalpy (H) balance equations).

The design of a DWC using multiobjective genetic algorithm with restrictions was studied by Gomez-Castro et al. (2008). Several mixtures were tested to see the effect of relative volatilities of the feed components on energy consumption, thermodynamic efficiency, total annual cost and theoretical control properties, with three thermally coupled schemes, viz. the traditional Petlyuk column, an alternative scheme with post-fractionator instead of pre-fractionator and a sequence of both pre- and post-fractionator. In most of the cases, they found that the alternative scheme with post-fractionator gave better thermodynamic efficiency and lower total annual costs. Gomez-Castro et al. (2011) also extended the multiobjective genetic algorithm with restrictions for the optimal design of multiple dividing wall columns for the separation of ternary mixture and found that the multiple dividing wall columns are preferable for the system, which has low composition of the middle-boiling component.

Vázquez – Castillo et al. (2009) considered a subset of five intensified configurations, for quaternary distillations of those reported by Rong and Turunen (2006), for the design and optimization of a DWC. They used genetic algorithm with restriction coupled to the Aspen Plus process simulator (Gutiérrez-Antonio and Briones-Ramírez, 2009) for the rigorous evaluation of the objective function. Numerical performance of this method was tested in the design of the columns for the separation of several mixtures to examine the effect of the relative volatilities of the feed components on the energy consumption, thermodynamic efficiency, total annual cost and theoretical control properties.

Guterrez- Antonio et al. (2011) used a rigorous design model for optimizing the Petlyuk sequences. Multi-objective genetic algorithms with constraints coupled with Aspen Plus simulation software were used for obtaining each data point during the search process. An optimal inter connection was shown to be different for each interconnecting streams.

Hwang et al. (2010) performed an experimental evaluation of a thermally coupled distillation column and evaluated column performance for the stable operation of the column, for the separation of a ternary mixture (methanol, ethanol and n-propanol) using a 100 mm sieve tray. The temperature profile along the column was obtained by measuring temperatures at seven different locations along the column. The column was found to be thermally stable. The experimental results were compared with the HYSYS simulation and it was found that neither a compressor nor a pump was necessary for the vapour and liquid flow between tray sections. They also presented the modelled temperature variation and showed that the model predictions were accurate. An analysis of dividing-wall columns based on both experimental and simulation studies had been presented by Niggemann et al. (2010). Different feed compositions of a ternary mixture of fatty alcohols were

examined in a purpose-built pilot plant while maintaining product specifications of ~99 wt % at steady-state conditions.

Niggemann et al. (2011) also simulated and analysed the startup of DWC. They presented a model predicting the dynamic discrete-continuous changes which are the characteristics of a DWC. The process model takes into account the heat transfer across the dividing wall as well as the vapor distribution below the dividing wall. The degree of accuracy of the model was determined by comparing the results of simplified scenarios, e.g. a constant vapor distribution ratio equal to the steady-state value. The detailed studies were carried out with strict product specifications so that the influence of process parameters could be quantified. The analysis revealed that the vapor split is self-adjusting and cause significant changes only at the beginning of the start-up before the vapor split reaches its steady-state value. Therefore, the simplification of a constant vapor split according to its steady- state value was considered and identified as a valid modeling approach.

2.4 Control of a DWC

Although a large amount of the existing literature focuses on the control of binary distillation columns, limited numbers of studies are reported on the control of a DWC. It appears that various authors have selected different ternary chemical systems to be separated and have explored many control structures (the selection and pairing of manipulated and controlled variables) with different control objectives and different control algorithms, from proportional integral derivative (PID) to model predictive control (MPC). Some authors control only two compositions, while others control three or even four compositions. The influence of pressure variations upon distillation operation does not seem to be properly recognized by the investigators, and contradictory statements are

found concerning the importance of pressure control on binary distillation. Li et al. (2006) investigated and reported that, if column pressure is controlled, instability may occur when both product purities are controlled in a decentralized control structure. Several studies work on inferential temperature control instead of – or in combination with – composition control.

One of the earliest study on control of a DWC was by Wolf and Skogestad (1995) in which they studied three point control, i.e. purities of three products were controlled. A controllability analysis of the diagonal feedback control using multiple input-multiple output (MIMO) linear analysis tools was carried out by Serra et al. (1999, 2000, 2001 and 2003) for the separation of different mixtures under different operating conditions, including optimal operation. As a result, a trade-off was found between energy minimization and controllability. As an alternative, application of dynamic matrix control (DMC) to the divided wall column (DWC) was also evaluated. Through simulation, the ability of DMC for disturbance rejection and set-point tracking was studied and compared with that of the feedback diagonal control. The influence of design and operating conditions on the divided wall column controllability was studied by Serra et al. (2000). Two designs for which the total distillation cost is minimized were compared and for each design, different optimal reflux to minimum reflux ratio was assumed. They compared three non- optimal designs with an optimal one. Adding trays to different column sections, the distribution of the distillation effort was changed. The effect of this change on the controllability was studied. The DWC has extra operational degrees of freedom and the operation that minimizes the boil-up was searched. The influence of the operating conditions over the controllability was studied comparing optimal and non-optimal nominal operations. A 3×3 operation scheme, which has favorable indices of multivariable controllability, was examined by Kim (2002b) to check the control performances of set-

point tracking and regulation with a model predictive control. Jana et al. (2005) developed a linearized control system design of a constrained multivariable distillation column.

The dynamic behavior of three thermally coupled distillation schemes and two conventional distillation sequences for the separation of ternary mixtures was compared by Segovia-Hernandez et al. (2004). Designs for the thermally coupled schemes were obtained and optimized for energy consumption to link their energy characteristics to their dynamic behavior. For the comparison of the dynamic behavior, responses to set point changes under closed loop operation with proportional-integral (PI) controllers were obtained. For each separation scheme, the parameters of the PI controllers of the three composition control loops were optimized using the integral of the absolute error criterion. The Petlyuk column showed the highest energy savings.

Juan et al. (2007) studied the control properties of thermally coupled distillation sequences for different operating conditions. They observed that the thermally coupled distillation sequences (TCDS) can provide significant energy savings with respect to the operation of sequences based on conventional distillation columns. TCDS exhibits a complex structure, with recycle streams, that appear to affect their controllability properties. One potential solution to this problem had been suggested through the operation of TCDS under conditions that do not provide minimum energy consumption. The basic idea was that if one changes the operation point, the control properties must change as well. They analyzed the dynamic behavior of two TCDS structures under different operating points, including the one with minimum energy consumption. The control analysis properties were analyzed with the application of the singular value decomposition technique at zero frequency and closed-loop dynamic responses using standard PI controllers. It was reported that the controllability properties of distillation sequences might change significantly depending on the selected operation point.

Segovia-Hernandez (2007) analyzed the dynamic behavior of two TCDS structures under different operating points, including the one with minimum energy consumption and found that the controllability properties of distillation sequences may change significantly depending on the selected operation point.

Plant wide design and control of acetic acid dehydration system via heterogeneous azeotropic distillation and divided wall distillation was studied by Wang et al. (2007). They proposed control strategies using temperature loops for the acetic acid dehydration system. The effects of liquid split and vapor split ratios on the energy efficiency and controllability of a divided wall column system for separating ethanol, *n*-propanol, and *n*-butanol were investigated by Wang and Wong (2007). They found that for a column with finite number of stages, the energy efficiency of the design depends on the designed value of liquid and vapour split with a trade-off between energy efficiency and controllability of end product composition. They proposed a composition plus temperature cascade scheme to stabilize the high efficiency operation, with variations in composition, to be separated into high purity products.

Tamayo-Galvan et al. (2008a) compared the theoretical control properties of six alternative schemes to the Petlyuk system by using the singular value decomposition (SVD) technique in the frequency domain. They found that the reduction in the number of interconnections and the use of unidirectional flows affected the dynamic properties of the complex schemes leading to potential operational advantages in thermally coupled distillation sequences. An analysis of control properties of two distillation sequences that arise from modifications to thermally coupled systems with side columns was presented by Tamayo-Galvan et al. (2008b). The results indicated that a reduction in the number of interconnections in alternate configurations does not necessarily provide an improvement of controllability properties.

Ling and Luyben (2009) proposed a new control structure that controls the purity of the products and also minimizes energy consumption for ternary separation of BTX, by controlling the composition of the heaviest component in the prefractionator. Ling and Luyben (2010) also explored the use of temperature measurement to avoid the use of expensive composition analyzers. They used two types of temperature control structure in their studies. The DWC control issues were explored by Diggelen et al. (2010). They compared various control strategies for the ternary separation of BTX. The performance of these control strategies and the dynamic response of the DWC was investigated in terms of the product composition and flow rate for various persistent disturbances in the feed flow rate and composition. Using the singular value decomposition technique on open-loop transfer function matrices, controllability indices were obtained by Vaca et al. (2009).

An overview of the available control strategies for a DWC was given by Kiss and Bildea (2011). The control strategies varying from the classic three-point control structure and PID controllers in a multi-loop framework to model predictive control (MPC) and other advanced control strategies were used. They concluded that the dividing-wall distillation column has good controllability properties, provided that an appropriate control structure is implemented. An analysis for the design of model predictive controllers for dividing wall columns with experimental investigation has been presented by Buck et al. (2011).

Ling et al. (2011) proposed a control structure by controlling the remixing of the intermediate at the top trays in the prefractionator section for the separation of benzene, toluene, and o-xylene and found that avoiding the remixing of toluene helps the divided-wall column work very close to the optimal conditions. Remixing profile analysis of intermediate compounds gave an easy to design and control the divided-wall column at energy saving conditions.

2.5 Structure Design using RSM

Response surface methodology (RSM) is a promising method for process optimization studies. RSM comprises a number of statistical techniques including Box-Behnken design (BBD) for model building and model exploitation. BBD under RSM allows the identification and quantification of interactive effect of various parameters. Using BBD and RSM for optimizing distillation is not very common, only a few investigators have used this technique for DWC optimization. Considering designing of a DWC to be a multivariable problem and these variables interact with each other and need to be optimized simultaneously to obtain the best design, Long and Lee (2012b) used BBD under RSM for the structural design of a DWC. They considered the five variables for the structural design and tested their method in the design and optimization of an acetic acid purification process and found that total annual cost decreased by 44.57% as compared to conventional distillation. They also reported that the optimization result of BBD effectively copes with the interactions between variables and predictions agreed well with the rigorous simulation results. So by BBD method, they optimized all the structural variables simultaneously, while Long et al. (2010) and Premkumar and Rangaiah (2009) optimized one variable at a time, while keeping the others constant.

2.6 Reactive and Extractive DWC

An experimental study on the reactive DWC for the hydrolysis of methyl acetate was carried out by Sander et al. (2007). Wang et al. (2008) studied the design and control strategies of a reactive distillation process with partially thermal coupling for the production of methanol and n-butyl acetate by trans-esterification reaction. The dynamics of a reactive Petlyuk column for the production of ethyl acetate was studied by Hernandez et al. (2009). They found that the reactive Petlyuk column can achieve set point changes in two control loops of temperature and it also eliminates disturbances in the feed

composition. The dynamic simulations indicate that it is possible to control either the composition of the top and bottoms products or two temperatures by manipulating the reflux rate and the heat duty supplied to the reboiler, respectively.

The feasibility study of using both reactive distillation and thermally coupled reactive distillation schemes for biodiesel production at high pressure conditions was presented by Gomez-Castro et al. (2010). They found a significant reduction in energy consumptions than that in a conventional process and a reactive distillation system by itself may produce high-purity biodiesel, but the thermally coupled system shows lower energy consumptions than the reactive distillation column. Nguyen and Demirel (2011) also found that the thermally coupled distillation sequences require less energy than that for conventional reactive distillation for biodiesel production.

Barroso-Munoz et al. (2011) implemented a reactive DWC in order to manipulate the internal flows associated with energy consumption. The reaction between ethanol and acetic acid was conducted within the prototype, and the experimental results indicated that a heterogeneous mixture of ethyl acetate and water was obtained as the top product. They claimed that the temperature profile measured during the experimental run can be used for controlling the batch distillation column in cyclic operation mode. Kiss and Rewagad (2011) controlled the optimal liquid split ratio by several control structures to minimize the reboiler duty, using dynamic model. The internal flow distribution was found to be the most important variable influencing the energy efficiency of DWC (Lee et al., 2011). A study of the design of reactive distillation with thermal coupling by using a multi objective genetic algorithm with restrictions coupled to Aspen Plus had been done by Miranda-Galindo et al. (2011). The results obtained in the Pareto front indicate that the energy consumption of the complex distillation sequence can be reduced significantly by varying operational conditions.

A multi objective stochastic technique to obtain the optimal design of an extractive DWC column was presented by Bravo et al. (2010). The approach was based on the use of genetic algorithms to determine the design that minimizes energy consumption and total annualized cost.

Although first patent for the DWC came in the year 1938 (Table 2.1), systematic research efforts began in the beginning of last decade of twentieth century. Fig 2.1 shows the numbers of publication on DWCs during the past years. It is clear form Fig. 2.1 that the publications increased significantly from the year 2007 onwards. There are a total of sixty eight publications as culled from the Web of Science by using the key words as 'divided wall column'. There are only five publications available on the DOF of a DWC, but no work is reported on the effect of feed thermal quality on the operation of a DWC. Figs. 2.2 and 2.3 show the number of research publications since 1993 on the optimization and control aspects of DWCs. A total of thirty three and twenty seven publications have been cited for the optimization and control, respectively. There are only two publications on the pressure drop aspects of a DWC and five publications reported on multi wall divided distillation columns.

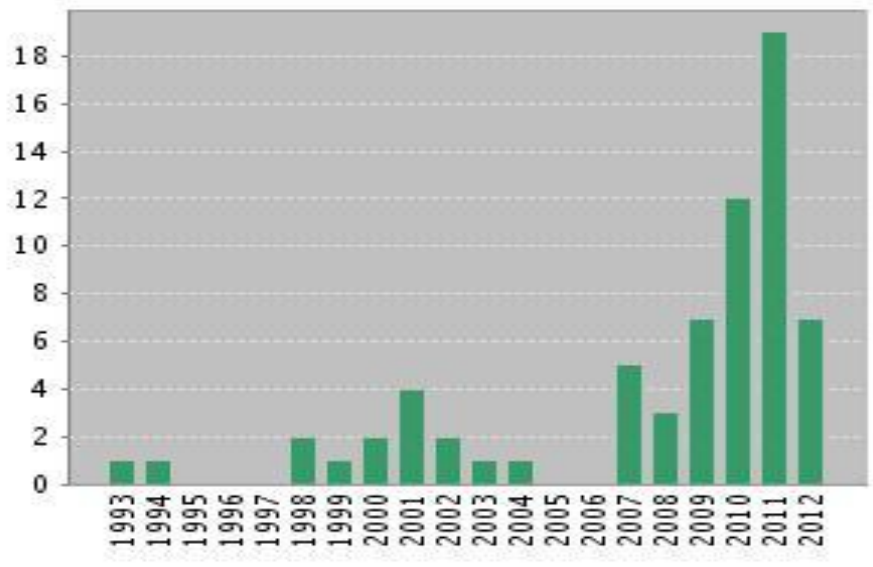

Figure 2.1: Year wise publication of research papers on DWC.
(Source: Web of science; keyword: divided wall column; accessed on 16.06.2012)

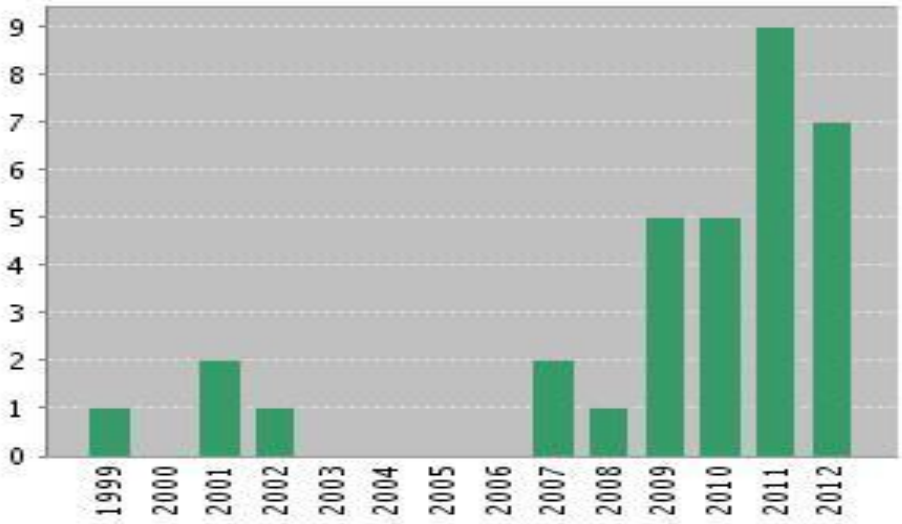

Figure 2.2: Year wise publication of research papers on optimization of DWC.
(Source: Web of science; keyword: 'divided wall column' refined with 'optimization'; accessed on 16.06.2012)

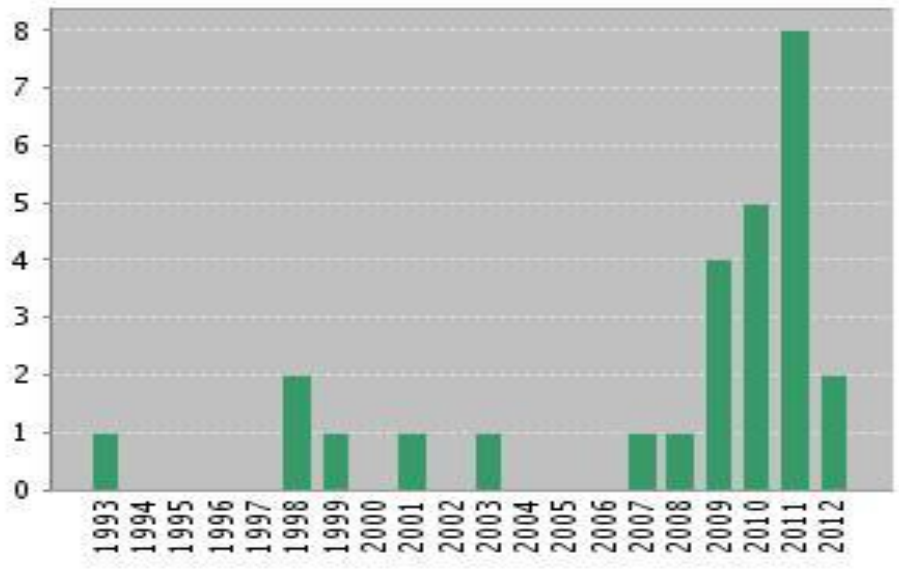

Figure 2.3: Year wise publication of research papers on control aspects of DWC.
(Source: Web of science; keyword: 'divided wall column' refined with 'control'; accessed on 16.06.2012).

A number of patents have been filed since the first patent in 1938 by Standard Oil. The list of patents on DWC is given in Table 2.1.

Table 2.1 Lists of Patents related to DWC

S. No.	Patent	Patent holder	Remarks, including names/types of products targeted by the patent	Year
1.	US 2 134 882: Fractionating apparatus and method of fractionation	Standard Oil	Dividing wall at lower end	1938
2.	US 2 471 134: Fractionation apparatus	Standard Oil	1 side draw	1949
3.	US 4 230 533: Fractionation method and apparatus	Phillips Petroleum	Control	1980
4.	DE 3302525: Destillationskolonne zur Zerlegung eines aus mehreren Frak-tionen bestehenden Zulaufproduktes	BASF	Multiple dividing walls, multiple side draws	1983
5.	DE 35 14 365: Destillations system, bestehend aus zwei Destillations-kolonnen zur destillativen energie-günstigen Zerlegung eines aus mehreren Fraktionen bestehenden Zulaufproduktes	BASF	Thermally coupled distillation columns	1984
6.	EP 0 122 367: Destillationskolonne	BASF	2 side draws	1984
7.	DE 35 10 365: Verfahren zur destilla-tiven Zerlegung eines Gemisches mittels einer Destillationskolonne	BASF	Separation of 2- or 3-component mixtures	1985
8.	EP 0 133 510: Verfahren zur Zerle-gung eines azeotropen Stoffge-misches	BASF	Azeotropic distillation	1985
9.	DE 35 22 234 : Verfahren zum energiegünstigen Betreiben einer Destillationskolonne	BASF	Control	1987
10.	EP 0 284 971: Verfahren zur Gewinnung von 1,3-Butadien	BASF	Thermally coupled distillation columns	1988
11.	EP 0 380 001: Verfahren zur Abtrennung geringer Mengen einer Mittelsiederfraktion aus einem Flüssigkeitsgemisch	BASF	Thermally coupled distillation columns	1990
12.	DE 43 36 984: Kolonne für überhitzte	Montz	Construction details,	1993

	Flüssigkeiten		integrated flash-box	
13.	EP 0 640 367: Destillationskolonne zur Trennung eines Flüssigkeitsge-misches in mehrere reine Fraktionen	BASF	Thermal insulation of the dividing wall	1995
14.	DE 43 36 983: Kolonne mit einer Trennwand	Montz	Construction details	1995
15.	DE 43 36 985: Kolonne zum Durch-führen thermischer Trennungen und/oder chemischer Reaktionen	Montz	Construction details, self-centering packing elements	1995
16.	DE 43 36 986: Kolonne mit Trenn-wand	Montz	Construction details	1995
17.	EP 0 684 060: Verfahren und Vor-richtung zur destillativen Trennung von Stoffgemischen	BASF	Adjusted liquid distribution	1995
18.	DE 196 18 152: Verfahren zur Tren-nung von Rohester im DMT-Prozess	Hüls	Thermally coupled distillation columns	1997
19.	EP 0804 951: Trennwandkolonne zur kontinuierlichen destillativen Zerle-gung von Mehrstoffgemischen	BASF	Unfixed wall elements	1997
20.	EP 0 780 147: Verfahren zur Rege-lung einer Trennwandkolonne oder einer thermisch gekoppelten Destilla-tionskolonne	BASF	Control	1997
21.	WO 1999/56 848 : Device and method for distillation	Sumitomo Heavy Industries	Lateral offset of the dividing wall	1999
22.	DE 199 58 464 : Verfahren zur Extrak-tivdestillation und Kolonne zur Durch-führung des Verfahrens	Krupp Uhde	Extractive distillation, integrated side column	2000
23.	EP 1 042 040: Rectifying column for extractive distillation of close-boiling or azeotropic mixtures	Krupp Uhde	Extractive distillation	2000
24.	DE 101 35 585: Verfahren und Vor-richtung zur Gewinnung einer reinen Benzol, Toluol und Xylole umfassen-den Aromatenfraktion aus Raffinerie-strömen durch Extraktivdestillation	Krupp Uhde	Extractive distillation, multiple dividing walls	2000
25.	EP 1 088 577: Kolonnentrennwand	Montz	Unfixed wall elements	2000
26.	DE 100 33 958985: Verfahren zur Reaktivdestillation	BASF	Reactive distillation	2001

27.	JP 2001 334 101: Distillation appara-tus and distillation method using the same	Kyowa Yuka	Multiple dividing walls	2001
28.	JP 2001 353 401: Distillation appa-ratus has partitions formed in dis-tillation regions obtained by partitioning tower housing	Kyowa Yuka	Multiple dividing walls	2001
29.	DE 100 22 465 : Verfahren und Vor-richtung zur Aufarbeitung eines C4-Schnitts aus der Fraktionierung von Erdöl	BASF	Reactive distillation	2001
30.	WO 2001/ 79 389: Plant for the extrac-tion of aromatic substances from a hydrocarbon mixture containing aro-matic and non-aromatic substances	Krupp Uhde	Extractive distillation, aromatics	2001
31.	DE 100 19 196: Verfahren zur Gewin-nung eines aus Benzol und Toluol oder Toluol und Xylol bestehenden Aromatenproduktes hoher Reinheit aus einem Nichtaromaten enthalten-den eng- oder azeotropsiedenden Vorprodukt und Anlage zur Druch-führung des Verfahrens	Krupp Uhde	Extractive distillation BTX	2001
32.	EP 1 080 766: Distillation of multicom-ponent fluid e.g. air, involves partial separation in first column, with mixture stream transferred one-way for final separation in second column	Air Products and Chemicals	Thermally coupled distillation columns	2001
33.	DE 101 63 335 : Trennwandkolonne mit ganz oder teilweise dampfförmigen Zulauf und/oder ganz oder teilweise dampfförmiger Seitenentnahme	BASF	Diagonal offset of the dividing wall	2001
34.	EP 1 151 781: Trennwandkolonne	BASF	Unfixed wall	2001
35.	EP 1 108 966: Process for separation of multicomponent fluids using a multizone distillation column	Air Products and Chemicals	Integrated side columns	2001
36.	EP 1 112 769: Verfahren zur Extrak-tivdestillation und Kolonne zur Durch-führung des Verfahrens	Krupp Uhde	Integrated side column	2001
37.	DE 199 63 017: Verfahren zum Be-treiben einer Trennwanddestillations-kolonne	Wacker	Control	2001
38.	DE 199 58 464: Verfahren zur Extrak-tivdestillation und Kolonne zur Durch-führung des Verfahrens	Krupp Uhde	Control extractive distillation	2001
39.	EP 0 126 288: Verfahren zur Durch-führung von chemischen Reaktionen und gleichzeitiger destillativer Zerle-gung eines Produktgemisches in mehrere Fraktionen mittels einer Destillationskolonne	BASF	Reactive distillation	2002

40.	WO 2002/45 811: Method and device for separating a substance mixture into the component parts thereof by means of extractive distillation in a separating wall column	Linde	Extractive distillation	2002
41.	WO 2002/094 408: Fixing parts and seals for partition elements of a multi-section partition	Montz	Unfixed wall elements in trayed columns	2002
42.	DE 103 52 294: Kolonne	Montz	Mixing elements at the ends of the dividing wall	2002
43.	EP 0141 356: Verfahren zur Gewin-nung eines konjugierten Diolefins und/oder Olefins aus einem C4- oder C5-Kohlenwasserstoffgemisch	BASF	Multiple dividing walls, extractive distillation	2003
44.	JP 2003 220 301: Distillation purification method has distillation column with four divided chambers to separate components of different boiling points in raw material	JGC	Dividing walls at upper and lower ends of the column	2003
45.	EP 1 317 947: Improved batch distillation	Air Products and Chemicals	Discontinuous operation	2003
46.	US 2 295 256: Process and device for fractional distillation of liquid mixtures, more particularly petroleum	Brugma	Thermally coupled distillation columns	2003
47.	US 6 645 350: Dividing wall column fractionation tray	UOP	Thermal insulation of the dividing wall	2003
48.	DE 103 19 159: Verfahren zur destilla-tiven Gewinnung von hochreinem Tri-ethylendiamin (TEDA)	BASF	Dividing wall at lower end, TEDA	2003
49.	EP 1 329 449: Kolonne zur Aufkon-zentrierung von Phthalsäureanhydrid	Lurgi	Dividing wall across the column, phthalic anhydride	2003
50.	US 6 551 465: Dividing wall column control system	UOP	Control	2003
51.	US 6 558 515: Dividing wall fractionation column control system and apparatus	UOP	Control	2003
52.	DE 10 2004 004 672: Verfahren zur	BASF	2 side draws	2004

	destillativen Gewinnung von reinen Isopropenylethern			
53.	EP 1 378 282: Distillation apparatus	Sumitomo Heavy Industries	Lateral offset of the dividing wall	2004
54.	US 2004/0182751: Low capital implementation of distributed distillation in ethylene recovery	BP America	Dividing wall at lower end, ethylene	2004
55.	WO 2004/103 937: Recovery of crude butadiene from a C4 fraction by extractive distillation in a partitioned column comprises controlling column parameters so that the bottoms stream consists of purified solvent	BASF	Dividing wall at upper end, butadiene	2004
56.	WO 2004/071 618: Control apparatus to control dividing wall section ope-ration of dividing wall fractional distillation zone, has controller regu-lating input of heat in reboiler, and flow rate controller regulating the rate of net bottom stream	UOP	Control	2004
57.	DE 10 2004 004 530: Destillations-verfahren	Kao	Control	2004
58.	WO 2004/052 491: Improved dis-tillation systems	Fluor	Control	2004
59.	DE 10 2005 002 129: Reaktor und Verfahren in einem Reaktor mit einem Reaktorinnenraum, der in zwei oder mehrere voneinander getrennte Reaktionsräume aufgeteilt ist	BASF	Multiple dividing walls, dividing walls in reactors	2005
60.	EP 1 598 098: Trennwandkolonne	BASF	Construction for high temperature differences	2005
61.	DE 10 2005 003 499: Verfahren und Vorrichtung zur Trennung von Stoff-gemischen	Linde	Integrated side column	2005
62.	DE 10 2005 029 643: Verfahren zur Gewinnung von Reinstyrol aus einer Pyrolysebenzinfraktion	Uhde	Dividing wall at the upper end, styrene	2005
63.	JP 2005 513 586: Distillation appara-tus, e.g. for liquid slurry, has actuator to move movable perforated panel of change tray to adjust flow rate of steam supplied from one distillation column to other distillation column	Kansai Kagaku Kikai Seisakusho	Control	2005
64.	EP 1 108 965 : Process for distillation of multicomponent fluid suitable for production	Air Products	Integrated side column	2006

	of an argon-enriched stream from a cryogenic air separation process			
65.	CN 1745868: Extraction rectification tower has isolating wall vertically arranged from tower top to lower part of tower to divide internal space of tower into three sub-spaces	Jiangsu ind. college	Dividing wall at the upper end	2006
66.	EP 1 127 601: Trennwandkolonne zur Auftrennung eines Vielstoffgemisches	BASF	Diagonal offset of the dividing wall	2007
67.	EP 1 647 318: Dividing wall column	Air Products and Chemicals	Arrangement of regular packings in dividing wall columns	2008
68.	US 5914012: Dividing wall distillation column	LG Chem. Ltd	Temperature and pressure control	2011
69.	EP 2409746: Dividing wall distillation columns for production of high-purity 2-ethylhexanol and fractionation method using same	LG Chem. Ltd.	Dividing wall, 2-ethyl hexanol	2012

2.7 Scope and Objective of the Present Work

An important motivation for studying integrated distillation column arrangements (either thermally coupled or divided wall column) is to reduce the energy requirement for the separation of a ternary mixture or multi-component mixture with desired purities of the components. On a global basis, distillation columns utilize a large portion of the total industrial energy requirement. An incremental enhancement in the energy efficiency can save huge amount of energy.

The increasing energy cost and concern on climatic behaviour in the recent times have made the DWC an attractive alternative to conventional distillation columns in CPI. The energy saving that can accrue with the use of complex integrated columns has not been fully exploited by the industry so far. This stems primarily from the lack of confidence on the design, operation and control of DWCs. Although a number of companies have started using DWCs in retrofitted column, new design, etc., the confidence level is yet to percolate down across the industry. Therefore, a better understanding of the characteristics of these systems is required.

Objective of the present work:

Based on the critical literature review, the following objectives have been set for the present work:

1. Studies on a divided wall distillation column with reference to
    a. Modelling of a divided wall distillation column.
    b. the rationalization of the degree of freedom analysis.
    c. the effect of column pressure drop
    d. the effect of feed quality
    e. Optimization of energy requirement
2. Case studies of ternary systems in a DWC for the energy efficiency.

Chapter – III

DIVIDED WALL DISTILLATION COLUMN : MODELLING AND DEGREE OF FREEDOM ANALYSIS

3.1 Introduction

A complete mathematical model of a tray distillation column is required to describe material, energy and momentum balance equations for each individual tray of the entire column subject to thermodynamic constraints of vapour- liquid equilibrium (VLE). Most of the existing models (Friday and Smith, 1964; Tomich, 1970; Naphtali and Sandholm, 1971; Hess and Holland, 1977; Hofeling and Seader, 1978) ignore momentum balance equations and rely only upon material and energy balance equations with VLE. These model equations are commonly known as MESH (material balance, vapour-liquid equilibrium, summation, and enthalpy (H) balance) equations. Several versions of these MESH equations have been used by different investigators by choosing different sets of independent and dependent variables (Friday and Smith, 1964; Tomich, 1970; Naphtali and Sandholm, 1971; Hess and Holland, 1977; Hofeling and Seader, 1978).

3.2 Simple Distillation Column

Let l and v are component flow rates in the liquid and vapour phases, respectively. The subscript (i) refers to stage number from where the stream is emanating and the subscript (j) refers to the component number. For a simple distillation column with one feed and two products (as shown in Fig. 3.1), the following set of equations can be written (Friday and Smith, 1964):

1) Component material (M) balance equation (for j=1 … C):

$$v_{2,j} - l_{1,j} - v_{1,j} = 0 \qquad \text{(condenser, } i\text{=1)} \qquad (3.1)$$

$$l_{i-1,j} + v_{i+1,j} - l_{i,j} - v_{i,j} = 0 \qquad (i\text{=2 … } N\text{-1; } i \neq f) \qquad (3.2)$$

$$l_{f-1,j} + v_{f+1,j} - l_{f,j} - v_{f,j} + F_j = 0 \qquad \text{(feed plate, } i\text{=}f\text{)} \qquad (3.3)$$

$$l_{N-1,j} - l_{N,j} - v_{N,j} = 0 \qquad \text{(reboiler, } i\text{=}N\text{)} \qquad (3.4)$$

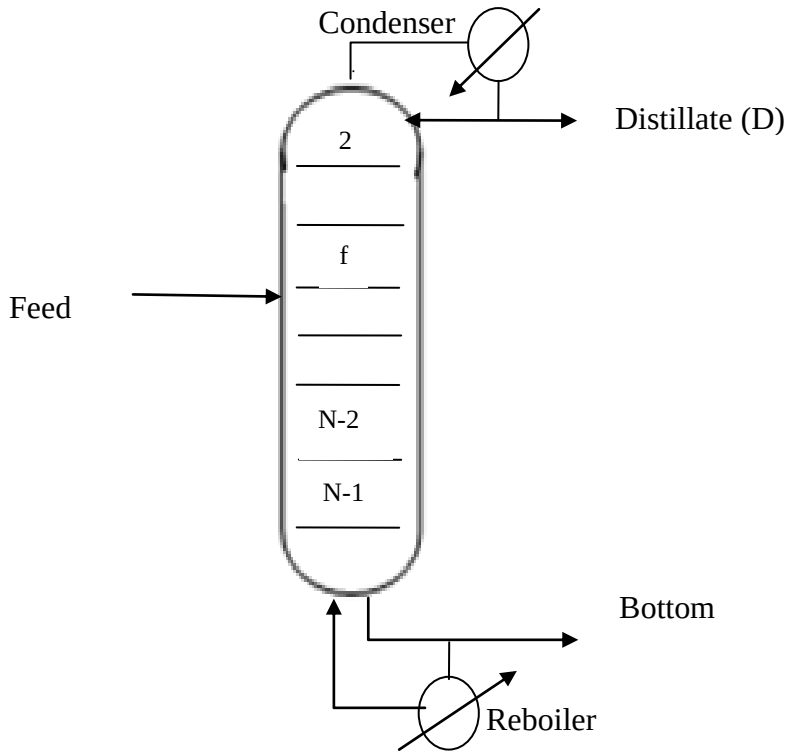

Figure 3.1: Simple distillation column

For condenser (i=1) and reboiler (i=N), $v_{1,j}$ and $l_{N,j}$ have special meanings as they refer to j^{th} component of distillate and bottom product, respectively. It may, however, be noted that an overall material balance equation (3.5) is not an independent equation as it can be obtained by the summation of equations (3.1)- (3.4) for all value of i and j.

$$\Sigma F_j = \Sigma v_{1,j} + \Sigma l_{N,j} \qquad (3.5)$$

2) Summation (S) equations:

Overall liquid flow rate:

$$L_i = \sum_{j=1}^{C} l_{i,j} \qquad (i=1 \ldots N) \qquad (3.6)$$

Overall vapour flow rate:

$$V_i = \sum_{j=1}^{C} v_{i,j} \qquad (i=1 \ldots N) \qquad (3.7)$$

Some authors use the above equations (3.6) and (3.7) in terms of mole fraction by dividing equation (3.6) by L_i and equation (3.7) by V_i. Thus, the summation equations may be written as:

$$1 = \Sigma\, x_{i,j} \qquad (i= 1,... N) \qquad (3.8)$$

$$1 = \Sigma\, y_{i,j} \qquad (i= 1,... N) \qquad (3.9)$$

3) Equilibrium (E) relation

$$y_{i,j} = K_{i,j}\, x_{i,j} \qquad (i=2,...,N;\ j=1..c) \qquad (3.10)$$

where, at a given temperature T_i and pressure P_i, equilibrium constants $K_{i,j}$ are dependent variables $\{K_{i,j} = K(T_i, P_i, l_{i,j}, v_{i,j})\}$ which can be obtained by a suitable thermodynamic equation of state such as those suggested by Redlich- Kwong (RK) (1949), Soave- Redlich- Kwong (SRK) (1972), Peng-Robinson (PR) (1976), etc., Above equilibrium relation (equation 3.10) can be expressed in terms of $l_{i,j}$ and $v_{i,j}$ (except for the total condenser) as follows

$$v_{i,j} - V_i K_{i,j}\left(\frac{l_{i,j}}{L_i}\right) = 0 \qquad (i=2 \ldots N;\ j=1,...c) \qquad (3.11)$$

In a condenser, reflux ratio (R) is maintained between the reflux stream and the distillate stream by using a splitter. Thus, the following C number of equations appears to represent the splitter in place of vapour-liquid equilibrium for a total condenser (i=1):

$$l_{1,j} - R v_{1,j} = 0 \qquad (3.12)$$

4) Enthalpy (H) balance equations:

$$V_2 H_2 - (L_1 + V_1) h_i - Q_C = 0. \qquad \text{(for condenser, } i=1) \qquad (3.13)$$

$$L_{i-1} h_{i-1} + V_{i+1} H_{i+1} - L_i h_i - V_i H_i = 0. \qquad (i=2\ldots N\text{-}1;\ i \neq f) \qquad (3.14)$$

$$L_{f-1} h_{f-1} + V_{f+1} H_{f+1} - L_f h_i - V_f H_f + HF \sum_{j=1}^{C} F_j = 0. \quad \text{(feed plate, } i=f) \qquad (3.15)$$

$$L_{N-1} h_{N-1} - L_N h_N - V_N H_N + Q_B = 0. \qquad \text{(reboiler, } i=N) \qquad (3.16)$$

In the above equations (3.13)- (3.16), $H_{i,j} = H(T_i, P_i, v_{ij})$ and $h_{i,j} = h(T_i, P_i, l_{ij})$ are respectively, vapour and liquid phase enthalpies which are generally obtained by integrating heat capacity of individual components with respect to a fixed reference temperature along with the enthalpy departure functions. Thus, these enthalpy parameters become dependent variables at a given temperature T_i and pressure P_i.

The influence of pressure variations upon distillation operation has not been considered by most of the investigators. As discussed earlier in the literature review, Chapter II, the stage pressure is generally selected arbitrarily, because the stage pressure does not affect significantly the distillation column calculations. This is because the vapour-liquid equilibrium and enthalpies are only weak functions of pressure. In an actual column, however, the pressure drop across each stage depends both on the design as well as the operating parameters such as tray type and vapour and liquid flow rates. Li et al. (2006) carried out the sensitivity analysis of distillation performance to operating pressure and found that the column operating pressure has significant impact on vapour- liquid equilibrium at high internal flow rates.

Lockett (1986) has presented a detailed analysis of the relations between hydrostatic pressure head created in the down comer and the pressure drop across sieve trays. Fig. 3.2 shows a sieve tray and tray hydraulic parameters. An abridged version of these correlations for sieve-tray column can be expressed as force balance equations, as given below:

5) Force balance (delta P) equations:

$$(P_i - P_{i-1}) - \rho_L \, g \, ht_i = 0 \qquad (i=2 \ldots N\text{-}1) \qquad (3.17)$$

Where,

$$ht_i = (h_w + h_{ow} + h_d + h_r)_i \qquad (3.18)$$

ht_i is the liquid head equivalent to the pressure drop between i^{th} tray and $(i\text{-}1)^{th}$ tray, and P_i is the absolute pressure of the vapour phase in the vapour-liquid disengagement space above i^{th} tray. For the estimation of the dependent variable ht_i, appearing in equation (18), the height of the liquid crest over the weir (h_{ow}), pressure drop through the dry plate (h_d), and residual head (h_r) can be obtained from the following relationships (The details are given by Lockett, 1986, and Towler and Sinnott, 2008):

$$h_{ow} = f_o(L_i, W_L) \qquad (3.19)$$

$$h_d = f_d(V_i, t_p, d_h) \qquad (3.20)$$

$$h_r = f_r(\sigma_L, t_p, d_h) \qquad (3.21)$$

Where, W_L, d_h, t_p, and σ_L are weir length, hole diameter, plate thickness and surface tension of liquid, respectively.

In the case of the reboiler ($i=N$), equation (3.17) is not applicable. However, pressure drop can be expressed as

$$(P_N - P_{N-1}) - \Delta P_{\mathrm{Re}} = 0 \qquad (i=N) \qquad (3.22)$$

where, ΔP_{Re} is the pressure drop in the reboiler, which can be estimated by the following equation (Towler and Sinnott, 2008)

$$\Delta P_{\mathrm{Re}} = \frac{f^o \, G_S^2 \, D_S \, (N_{Pass} + 1)}{2 g \rho \, D_e \, \varphi_S} \qquad (3.23)$$

Here, f°, D_S, N_{Pass}, ρ, D_e, ϕ_S are friction factor, shell side diameter, number of passes, density of liquid, equivalent diameter, and ratio of viscosity of liquid to the viscosity of water, respectively.

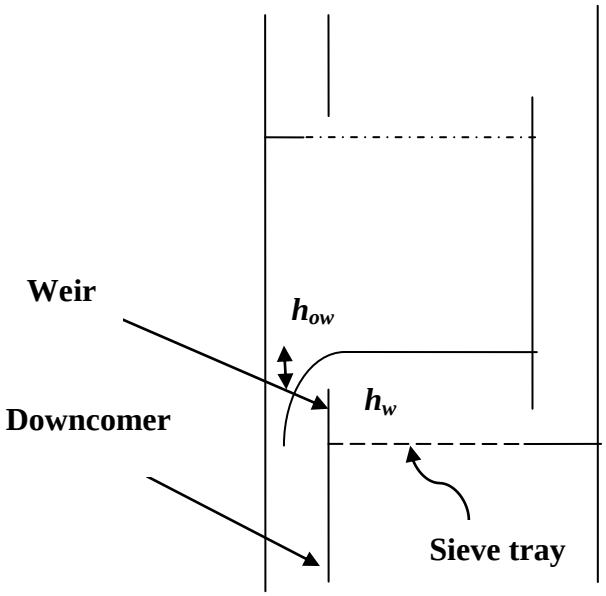

Figure 3.2: Hydraulic parameters for a sieve tray.

3.2.1 Simple Distillation Column with One Intermediate Product

In such a distillation column, a third product stream is taken out as a side draw from an intermediate stage (say from stage number N_{S3}). Equations (3.2) and (3.14) are rewritten for $i = N_{S3}$ and added to the set of material and energy balance equations, (3.1- 3.4) and (3.12-3.16) as follows:

$$l_{Ns3-1,j} + v_{NS3+1,j} - l_{NS3,j} - v_{Ns3,j} - S_3 l_{NS3,j} / L_{NS3} = 0 \qquad (i=N_{S3}) \qquad (3.24)$$

and $$L_{NS3-1} h_{NS3-1} + V_{NS3+1} H_{NS3+1} - L_{NS3} h_{NS3} - V_{Ns3} H_{NS3} - S_3 h_{NS3} = 0. \ (i=N_{S3}) \qquad (3.25)$$

3.2.2 Divided Wall Distillation Column

A typical DWC as shown in Figure 3.3 consists of a condenser, a reboiler and *N–2* full size trays. The trays numbered N_{s1}+1 to N_{s2} are divided into two parts. For applying the conventional MESH equations plus the pressure drop (ΔP) equation, taken together as MESHD equations, the trays are numbered sequentially from top to bottom (including feed tray and all the divided trays of section 1) in the same way as discussed earlier for a simple distillation column. Thus the condenser is numbered as stage 1, top most tray of the divided section 1 is N_{s1}+1, last tray of the divided section 1 is N_{s2}, and the reboiler is numbered as stage number *N*. Similarly, top-down numbering of second section of the column starts from *N*+1 and continues to N_T, i.e., the last divided tray in section 2.

Thus in the DWC shown in Fig. 3.1, trays numbered 2 to N_{s1} are full size trays, whereas trays below N_{s1} (up to N_{s2}) are divided into two parts. The first tray of the first half in section 1, i.e., the first divided tray just below tray number N_{s1} is numbered as N_{s1}+1, whereas the second half of the same tray (in section 2) is numbered as *N*+1. This scheme of nomenclature of stages makes a DWC exactly the same as a pair of thermally coupled columns in which the main column (including divided section between stage number N_{s1} to stage number N_{s2}) has *N* stages and the post-fractionator (section 2) has (N_{s2} – N_{s1}) stages such that the total number of stages, $N_T = N + (N_{s2} - N_{s1})$.

Liquid stream originating from stage number N_{S1} is divided into two parts: L_{NS1} and *L*s, among them L_{NS1} goes to stage number N_{S1}+1 of section 1 and *L*s goes to stage number *N*+1, i.e., to the uppermost tray of section 2 of the DWC. Similarly, vapour stream originating from N_{S2} is also divided into two parts (V_{NS2} and *V*s): V_{NS2} goes to stage N_{S2}-1, and *V*s goes to the bottom stage of section 2.

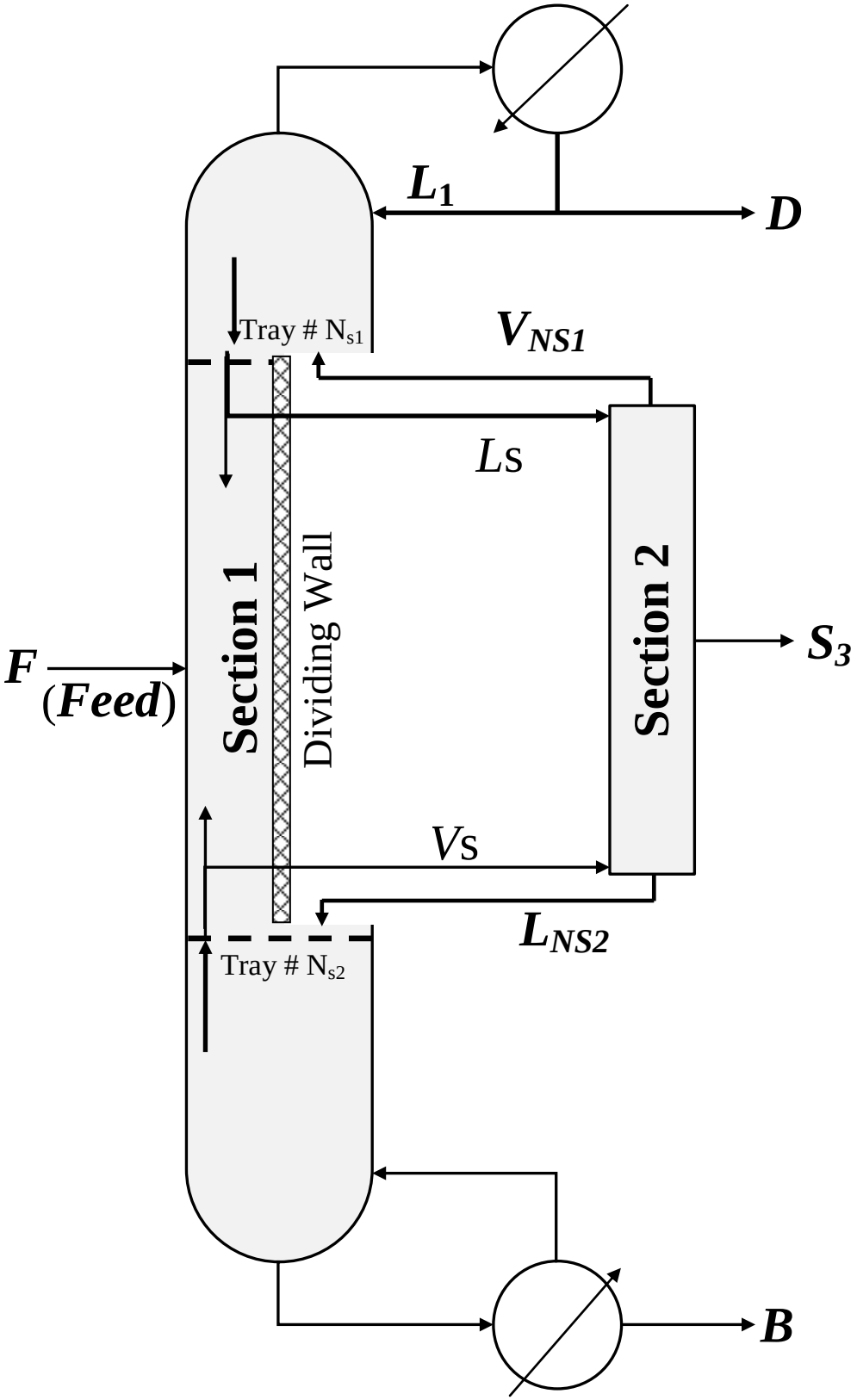

Figure 3.3: Divided wall column (DWC) with inter connecting stream.

The main column (column 1) has two side draws, one liquid *L*s emanating from stage N_{s1} and the other vapour stream *V*s emanating from stage N_{s2}. A secondary stream S_3 is withdrawn from stage number N_{S3} which is in the second half of the divided section. To model these additional columns and connecting streams, the model equations, equations (3.1) to (3.4), (3.6), (3.7) and (3.10) to (3.17) are to be modified, as given below:

1) Component material (M) balance equation (for all j=1 … C):

$$l_{Ns1-1,j} + v_{NS1+1,j} - l_{NS1,j} - v_{Ns1,j} - R_1 l_{NS1,j} + v_{N+1,j} = 0 \quad (i=N_{S1}) \tag{3.26}$$

Where, $R_1 = Ls / L_{NS1}$

$$l_{Ns2-1,j} + v_{NS2+1,j} - l_{NS2,j} - v_{Ns2,j} - R_2 v_{NS2,j} + l_{NT,j} = 0 \quad (i=N_{S2}) \tag{3.27}$$

Where, $R_2 = Vs / V_{NS2}$

4) Enthalpy (H) balance equation:

$$L_{NS1-1}h_{NS1-1} + V_{NS1+1}H_{NS1+1} - L_{NS1}h_{NS1} - R_1 L_{NS1}h_{NS1} - V_{Ns1}H_{NS1} + V_{N+1}H_{N+1} = 0. (i=N_{S1}) \tag{3.28}$$

$$L_{NS2-1}h_{NS2-1} + V_{NS2+1}H_{NS2+1} - L_{NS2}h_{NS2} - R_2 L_{NS2}h_{NS2} - V_{Ns2}H_{NS2} + L_{NT}H_{NT} = 0. (i=N_{S2}) \tag{3.29}$$

5) Pressure balance equation (between two sections):

$$(P_{NS2} - P_{NS1}) - (P_{N+1} - P_{NT}) = 0 \tag{3.30}$$

3.3 Degree of Freedom (DOF) Analysis

The degrees of freedom (DOF) of a system are independent of the way in which dependent and independent variables of the system are arranged. The model equations lead to $N(2C+1)$ independent equations for a simple distillation column with one feed and two product (top and bottom) streams, where *C* is the number of components in the feed and *N* is the number of stages in the column including the condenser and the reboiler.

A summary of all independent and dependent variables and the number of independent MESH equations appearing in above model equations (3.1) to (3.16) are presented in Table 3.1.

Table 3.1 Summary of number of independent variables and independent MESH equations for a simple distillation column.

Equation No.	Variable		No. of new independent variables introduced	No. of independent equations
	Independent	Dependent		
3.1-3.4	$l_{i,j}$, $v_{i,j}$, F_j	—	$2NC+C$	NC
3.6 and 3.7	—	L_i, V_i	—	—
3.10 and 3.11	$(T_i)_{i=2\ldots N}$, $(P_i)_{i=2\ldots N}$	$K_{i,j}$	$2N$-2	NC-C
3.12-3.16	R, Q_C, P_1, HF, Q_B	H_i, h_i	5	$N+C$
Total:			$2N(C+1)+C+3$	$N(2C+1)$

Therefore, for a column with total number of stages N and the number of components C, the total number of independent variables, i.e., $(l_{i,j}, v_{i,j}, P_i, F_j)_{i=1\ldots N,\, j.=1\ldots C}$, $(T_i)_{i=2\ldots N}$, R, HF, Q_C, Q_B becomes $2N(C+1)+C+3$, and the number of independent equations (equations (3.1)-(3.4) and (3.11)-(3.16) becomes $N(2C+1)$. Thus it is possible to find the values of unknowns by solving these equations simultaneously only after introducing $N+C+3$ number of additional equations as degrees of freedom. Normally, N number of degrees of freedom are used to specify pressure on each stage (including condenser and reboiler). In most of the commercial software, this is done by assuming constant pressure along the column or by assuming constant pressure drop across each stage. Out of the remaining $C+3$ degrees of freedom, $C+1$ are used in specifying feed composition and feed enthalpy. For the present set of model equations, remaining two degrees of freedom can be used to specify any two of R, Q_C, Q_B, and $v_{1,1}$ or $l_{N,1}$ (either the purity of the distillate or the purity of the bottom product), etc. It is possible to arrange model equations in different ways that may use other variables

like distillate, bottom product and/or reflux flow rate, boil-up ratio, condenser temperature, etc., as variable parameters and can be specified as degrees of freedom, For example Q_c in equation (3.13) can be replaced in terms of condenser temperature or the degree of sub-cooling. In any case, however, the number of parameters to be specified cannot exceed two, after the feed and stage pressures are specified.

When tray hydrodynamics is taken into account, additional N-1 independent equations (equation 3.22) are available to correlate stage pressures that reduce the degrees of freedom for a simple distillation column with three products from $N+C+3$ to $C+4$. After specifying feed composition and enthalpy, only three degrees of freedom, including condenser pressure or pressure at any one stage in the column, are needed to be specified for the simulation or control of an ordinary distillation column.

Many investigators have included some of the parameters appearing in equations (3.19) - (3.21), number of stages N, feed plate location f, as contributing to the degrees of freedom. However, these parameters can be assigned freely at the time of design but not at the time of simulation or operation. Therefore, for simulation of an ordinary distillation column with a known feed stream, the degree of freedom is reduced to three that includes condenser pressure (or pressure at some known location inside the column).

On the other hand, the designers have many more parameters that can be used to optimize the process. These parameters may include weir length (W_L), column diameter (D_t), hole diameter (d_h), plate thickness (t_p), weir height (h_w), number of trays in the main column (N), feed plate location (f), etc. An exhaustive list of these designers' freedom may include several more parameters including the number and arrangement of holes on a tray. In the present work, however, degree of freedom at the time of simulation of an existing column is considered for which design parameters are assumed to be constant.

For a simple distillation column with a side stream, the introduction of one side product does not introduce any new equation but includes one extra variable S_3, which may either be the side product flow rate or the side product purity. Therefore, the degrees of freedom of a single column with a known feed and three products become C+5 which is one more than that for the column with only two products. As discussed earlier, in this case also, C+1 degrees of freedom are used to specify feed and one for condenser pressure leaving aside three parameters to be specified from S_3 , R, Q_C, Q_B, purity of distillate or bottom product, flow rates of distillate, bottom product or reflux streams, boil-up ratio, etc.

In comparison to a simple distillation column with three product streams, a DWC has one additional equation (3.30) for pressure balance between two sections and two additional independent variables (Ls and Vs). Thus, the degrees of freedom of a DWC is just one more than that obtained for a simple distillation column with three product streams. The number of these MESHD equations and variables for DWC are summarized in Table 3.2.

It is evident from Table 3.2 that in case of a DWC, the DOF, i.e. the difference between the number of independent variables and the number of independent equations is found to be C+6. If C+2 variables representing feed properties (F_j and H_F) and condenser pressure are known, the DOF of an existing DWC, with fixed number of stages (N_T) and fixed location of divided segment and intermediate product stages (N_{S1}, N_{S2}, and N_{S3}), reduces to four which is at least one less than that reported by many investigators for the steady state operation of a DWC. Ideally these four degrees of freedom can be used to specify any four independent variables appearing in equations (3.1) to (3.30). However, parameters that can lead to easier convergence may include any four from reflux ratio R, liquid split ratio R_1, side draw S_3, Q_C, Q_B, $v_{1,1}$ or $l_{N,1}$.

Table 3.2 Summary of number of independent variables and independent MESHD equations for a DWC.

Equation No.	Variables		No. of independent variables	No. of independent equations
	Independent	Dependent		
3.1-3.44, 3.24, 3.26, 3.27	$l_{i,j}$, $v_{i,j}$, F_j, S_3, Ls, Vs	R_1, R_2	$2N_TC+C+3$	N_TC
3.6 and 3.7	—	L_i, V_i	—	—
3.10 and 3.11	$(T_i)_{i=2...NT}$ $(P_i)_{i=2...NT}$	$K_{i,j}$	$2N_T$-2	N_TC-C
3.12- 3.16, 3.25, 3.28, 3.29	R, Q_C, P_1, Q_B, H_F	H_i, h_i	5	N_T+C
3.17, 3.22, 3.30	—	ht_i, ΔP_{Re}	—	N_T
3.18- 3.21	—	$(h_{ow})_i$, $(h_d)_i$, $(h_r)_i$	—	—
Total:			$2N_T(C+1)+C+6$	$2N_T(C+1)$

Thus, for a given DWC or a Petyluk column operating under steady state conditions with known feed and condenser pressure, the DOF is four. This is one more than that for a conventional distillation column with three product streams (distillate, bottoms and the intermediate product). Therefore, when the model equations representing pressure drop are taken into consideration, no extra degree of freedom is left which can be used to specify simultaneously both the connecting streams between two columns.

Chapter – IV

PROBLEM DEFINITION AND SOLUTION TECHNIQUE

4.1 Schematic Representation of a DWC

A typical DWC, as shown in Figure 4.1, consists of a condenser, a reboiler and *N–2* number of full size trays, out of which trays numbered N_{s1}+1 to N_{s2} are divided into two parts. For applying the conventional MESH equations plus the pressure drop (ΔP) equation, taken together as MESHD equations, the trays are numbered sequentially from top to bottom (including feed tray and all the divided trays of section 1) in the same way as that for a simple distillation column. Thus the condenser is numbered as stage 1, top most tray of the divided section 1 is numbered as N_{s1}+1, last tray of the divided section 1 as N_{s2}, and the reboiler is numbered as stage number *N*. Similarly, top-down numbering of second section of the DWC starts from *N*+1 and continues to N_T, i.e., the last divided tray in section 2. Thus in the DWC, trays numbered 2 to N_{s1} are full sized trays, whereas trays below N_{s1} (up to N_{s2}) are divided into two parts. The first tray of first half in section 1, i.e., the first divided tray just below tray number N_{s1} is numbered as N_{s1}+1 whereas the second half of the same tray (in section 2) is numbered as *N*+1. This scheme of nomenclature for stages makes a DWC exactly the same as a pair of thermally coupled columns in which main column (including divided section between stage number N_{s1} to stage number N_{s2}) has *N* stages and the post-fractionator (section 2) has ($N_{s2} - N_{s1}$) stages such that the total number of stages, $N_T = N + (N_{s2} - N_{s1})$.

Liquid stream originating from stage number N_{S1} is divided into two parts: L_{NS1} and *Ls* with L_{NS1} going to stage number N_{S1}+1 of section 1 and *Ls* going to stage number *N*+1, i.e., to the uppermost tray of section 2 of the DWC. Similarly, vapour stream originating from N_{S2} is also divided into two parts (V_{NS2} and *Vs*): V_{NS2} going to stage N_{S2}-1,

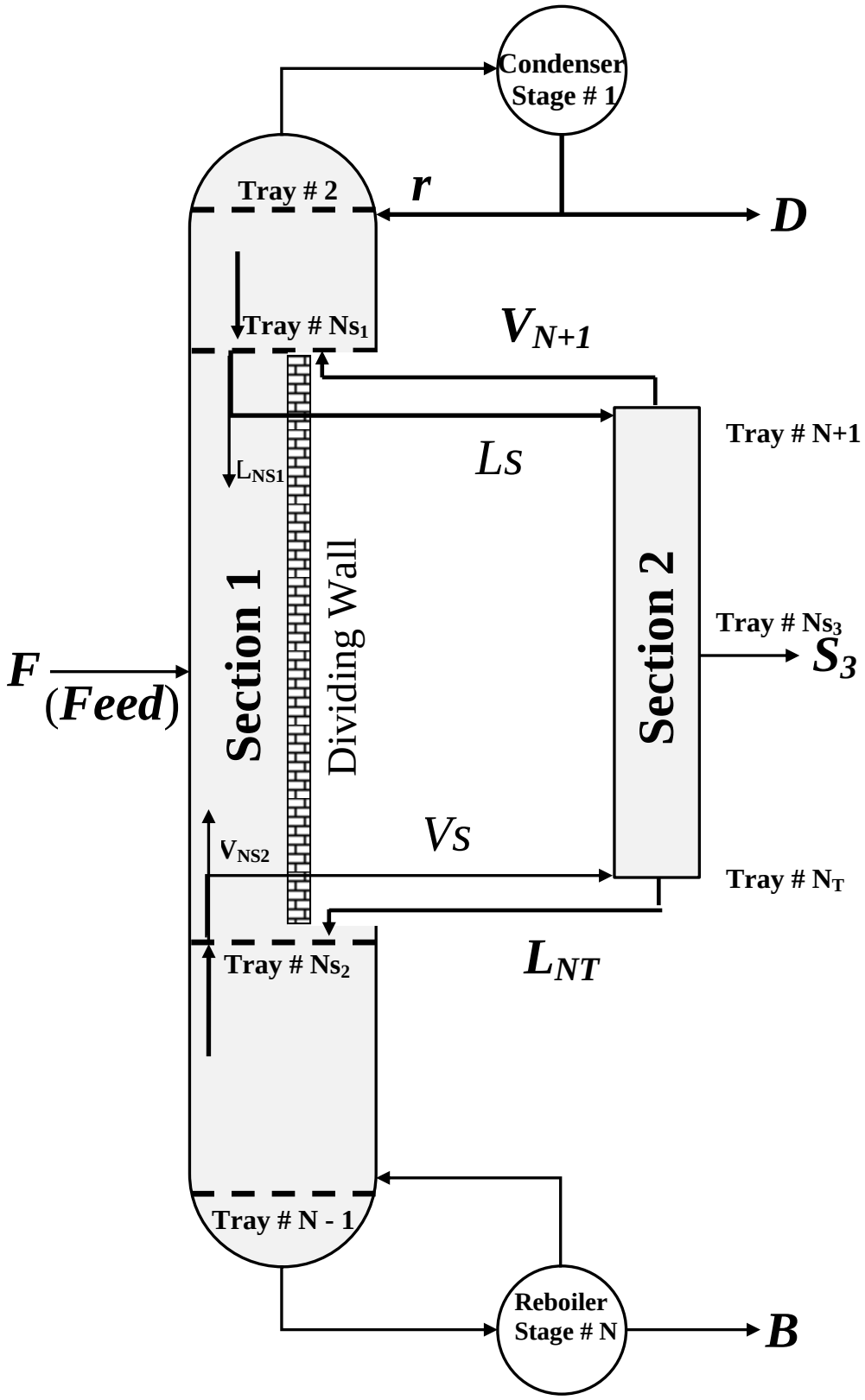

Figure 4.1: Schematic diagram of a Divided wall column (DWC) with streams and tray numbering.

and *Vs* going to the bottom stage of section 2. Thus, the main column (column 1) has two side draws, one liquid *Ls* originating from stage N_{s1} and the other vapour stream *Vs* originating from stage N_{s2}. A secondary stream S_3 (rich in component B) is withdrawn from stage number N_{S3} which is in the second half of the divided section.

4.2 Simulation of a DWC

Simulation of a DWC is a challenging task, as it involves a number of variables and recycle streams. A number of researchers in the past have ignored the effect of pressure drop during simulation stage as they found its impact to be insignificant on vapour-liquid equilibrium (Friday and Smith, 1964; Tomich, 1970; Naphtali and Sandholm, 1971; Hess and Holland 1977; Hofeling and Seader, 1978). However, Li et al. (2006) pointed out that the column operating pressure has significant impact on vapour liquid equilibrium at high internal flow rates.

For a simple column, the stage-wise arrangement of the equations gives a block tri-diagonal matrix structure, since the MESH equations contain streams emerging from stage number *i*-1, *i*, and *i*+1 only. For a cascade of columns, however, the off-diagonal elements also appear due to introduction of a few terms like $l_{p,j}$, $v_{p,j}$, and T_p representing 'connecting streams' originating from stage number *p* and reaching to the i^{th} stage. Hofeling and Seader (1978) used a modified Thomas algorithm to solve the model equations for such configurations. Similar technique is used in almost all commercially available software for solving distillation problems. It is interesting to note that the equilibrium constant $K_{i,j}$ depends both on temperature T_i and pressure P_i, however, no commercial software takes pressure as an iteration variable as $K_{i,j}$ is only a weak function of pressure. However, the ASPEN Plus™ can calculate pressure drop across each individual stage using hydrodynamic considerations separately as an external parameter.

In the present work, for rigorous simulation, the MultiFrac model of ASPEN Plus™ has been used for solving the case. MultiFrac model library is suitable for solving complex cascade of several columns. Different columns can be interconnected by using 'Connecting Streams'. MultiFrac uses these connecting streams as internal variable streams and no extra specification (or extra degree of freedom) is required for model solution.

MultiFrac uses the inside-out approach for column convergence. MultiFrac also has the Newton algorithm, which uses a Napthali-Sandholm formulation. It solves the column-describing equations and design specifications simultaneously, using Newton's method. This method can enhance convergence for highly-nonideal systems, such as azeotropic distillation.

For calculating the pressure drop, 'Tray Rating' feature of ASPEN Plus™ was used. Sieve trays were used in the DWC. Sieve trays are used extensively in plate distillation columns for vapour-liquid contacting, even for systems with moderate fouling characteristics. Large amount of data are available for design of sieve trays and the sieve tray design is easy and non-proprietary. Properly designed sieve trays have capacity and efficiency comparable to other trays. The initial estimate for the design variables were obtained by decomposing the DWC in to three-column model by using the short-cut method of Amminudin et al. (2001).

4.2.1 DWC Flowsheet in Aspen Plus

For the present simulation, just one icon of MultiFrac model was selected from the model library as one block (B1 in this case) and four input/output streams were connected to this block (Fig. 4.2.1). The stream numbers 6, 5, 7 and 4 represented the feed (F), distillate (D), side stream (S) and bottom product (B), respectively. Components and feed streams were specified in appropriate form.

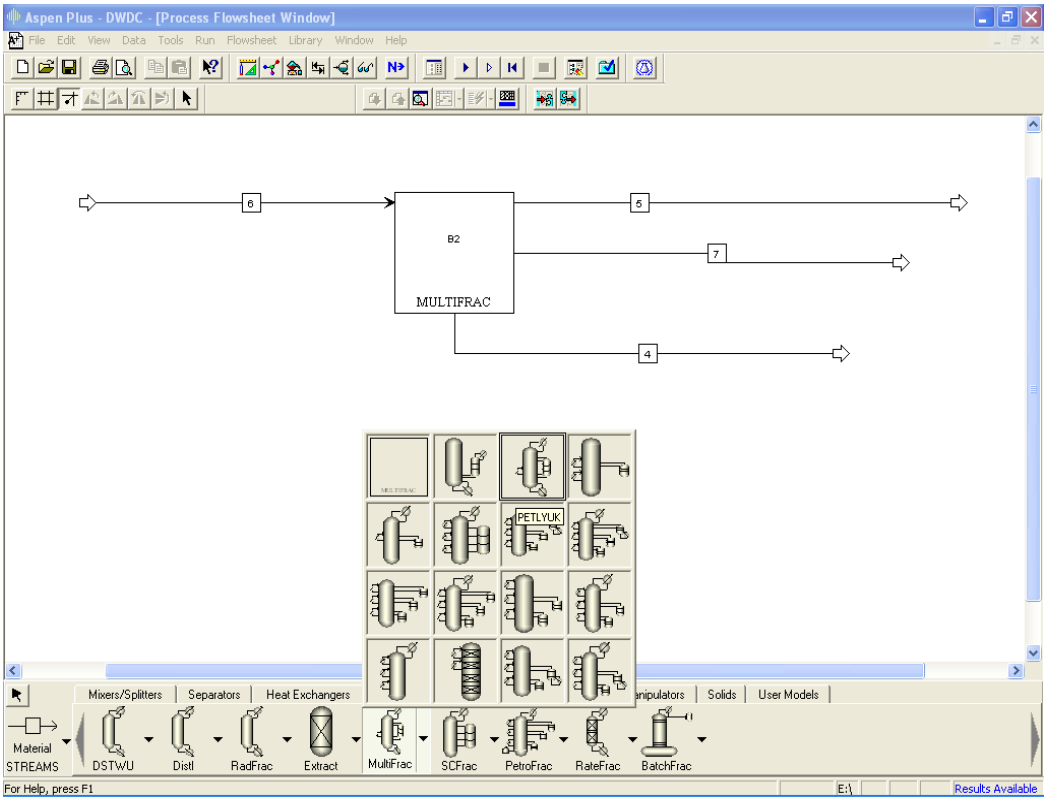

Figure 4.2.1: Flow sheet of a DWC using MultiFrac model on Aspen Plus platform.

To introduce columns other than main column, on the left pan of "Data Browser", "Columns" folder was selected and "New" button on the right pan was clicked to add second column in the same block (Fig. 4.2.2).

Separate "Setup" forms are available to specify number of stages, condenser, and reboiler type, etc. for each column. In case of post fractionator, option "None" was selected for both condenser and reboiler (Fig. 4.2.3). To establish connection between two columns, four connect streams were added (Fig. 4.2.4) and connectivity was specified in separate forms for each stream by providing information about its flowrate (in case of split stream), phase, source and destination stages (Fig. 4.2.5). The same form was used to change vapor split ratio by changing vapor flow rate (marked by a circle in Fig. 4.2.5).

For calculating pressure drop in each column, separate "Tray Rating" objects were created and the column segment through which pressure drop was required, were defined as starting and ending stages (Fig. 4.2.6).

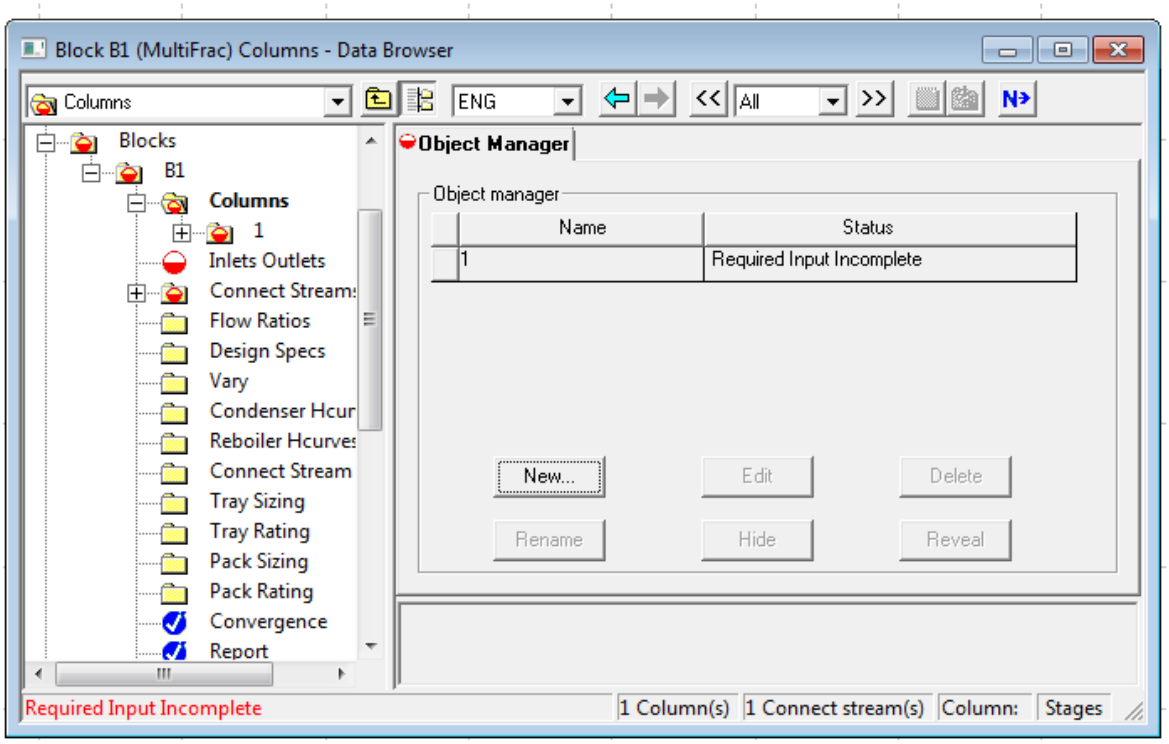

Figure 4.2.2: Form to add new columns in the same block ("B1" in this figure).

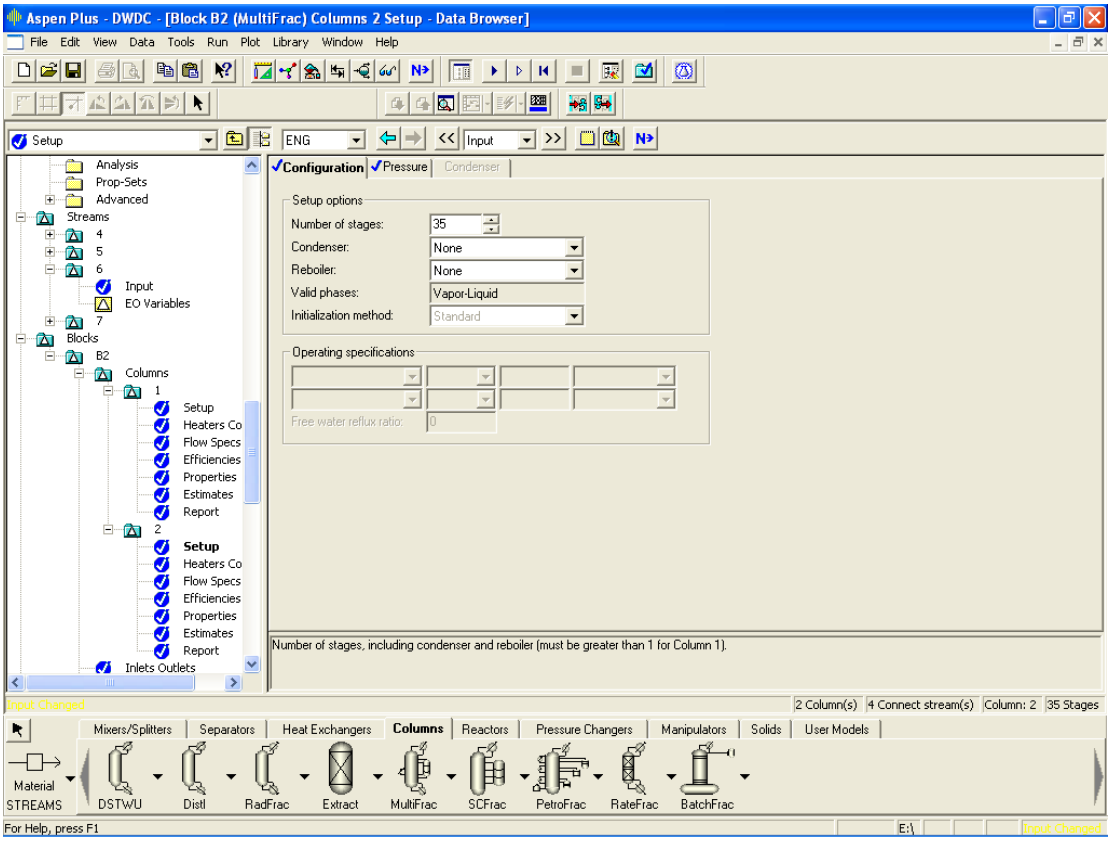

Figure 4.2.3: Postfractionator setup form.

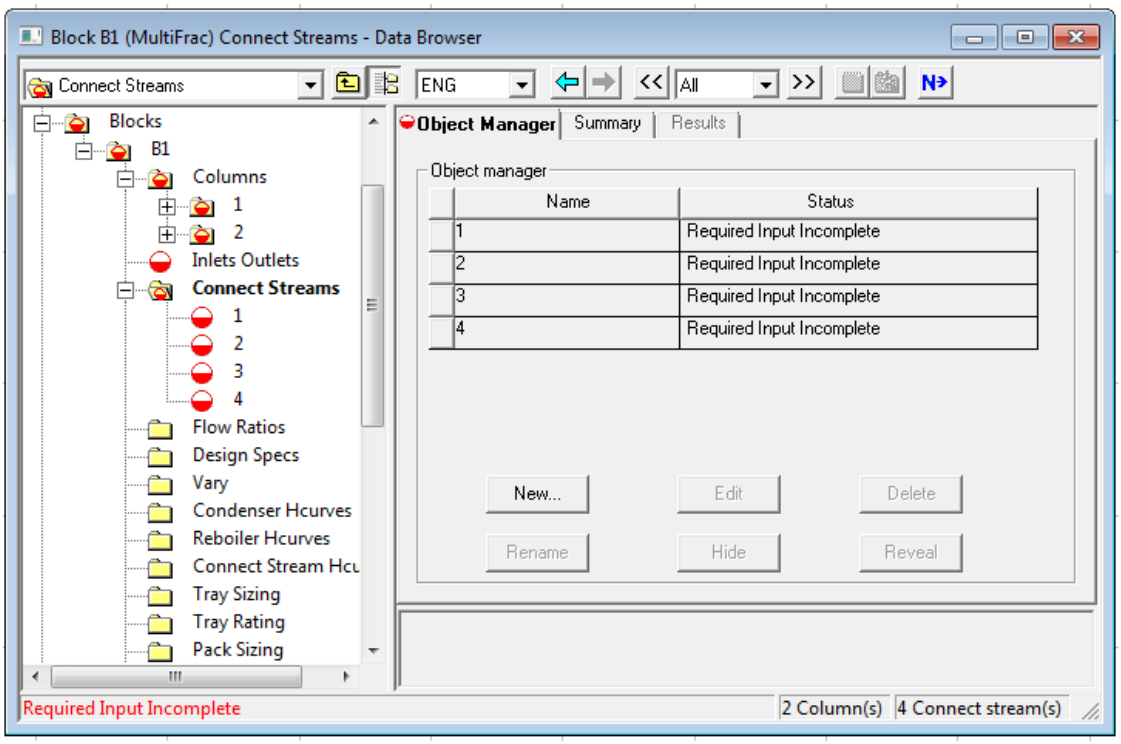

Figure 4.2.4: Four "Connect streams" added to connect main column and postfractionator.

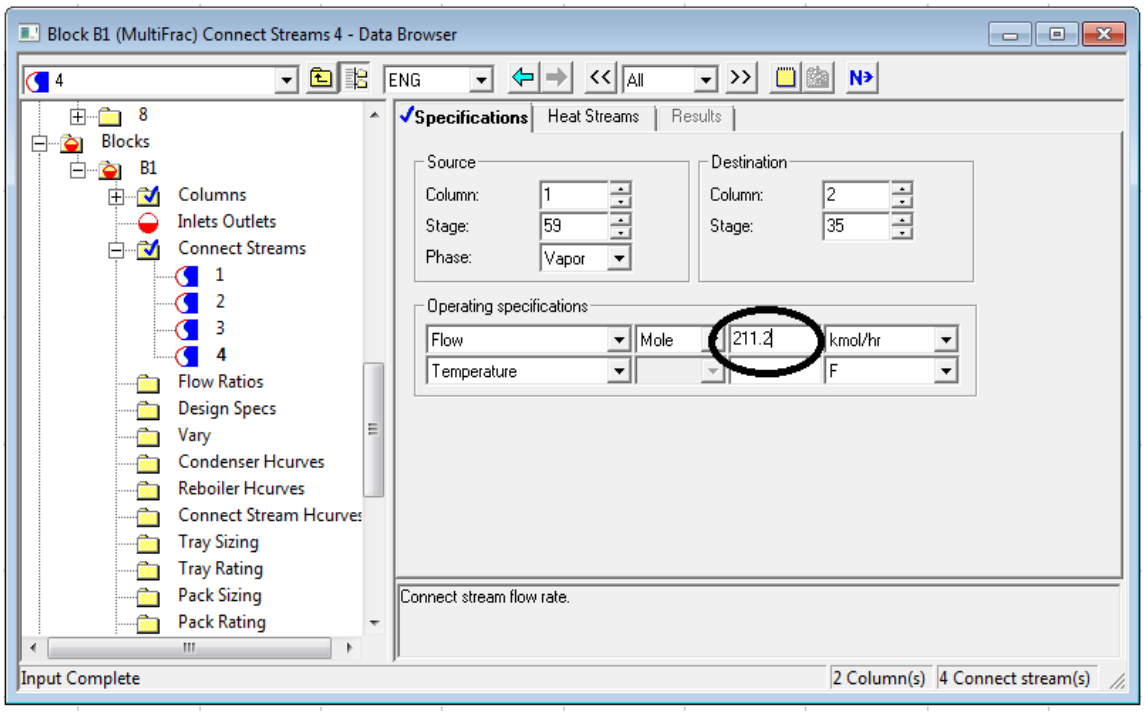

Figure 4.2.5: Source, destination, phase, and flow rate are required to specify a connect stream.

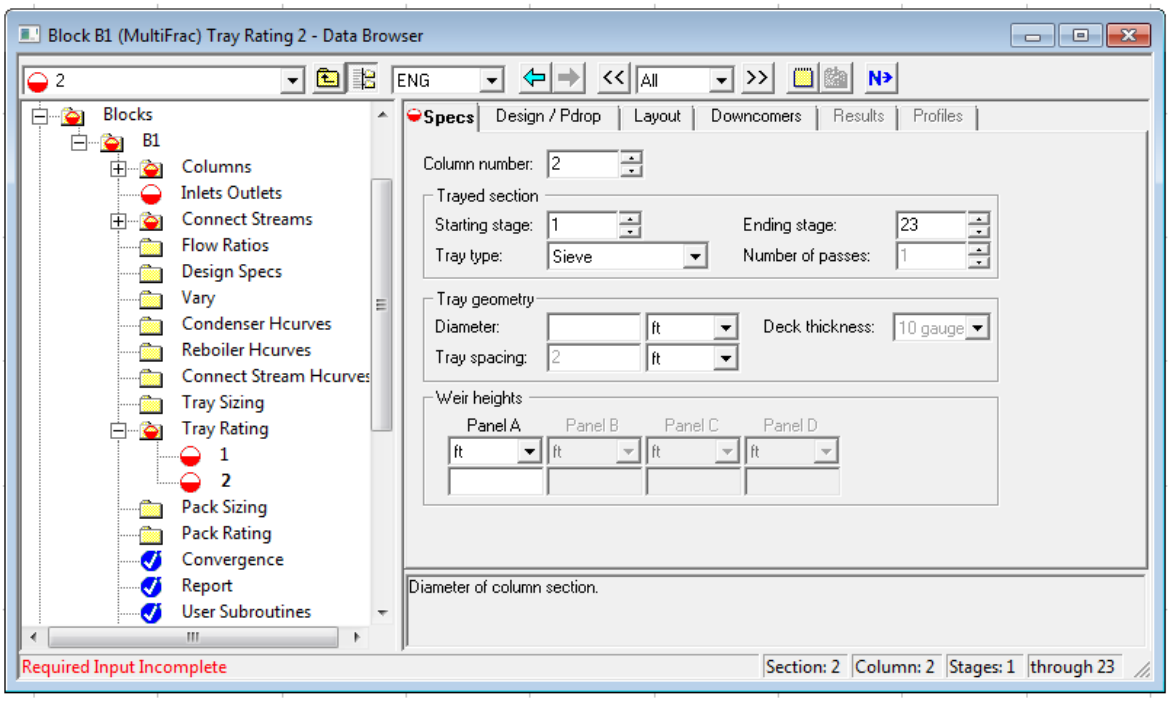

Figure 4.2.6: Tray rating form to specify tray type, tray diameter, and column segment.

4.3 Optimization

The design obtained by simulation may not be the optimum. The optimal design of a DWC is obtained by minimizing the energy duty, as it accounts for the major fraction of the operating cost.

The optimal design and operation of a DWC involve a number of variables and are marked by non-linearity. These variables interact with each other and need to be optimized simultaneously for optimal operation and design. Most of the available optimization codes optimize only one variable at a time, keeping the other variables constant. These methods do not guarantee a global optimal solution as also the identification and quantification of interactive effects of various parameters on the energy requirement. The optimization of a staged DWC is a mixed integer non-linear programming problem. The commercially available process simulators are not able to perform such an optimization of a DWC. The problem can be tackled only with the coupling of an external sub-routine/ software for

optimization with process simulators. This procedure can be implemented using ASPEN Plus and Design Expert softwares.

In the present work, the Aspen Plus software in conjunction with an external optimization technique has been used for the simulation and optimization of a DWC.

Response surface methodology (RSM) is a promising method for process optimization studies. It has been used to optimize process parameters for a number of processes (Kalil et al., 2000; Mannan et al., 2007; Kumar et al., 2007; Tarangini et al., 2009). RSM is a statistical technique for designing experiments, building models, evaluating the effects of various parameters, and for identifying optimum conditions for desirable responses (Box and Hunter, 1957; Box and Behnken, 1960). RSM comprises a number of statistical techniques including Box-Behnken design (BBD) for model building and model exploitation. RSM is an useful method in the selection of such factors as affect the responses with statistical significance and also to establish regression models. RSM can be useful for impinging on the desired target, and for optimizing a response. This also helps in making a process robust. In case of multiple -response problems, the desired responses can be optimized either singly in isolation or simultaneously. However, RSM also has some drawbacks, e.g. its sensitivity to system noise. This undermines the robustness of the RSM. BBD is used extensively for the design of experiments and estimation of optimum operating conditions. BBD under RSM permits identification of interactive effects of various parameters and their values.

BBD under RSM has been applied for optimization of a number of chemical and physical processes (Muthukumar et al., 2003; Kumar et al., 2007; Tan et al., 2008). Recently, Long and Lee (2012 b) have also used RSM for the optimum structural design of a DWC.

BBD under RSM allows the identification and quantification of interactive effects of various parameters. This method is simple and efficient and has the advantage of reducing the number of simulation runs which are needed to evaluate the effect of multiple parameters and their interactions on the process (Kumar et al., 2007).

RSM was applied to the simulated data using the Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, US). The simulated data were analyzed by regression analysis to fit the equations developed and also for the evaluation of the statistical significance of the equations.

4.3.1 Response surface methodology (RSM)

RSM is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response (Cochran and Cox, 1962). It is possible to represent factors in quantitative form in many conditions. Then these factors can be thought of having a functional relationship or response as follows:

$$Y = f(x_1, x_2, ..., x_k) \pm \varepsilon_r \qquad 4.3.1$$

where, Y is the response which depends on the input factors: $x_1, x_2, ..., x_k$ of k quantitative factors,, f is the unknown but a real response function, and ε_r is the residual error which describes the differentiation that can be included by the function *f*. The methodology as adopted is called the response surface methodology (RSM). This is the relationship between the response and the input parameters as the surface of the $x_1, x_2, ..., x_k$ coordinated in the graphical sense.

In most RSM problems, the form of the relationship between the response and the variables is unknown. Therefore, the first step in RSM is to find a suitable approximation for the true functional relationship between y and the set of independent variables. Generally, a low-order polynomial is employed in some region of the independent

variables. If the response is well modeled by a linear function of the variables, then the approximating function is the first-order model:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + ... + \beta_k\ x_k + \varepsilon_r \qquad 4.3.2$$

The polynomial of higher degree must be used, such as the second-order model, if there is a curvature in the system,

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i\ x_i + \sum_{i=1}^{k} \beta_{ii}\ x_i^{\,2} + \sum\sum_{i<j} \beta_{ij}\ x_i\ x_j + \varepsilon_r \qquad 4.\ 3.3$$

Mostly all RSM problems use one or both of these models. In order to estimate the regression coefficients, a number of experimental design techniques are available such as face centered central composite design, central composite design, etc. Montgomery (2004) has proposed that the scheme based on rotatable design fits the second order response surfaces quite accurately.

4.3.2 Box-Behnken design (BBD)

Three-level designs for fitting response surfaces was proposed by Box and Behnken (1960). The best performance of a BBD depends on some prior knowledge of the system being optimized. It requires an experiment or simulation run according to $N_{exp} = k^2 + k + c_p$, where, k is the factor number and c_p is the replicate number of the central point. These designs are formed by combining 2^k factorials with incomplete block designs. BBD is a spherical, revolving design, viewed as a cube (Fig. 4.3).

Thus all the points lie on a sphere of radius $\sqrt{2}$. It consists of a central point and the middle points of the edges. The resulting designs are usually very efficient in terms of the number of required runs, and they are either rotatable or nearly rotatable. Table 4.1 shows a three-variable BBD.

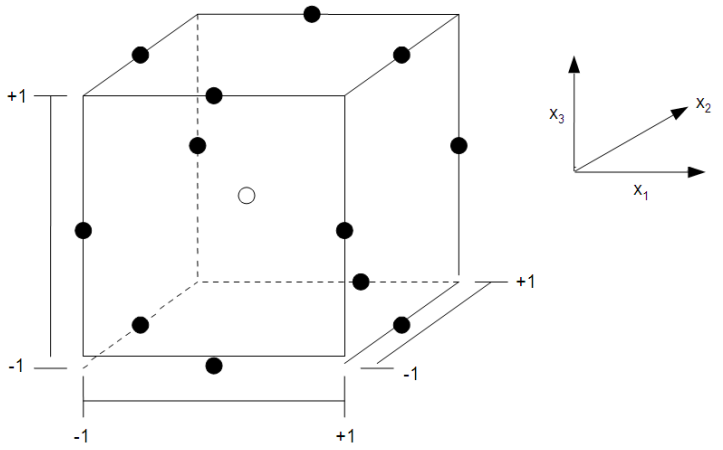

Figure 4.3: Box-Behnken design for three factors (k = 3) (Montgomery, 2004**)**

Table 4.1 A three-variable Box-Behnken design.

Run	x_1	x_2	x_3
1	-1	-1	0
2	-1	1	0
3	1	-1	0
4	1	1	0
5	-1	0	-1
6	-1	0	1
.7	1	0	-1
8	1	0	1
9	0	-1	-1
10	0	-1	1
11	0	1	-1
12	0	1	1
13	0	0	0
14	0	0	0
15	0	0	0
16	0	0	0
17	0	0	0

The BBD does not contain any points at the vertices of the cubic region created by the upper and lower limits for each variable. This could be advantageous when the points on the corners of the cube represent factor-level combinations that are prohibitively expensive or impossible to test because of physical process constraints. As compared to other RSM techniques, the BBD requires less experimental or simulation runs. BBD is slightly more efficient than the central composite design and much more efficient than the

three-level full factorial designs (Ferreira et al., 2004). The central composite design requires a greater number of experimental or simulation runs, which is calculated according to $N_{exp} = k^k + 2^k + c_p$, where, k is the variable number and c_p is the number of central points. A face centered central composite design is a special case of central composite design. It is not rotatable because the axial point is always set equal to one, no matter how many factors are included in the experiment or simulation. Because of this the axial points will trace out a cuboidal region on the response surface. They are, therefore, sometime called cuboidal designs (Evans, 2003).

These designs are generally used for fitting the second order model. It is important to noted that the second order model provides good prediction through out the region of interest. Box and Hunter (1957) suggested that the second order response surface design should be rotatable. Rotatability is a reasonable basis for the selection of response surface design. Because the purpose of RSM is the optimization of the location of the optimum that is unknown prior to running the experiment or simulation. It makes sense to use design that provides equal precisions of estimation in all directions. The cubic model is found to be aliased and is inappropriate for further investigations. For an aliased model the numbers of simulation or experimental runs are not enough for independent estimation of all the terms for that model. If the number of independent points in the design is less than the number of terms in the model, then some of the parameters cannot be estimated independently.

The sequential F-test and other adequacy measures are generally used for selecting the best model (Muthukumar et al., 2003). An F-test is any statistical test in which the test statistic has an F-distribution under the null hypothesis. It is most often used when comparing statistical models that have been fit to a data set, in order to identify the model that best fits the population from which the data were sampled.

The least squares method is used to estimate the parameters in the approximating polynomials. The response surface analysis is then performed using the fitted surface. If the fitted surface is an adequate approximation of the true response function, then analysis of the fitted surface will be approximately equivalent to analysis of the actual system. Designs for fitting response surfaces are called response surface designs.

Chapter –V

RESULTS AND DISCUSSION

This chapter presents the results and discussions of the modelling and optimization studies carried out for a DWC using ternary mixtures as case studies. Degree of freedom (DOF) analysis, pressure drop analysis, and the effects of various parameters on the operation and energy efficiency of a DWC are presented in various sections of this chapter.

5.1 Verification of Available DOF in a DWC

In order to verify actual degrees of freedom available in a DWC, let us take the case of fractionation of benzene-toluene-*p*-xylene (BTX) mixture obtained from a naphtha reformer. This example is similar to that used by Kim (2006). The DWC was considered to have 89 number of stages (sieve trays)(N) in the main column; the number of sieve trays in the divided segment ($N_{s2} - N_{s1}$) was taken as 35; whereas the starting and ending trays of the divided segment N_{s1} and N_{s2} were taken as 24^{th} and 58^{th}, respectively. Feed was introduced at stage number 44 of the main column and the side product S_3 was withdrawn from stage number 109 (tray number 20 if counted from top of the second column). Other operating parameters required to be specified to operate a DWC under varying conditions are listed in Table 5.1.

For the given case study, the total number of degrees of freedom is found to be N_T+C+6, as shown in Table 5.1. Here, C+1 variables represent feed properties (sum of the DOF observed at serial number 1, 2 and 3) and N_T number of stage pressures are required to be specified since the software used does not perform pressure drop calculations (equations 3.17 and 3.22) at the time of solving MESH equations. For calculating pressure drop, 'Tray Rating' feature of ASPEN Plus™ was used. For making hydrodynamic calculations using 'Tray Rating', additional column design specifications are required. These specifications are listed in Table 5.2.

Table 5.1 Feed, product and connect stream specifications.

S.No.	Parameter	Value	Degrees of Freedom Used
1	Feed Pressure	150 kPa	1
2	Feed rate (ΣF_j)	801.8 kmol/h	1
3	Feed composition (mol fraction)	Benzene = 0.1096 Toluene = 0.4217 Xylene = 0.4687	C-1
4	Column pressure (P_i)	116 KPa	N_T
5	Distillate rate (D)	88.65 kmol/h	1
6	Reflux rate ($R*D$)	1792 kmol/h	1
7	Product rate (S_3)	337.8 kmol/h	1
8	L_s	529.8 kmol/h	1
9	V_s	340- 1055kmol/h	1
	Total		N_T+C+6

Table 5.2 Tray design specifications (for BTX separation).

Tray diameter	1.80 m
Tray spacing	0.6096 m
Ratio of sieve hole area to tray active area	0.12
Weir height (h_w)	50 mm
Hole diameter	5 mm

The difference in calculated pressure drops $\{\Delta(\Delta P)=\Delta P_2-\Delta P_1\}$ was recorded at different values of vapour split (Vs) (in the range of 340-1055 kmol/h) while keeping the reflux flow rate and liquid split L_s constant (as listed in Table 5.1). For easier convergence of the simulator, molar flow rates of the reflux and connect stream r, Vs and L_s, instead of split ratios (R_1 and R_2), were used as input parameters. Table 5.3 shows the variation in ΔP as a function of vapour split at a fixed value of reflux ratio R_1 and R_2. It is observed that with an increase in vapour flow rate , (Vs), to section 2, the pressure drop in the divided segment of section 1 (ΔP_1) decreases with a simultaneous increase in the pressure drop in section 2 (ΔP_2). This results in an increase in $\Delta(\Delta P)$ with an increase in Vs. Obviously, only one value of vapour split (Vs) is feasible (at a given value of r and L_s or R_1), which gives $\Delta(\Delta P)$ equal to zero as indicated by italicized bold data row in Table 5.3.

On the basis of the above observation, it may be concluded that the specification of Vs in Table 5.1 is redundant and that it cannot be treated as a free variable. Therefore, the

number of variables that can be freely assigned, reduces to four. Most of the investigators have assumed the remaining five parameters (at serial numbers 5 to 9) as DOF of a DWC. However, after comparing the difference in pressure drop on the two sides of the DWC with the resulting liquid and vapour flow rates after convergence was achieved, it becomes evident that the vapour split stream, *V*s, cannot be specified arbitrarily.

Table 5.3 Variation in ΔP as a function of vapour split ratio at *r* =1792 kmol/h (*R*=20.84); L_s=840 kmol/h.

L_{23} (kmol/h)	L_{24} (kmol/h)	R_1	*V*s (kmol/h)	V_{58} (kmol/h)	V_{59} (kmol/h)	R_2	ΔP_1 (atm)	ΔP_2 (atm)	Δ(ΔP) (atm)	Δ(ΔP) (kPa)
1544	689.6	1.218	340	906.8	1251	0.375	1.385	0.262	1.122	113.72
1581	735.2	1.142	540	693.7	1236	0.778	0.974	0.428	0.546	55.35
1694	***841.9***	***0.99***	***738.25***	***497.7***	***1236***	***1.483***	***0.662***	***0.662***	***0.000***	***0.00***
1586	745.7	1.126	900	347.5	1249	2.589	0.490	0.934	-0.444	-44.98
1599	758.9	1.106	1050	210.4	1262	4.990	0.374	1.204	-0.828	-83.89

It is also noted that an arbitrary value of *V*s (or R_2) not only creates an imbalance in the pressure drop in the two sides of the divided wall column, but also severely distorts the concentration profile. Figure 5.1 presents concentration profiles of toluene in the second column (from where toluene rich product is taken out).

Considering the detailed mathematical model, which includes the MESHD (conventional MESH equation plus the pressure drop) equations, the degree of freedom for thermally coupled and divided wall distillation column (DWC) for steady state operation with known feed and condenser pressure comes to be four. Although pressure drop calculations are insignificant for a simple distillation column simulation, the tray hydraulics play an important role in the performance of the interlinked thermally coupled columns or DWCs. Therefore, the pressure drop calculations are unavoidable. When model equations representing pressure drop are taken into consideration, no extra degree of freedom is left to be specified simultaneously for both the connecting streams between two columns.

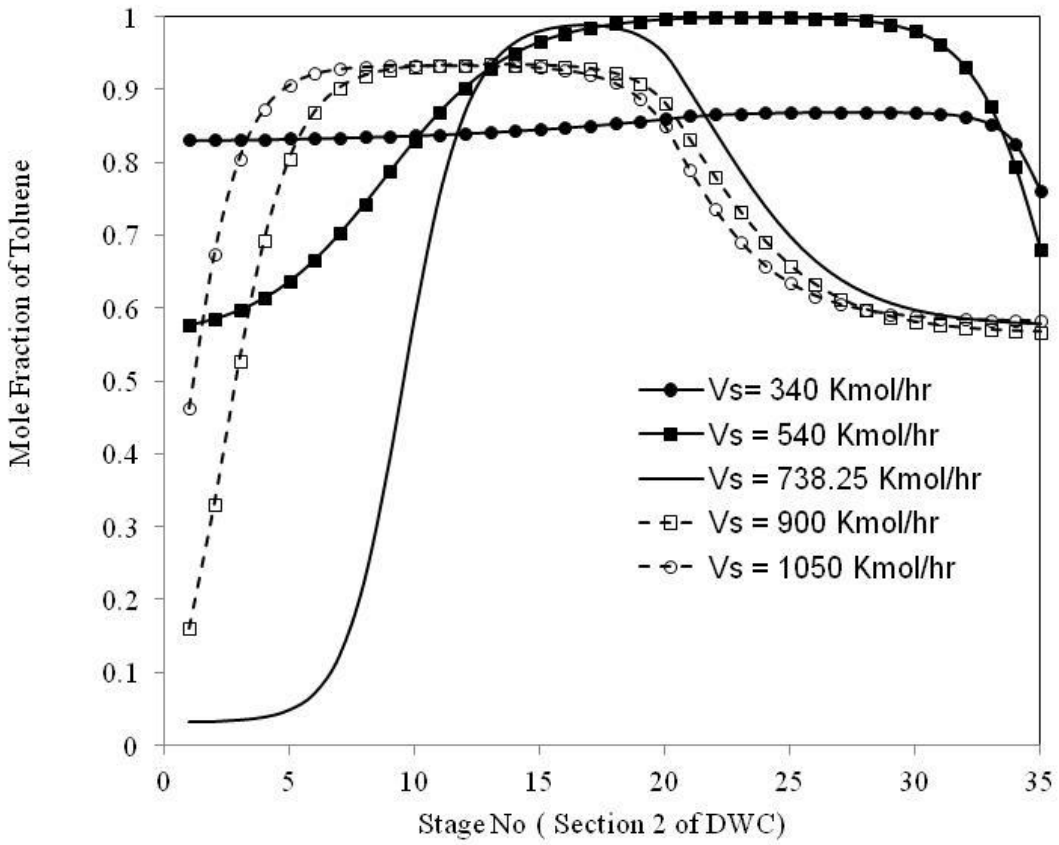

Figure 5.1: Concentration profile of toluene in DWC

When compared to an existing simple distillation column with one feed and two products, a DWC with one feed and three products has two extra degrees of freedom. Therefore, out of these two degrees of freedom, one is required to specify a parameter related to the third product stream (such as product flow rate), and the other can be used to fix any one of the four connecting streams between the two sections of the column. Several investigators, particularly those working on the control aspects of a DWC (Serra et al., 2000; Juan et al., 2007), have attempted to control two (or more) connecting streams and felt that the controllability of a DWC is difficult. Therefore, it is recommended that control strategies for a DWC should be re-examined and the splitting of vapour should be predicted using hydrodynamic correlations.

5.2 Importance of Pressure Drop in a DWC

Pressure drop calculations are extensively used for providing tray spacing at the time of designing a column, but these are rarely performed for the simulation purposes. This is because of the fact that a minor change in pressure (from condenser to reboiler) has insignificant impact on the vapour-liquid-equilibrium (VLE). However, pressure difference plays an important role in deciding vapour and liquid flow rates across a tray (or trays), particularly in case of interconnected or divided wall distillation column. In case of a DWC, the feasible vapour split ratio below the divided wall section is naturally adjusted in such a way that the pressure drop in the two parallel branches of the DWC are equal. In the present work, the simulation of a DWC using the MultiFrac model of Aspen Plus^{TM} was carried out to study the feasible vapour split as a function of reflux ratio and liquid split ratio. Simple models are used to predict the pressure drops.

The separation of a ternary mixture of benzene-toluene-*p*-xylene (BTX) of the naphtha reformer, as used by Kim (2006) was considered as the case study for the optimal design of a DWC.

5.2.1 Pressure drop

In case of a DWC, the role of vapour split at the bottom of the divided segment is crucial and important from the point of view of the performance of a column. At the design stage, the positioning of the dividing wall is decided to obtain optimum vapour split ratio and it cannot be changed at a later stage (Ling and Luyben, 2009). Vapour flow rate on the two sides of the divided section is adjusted naturally in such a way that the pressure drops are equal on both sides as the vapour inlet and the outlet from both sides share common trays. During operation, the vapour split deviates from the designed value with any change in other operating parameters. The pressure drop across each individual tray depends on three factors: (i) the vapour flow through the holes or orifice of a dry sieve tray

(h_d), (ii) the static head of liquid on the plate (h_w+h_{ow}), where h_w is the weir height and h_{ow} is the liquid overflow from the weir, and (iii) the residual head (h_r) required to push vapour through holes of the tray in wet condition. In the present case, a simple adaptive model is used to predict these pressure drops. Net pressure drop is taken as the sum of the above three components. The total pressure drop in terms of liquid head across i^{th} tray (h_t) of a sieve tray column can be written as:

$$h_t = h_d + (h_w + h_{ow}) + h_r \quad (5.1)$$

The weir height (h_w) is a design variable and remains constant during operation, whereas the weir liquid crest (h_{ow}) depends mainly on the liquid flow rate, and is calculated by the Francis weir formula (equation 5.2). The Pressure drop through the dry plate (h_d) is estimated using a simple expression for flow through an orifice (equation 5.3).

$$h_{ow} = 750\left[\frac{L_w}{\rho_L W_L}\right]^{2/3} \quad (5.2)$$

$$h_d = 51\left[\frac{u_h}{C_0}\right]^2 \frac{\rho_L}{\rho_v}, \text{ and} \quad (5.3)$$

The residual head (h_r) due to wetting of the tray and froth formation is a function of liquid surface tension, froth density and froth height. However, the value of h_r is not large and, therefore, the use of an elaborate method for its estimation is generally not required. A simple and widely used correlation as given by Towler and Sinnott (2008) may suffice:

$$h_r = \frac{12.5\times10^3}{\rho_v} \quad (5.4)$$

Where, L_w is the liquid flow rate (kg/s), u_h is the vapour velocity through sieve tray holes (m/s), W_L is the weir length (m) and ρ_L and ρ_V are the liquid and vapour density (kg/m^3), respectively. C_0 is the orifice coefficient ($0.62 < Co < 0.95$) and is a function of

the plate thickness. Assuming the liquid phase to behave as an ideal solution, the liquid flow rate L_w can be calculated by using the following equation:

$$L_W = L_i M_{Li} \tag{5.5}$$

Where, L_i is the molar flow rate (kmol/s) of the liquid stream leaving the i^{th} tray, M_{Li} ($=\Sigma x_j.MW_j$) is the average molecular weight (kg/kmol) of the liquid stream, x_j is the mole fraction of the j^{th} component and MW_j is the molecular weight of the j^{th} component in the liquid stream. Similarly, the vapour velocity through sieve tray holes (u_h) can be calculated by using the following equation:

$$u_h = \left[\frac{V_{i+1} M_V}{A_h} \left(\frac{RT_{i+1}}{P_{i+1}} \right) \right] \tag{5.6}$$

Where, the vapour is considered to behave as an ideal gas, A_h is the total cross-sectional area of all the holes on a tray (m^2) and V_{i+1}, M_V and (RT_{i+1}/P_{i+1}) are, respectively, the molar vapour flow rate (kmol/s), average molecular weight (kg/kmol) and molar density of ideal gas leaving the $(i+1)^{th}$ tray and entering the i^{th} tray (kmol/m^3).

5.2.2 Simulation

The case study of Kim (2006), uses a divided wall column (Fig. 5.2) which consists of 89 stages, with 35 stages (from stage number 24 to 58) divided into two parts. For modelling of this DWC, a pair of thermally coupled columns (Fig. 5.3) was considered in which the main column (column 1) has 89 stages and the post-fractionator (column 2) has 35 stages.

Vapour from the top stage of column 2 (V_P) is returned to below stage 23 of column 1 (main column) and the liquid from the bottom stage of column 2 (L_P) is returned to above of the stage 59.

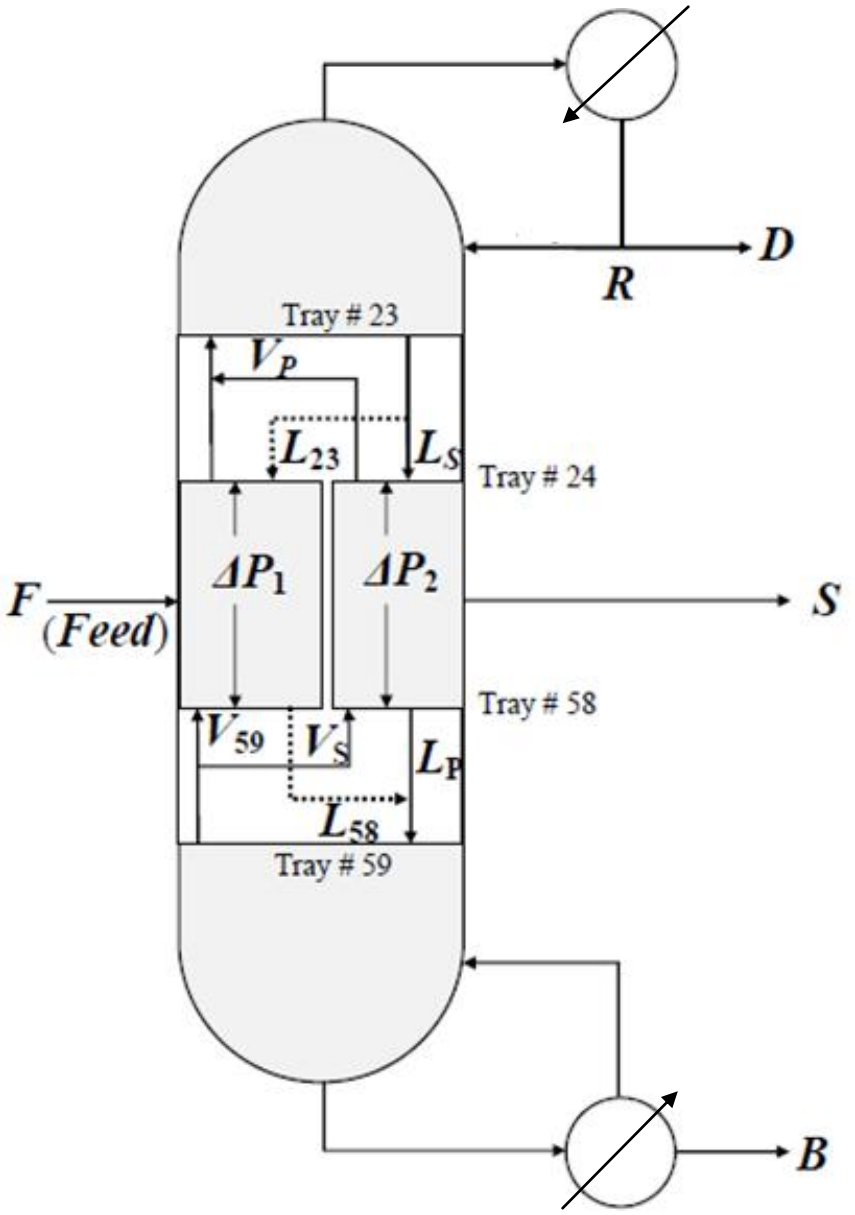

Figure 5.2: Divided wall distillation column (DWC) for pressure drop study.

Liquid stream originating from stage 23 of column 1 is split into two parts and one part (L_S) is sent to the top plate of column 2 and the other part (L_{23}- Ls) to the next tray (i.e. tray number 24) of column 1. Similarly, the vapour stream originating from stage 59 is also split into two parts, with one part (V_S) being sent to column 2 and the other fraction (V_{59}- V_S) going to tray 58 of column 1.

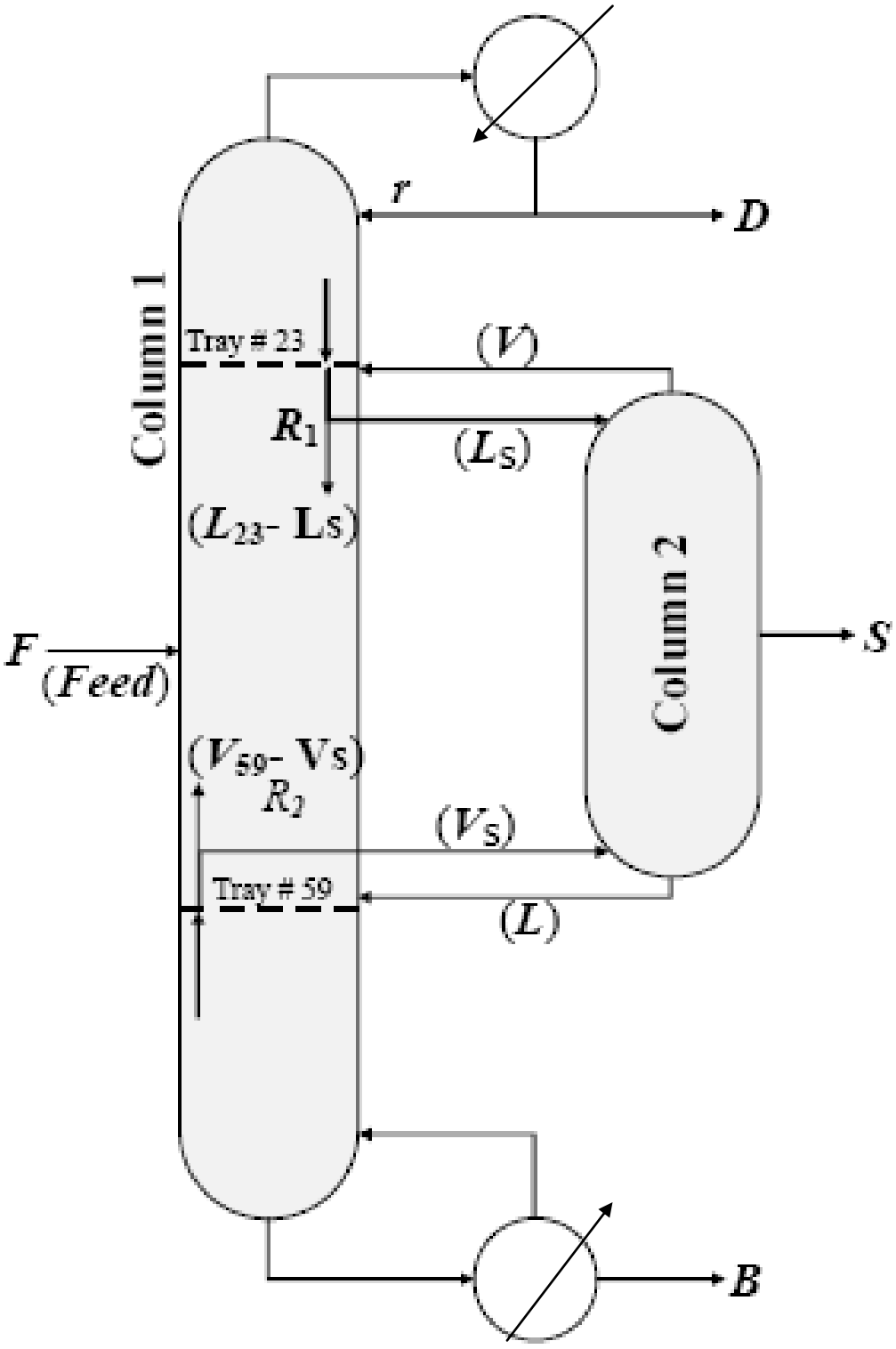

Figure 5.3: Thermally coupled analogue of DWC.

Other parameters which are required to be specified for the operation of a DWC under varying operating conditions are listed in Table 5.4.

Table 5.4 Column, feed, product and connect stream Specifications

Column 1		***Column 2***	
No of stages	89	No of stages	35
Feed stage	44	Product draw stage	20
Feed	• Super heated (150 kPa, 135°C) • Saturated liquid (150 kPa)	Product stream	Saturated liquid
Feed rate	801.8 kmol/h	Product rate (S)	337.8 kmol/h
Feed composition (mol fraction)	Benzene = 0.1096 Toluene = 0.4217 *p*-xylene = 0.4687	–	–
Column pressure	116 KPa	Column pressure	116 KPa
Distillate rate (D)	88.65 kmol/h		
Reflux rate	1000-2500 kmol/h		
Connect Streams:	***From***	***To***	***Value***
L_S	Column 1, Stage 24	Column 2, Stage 1	400-1800 kmol/h
V_S	Column 1, Stage 58	Column 2, Stage 35	340-1240 kmol/h
V_P (Internal Stream)	Column 2, Stage 1	Column 1, Stage 24	–
L_P (Internal Stream)	Column 2, Stage 35	Column 1, Stage 58	–

It may be mentioned here that the feed flow rate, composition, number of trays in column 1 and 2 and the location of the feed, product and connect streams are considered as design variables and are, therefore, assumed to be constant in the present study. Apart from these fixed design parameters, five operating parameters in terms of flow rates i.e., flow rates of (1) reflux, (2) distillate (3) product, (4) liquid connect stream (in place of liquid split ratio), and (5) vapour connect stream (in place of vapour split ratio) were used for the simulation runs. These five (instead of four) operating parameters are used to satisfy the required degrees of freedom, since the pressure drop correlations were not used in the model equations. As discussed earlier, this leads to an extra degree of freedom. Although the software requires pressure at each tray for VLE calculation, these pressures are not based on hydrodynamic calculations. However, the software has an additional

feature to calculate hydrodynamic pressure drop across each tray after the convergence is achieved. This feature was used to calculate pressure drop in the divided section of column 1 (between stage 24 and 58) and the column 2. The differences in calculated pressure drops $\{\Delta(\Delta P)=\Delta P_2-\Delta P_1\}$ were noted for different values of vapour split (V_S) while keeping the reflux flow rate r and the liquid split L_S constant. For easier convergence of the simulation runs, the molar flow rates of the reflux and the connect streams r, V_S and L_S, instead of reflux or split ratios (R_1 and R_2), were used as input parameters.

5.2.3 Discussion

The variation in $\Delta(\Delta P)$ as a function of vapour split at different reflux ratios at two corresponding farthest values of liquid splits are shown for the fractionation of BTX in Fig. 5.4.

It is observed that with an increase in vapour flow rate to column 2 (V_S), the pressure drop in the divided segment of column 1 (ΔP_1) decreases and simultaneously, the pressure drop in column 2 (ΔP_2) increases, leading to almost a linear increase in $\Delta(\Delta P)$ with V_S. Obviously, only those values of vapour split (V_S) are feasible (at a given value of r or R and L_S or R_1), which give $\Delta(\Delta P)$ equal to zero as indicated by small circles in Fig. 5.4. Due to almost linear variation in difference in the section pressure drop and V_S (Fig. 5.4), the determination of the feasible value of vapour split at a fixed pair of values for r and L_S was an easy task. These pressure drops at feasible operating conditions along with other liquid and vapour flow rates are given in Table 5.5.

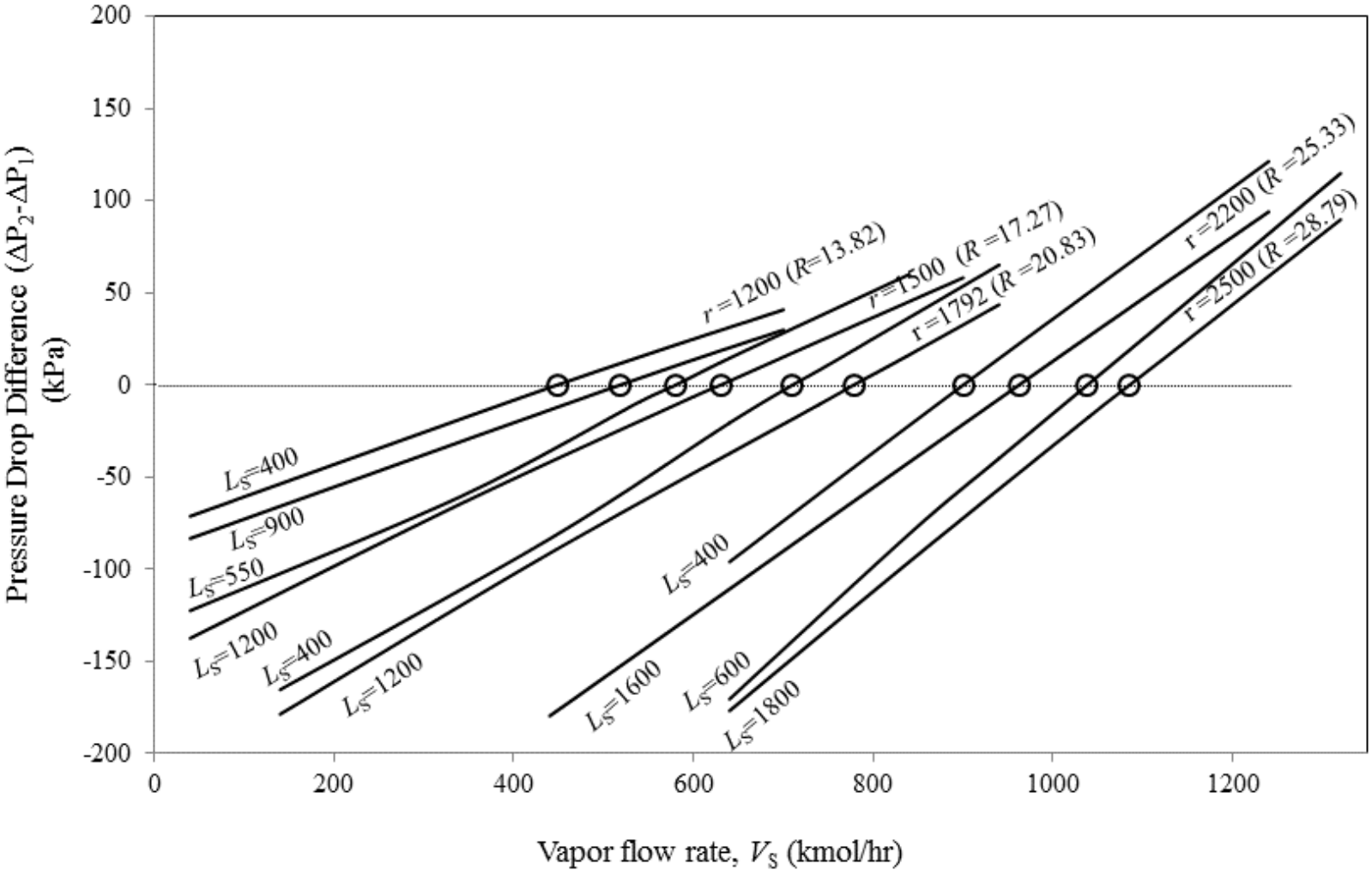

Figure 5.4: Feasible values of vapour split a different reflux ratios and liquid split ratios.

Table 5.5 Variation in ΔP (=ΔP_1=ΔP_2) as a function of reflux ratio, liquid split and feasible vapour split ratio.

r (kmol/h)	R	L_S (kmol/h)	L_{23} (kmol/h)	L_{23}- Ls (kmol/h)	R_1	V_S (kmol/h)	V_{59}-Vs (kmol/h)	V_{59} (kmol/h)	R_2	ΔP (kPa)
		400	1050	649.7	0.62	518	211.2	730.2	2.45	37.14
1200	13.82	650	1033	380.6	1.71	480	233.7	714.9	2.05	36.34
		900	980.9	78.60	11.45	448	263.2	712.6	1.70	36.04
		400	1327	926.4	0.43	648	353.9	1003	1.83	51.63
		550	1320	769.7	0.71	630	362.7	994.1	1.74	51.45
1500	17.27	700	1310	609.4	1.15	610	370.9	981.8	1.64	51.13
		850	1290	431.7	1.97	592	383.4	976.6	1.54	51.14
		1200	1245	43.74	27.43	580	403.7	985.7	1.44	50.09
		400	1592	1192	0.34	778	489.9	1269	1.59	69.33
		529.8	1591	1061	0.50	768	493.5	1263	1.56	68.93
		700	1581	880.3	0.80	751	498.2	1250	1.51	68.37
1792	20.84	1000	1566	560.6	1.78	725	513.5	1241	1.41	68.69
		1200	1526	316.4	3.79	718	525.8	1247	1.37	68.70
		1400	1508	104.9	13.35	710	538.6	1251	1.32	68.30
		400	1962	1562	0.26	962	678.4	1642	1.42	99.42
2200	25.33	1000	1951	950	1.05	912	687.1	1597	1.33	98.71
		1600	1883	275.0	5.82	900	718.9	1623	1.25	98.81
		600	2241	1640	0.37	1085	823.3	1910	1.32	125.59
		840	2231	1390	0.60	1070	824.4	1895	1.30	124.92
2500	28.79	1080	2228	1148	0.94	1045	827.4	1869	1.26	125.94
		1320	2228	907.6	1.45	1007	813	1818	1.24	126.39
		1800	2157	346.5	5.19	1038	855.4	1897	1.21	125.18

Fig. 5.5 shows the feasible vapour split ratio as a function of liquid split ratio. It is surprising to note that the vapour split ratio R_2 is almost independent of liquid split ratio R_1, except in the case of a low reflux, r =1200 kmol/h (Fig. 5.5). However, R_2 depends on the reflux flow rate (r). This seemingly surprising result is because of the fact that the major contribution to pressure drop is due to the vapour flow through the holes of the sieve tray. The liquid head over the tray is very low (of the order of a few centimeters of liquid only). On the other hand, the gas phase velocity (u_h) is in the turbulent regime and, therefore, the pressure drop (h_d) is proportional to the square of u_h (equation 5.3). A change in the liquid split ratio has only a minor effect on the liquid crest over the weir, h_{ow} (as h_{ow} is proportional to $L_w^{0.66}$) that has virtually insignificant effect on the pressure drop on either side of the divided segment. This leads to immeasurable change in vapour split that gives equal pressure drop on both sides. On the other hand, an increase in the reflux flow rate (r) needs more intense heat duties of the condenser and the reboiler, and,

therefore, leads to a considerable increase in vapor flow rate along the column. This increase in vapour flow rate ultimately affects the pressure drop significantly. This also results in a minor but measurable change in vapour split ratio (Fig. 5.5).

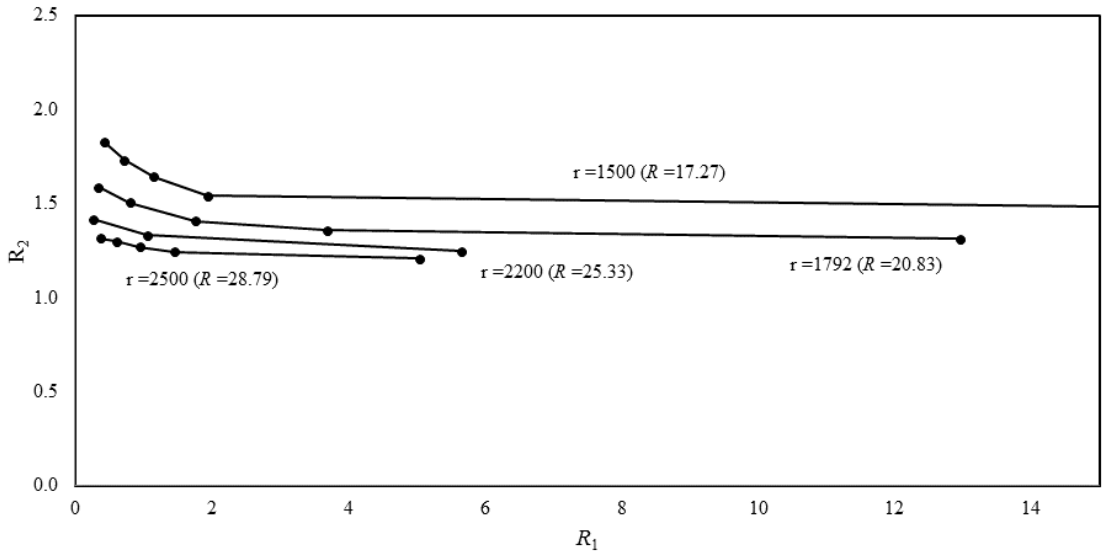

Figure 5.5: Vapor split ratio $R_2[V_S/(V_{59} - Vs)]$ as a function of liquid split ratio R_1 $[L_S/(L_{23} - Ls)]$.

Another interesting result is observed in Fig. 5.6 which shows that the variation in pressure drop with vapour flow rate is widely different in the two sections. This is observed even when the number of trays as well as the tray design in column 1 (trays 24 to 58) and in column 2 (trays 1 to 35) are exactly the same. It is observed that the equalization of pressure drop leads to nearly equal vapour flow rate on both the sides of the DWC when the feed is a saturated liquid (represented by filled and hollow circles in Fig. 5.6). However, the same is not the case for superheated feed (represented by filled and hollow triangles). In case of superheated feed, vapour flow rate is more on the feed side than that on the product side of the dividing wall. A positive intercept on the y-axis for the superheated feed indicates that even if the vapour flow rate (V_{59}- V_S) entering the feed side of the divided segment of the column (column 1) is reduced to zero, a finite pressure drop occurs in this section. This pressure drop is because of the presence of vapour fraction of

the superheated feed that enters at tray 44 in this section. For saturated feed (marked by solid circles), the intercept becomes insignificant. But even in this case, the variations in pressure drop on the two sides of the column are not the same. This is because of the fact that the saturated liquid feed, which is at a slightly higher pressure than the column pressure, flashes and a fraction of the liquid is converted into vapour resulting in the additional amount of vapour flow on the feed tray. In the second column (column 2), the vapour flow rate is mainly controlled by vapour split stream (V_S) at the bottom of the divided segment, and, therefore, the pressure drop is not affected appreciably by the feed condition.

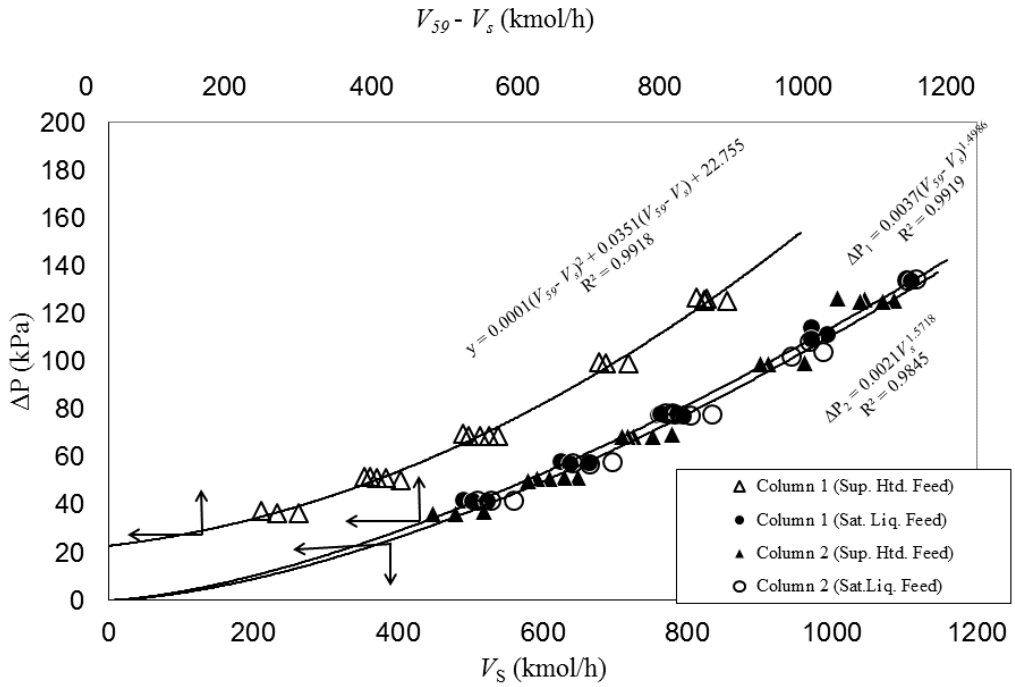

Figure 5.6: Variation of pressure drop ($\Delta P = \Delta P_1 = \Delta P_2$) in two column segments with inlet vapour flow rate.

Fig. 5.7 presents concentration profiles of toluene in the second column (from where the toluene rich product stream is taken out) at a reflux ratio R equal to 20.84. At this reflux ratio, the feasible vapour flow rate, V_S, is roughly constant (between 710 to 768 kmol/h) for a wide range of liquid split ratio ($0.5 < R_1 < 13.35$) (Table 5.5).

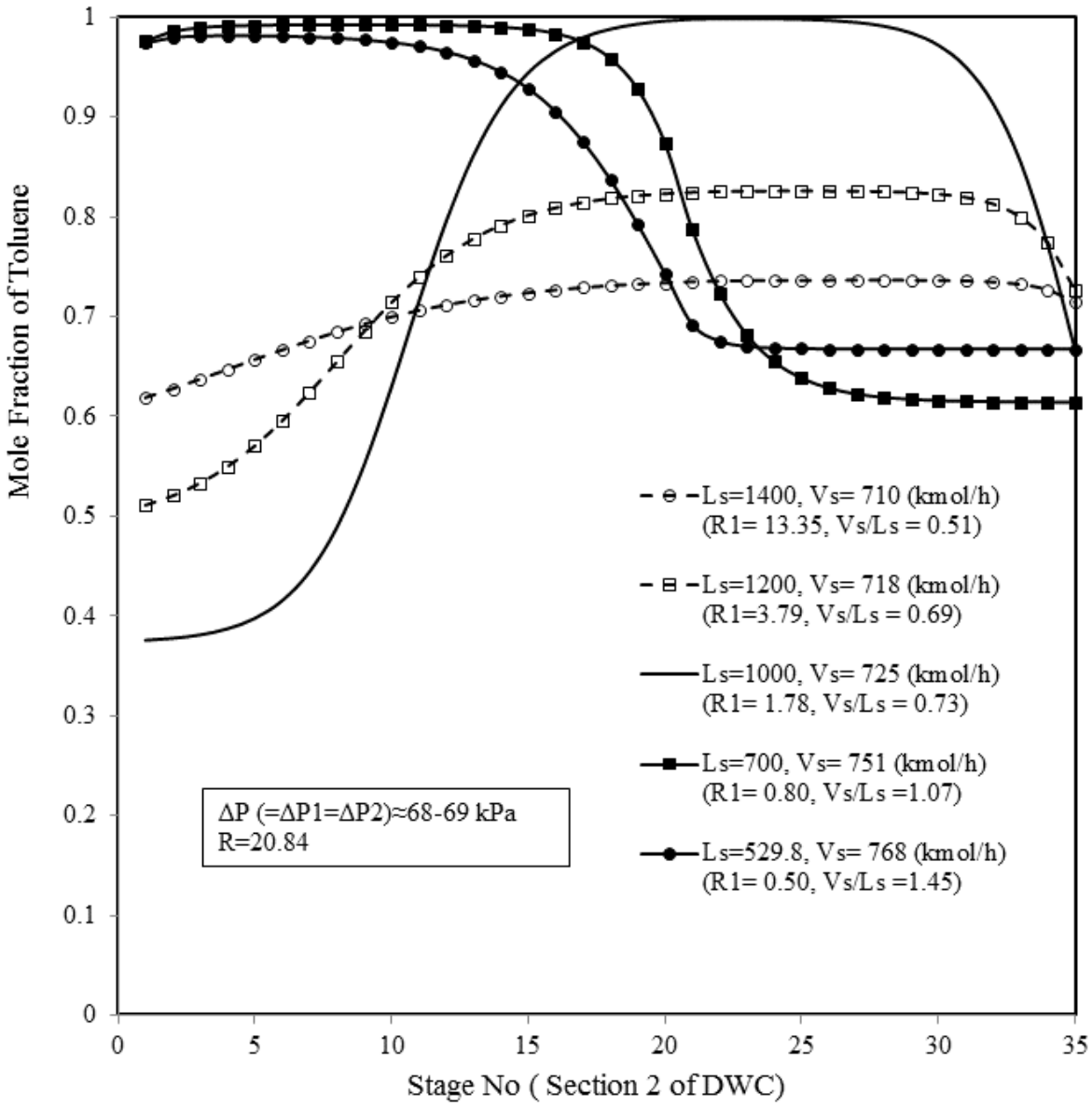

Figure 5.7: Concentration profile of toluene (intermediate product) in the post-fractionator section of DWC

It can be seen in Fig. 5.7 that with a decrease in liquid flow rate, or with an increase in vapour to liquid flow rate ratio (V_S/L_S), toluene concentration builds up in the upper part of the second column. At a very low value of V_S/L_S, toluene concentration remains almost constant along the second column. At this V_S/L_S value, the amount of vapour may not be sufficient for the stripping of toluene in the liquid flowing through the product side of the DWC. With a decrease in liquid flow rate (or with a relative increase in

vapour flow rate), the toluene concentration starts building up in the lower part of the second column.

With a further increase in V_S/L_S ratio, the concentration of toluene is observed to be high in the upper part of the divided section. This means that the toluene concentration near the product tray (tray number 20 in this case) depends strongly on V_S/L_S ratio. While it is difficult to control the vapour split ratio due to its natural selection on the basis of pressure drop on the two sides of the DWC, the liquid split ratio can easily be used to manipulate product concentration by changing the V_S/L_S ratio.

The results are interesting in that they show a little effect of liquid split ratio on the feasible vapour split ratio and significantly different pressure profiles in the two sides of the DWC. It was also found that the variation in vapour flow rate leads to a large variation in the concentration profile. These results indicate that the pressure drop may be one of the key parameters that should be considered for the optimal design and control of a DWC. Although a number of investigators cursorily reported the difficulty experienced in controlling a DWC, the results of the present study indicate that the composition of the middle product (side draw) can be regulated easily by controlling the liquid split ratio so as to maintain V_S/L_S ratio in the product side of the DWC.

In order to study the effect of column pressure or hydraulic pressure drop on concentration profile in a simple distillation column, the fractionation of benzene-toluene-*p*-xylene (BTX) of a naphtha reformer is considered. Operating parameters required to be specified to operate a simple distillate column under varying conditions are listed in Table 5.6. The rigorous RADFRAC model of ASPEN Plus™ has been used for solving the case.

The concentration profile of toluene for the fractionation of BTX using a simple distillation column at different values of column pressure and pressure drop are presented

in Fig. 5.8. It is clear from this figure that the column pressure or pressure drop do not show appreciable effect on the concentration profile in a simple distillation column.

Table 5.6 Operating parameters for the fractionation of BTX, using a simple distillation column

Parameter	***Value***
Number of stages	124
Feed (HF) Pressure	150 kPa
Feed rate (ΣF_j)	801.8 kmol/h at stage number 44
Feed composition (mol fraction)	Benzene = 0.1096 Toluene = 0.4217
Column pressure (P_i)	70 - 146 kPa
Distillate rate (D)	88.65 kmol/h
Reflux rate ($R*D$)	1792 kmol/h
Side draw rate (S)	337.8 kmol/h at stage number 64

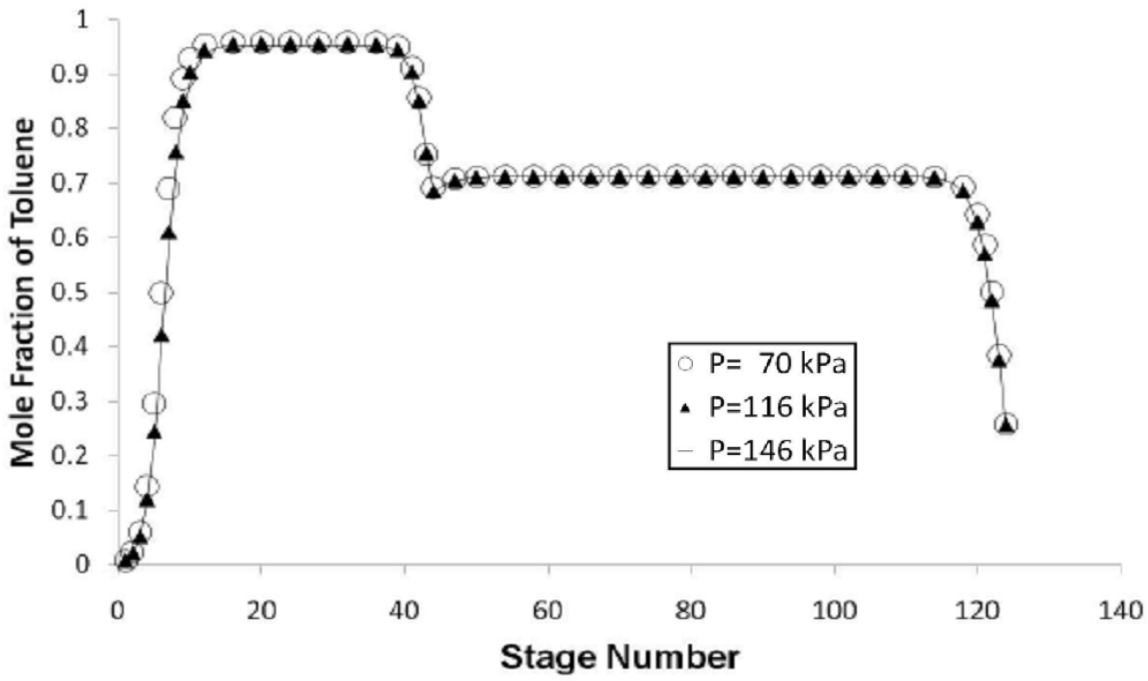

Figure 5.8: Concentration profile of toluene in a simple distillation column.

5. 3 Effect of Feed Quality on the Performance of a DWC

The thermal condition of the feed, *q* is defined as the ratio of the heat required to make the feed as saturated vapour (H_v - H_f) and the latent heat of vaporization of the feed mixture (H_v – H_L).

The feed quality, *q* is taken as a manipulative variable that can be used for the optimized operation of a DWC. The feed quality, *q* changes the profile of the pressure drop across the dividing wall. The pressure difference plays an important role in deciding vapour and liquid flow rates across a tray (or trays) in case of interconnected or divided wall distillation column (DWC). In case of a DWC, the feasible vapour split ratio below the divided wall section is naturally adjusted in such a way that the pressure drop in the two parallel branches of the DWC becomes equal. However, the impact of feed quality on the performance of a DWC is not well studied.

Generally, feed to a distillation column originates from another distillation column or from other units. Knowing the effect of thermal condition of the feed on the performance of a DWC, the energy efficiency as well as the control of a DWC may be improved upon by adjusting the feed quality at its optimal condition from the preceding unit operation.

By varying the feed quality, the performance of a DWC can be studied and the relation between 'natural' or 'feasible' vapour split as a function of reflux ratio and liquid split ratio of DWC can be observed. The feed quality can be varied from superheated vapour (i.e. $q < 0$) to sub-cooled liquid feed (i.e. $q > 1$). For the quantitative study of the effect of feed quality on the fractionation in a DWC the fractionation of BTX mixture as obtained from a naphtha reformer can be taken as a case study , similar to that discussed earlier in section 5.2.

Fig. 5.4 showed almost a linear variation in the difference in the section pressure drop and V_S and, therefore, the feasible value of vapour split at a fixed pair of values for r and L_S can be obtained easily. The pressure drops at feasible operating conditions along with other liquid and vapour flow rates are already listed in Table 5.5 for saturated liquid feed. It is noted that the feed quality influences the pressure drop across the divided wall as well as vapour split ratio.

Fig. 5.9 (a-e) shows the variation of the feasible vapour split ratio, R_2 ($=V_S/V_{58}$) as a function of liquid split ratio, R_1 ($=L_S/L_{23}$) for varying values of reflux rate (r) and for varying feed quality from subcooled liquid to superheated vapour feed to the DWC. It is seen from Fig. 5.9 (a, b) that the vapour split ratio R_2 is almost independent of liquid split ratio R_1 and the reflux flow rate for sub-cooled ($q > 1$) and saturated liquid ($q = 1$) feed. There is a marginal effect of feed as a liquid-vapour mixture (two phase). However, for saturated vapor and superheated vapour feed, the influence of liquid split ratio on the feasible vapour split ratio and R_2 is strongly dependent on the reflux flow rate (r) (Fig. 5.9 d-e). This seemingly strange result is because of the fact that the pressure drop depends strongly on the vapour flow rate (equations 5.3 and 5.6), whereas a change in liquid flow rate leads to only a marginal change in pressure drop due to variation in h_{ow} (equation 5.2). That is why the variation in pressure drop in the two sides of the columns with changing liquid flow rate (L_S) is not appreciable. On the other hand, an increase in reflux flow rate (r) needs more intense heat duties of condenser and reboiler, and, therefore, leads to considerable increase in vapor flow rate throughout the column, which ultimately affects the pressure drop significantly.

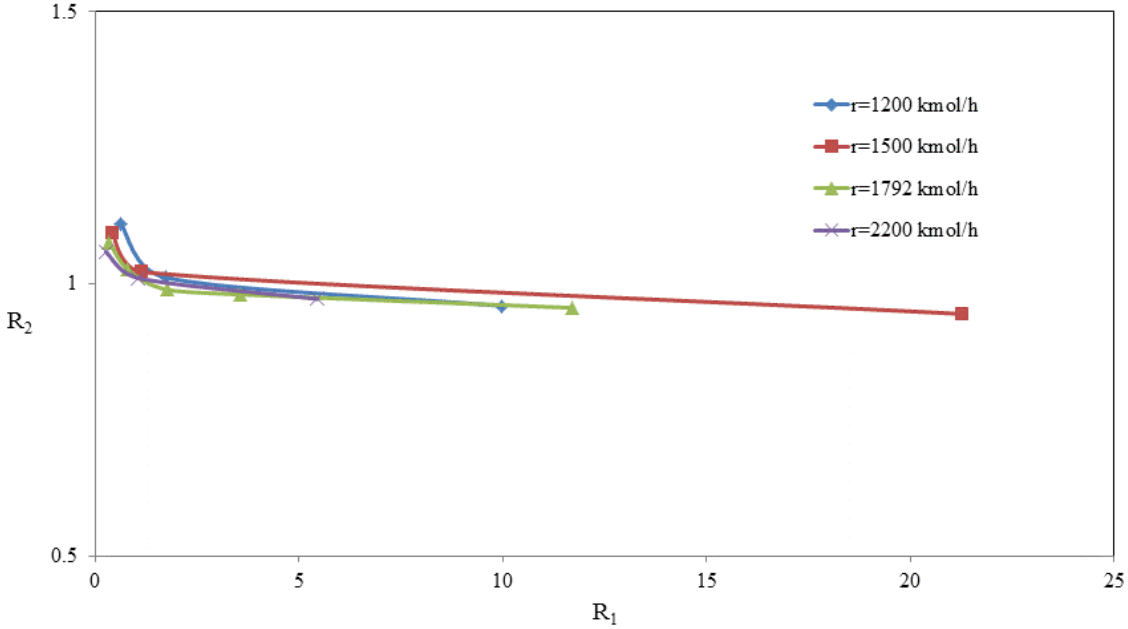

Figure 5.9 a: Feasible vapor split ratio R_2 as a function of liquid split ratio R_1 for subcooled liquid feed.

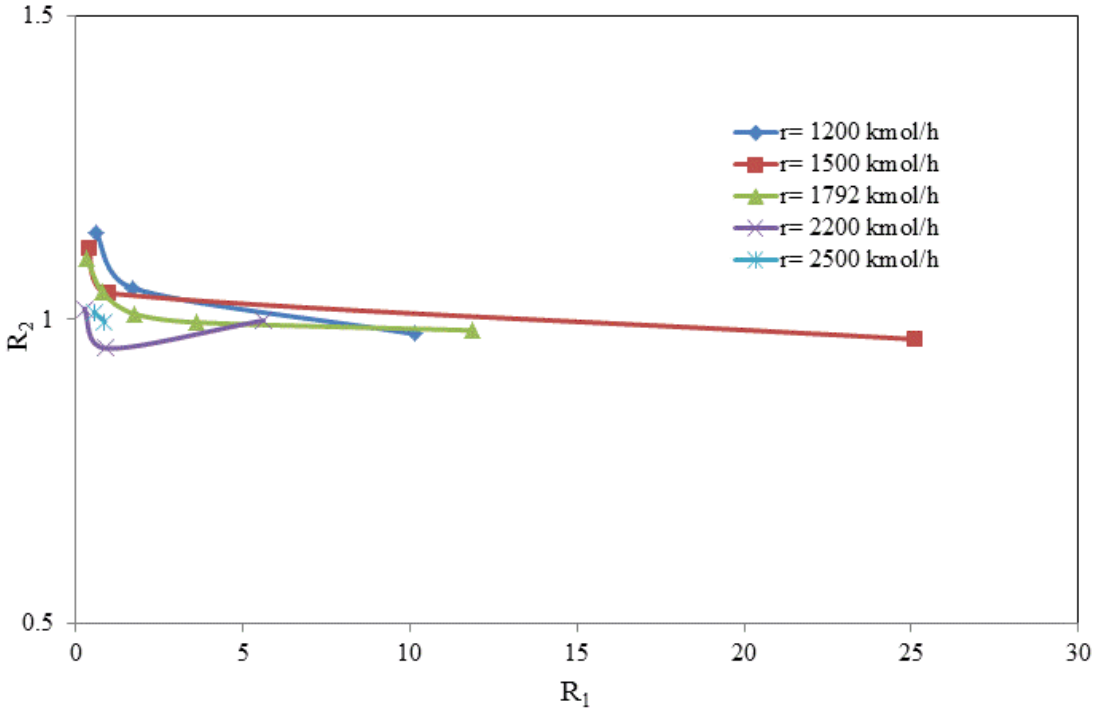

Figure 5.9 b: Feasible vapor split ratio R_2 as a function of liquid split ratio R_1 for saturated liquid feed.

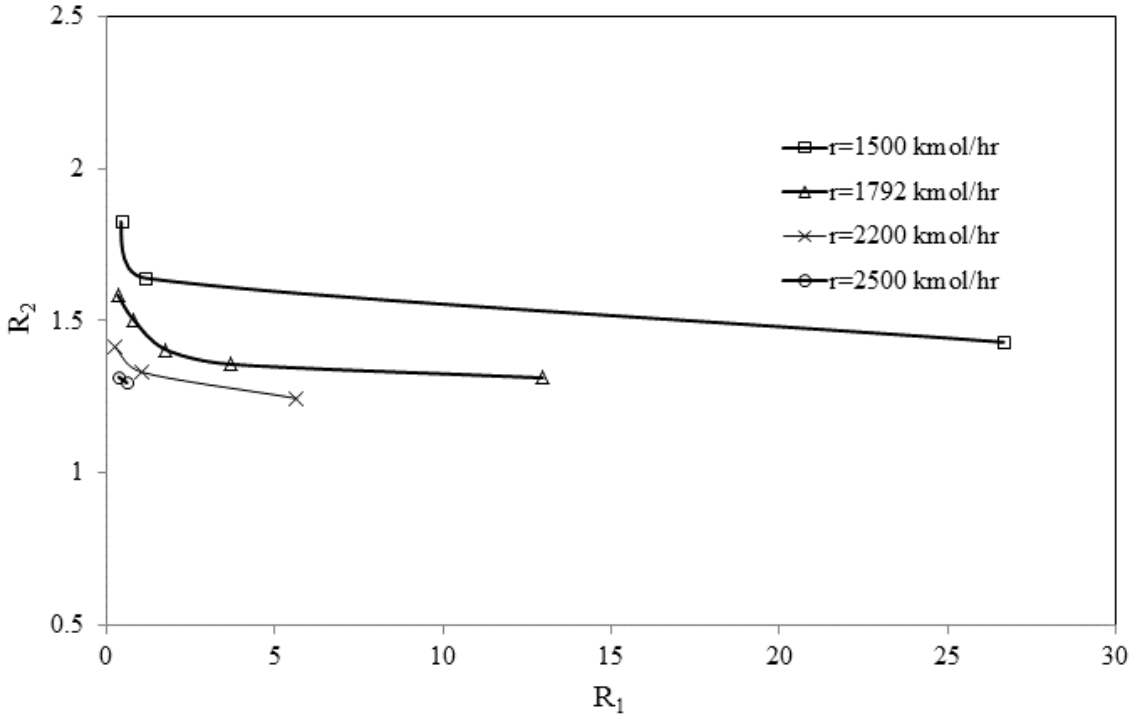

Figure 5.9 c: Feasible vapor split ratio R_2 as a function of liquid split ratio R_1 for two phase feed.

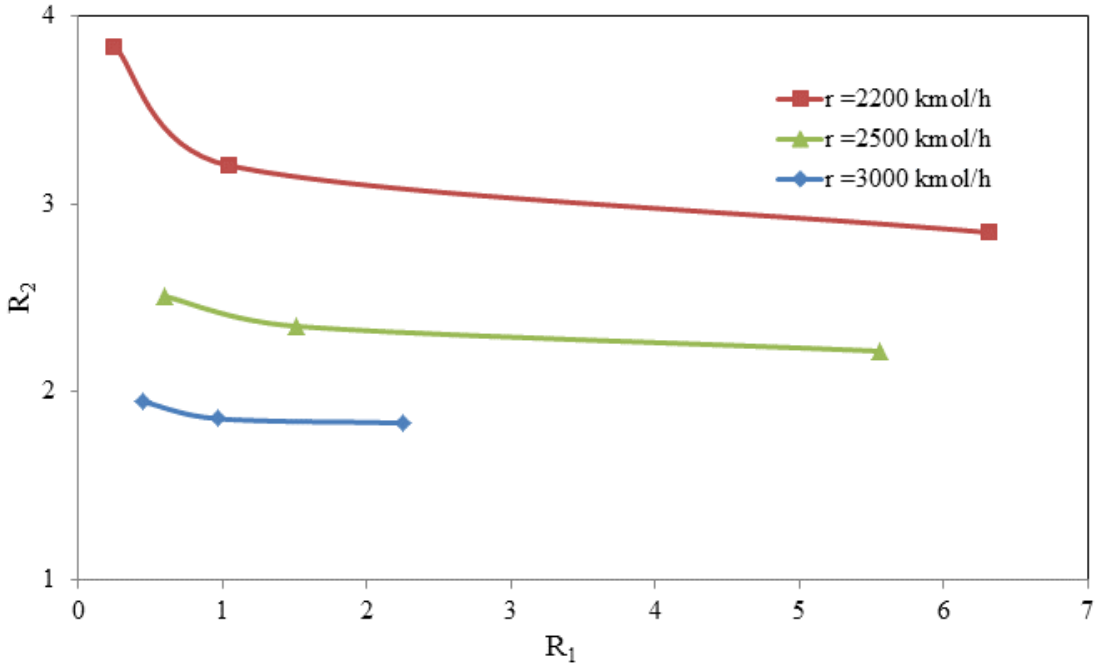

Figure 5.9 d: Feasible vapor split ratio R_2 as a function of liquid split ratio R_1 for saturated vapour feed.

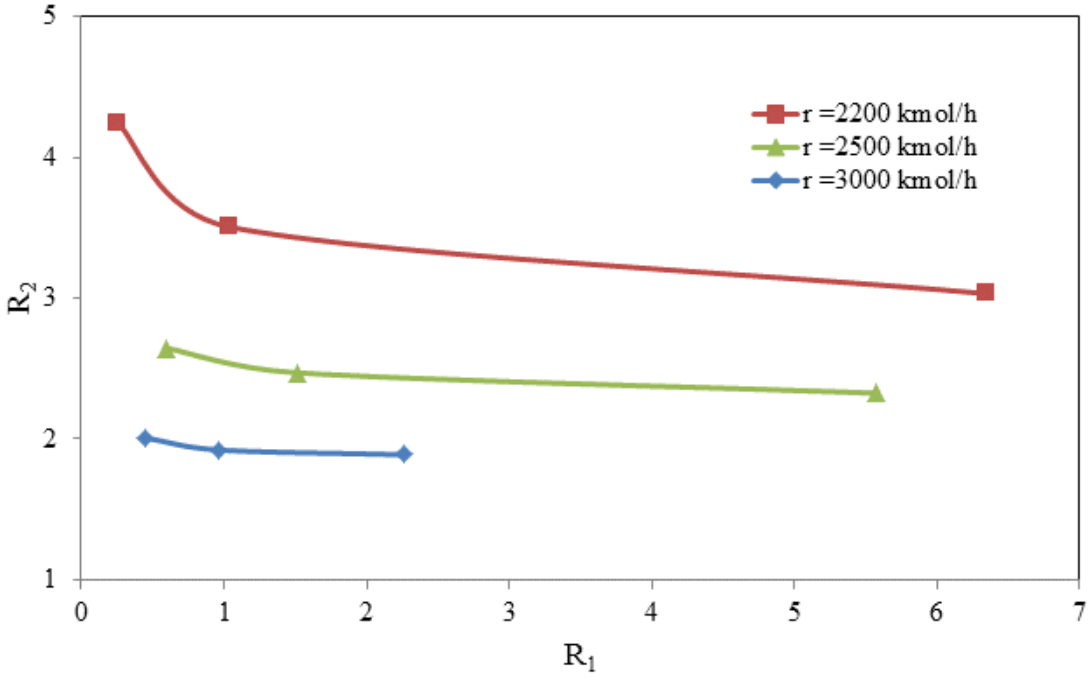

Figure 5.9 e: Feasible vapor split ratio R_2 as a function of liquid split ratio R_1 for superheated vapour feed.

Fig. 5.10 (a-e) shows the variation of the pressure drop (when the pressure drops in the two segments of the divided wall column are equal, i.e., $\Delta P_1 = \Delta P_2 = \Delta P$) with inlet vapour flow rate at various values of reflux flow rate, r and, for different feed quality, q.

For sub-cooled and saturated liquid feeds (Fig 5.10 a, b), the pressure drops are same at the same values of the internal vapour flow rate in the two segments. Although the saturated liquid feed does not contain any vapour fraction, a slightly higher pressure of the feed than the column pressure, leads to flashing of the feed with additional vaporization of the liquid available on the tray. In the second column (column 2), the feed quality has no appreciable effect on the pressure drop since the vapour flow rate in this column is mainly controlled by vapour split stream (V_S) at the bottom of the divided segment.

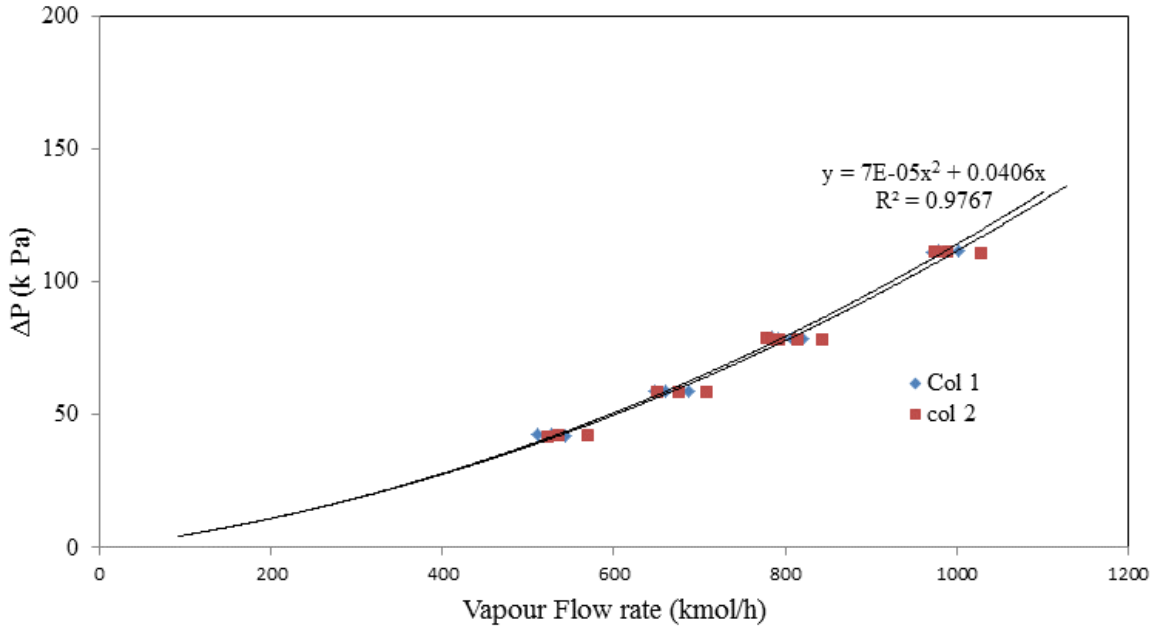

Figure 5.10 a: Variation of pressure drop ($\Delta P = \Delta P_1 = \Delta P_2$) in two column segments with inlet vapour flow rate for subcooled liquid feed.

Another interesting fact is revealed in Fig. (5.10 c-e) where it is found that the behavior of the pressure drop in the two segments of the column is widely different for two phase, saturated vapour and superheated vapour feeds. This is despite the fact that the columns 1 and 2 have same number of similar trays. A positive intercept on the y-axis in case of superheated feed indicates that even if the vapour flow rate (V_{59}) entering the feed side of divided segment of the column (column 1) is reduced to zero, a finite pressure drop is observed in this section. This pressure drop is because of the presence of vapour fraction of the superheated feed that enters at tray 44 in this section.

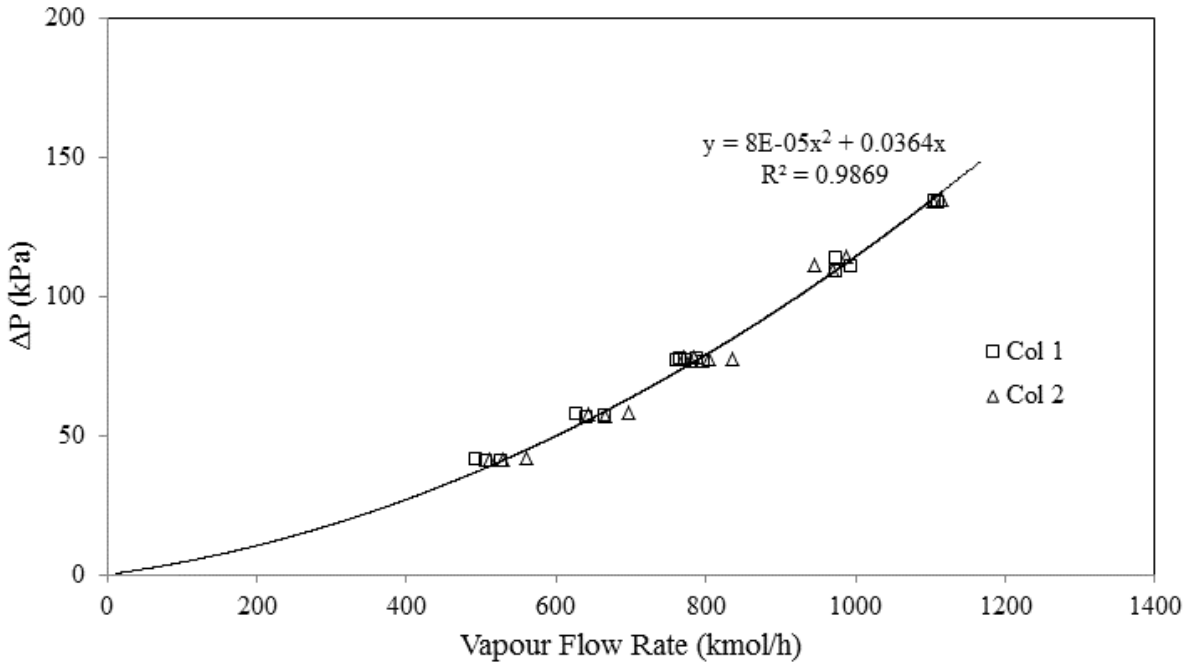

Figure 5.10 b: Variation of pressure drop ($\Delta P = \Delta P_1 = \Delta P_2$) in two column segments with inlet vapour flow rate for saturated liquid feed.

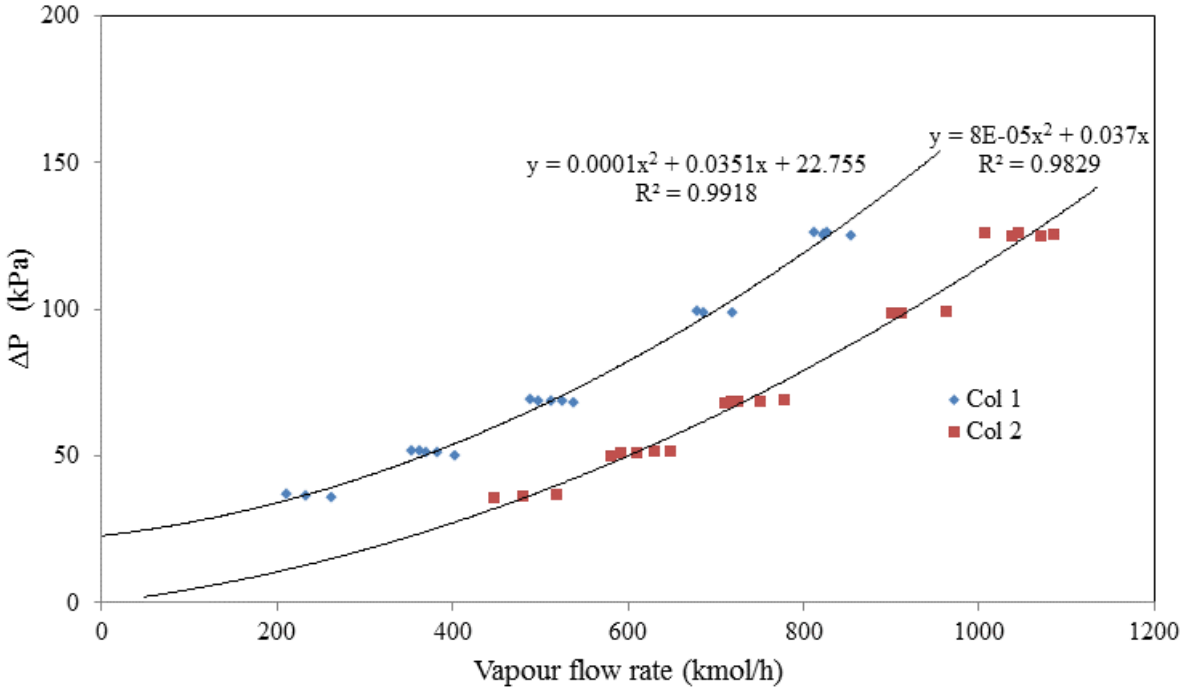

Figure 5.10 c: Variation of pressure drop ($\Delta P = \Delta P_1 = \Delta P_2$) in two column segments with inlet vapour flow rate for two phase feed.

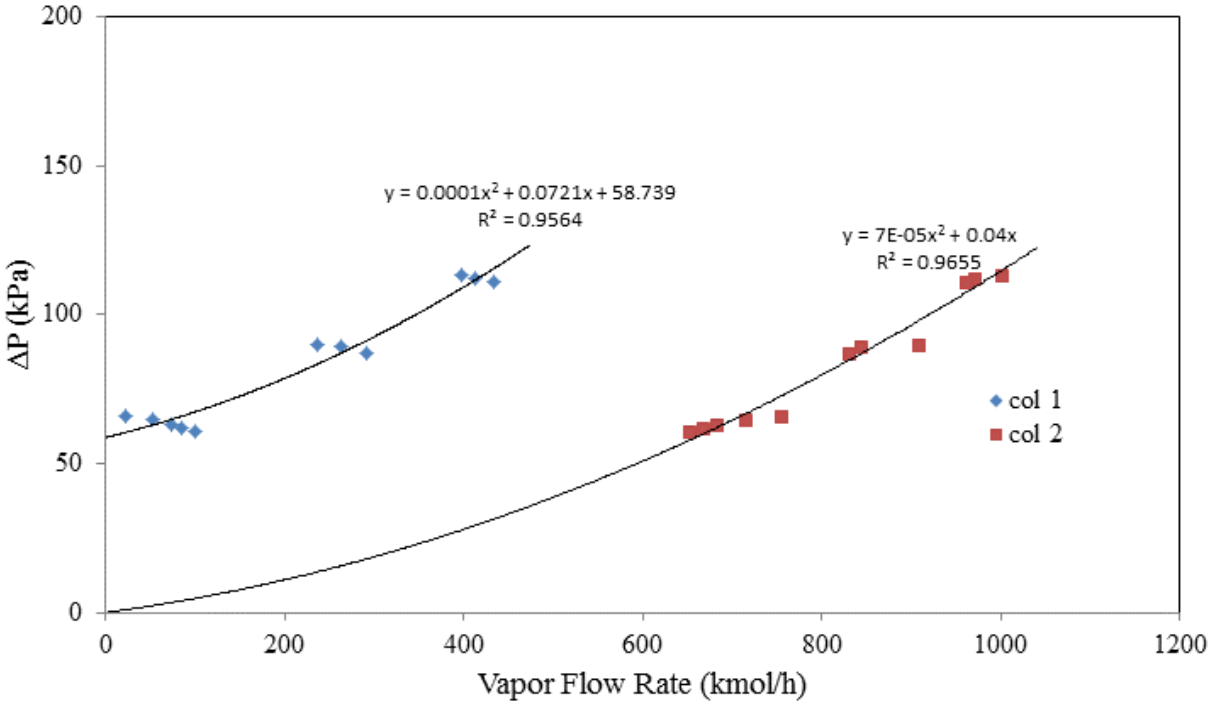

Figure 5.10 d: Variation of pressure drop ($\Delta P = \Delta P_1 = \Delta P_2$) in two column segments with inlet vapour flow rate for saturated vapour feed.

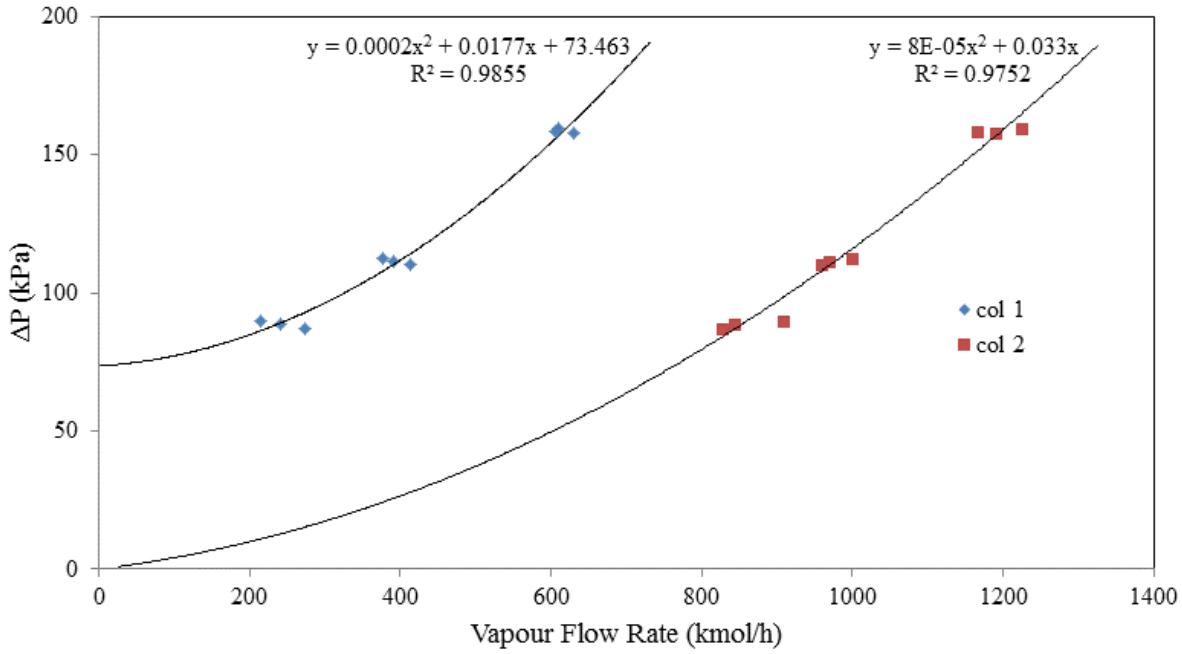

Figure 5.10 e: Variation of pressure drop ($\Delta P = \Delta P_1 = \Delta P_2$) in two column segments with inlet vapour flow rate for superheated vapour feed.

When the different feed composition of BTX mixture (0.2, 0.5 and 0.3 mole fraction of benzene, toluene and xylene, respectively) was taken, it was found that the vapour split ratio is independent of liquid split ratio and reflux rate for saturated liquid feed, as shown in Fig. 5.11.

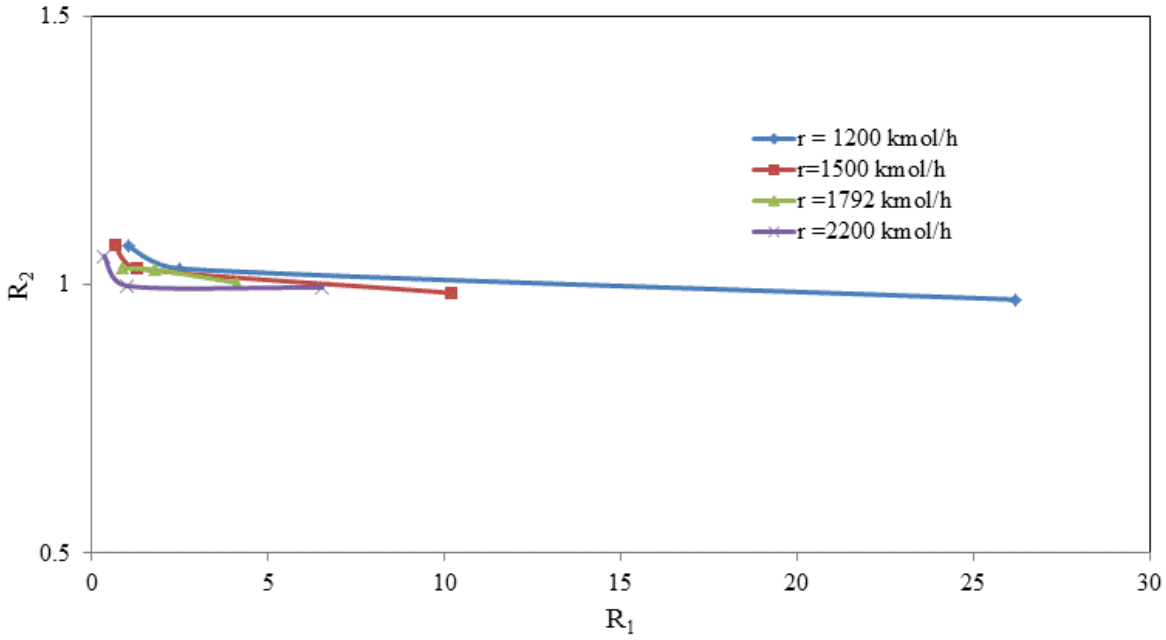

Figure 5.11: Feasible vapor split ratio as a function of liquid split ratio for saturated liquid feed with different feed composition.

Thus, if the DWC is operated with saturated liquid feed, the changes in liquid split will not affect the vapour split. Therefore, operating a DWC with saturated liquid feed should provide some flexibility in changing the liquid split. However, if the column is operated with saturated vapour feed or superheated vapour feed, the vapour split will change with any change in liquid split, thereby offering no flexibility during the operation of the DWC.

During the operation of a DWC, the liquid split can easily be manipulated. Calculations were made for assessing the impact of liquid split on the middle product (i.e. toluene) composition. To achieve this, the liquid split is varied while the vapour split is kept constant. Fig 5.12 shows the variation of toluene composition with respect to liquid split.

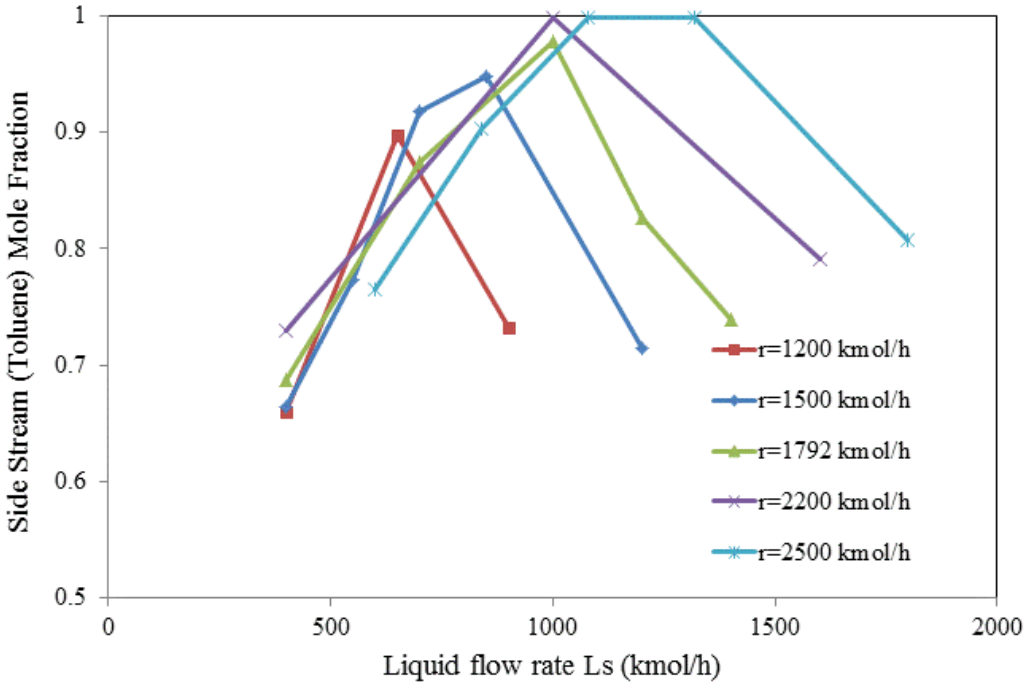

Figure 5.12: Cocentration profile of toluene (side stream) in the post-fractionator section

For saturated liquid feed, there is no effect of liquid split and reflux rate on feasible vapour split. The middle product composition varies with liquid split, reaching a maximum value at a certain value of liquid split. The maximum composition of toluene increases as the reflux ratio is varied from 1200 to 2500 kmol/h. Therefore, it may be suggested that the DWC can be operated and easily controlled for a saturated liquid feed.

5.4 Process Parametric Optimization of a DWC

The optimal design of divided wall distillation columns involves a number of variables and is a non-linear problem. A number of researchers (e.g Lee et al., 2011; Herna´ndez et al., 2011) reported that many process parameters, namely reflux rate, liquid split and vapour split affect the product quality and energy efficiency of a divided wall distillation column. Triantafyllou and Smith (1992) suggested that the vapour and liquid split rates should not be set arbitrarily and that they must be optimized in order to find the minimum energy requirement for a given number of plates. The energy consumption in the reboiler depends strongly on the values of interconnecting flows of a DWC (Herna´ndez et al., 2002**;** Serra et al., 2003). Herna´ndez and Me´ndez (2005) observed that the energy consumption depends strongly on the values of the vapor recycle streams. Rangaiah et al. (2009) also noted that the vapour and liquid splits in the column have significant impact on the energy requirements of a DWC.

The operating cost is the major fraction of the total annual cost of a distillation column. Therefore, the DWC should be optimized by minimizing the energy duty. The process parameters were optimized for improving the product quality and energy efficiency of a DWC and the structural design variables such as the number of trays in the column, and the location of feed and side draw, product and connect streams are fixed together with the feed composition and the feed rate.

The classical optimization of a DWC involves varying one variable (i. e., reflux rate (*r*), liquid split (*Ls*) and vapour split (*Vs)*) at a time while maintaining all other variables at a fixed level. This procedure, however, is labour-intensive, time-consuming and expensive. To overcome this difficulty, the Box-Behnken design (BBD) under response surface methodology (RSM) can be employed to optimize the operational and the

design parameters of a DWC for the purity of product quality and energy efficiency. Therefore, the objectives of this study are set as follows:

(i) The simulation of DWCs for different applications using commercial simulation software ASPEN Plus™,

(ii) The investigation of the effect of process variables on the product quality and energy efficiency, and

(iii) To propose a method based on relative importance of process variables, to make the optimization of a DWC fast and requiring less number of simulation runs.

The RSM was applied to optimize the process parameters for energy consumption, for three different mixtures namely,

(i) the fractionation of benzene-toluene-*p*-xylene (BTX) ternary mixture of the naphtha reformer similar to that used by Kim (2006);

(ii) the fractionation of n-butane, n-pentane, n-hexane ternary mixture as that taken by Gómez–Castro et al. (2008); and

(iii) the separation of a multicomponent light hydrocarbon mixture as that taken by Rangiah et al. (2009).

Initial estimates for the design variables for each system were obtained by decomposing the DWC into short cut columns as shown by Amminudin et al. (2001). For steady state rigorous simulation, the MultiFrac model of the process simulator ASPEN Plus™ has been used for all the systems. The parameters required to be specified to operate the DWC under varying operating conditions are listed in Table 5.7.

Table 5.7 Column, feed, product and connect stream specifications for three case studies.

Case no.	System	Column Data											
		No of stages in main column (N)	No of stages in post fractionator ($N_{S2}-N_{S1}$)	side draw stage (N_{S3})	Liquid split stage N_{S1}	Vapour split stage N_{S2}	Feed stage	Feed rate (kmol/h)	Feed composition (mol fraction)	Feed condition	Column pressure (kPa)	Distillate rate (kmol/h)	Side draw rate (kmol/h)
(i)	BTX	89	35	20	23	58	44	801.8	Benzene = 0.1096 Toluene = 0.4217 *p*-xylene = 0.4687	150 kPa, 135°C	116	88.65	337.8
(ii)	n C_4, n C_5, n C_6	38	17	9	9	27	18	45.359	n-Butane = 0.40 n-Pentane = 0.20 n-Hexane = 0.40	170.99 kPa, saturated liquid	144.79 kPa	18.27	8.618
(iii)	Light hydrocarbon (C_2-nC_6)	65	50	17	11	62	33	1600	Ethylene = 0.0128 Propene = 0.0760 Propane = 0.2312 i- Butane = 0.1443 1-Butene = 0.2683 n-Butane = 0.0409 i-Pentane = 0.0940 n-Pentane = 0.1008 n-Hexane = 0.0317	1490 kPa, 90% liquid	1390 kPa	503	651

For easier convergence of the simulator, molar flow rates of the reflux and connect stream *r*, *Ls* and *Vs* were used as input parameters. A range of values of the reflux rate *r*, liquid split *Ls*, and the vapour split *Vs* were taken as the variable input parameters for optimization. The factor levels were coded as −1 (low), 0 (central point or middle) and 1 (high) (Evans, 2003). The input parameters used in the present work are given in Table 5.8. The range of process variables *Ls*, *Vs* and *r* are chosen from the extreme values of these variables, i.e. below and above these extreme values, the simulation does not converge.

The simulated data were analyzed using the statistical software, Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, US), for regression analysis to fit the equations developed and also for the evaluation of the statistical significance of the equations.

Table 5.8 Experimental design levels of chosen variables for three case studies.

Variables	Levels in Box–Behnken design								
Coded level	Low (-1)			Medium (0)			High (+1)		
Systems	Case (i)	Case (ii)	Case (iii)	Case (i)	Case (ii)	Case (iii)	Case (i)	Case (ii)	Case (iii)
r (kmol/h)	1500	84	1350	1750	163	1825	2000	242	2300
Ls(kmol/h)	640	27	750	890	50	930	1140	73	1110
Vs(kmol/h)	469	10	100	719	60	380	969	110	660

The results of the product quality and the energy efficiency (responses) for a DWC were measured according to the design matrix for all the three systems. The detailed simulation and optimization procedures are discussed here only for the benzene-toluene-*p*-xylene (BTX) ternary system.

Case (i) Separation of BTX mixture

The design matrix for the product quality and the energy efficiency (responses) for the BTX mixture are listed in Table 5.9.

Table 5.9 Simulated values of the product quality and energy efficiency for a DWC for case (i)

Std order	Run order	*Ls*	*Vs*	*r*	Response Y [a]				
					D	S	B	Qc * 10^8 BTU/h	Qb * 10^8 BTU/h
5	1	640	719	1500	0.91829	0.8325	0.86771	0.441432	0.332793
3	2	640	969	1750	0.89417	0.7585	0.80678	0.517261	0.40769
16	3	890	719	1750	0.82113	0.45189	1	0.523568	0.414659
1	4	640	469	1750	0.99115	0.99853	0.99993	0.507582	0.401531
4	5	1140	969	1750	0.98012	0.94709	0.95625	0.508769	0.401864
15	6	890	719	1750	0.82113	0.45189	1	0.523568	0.414659
12	7	890	969	2000	0.97378	0.977	0.98464	0.582217	0.47578
17	8	890	719	1750	0.82113	0.45189	1	0.523568	0.414659
2	9	1140	469	1750	0.92087	0.7303	0.77512	0.514757	0.405061
6	10	1140	719	1500	0.99106	0.76717	0.79172	0.435078	0.326001
9	11	890	469	1500	0.98612	0.80118	0.82352	0.435537	0.326795
10	12	890	969	1500	0.87422	0.91346	0.95097	0.44491	0.337338
8	13	1140	719	2000	0.991	0.87364	0.88756	0.580111	0.472194
13	14	890	719	1750	0.82113	0.45189	1	0.523568	0.414659
14	15	890	719	1750	0.82113	0.45189	1	0.523568	0.414659
11	16	890	469	2000	0.98389	0.92379	0.93436	0.58099	0.473738
7	17	640	719	2000	0.9886	0.89716	0.90928	0.580409	0.47279

[a] D, S and B are mole fractions of benzene, toluene and p-xylene in the distillate, side stream and bottom product, respectviely and Q_c and Q_b are condenser and reboiler duty, respectively.

From the design matrix for optimization of a DWC by BBD, we need only seventeen simulation runs, out of which five runs are repeated. So only thirteen simulation runs are actually required. The sequential F-test and other adequacy measures were used for selecting the best model (Muthukumar et al., 2003). A manual regression method was used to fit the second order polynomial equation (4.3.3) to the simulated data and to identify the relevant model terms. To decide about the adequacy of the model for product quality and energy efficiency of a DWC, two different tests, such as the sequential model sum of squares and model summary statistics were carried out and p values for all the regressions were lower than 0.01 and the quadratic model. This means that at least one of

the terms in the regression equation had a significant correlation with the response variable. Table 5.10 (a, b) shows the selection of a satisfactory model for the purity of side stream and the reboiler duty, respectively.

By selecting the manual regression method, which eliminated the insignificant model terms automatically, the resulting ANOVA for the reduced quadratic models summarizes the analysis of variance of each response and shows the significant model terms. For BTX separation, Table 5.11(a, b) shows the ANOVA results for the purity of side stream and the reboiler duty of the DWC, with a model F- value of 120.49 and 2163.89, respectively, implying that the model is significant.

Table 5.10 (a) Selection of a satisfactory model for the purity of side stream (S) for case (i)

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	9.457445	1	9.457445			
Linear	0.022034	3	0.007345	0.140784	0.9337	
2FI	0.05348	3	0.017827	0.285353	0.8349	
Quadratic	0.620238	3	0.206746	322.2367	< 0.0001	suggested
Cubic	0.004491	3	0.001497	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	10.15769	17	0.597511			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.228408	0.031466	-0.19204	-0.43229	1.002954	
2FI	0.249946	0.10784	-0.42746	-1.10986	1.477417	
Quadratic	0.02533	0.993586	0.98534	0.89738	0.071859	suggested
Cubic	0	1	1	+		aliased

Table 5.10 (b) Selection of a satisfactory model for reboiler duty (Q_b) for case (i)

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	2.806168	1	2.806168			
Linear	0.040879	3	0.013626	304.1759	< 0.0001	
2FI	4.95E-05	3	1.65E-05	0.309972	0.8178	
Quadratic	0.000518	3	0.000173	81.12144	< 0.0001	suggested
Cubic	1.49E-05	3	4.97E-06	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	2.847629	17	0.167508			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.006693	0.985954	0.982713	0.97875	0.000881	
2FI	0.007299	0.987149	0.979438	0.967863	0.001332	
Quadratic	0.001459	0.999641	0.999179	0.994251	0.000238	suggested
Cubic	0	1	1		+	aliased

Table 5.11(a) ANOVA for response surface quadratic model (for purity of side stream S) for case (i)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks[a]
Model	0.695753	9	0.077306	120.4898	< 0.0001	Significant
Ls	0.003549	1	0.003549	5.530901	0.0510	
Vs	0.002529	1	0.002529	3.942323	0.0875	
R	0.015956	1	0.015956	24.86938	0.0016	Significant
Ls^2	0.125635	1	0.125635	195.8156	< 0.0001	Significant
Vs^2	0.230507	1	0.230507	359.271	< 0.0001	Significant
r^2	0.200083	1	0.200083	311.851	< 0.0001	Significant
Ls.Vs	0.052171	1	0.052171	81.31447	< 0.0001	Significant
Ls.r	0.000437	1	0.000437	0.681142	0.4364	
Vs. r	0.000872	1	0.000872	1.359601	0.2818	
Residual	0.004491	7	0.000642			
Lack of fit	0.004491	3	0.001497			
Pure error	0	4	0			
Cor. total	0.700244	16				

[a] R^2=0.9936, predicted R^2=0.8974, adjusted R^2= 0.9853, adequate precision = 26.983.

Table 5.11(b) ANOVA for response surface quadratic model (for reboiler duty Q_b) for case (i)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks [a]
Model	0.041447	9	0.004605	2163.897	< 0.0001	Significant
Ls	1.17E-05	1	1.17E-05	5.508194	0.0513	
Vs	3.02E-05	1	3.02E-05	14.19688	0.0070	Significant
R	0.040837	1	0.040837	19188.73	< 0.0001	Significant
Ls^2	0.00018	1	0.00018	84.76082	< 0.0001	Significant
Vs^2	7E-05	1	7E-05	32.88775	0.0007	Significant
r^2	0.000216	1	0.000216	101.6853	< 0.0001	Significant
Ls.Vs	2.19E-05	1	2.19E-05	10.28277	0.0149	Significant
Ls.r	9.6E-06	1	9.6E-06	4.50975	0.0713	
Vs. r	1.81E-05	1	1.81E-05	8.489258	0.0225	Significant
Residual	1.49E-05	7	2.13E-06			
Lack of fit	1.49E-05	3	4.97E-06			
Pure error	0	4	0			
Cor. total	0.041462	16				

[a] R^2=0.9996, predicted R^2=0.9943, adjusted R^2= 0.9992, adequate precision = 132.547.

An inverse transformation for D and B and no transformation for S, Q_b, Q_c were applied to the simulated data, the interaction of two factors (2FI) and the linear model were suggested to be insignificant using the response surface methodology. The model summary statistics showed that the regression coefficient (R^2 = 0.9861, 0.9936, 0.9657,

0.9996, 0.9998) were the highest for the quadratic model with minimum standard deviation (0.016, 0.025, 0.029, 0.0014 and 0.00118) for the purity of distillate D, side stream S and bottom product B, reboiler duty Q_b and the condenser duty Q_c of the DWC, respectively, for the separation of BTX mixture.

For the purity of distillate, side stream and bottom product, reboiler duty and condenser duty of DWC showed adequate precision ratio (> 4), thus indicating an adequate precision ratio above 4 indicates adequate model efficacy. It means that the model can be used to navigate the design space.

The ANOVA analysis indicates a relationship between the purity of distillate, side stream and bottom product, reboiler duty and condenser duty of DWC in terms of liquid split (*Ls*), vapour split (*Vs),* and the reflux rate (*r*). By eliminating the insignificant interaction terms, the final mathematical equation in terms of actual (natural) factors (confidence level above 95%) are determined by Design-Expert software.

A normal probability plot and a dot diagram of the residuals are shown in Figure 5.13 for reboiler duty Q_b. The data points on this plot lie reasonably close to a straight line, indicating that the underlying assumptions of the analysis were satisfied. Figure 5.14 shows the relationship between the actual and predicted values of $Q_{b,}$ for a DWC. It can be seen from Fig. 5.14 that the residuals are in the proximity of the straight diagonal line. Therefore, it is concluded that the developed models are adequate because the residuals for the prediction of each response are minimum. Similar plots were obtained and data analysis were done for product purity D, S, B and condenser duty Q_c.

The 3D response surface plots of the effect of *Ls* and *Vs* on the purity of S and Q_b of a DWC are shown in Figures 5.15- 5.16. To verify the adequacy of the developed models, the confirmation simulation runs for the purity of the distillate of a DWC were

carried out using new test conditions, although within the simulation ranges defined earlier.

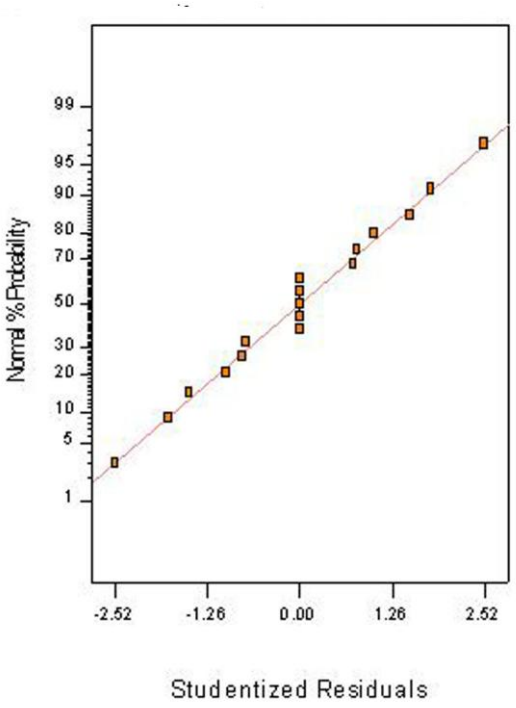

Figure 5.13: Normal % probabilities versus studentized residuals for the reboiler duty Q_b for case (i).

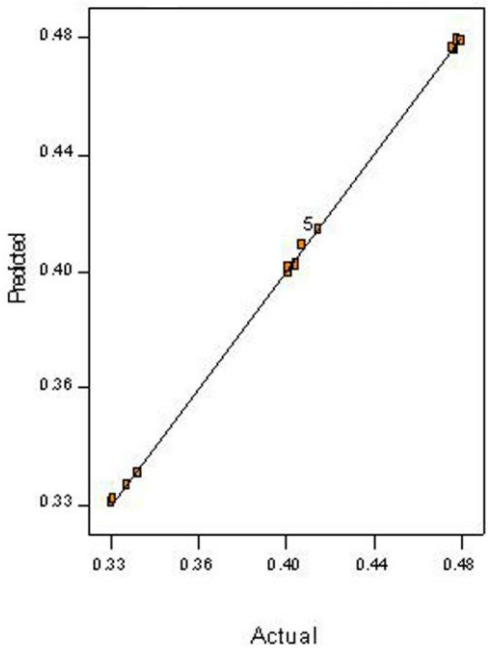

Figure 5.14: Scatter diagram for the predicted response versus actual response for the reboiler duty, Q_b for case (i).

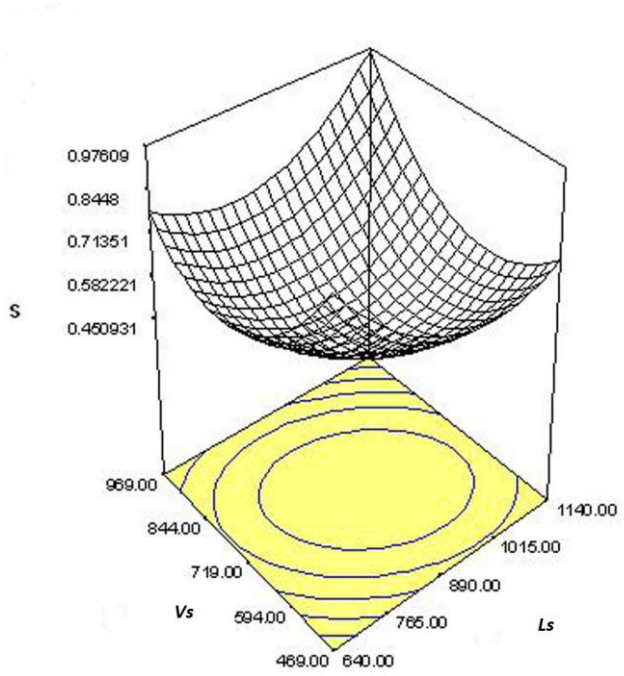

Figure 5.15: 3D response surface graph of liquid split (*Ls*) verses vapour split (*Vs*) at a reflux rate *r* = 1750 kmol/h for the purity of side stream in a DWC

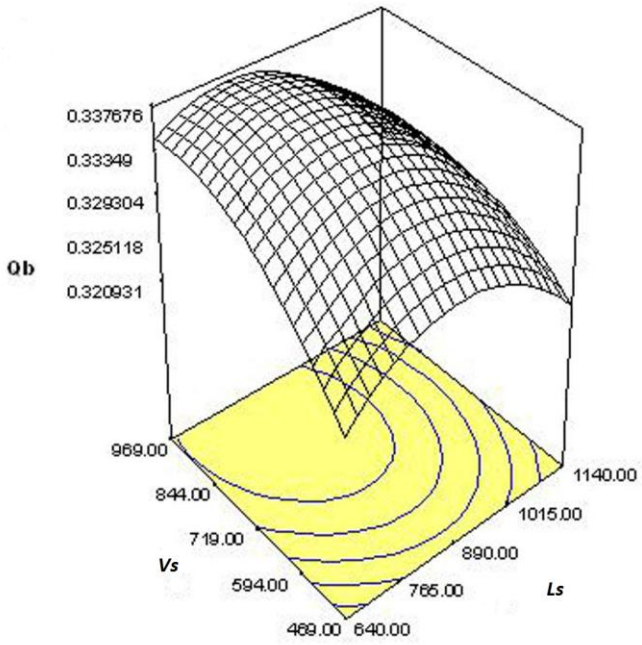

Figure 5.16: 3D response surface graph of liquid split (*Ls*) versus vapour split (*Vs*) at a reflux rate *r* = 1500 kmol/h for the reboiler duty Q_b of a DWC

Case (ii) Separation of n- C4, n- C5, n- C6

The design matrix for the product quality and the energy efficiency (responses) for the nC_4-nC_6 mixture are listed in Table 5.12. Table 5.13(a, b) shows the selection of satisfactory model for the purity of side stream and the reboiler duty, respectively.

Table 5.12 Simulated values of the product quality and energy efficiency for a DWC for case (ii).

Std order	Run order	*r*	*Ls*	*Vs*	Response Y [a]				
					D	S	B	Qb	Qc
12	1	163	73	110	0.93841	0.88198	0.98132	1649850	-1569670
14	2	163	50	60	0.98843	0.97087	0.9733	1632050	-1545700
6	3	242	50	10	0.95273	0.91438	0.98226	2402340	-2320210
2	4	242	27	60	0.99278	0.79496	0.88689	2368720	-2291770
9	5	163	27	10	0.918	0.27963	1	1645930	-1579390
15	6	163	50	60	0.98843	0.97087	0.9733	1632050	-1545700
1	7	84	27	60	0.87824	0.48288	0.85459	879608	-823725
10	8	163	73	10	0.9314	0.70311	0.90476	1641490	-1573040
3	9	84	73	60	0.95772	0.69466	0.74021	875094	-803789
7	10	84	50	110	0.90383	0.56002	0.78055	890696	-816851
11	11	163	27	110	0.9354	0.59698	0.85127	1633930	-1571130
4	12	242	73	60	0.9928	0.99981	0.98248	2380170	-2291760
13	13	163	50	60	0.98843	0.97087	0.9733	1632050	-1545700
8	14	242	50	110	0.97536	0.80258	0.90768	2379870	-2304090
5	15	84	50	10	0.88426	0.36816	0.77075	879176	-821588
16	16	163	50	60	0.98843	0.97087	0.9733	1632050	-1545700
17	17	163	50	60	0.98843	0.97087	0.9733	1632050	-1545700

[a] D, S and B are mole fractions of n-C_4, n – C_5 and n – C_6 in the distillate, side stream and bottom product, respectviely, and Q_c (BTU/h) and Q_b (BTU/h) are condenser and reboiler duty, respectively.

Table 5.13 (a) Selection of a satisfactory model for the purity of side stream (S) for case (ii).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	9.839731	1	9.839731			
Linear	0.446854	3	0.148951	4.724179	0.0193	
2FI	0.027859	3	0.009286	0.243077	0.8644	
Quadratic	0.346052	3	0.115351	22.44527	0.0006	suggested
Cubic	0.035974	3	0.011991	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	10.69647	17	0.629204			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.177566	0.521576	0.41117	0.246911	0.645201	
2FI	0.195455	0.554093	0.286548	0.25846	1.078171	
Quadratic	0.071688	0.95801	0.904023	0.728162	0.57559	suggested
Cubic	0	1	1		+	aliased

Table 5.13 (b) Selection of a satisfactory model for reboiler duty (Q_b) for case (ii).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	4.54E+13	1	4.54E+13			
Linear	4.51E+12	3	1.5E+12	16880.43	< 0.0001	
2FI	4.56E+08	3	1.52E+08	2.167488	0.1551	
Quadratic	6.51E+08	3	2.17E+08	30.12075	0.0002	suggested
Cubic	50438317	3	16812772	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	4.99E+13	17	2.94E+12			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	9436.9	0.999743	0.999684	0.999469	2.39E+09	
2FI	8375.806	0.999844	0.999751	0.999228	3.48E+09	
Quadratic	2684.301	0.999989	0.999974	0.999821	8.07E+08	suggested
Cubic	0	1	1		+	aliased

Case (iii) Separation of light hydrocarbon mixture

For the separation of C_2 – nC_6 light hydrocarbon mixture, the recovery of n-C_3 in distillate, all C_4 products in side stream and i-C_5 in bottom product, respectively, are considered. The design matrix for the product quality and the energy efficiency (responses) for the given mixture are listed in Table 5.14. Table 5.15(a, b) shows the selection of satisfactory model for the purity of side stream and the reboiler duty, respectively.

Table 5.14 Simulated values of the product quality and energy efficiency for a DWC for case (iii).

Std order	Run order	*r*	*Ls*	*Vs*	Response Y [a]				
					D	S	B	Qb BTU/h	Qc BTU/h
5	1	1350	930	100	0.64278	0.51898	0.2974	5262.2	-5926.32
10	2	1825	1110	100	0.70823	0.6518	0.50476	7050.9	-7802.74
4	3	2300	1110	380	0.79972	0.799377	0.60614	9043.67	-9555.45
12	4	1825	1110	660	0.87544	0.82515	0.53041	6864.06	-7375.55
15	5	1825	930	380	0.82247	0.791735	0.57048	6986.28	-7525.44
16	6	1825	930	380	0.82247	0.791735	0.57048	6986.28	-7525.44
17	7	1825	930	380	0.82247	0.791735	0.57048	6986.28	-7525.44
8	8	2300	930	660	0.93363	0.885585	0.57764	8658.22	-9070.31
2	9	2300	750	380	0.91319	0.863971	0.57582	8709.6	-9149.53
6	10	2300	930	100	0.73844	0.75841	0.61654	9182.48	-9743.68
3	11	1350	1110	380	0.74509	0.68548	0.43493	5847.87	-5718.88
14	12	1825	930	380	0.82247	0.791735	0.57048	6986.28	-7525.44
11	13	1825	750	660	0.72805	0.67128	0.39623	7438.13	-7765.61
7	14	1350	930	660	0.69219	0.62948	0.42646	5544.85	-5794.13
9	15	1825	750	100	0.72662	0.72536	0.58207	7151.22	-7764
13	16	1825	930	380	0.82247	0.791735	0.57048	6986.28	-7525.44
1	17	1350	750	380	0.73102	0.65117	0.4575	5256.06	-5745.83

[a] D, S and B are mole fractions of n-C_4, n – C_5 and n – C_6 in the distillate, side stream and bottom product, respectviely and Q_c and Q_b are condenser and reboiler duty respectively.

Table 5.15 (a) Selection of a satisfactory model for the purity of side stream (S) for case (iii).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	9.3755	1	9.3755			
Linear	0.100747	3	0.033582	9.736203	0.0012	Suggested
2FI	0.015446	3	0.005149	1.751619	0.2197	
Quadratic	0.022549	3	0.007516	7.687129	0.0128	Suggested
Cubic	0.006845	3	0.002282	63660000	< 0.0001	Aliased
Residual	0	4	0			
Total	9.521088	17	0.560064			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.05873	0.692006	0.62093	0.435149	0.082235	Suggested
2FI	0.054216	0.798101	0.676962	0.294667	0.102688	
Quadratic	0.03127	0.952986	0.89254	0.647783	0.109513	Suggested
Cubic	0	1	1		+	Aliased

Table 5.15 (b) Selection of a satisfactory model for reboiler duty (Q_b) for case (iii).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	8.6E+08	1	8.6E+08			
Linear	23413437	3	7804479	140.8685	< 0.0001	Suggested
2FI	235493.2	3	78497.73	1.619377	0.2464	
Quadratic	131577.4	3	43859.14	0.869327	0.5007	
Cubic	353162.9	3	117721	63660000	< 0.0001	Aliased
Residual	0	4	0			
Total	8.85E+08	17	52030850			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	235.3775	0.970156	0.96327	0.940797	1428785	
2FI	220.1682	0.979914	0.967863	0.910386	2162715	
Quadratic	224.6149	0.985366	0.966552	0.765862	5650607	suggested
Cubic	0	1	1		+	

Using the point prediction option in the software, the response of the validation simulations were predicted using the previously developed models. The optimized values of *Ls*, *Vs* and *r* for all the systems were estimated for product quality and energy efficiency and these values are given in Table 5.16.

Table 5.16 Optimum column results for all the systems studied.

Process parameters	Optimized results		
	Case (i) BTX	Case (ii) n-C4, n-C5, n-C6	Case (iii) light hydrocarbon
Ls (kmol/h)	643.15	57.87	1110
Vs(kmol/h)	575.35	66.31	615.57
r (kmol/h)	1500.26	154.28	2047.23
Reboiler duty Q_b (kW)	9627.60	452	7629.93

The number of ASPEN runs that are needed to optimize the system using the Box-Behnken Design approach reduced significantly and only thirteen simulation runs were needed to optimize the systems. The optimized reboiler duty for DWC by this method for the separation of light hydrocarbons is 7629.9 kW, and is comparable to that reported by Rangiah et al. (2009), for a specified separation.

5.5 Optimization of a DWC for the Separation of C4-C6 Normal Paraffin Mixture

A number of authors have optimized the operating conditions of distillation columns including a DWC by neglecting the consideration of pressure drop. As shown earlier, the consideration of pressure drop during distillation column simulation is necessary. The positioning of the dividing wall is decided at the design stage to obtain optimum vapour split ratio and this cannot be changed at a later stage. On the other hand, at the time of operation, depending upon tray hydrodynamics, vapour flow rates on the two sides of the divided section are adjusted naturally in such a way that the pressure drops on both sides of the divided segment of the column are equal. This leads to a deviation in the vapour split from the designed value. Moreover, the vapour flow rate to liquid flow rate ratio (Vs/Ls) in the divided segment plays an important role on the product concentration (Fig. 5.7 of section 5.2). In the present work, the data at different operating conditions are generated using Aspen Plus and the optimum operating conditions are obtained by using BBD under RSM. However, the simulator used does not take pressure drop as a variable parameter and the vapor split is required to be defined by the user. Therefore, it is necessary that only those pairs of *Ls* and *Vs* values should be selected for optimization at which the pressure drop across both the sides of the dividing wall is zero.

Aspen plus is used for the rigorous simulation and BBD under RSM is used for the optimization of the operational parameters of a DWC, for the purity of product quality in such a way that the reboiler duty is minimized (or energy efficiency is maximized). It is also targeted that the difference between the pressure drops across the two sections of the divided wall is zero. The reboiler duty is considered as the energy requirement for a DWC. The fractionation of n-butane, n-pentane and n-hexane (C4-C6) ternary mixture, as investigated by Gómez–Castro et al. (2008), in a DWC is taken as a case study. The use

of BBD is expected to reduce significantly the number of simulation runs for the optimization of a DWC in comparison to other methods.

The impurities that can be allowed in each of the three components in the distillate and bottom products, and side stream are taken to be not more than 5 %. The other parameters required to be specified to operate the DWC under varying operating conditions are listed in Table 5.17.

Table 5.17 Column, feed, product and connect stream specifications for paraffin mixture.

Main Column		***Section 2 of Main Column***	
No of stages	38	No of stages	17
Feed stage	18	Product draw stage	9
Column pressure	144.79 kPa	Column pressure	144.79 kPa
Distillate rate	18.275 kmol/h		
Reflux rate (*r*)	84-242 kmol/h		
Feed rate	45.359 kmol/h	Product rate (*S*)	8.618 Kmol/h
Feed condition	(172.36 kPa, saturated liquid)	Product stream	Saturated liquid
Feed composition (mol fraction)	n-Butane = 0.40 n-Pentane = 0.20 n-Hexane = 0.40	–	–
Connect Streams:	***From***	***To***	***Value***
Ls	Column 1, Stage 9	Column 2, Stage 1	27-73 kmol/h
Vs	Column 1, Stage 27	Column 2, Stage17	10-110 kmol/h
L_{NS1} (Internal Stream)	Column 2, Stage 1	Column 1, Stage 9	–
V_{NS2} (Internal Stream)	Column 2, Stage 17	Column 1, Stage 27	–

Sieve trays are used extensively in plate distillation columns for vapour-liquid contacting, even for systems with moderate fouling characteristics. Large amount of data are available for design of sieve trays and the sieve tray design is easy and non-proprietary. Properly designed sieve trays have capacity and efficiency comparable to other trays Therefore, the sieve trays are used in the tray rating. The additional column design specifications required for making hydrodynamic calculations are listed in Table 5.18.

Table 5.18 Tray design specifications for paraffin mixture.

Tray diameter	0.67 m
Tray spacing	0.60 m
Ratio of sieve hole area to tray active area	0.12
Weir height (h_w)	0.05 m
Hole diameter	5 mm

The structural design variables are taken as the number of trays in the column, and the location of feed and side draw, product and connect streams are fixed together with the feed composition and feed rate. For the separation of C4-C6 normal paraffin mixture, a three-level, three-factorial BBD is applied to study the DWC process parameters affecting the product quality, energy efficiency and pressure drop across the divided wall (ΔP). The factor levels are coded as −1 (low), 0 (central point or middle) and 1 (high) (Evans, 2003). Table 5.19 shows the input parameters. The range of the values of the process variables namely, *Ls*, *Vs* and *r*, are chosen from the extreme values of these variables beyond which the convergence of the results of simulation is not achieved.

Table 5.19 Experimental design levels of chosen variables for paraffin mixture.

Variables	Levels in Box–Behnken design		
Coded level	Low (-1)	Medium (0)	High (+1)
r (kmol/h)	84	163	242
Ls (kmol/h)	27	50	73
Vs (kmol/h)	10	60	110

RSM was applied to the simulated data using the Design-Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, US). The simulated data were analyzed by regression analysis to fit the equations developed and also for the evaluation of the statistical significance of the equations. The results of the product quality, the energy efficiency and ΔP (responses) for a DWC were analysed according to the design matrix and are listed in Table 5.20.

Table 5.20 Simulated values of the product quality, energy efficiency and ΔP for paraffin mixture.

Std order	Run order	*r* (kmol/h)	*Ls* (kmol/h)	*Vs* (kmol/h)	Response Y [a]					
					D	S	B	Qb BTU/h	Qc BTU/h	Δ P psi
12	1	163	73	110	0.938	0.882	0.981	1649850	-1569670	-5.552
14	2	163	50	60	0.988	0.971	0.973	1632050	-1545700	-1.290
6	3	242	50	10	0.953	0.914	0.982	2402340	-2320210	1.996
2	4	242	27	60	0.993	0.795	0.887	2368720	-2291770	-0.347
9	5	163	27	10	0.918	0.280	1.000	1645930	-1579390	0.854
15	6	163	50	60	0.988	0.971	0.973	1632050	-1545700	-1.290
1	7	84	27	60	0.878	0.483	0.855	879608	-823725	-1.129
10	8	163	73	10	0.931	0.703	0.905	1641490	-1573040	0.572
3	9	84	73	60	0.958	0.695	0.740	875094	-803789	-1.420
7	10	84	50	110	0.904	0.560	0.781	890696	-816851	-5.137
11	11	163	27	110	0.935	0.597	0.851	1633930	-1571130	-5.084
4	12	242	73	60	0.993	1.000	0.982	2380170	-2291760	-0.527
13	13	163	50	60	0.988	0.971	0.973	1632050	-1545700	-1.290
8	14	242	50	110	0.975	0.803	0.908	2379870	-2304090	-5.266
5	15	84	50	10	0.884	0.368	0.771	879176	-821588	0.097
16	16	163	50	60	0.988	0.971	0.973	1632050	-1545700	-1.290
17	17	163	50	60	0.988	0.971	0.973	1632050	-1545700	-1.290

[a] D, S and B are mole fractions of n-C_4, n – C_5 and n – C_6 in the distillate, side stream and bottom product, respectviely, Q_c and Q_b are condenser and reboiler duty respectively and Δ P is pressure drop across the divided wall

The best model was selected on the basis of the sequential F-test and other adequacy measures (Muthukumar et al., 2003). A manual regression method was used to fit the second order polynomial equation (4.3.3) to the simulated data and to identify the relevant model terms. The cubic model was found to be aliased and, therefore, was not used for further processing of the simulated data.

The sequential model sum of squares and model summary statistics were carried out to test the adequacy of the model for product quality and energy efficiency of a DWC, and the p values for all the regressions were found to be lower than 0.01. This exemplified that at least one of the terms in the regression equation had a significant correlation with the response variable.

Table 5.21 (a-f) show the selection of a satisfactory model for the purity of distillate (D), purity of side stream (S), purity of bottom product (B), reboiler duty (Q_b), condener duty (Q_c) and pressure drop across the divided wall (ΔP), respectively.

Table 5.21(a) Selection of a satisfactory model for the purity of distillate (D).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	15.44352	1	15.44352			
Linear	0.012189	3	0.004063	4.152032	0.0287	
2FI	0.001608	3	0.000536	0.48222	0.7020	
Quadratic	0.010565	3	0.003522	44.93057	< 0.0001	suggested
Cubic	0.000549	3	0.000183	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	15.46843	17	0.909908			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.031282	0.489317	0.371467	0.172305	0.020619	
2FI	0.033337	0.553858	0.286173	-0.28909	0.032113	
Quadratic	0.008853	0.977975	0.949657	0.747597	0.008779	suggested
Cubic	0	1	1		+	aliased

Table 5.21(b) Selection of a satisfactory model for the purity of side stream (S).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	9.839731	1	9.839731			
Linear	0.446854	3	0.148951	4.724179	0.0193	
2FI	0.027859	3	0.009286	0.243077	0.8644	
Quadratic	0.346052	3	0.115351	22.44527	0.0006	suggested
Cubic	0.035974	3	0.011991	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	10.69647	17	0.629204			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.177566	0.521576	0.41117	0.246911	0.645201	
2FI	0.195455	0.554093	0.286548	-0.25846	1.078171	
Quadratic	0.071688	0.95801	0.904023	0.728162	0.57559	suggested
Cubic	0	1	1		+	aliased

Table 5.21 (c) Selection of a satisfactory model for the purity of bottom product (B).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	14.14924	1	14.14924			
Linear	0.04938	3	0.01646	3.228009	0.0577	
2FI	0.025491	3	0.008497	2.082703	0.1662	
Quadratic	0.039918	3	0.013306	105.9568	< 0.0001	suggested
Cubic	0.000879	3	0.000293	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	14.26491	17	0.839112			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.071408	0.42691	0.294658	-0.04456	0.120822	
2FI	0.063873	0.647288	0.435661	-0.16754	0.135047	
Quadratic	0.011206	0.9924	0.982629	0.878401	0.014065	suggested
Cubic	0	1	1		+	aliased

Table 5.21(d) Selection of a satisfactory model for reboiler duty (Q_b).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	4.54E+13	1	4.54E+13			
Linear	4.51E+12	3	1.5E+12	16880.43	< 0.0001	
2FI	4.56E+08	3	1.52E+08	2.167488	0.1551	
Quadratic	6.51E+08	3	2.17E+08	30.12075	0.0002	suggested
Cubic	50438317	3	16812772	63660000	< 0.0001	aliased
Residual	0	4	0			
Total	4.99E+13	17	2.94E+12			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	9436.9	0.999743	0.999684	0.999469	2.39E+09	
2FI	8375.806	0.999844	0.999751	0.999228	3.48E+09	
Quadratic	2684.301	0.999989	0.999974	0.999821	8.07E+08	suggested
Cubic	0	1	1		+	aliased

Table 5.21 (e) Selection of a satisfactory model for condener duty (Q_c).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	4.13E+13	1	4.13E+13			
Linear	4.41E+12	3	1.47E+12	8270.492	< 0.0001	
2FI	1.38E+08	3	45877522	0.21095	0.8865	
Quadratic	2.03E+09	3	6.78E+08	33.812	0.0002	suggested
Cubic	1.4E+08	3	46797669	63660000	< 0.0001	aliased
Residual	0	4	0	8270.492	< 0.0001	
Total	4.57E+13	17	2.69E+12			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	13337.17	0.999476	0.999355	0.999084	4.04E+09	
2FI	14747.23	0.999507	0.999212	0.99822	7.86E+09	
Quadratic	4478.409	0.999968	0.999927	0.999491	2.25E+09	suggested
Cubic	0	1	1		+	aliased

Table 5.21 (f) Selection of a satisfactory model for pressure drop across the divided wall (ΔP).

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	44.14475	1	44.14475			
Linear	77.05738	3	25.68579	50.17157	< 0.0001	
2FI	1.040096	3	0.346699	0.61741	0.6194	
Quadratic	5.581058	3	1.860353	379.4991	< 0.0001	Suggested
Cubic	0.034315	3	0.011438	63660000	< 0.0001	Aliased
Residual	0	4	0			
Total	127.8576	17	7.521036			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.715513	0.920496	0.902149	0.839523	13.434	
2FI	0.749358	0.932921	0.892674	0.680073	26.78201	
Quadratic	0.070015	0.99959	0.999063	0.993441	0.549038	Suggested
Cubic	0	1	1	+		Aliased

The manual regression method eliminated the insignificant model terms automatically and the resulting analysis of variance (ANOVA) for the reduced quadratic model summarizes the results for each response and shows the significant model terms. Table 5.22(a- f), shows the ANOVA results for the purity of distillate (D), purity of side stream (S), purity of bottom product (B), reboiler duty (Q_b), condener duty (Q_c) and the pressure drop across the divided wall of the DWC, with a model F- value of 34.5, 17.7, 101.5, 69561, 24462 and 1897, respectively. These F values are much larger than 5 and imply that the model is significant.

Table 5.22 (a) ANOVA for response surface quadratic model (for purity of distillate D).

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	0.024362	9	0.002707	34.5353	< 0.0001	Significant Highly
r	0.010485	1	0.010485	133.768	< 0.0001	Significant
l	0.00115	1	0.00115	14.66976	0.0065	Significant
v	0.000555	1	0.000555	7.075776	0.0325	Significant
r^2	0.001275	1	0.001275	16.26606	0.0050	Significant
l^2	0.00103	1	0.00103	13.14629	0.0084	Significant Highly
v^2	0.007422	1	0.007422	94.68562	< 0.0001	Significant
rl	0.001578	1	0.001578	20.13828	0.0028	Significant
rv	2.34E-06	1	2.34E-06	0.029865	0.8677	
lv	2.7E-05	1	2.7E-05	0.344315	0.5758	
Residual	0.000549	7	7.84E-05			
Lack of fit	0.000549	3	0.000183			
Pure error	0	4	0			
Cor. total	0.024911	16				

R^2=0.9780, predicted R^2=0.7476, adjusted R^2= 0.9497, adequate precision = 16.816.

Table 5.22 (b) ANOVA for response surface quadratic model (for purity of side stream S).

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks[a]
Model	0.820765	9	0.091196	17.74	0.0005	Significant
r	0.247108	1	0.247108	48.1	0.0002	Significant
Ls	0.158234	1	0.158234	30.8	0.0009	Significant
Vs	0.041512	1	0.041512	8.1	0.0250	Significant
r^2	0.034842	1	0.034842	6.78	0.0352	Significant
Ls^2	0.078827	1	0.078827	15.3	0.0058	Significant
Vs^2	0.201239	1	0.201239	39.1	0.0004	Significant
r. Ls	1.2E-05	1	1.2E-05	0.0023	0.9628	
r. Vs	0.023052	1	0.023052	4.5	0.0719	
Ls. Vs	0.004794	1	0.004794	0.93	0.3663	
Residual	0.035974	7	0.005139			
Lack of fit	0.035974	3	0.011991			
Pure error	0	4	0			
Cor. total	0.856739	16				

[a] R^2=0.9580, predicted R^2=0.7282, adjusted R^2= 0.9040, adequate precision = 13.098.

Table 5.22 (c) ANOVA for response surface quadratic model (for purity of bottom product B).

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	0.114789	9	0.012754	101.5626	< 0.0001	Significant Highly
r	0.047003	1	0.047003	374.2868	< 0.0001	Significant
l	3.21E-05	1	3.21E-05	0.255453	0.6288	
v	0.002344	1	0.002344	18.66853	0.0035	Significant Highly
r^2	0.034594	1	0.034594	275.4712	< 0.0001	Significant
l^2	0.001162	1	0.001162	9.255781	0.0188	Significant
v^2	0.002103	1	0.002103	16.74443	0.0046	Significant Highly
rl	0.011022	1	0.011022	87.76685	< 0.0001	Significant
rv	0.00178	1	0.00178	14.17409	0.0070	Significant Highly
lv	0.012689	1	0.012689	101.0415	< 0.0001	Significant
Residual	0.000879	7	0.000126			
Lack of fit	0.000879	3	0.000293			
Pure error	0	4	0			
Cor. total	0.115668	16				

R^2=0.9924, predicted R^2=0.8784, adjusted R^2= 0.9826, adequate precision = 31.051.

Table 5.22 (d) ANOVA for response surface quadratic model (for reboiler duty Q_b)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks[a]
Model	4.51E+12	9	5.01E+11	69560.8	< 0.0001	Significant Highly
r	4.51E+12	1	4.51E+12	625884.5	< 0.0001	Significant
Ls	42393632	1	42393632	5.9	0.0457	Significant Slightly
Vs	26608513	1	26608513	3.7	0.0961	Significant
r^2	1.26E+08	1	1.26E+08	17.5	0.0041	Significant
Ls^2	1982901	1	1982901	0.275	0.6161	Highly
Vs^2	5.51E+08	1	5.51E+08	76.4	< 0.0001	Significant
r. Ls	63712324	1	63712324	8.842	0.0207	Significant
r. Vs	2.89E+08	1	2.89E+08	40.1	0.0004	Significant
Ls. Vs	1.04E+08	1	1.04E+08	14.4	0.0068	Significant
Residual	50438317	7	7205474			
Lack of fit	50438317	3	16812772			
Pure error	0	4	0			
Cor. total	4.51E+12	16				

[a]R^2=1.00, predicted R^2=0.9998, adjusted R^2= 1.00, adequate precision = 741.106

Table 5.22 (e)ANOVA for response surface quadratic model (for condener duty Q_c)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	4.42E+12	9	4.91E+11	24462.65	< 0.0001	Significant Highly
r	4.41E+12	1	4.41E+12	220044.2	< 0.0001	Significant
l	96299442	1	96299442	4.801493	0.0646	Significant
v	1.32E+08	1	1.32E+08	6.577817	0.0373	Significant
r^2	332171.6	1	332171.6	0.016562	0.9012	
l^2	2.27E+08	1	2.27E+08	11.31626	0.0120	Significant Highly
v^2	1.73E+09	1	1.73E+09	86.22019	< 0.0001	Significant
rl	99261369	1	99261369	4.949175	0.0615	
rv	32393172	1	32393172	1.615125	0.2444	
lv	5978025	1	5978025	0.298065	0.6021	
Residual	1.4E+08	7	20056144			
Lack of fit	1.4E+08	3	46797669			
Pure error	0	4	0			
Cor. total	4.42E+12	16				

R^2=1.00, predicted R^2=0.9995, adjusted R^2= 0.9999, adequate precision = 440.712

Table 5.22 (f) ANOVA for response surface quadratic model (for ΔP).

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks[a]
Model	83.67854	9	9.297615	1896.6	< 0.0001	Significant
r	1.483477	1	1.483477	302.6	< 0.0001	Highly Significant
Ls	0.186557	1	0.186557	38.1	0.0005	Significant
Vs	75.38735	1	75.38735	15378.5	< 0.0001	Highly Significant
r^2	0.45804	1	0.45804	93.4	< 0.0001	Highly Significant
Ls^2	0.046172	1	0.046172	9.41	0.0181	Significant
Vs^2	5.255168	1	5.255168	1072	< 0.0001	Highly Significant
r. Ls	0.003129	1	0.003129	0.638	0.4506	
r. Vs	1.028318	1	1.028318	209.8	< 0.0001	Highly Significant
Ls. Vs	0.00865	1	0.00865	1.764	0.2257	
Residual	0.034315	7	0.004902			
Lack of fit	0.034315	3	0.011438			
Pure error	0	4	0			
Cor. total	83.71285	16				

[a]R^2=0.9996, predicted R^2=0.9934, adjusted R^2= 0.9991, adequate precision = 139.695

The interaction of two factors (2FI) and the linear model were found to be insignificant using the RSM. The model summary statistic showed the regression coefficient (R^2) to be the highest for the quadratic model for the purity of the distillate D (0.978), side stream S (0.958) and bottom product B (0.9924);the reboiler duty Q_b (1.0), condenser duty Q_c (1.0), and the difference in pressure drop across the divided wall ΔP (1.0), respectively. Only 0.04% of the variation for the product quality and energy efficiency could not be explained by the model.

For the purity of the distillate, side stream and bottom product, the reboiler duty, condenser duty and the difference in pressure drop across the divided wall of DWC, adequate precision ratios of 16.8, 13.1, 31.1, 741.1, 440.7 and 139.7, respectively, were obtained. An adequate precision ratio above 4 indicates adequate model efficacy and that the model can be used to navigate the design space.

From ANOVA analysis, it was clear that the reflux rate *r* and square of vapour split *Vs* are highly significant for the reboiler duty of a DWC. Similarly, for the pressure

drop across the divided wall, the reflux rate *r* and vapour split *Vs* and interaction between *r* and *Vs* are highly significant as compared to liquid split *Ls*. This seemingly strange result is due to the fact that the pressure drop depends strongly on the vapor flow rate whereas a change in liquid flow rate leads to only minor change in pressure drop due to variation in h_{ow}.

A normal probability plot and a dot diagram of these residuals are shown in Figure 5.17 for reboiler duty Q_b. The data points on this plot lie reasonably close to a straight line. This means that the assumptions used in the analysis are satisfied. Figure 5.18 shows the relationship between the actual and predicted values of $Q_{b,}$ for a DWC. It can be seen from Figure 5.18 that the residuals are in the proximity of the straight diagonal line. Therefore, the developed models can be considered to be adequate because the residuals for the prediction of each response are the minimum. Similar plots and data analysis were obtained for the product purity D, S, B, condenser duty Q_c and pressure drop ΔP.

The 3D response surface plots of the effect of *Ls* and *Vs* for the purity of S and reboiler Q_b of a DWC are illustrated in Figure 5.19 and 5.20.

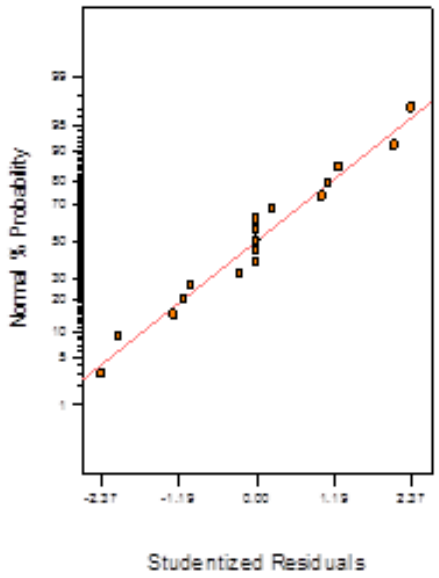

Figure 5.17: Normal% probabilities versus studentized residuals for the reboiler duty Q_b.

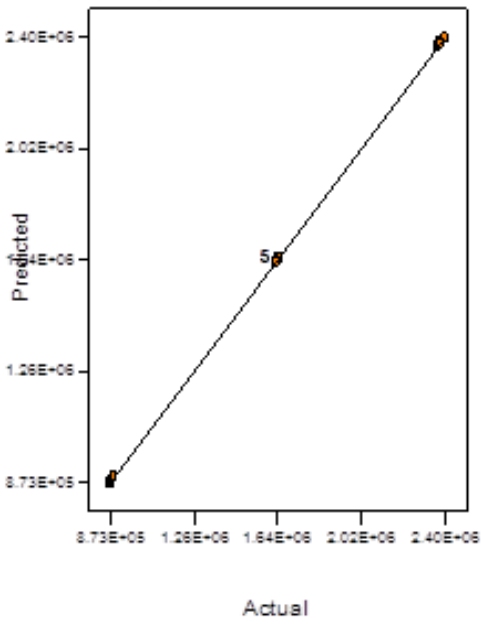

Figure 5.18: Scatter diagram for the predicted response versus actual response for the reboiler duty.

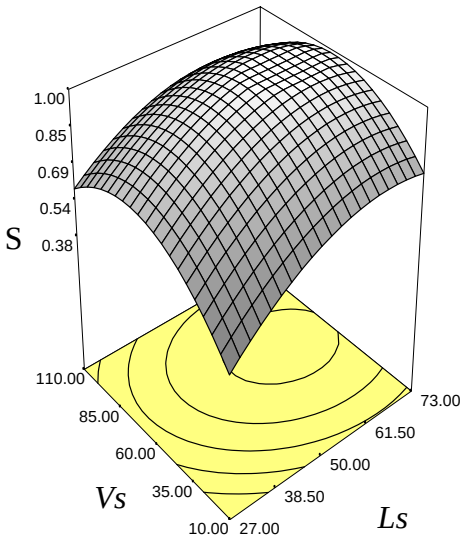

Figure 5.19: 3D response surface graph of liquid split (*Ls*) versus vapour split (*Vs*) at reflux rate *r* = 167.70 kmol/h for the purity of side stream in a DWC.

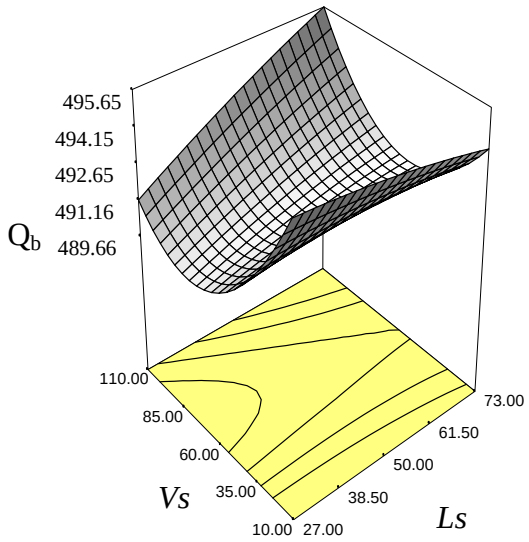

Figure 5.20: 3D response surface graph of liquid split (*Ls*) versus vapour split (*Vs*) at reflux rate *r* = 167.70 kmol/h for the reboiler duty Q_b of a DWC.

The point prediction option in the software was used for the optimization of the process parameters. The adequacy of the developed models was verified by carrying out the confirmatory simulation runs using test conditions, within the simulation ranges defined earlier. The final column design parameters are given in Table 5.23.

Table 5.23 Final column design parameters

Parameters	Final value
Number of trays in main column	38
Feed stage location	18
Liquid split location	9
Vapour split location	27
Side stream location (section 2 of DWC)	9
Ls (kmol/h)	61.89
Vs (kmol/h)	34.58
r (kmol/h)	167.7
Distillate purity (mole fraction of C4)	0.99
Side stream purity (mole fraction of C5)	0.979
Bottom Product Purity (mole fraction of C6)	0.99
Reboiler duty Q_b (kW)	487.58

The optimum values for *r*, *Ls* and *Vs* were estimated to be 167.7 kmol/h, 61.9 kmol/h and 34.6 kmol/h, respectively. At these values of *r*, *Ls* and *Vs*, the mole fractions of C4 in the distillate, C5 in the side stream and C6 in the bottom stream were 0.99, 0.979 and 0.99, respectively, and the reboiler duty was found to be 487.58 KW. The product purities are very high. Also, the energy requirement in the reboiler by this method for the separation of C4-C6 normal paraffin mixture is found to be less than 499.83 KW as reported by Gomez-Castro et al. (2008).

5.6 Optimization of Structural and Operational Variables for the Energy Efficiency of a Divided Wall Distillation Column

The structural and process parameters of a DWC have been optimized simultaneously for the separation of benzene-toluene-*p*-xylene (BTX) mixture of the naphtha reformer for the energy efficiency. The reboiler duty and the heat required to preheat the feed are considered as the total energy requirement for the DWC.

The system has nine structural variables and four process variables including the location of the feed tray, the location of the side stream tray, and the number of trays in the main column and in the post-fractionator, location of the divided wall, number of trays in divided wall section, reflux rate, liquid spilt, vapour split and the feed quality. These variables are used for the optimization of the product purities and the reboiler and condenser duties. While doing so, it is also targeted that the difference between the pressure drops across the two sections of the DWC is zero. The Peng-Robinson property model is use in the simulation.

The parameters required to be specified for the operation of the DWC under varying operating conditions are listed in Table 5.24. For easier convergence of the simulator, molar flow rates of the reflux (*r*) and the connecting streams (*Ls* and *Vs*) were used as input parameters.

Table 5.24 Column, feed, product and connect stream specifications.

Main Column		***Section 2 of Main Column***	
No of stages (N)	84-94	No of stages (N_{S2} –N_{S1})	27-39
Feed stage	40-50	Product draw stage (N_{S3})	14-26
Column pressure	116 KPa	Column pressure	116 KPa
Distillate rate	88.65 kmol/h		
Reflux rate (r)	1400-2000 kmol/h		
Feed rate	801.8 kmol/h	Product rate (S)	337.8 kmol/h
Feed condition	(150 kPa, 135°C)	Product stream	Saturated liquid
Feed composition (mol fraction)	Benzene = 0.1096 Toluene = 0.4217 *p*-xylene = 0.4687	–	–
Connect Streams:	***From***	***To***	***Value***
Ls	Column 1, Stage (N_{S1})	Column 2, Stage 1	640-1140 kmol/h
Vs	Column 1, Stage (N_{S2})	Column 2, Stage (N_{S2} –N_{S1})	469-969 kmol/h
V_{N+1}(Internal Stream)	Column 2, Stage 1	Column 1, Stage (N_{S1})	–
L_{NT} (Internal Stream)	Column 2, Stage (N_{S2} –N_{S1})	Column 1, Stage (N_{S2})	–

As explained earlier, sieve trays have been taken in the DWC. For hydrodynamic calculations using 'Tray Rating', the additional column design specifications as listed in Table 5.25 were used.

Table 5.25 Tray Design Specifications.

Tray diameter	1.80 m
Tray spacing	0.61 m
Ratio of sieve hole area to tray active area	0.12
Weir height (h_w)	50 mm
Hole diameter	5 mm

A three level BBD was applied to estimate the effect of the structural and process parameters on the energy efficiency, purity of distillate, side stream and bottom products, condenser duty and the pressure drop across the divided wall of a DWC. Various ranges of values of the structural and process parameters were taken as the variable input parameters. The input parameters used in the present work are given in Table 5.26. In the preliminary analysis to understand the effect of the feed quality, q, it was found that the optimum energy requirement occurs in the saturation region of the feed, The feed quality, q was varied between zero and one ($0 \leq q \leq 1$) for the simulation runs.

Table 5.26 Experimental design levels of chosen variables.

Variables	Levels in Box–Behnken design		
Coded level	Low (-1)	Medium (0)	High (+1)
F Location	40	45	50
S Location (N_{S3})	14	20	26
L Location (N_{S1})	21	24	27
V Location (N_{S2})	54	57	60
N	84	89	94
Ls (kmol/h)	640	890	1140
Vs (kmol/h)	469	719	969
r (kmol/h)	1400	1700	2000
q	0	0.5	1.0

The simulated data were analyzed using the statistical software, Design-Expert software version 6.0.6 (STAT-EASE Inc. Minneapolis US), for regression analysis to fit the equations developed and also for the evaluation of the statistical significance of the equations.

A manual regression method was used to fit the second order polynomial Eq. (4.3.3) to the simulated data and to identify the relevant model terms. To decide the adequacy of the model for product quality and energy efficiency of a DWC, two different tests such as the sequential model sum of squares and model summary statistics were carried out and the p values were found to be lower than 0.01 (see Table 5.27) for the energy efficiency. For the purity of products, condenser duty and the pressure drop across the dividing wall, the results are shown in Appendix-I.

An arc sine square root transformation for D, cubic power transformation for B, natural log transformation for Qc and no transformation for S, Q_b, and delta p were applied to the simulated data. The interactions of two factors (2FI) were suggested to be insignificant using the RSM. The model summary statistics showed the highest regression coefficient $R^2 = 0.9882$ for the quadratic model. ANOVA analysis confirmed that the form of the model chosen to explain the relationship between the factors and the response was correct. Table 5.28 shows the ANOVA results for the energy efficiency of a DWC, with a model F- value of 749.9 implying that the model is significant. For the purity of products,

condenser duty and the pressure drop across the dividing wall, the results are given in Appendix-I. From the ANOVA analysis, it is clear that the structural variables of a DWC are not significant and that only the process variables- reflux rate, liquid split and vapour split are highly significant for the energy efficiency of a DWC.

Table 5.27 Selection of a satisfactory model for energy efficiency [reboiler duty (Q_b) + feed enthalpy].

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	5.16115E+17	1	5.16E+17			
Linear	2.86607E+15	9	3.18E+14	4220.54139	< 0.0001	
2FI	1.87572E+12	36	5.21E+10	0.60968319	0.9504	
Quadratic	1.86345E+12	9	2.07E+11	2.92158845	0.0051	Suggested
Cubic	3.08005E+12	39	7.9E+10	1.27201897	0.2343	Aliased
Residual	2.23513E+12	36	6.21E+10			
Total	5.1899E+17	130	3.99E+15			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	274686.9	0.996851	0.996615	0.996261	1.07E+13	
2FI	292335.1	0.997503	0.996166	0.993699	1.81E+13	
Quadratic	266212.3	0.998151	0.99682	0.993818	1.78E+13	Suggested
Cubic	249172.3	0.999223	0.997214	0.890422	3.15E+14	Aliased

Table 5.28 ANOVA for response surface quadratic model (for energy efficiency of DWC).

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	2.86981E+15	54	5.31E+13	749.899043	< 0.0001	significant
F location	7009256250	1	7.01E+09	0.09890441	0.7540	
S location	85442292250	1	8.54E+10	1.20563713	0.2757	
L location	92112250	1	92112250	0.00129975	0.9713	
V location	899652250	1	9E+08	0.01269458	0.9106	
N	49133090250	1	4.91E+10	0.69329458	0.4077	
Ls	8.37784E+11	1	8.38E+11	11.8215882	0.0010	significant
Vs	4.97476E+12	1	4.97E+12	70.1966068	< 0.0001	Highly significant
r	2.86E+15	1	2.86E+15	40356.1787	< 0.0001	Highly significant
q	1.11823E+11	1	1.12E+11	1.57788339	0.2130	
(F location)^2	45992980786	1	4.6E+10	0.64898593	0.4230	
(S location)^2	1.91945E+11	1	1.92E+11	2.70845433	0.1040	
(L location)^2	60078001000	1	6.01E+10	0.84773321	0.3601	
(V location)^2	30824010004	1	3.08E+10	0.43494351	0.5116	
N^2	97899893442	1	9.79E+10	1.38142064	0.2436	
Ls^2	59159172250	1	5.92E+10	0.83476803	0.3638	
Vs^2	2.81864E+11	1	2.82E+11	3.97725723	0.0498	significant
r^2	2.62321E+11	1	2.62E+11	3.7014852	0.0582	

q^2	2.81313E+11	1	2.81E+11	3.96947534	0.0500	
F location * S location	1198051250	1	1.2E+09	0.01690515	0.8969	
F location * L location	1267561250	1	1.27E+09	0.01788598	0.8940	
F location * V location	29095830625	1	2.91E+10	0.41055796	0.5236	
F location * N	28500781250	1	2.85E+10	0.4021615	0.5279	
F location * *Ls*	2492180000	1	2.49E+09	0.03516601	0.8518	
F location * *Vs*	29044680625	1	2.9E+10	0.40983621	0.5240	
F location * *r*	2842580000	1	2.84E+09	0.04011035	0.8418	
F location * *q*	16407661250	1	1.64E+10	0.23152101	0.6318	
S location * L location	7362911250	1	7.36E+09	0.10389467	0.7481	
S location * V location	99971561250	1	1E+11	1.410653	0.2387	
S location * N	1.81583E+11	1	1.82E+11	2.56222787	0.1136	
S location * *Ls*	968000000	1	9.68E+08	0.01365901	0.9073	
S location * *Vs*	1026045000	1	1.03E+09	0.01447805	0.9045	
S location * *r*	1.63317E+11	1	1.63E+11	2.30449175	0.1332	
S location * *q*	85594531250	1	8.56E+10	1.2077853	0.2753	
L location * V location	429245000	1	4.29E+08	0.00605688	0.9382	
L location * N	500000	1	500000	7.0553E-06	0.9979	
L location * *Ls*	6456122500	1	6.46E+09	0.09109939	0.7636	
L location * *Vs*	19845000	1	19845000	0.00028002	0.9867	
L location * *r*	55125000	1	55125000	0.00077784	0.9778	
L location * *q*	2683240000	1	2.68E+09	0.03786197	0.8462	
V location * N	101250	1	101250	1.4287E-06	0.9990	
V location * *Ls*	31601250	1	31601250	0.00044591	0.9832	
V location * *Vs*	22899255625	1	2.29E+10	0.32312093	0.5714	
V location * *r*	63845000	1	63845000	0.00090089	0.9761	
V location * *q*	55261501250	1	5.53E+10	0.77976978	0.3800	
N * *Ls*	11250	1	11250	1.5874E-07	0.9997	
N * *Vs*	2645000	1	2645000	3.7322E-05	0.9951	
N * *r*	1.82436E+11	1	1.82E+11	2.57426769	0.1128	
N * *q*	12144611250	1	1.21E+10	0.17136706	0.6801	
Ls * *Vs*	800000000	1	8E+08	0.01128843	0.9157	
Ls * *r*	2.06917E+11	1	2.07E+11	2.91971747	0.0916	
Ls * *q*	4.47093E+11	1	4.47E+11	6.30872243	0.0142	significant
*Vs** *r*	1333861250	1	1.33E+09	0.01882151	0.8912	
Vs * *q*	15833101250	1	1.58E+10	0.22341365	0.6378	
*r** *q*	2.7059E+11	1	2.71E+11	3.8181783	0.0544	Slightly significant
Residual	5.31517E+12	75	7.09E+10			
Lack of Fit	3.57797E+12	42	8.52E+10	1.61826416	0.0778	
Pure Error	1.73721E+12	33	5.26E+10			
Cor Total	2.87512E+15	129				

R^2=0.9982, predicted R^2=0.9938, adjusted R^2= 0.9968, adequate precision = 103.350.

Highly significant model terms were found to be *Vs* and *r*, while *Ls*, Vs^2 and *Ls. q* were found to be significant. Model values greater than 0.10 indicated that the model terms were not significant. Adequate precision of 103.3 (which is more than 4) indicates an adequate signal and the model can be used to navigate the design space.

The ANOVA analysis indicates a relationship between the purity of the distillate, side stream, and the bottom product, the reboiler duty and the condenser duty in terms of liquid split (*Ls*), vapour split (*Vs),* and the reflux rate (*r*). By eliminating the insignificant interaction terms, an empirical mathematical equation was obtained by using the Design-Expert software, in terms of actual (natural) factors:

$$Qb = +5.88E+7 - 1989.32\ Ls + 3715.95\ Vs + 28710.80\ r + 1.79\ Vs^2 - 1337.30\ Ls\ q \quad (5.6.1)$$

Thus, the energy efficiency of a DWC was directly related to Vs^2, *Ls*, *Vs*, *r* and the interaction term *Ls q*. It is seen from Eq. (5.6.1) that the energy efficiency of a DWC is linear with respect to *Ls*, r, *Ls q*, but quadratic with respect to the vapour split (*Vs*). This indicates that there is a liquid split -to- feed quality and vapour split -to- vapour split interaction for the energy efficiency.

A normal probability plot and a dot diagram of the residuals are shown in Figure 5.21. The data points on this plot lie reasonably close to a straight line, which exemplifies that the underlying assumptions of the analysis were satisfied. Figure 5.22 shows the relationship between the actual and predicted values of the energy efficiency for a DWC. It can be seen from Figure 5.22 that the residuals are in the proximity of the straight diagonal line. For the purity of products, condenser duty and the pressure drop across the dividing wall, the figures are shown in Appendix-I.

The 3D response surface plots of the effect of structural and process parameters for the energy efficiency of a DWC are visualized in Figs. 5.23- 5.25. To verify the adequacy of the developed models, the confirmation simulation runs for the energy efficiency of a DWC were carried out using new test conditions, which were found to be within the simulation ranges defined earlier.

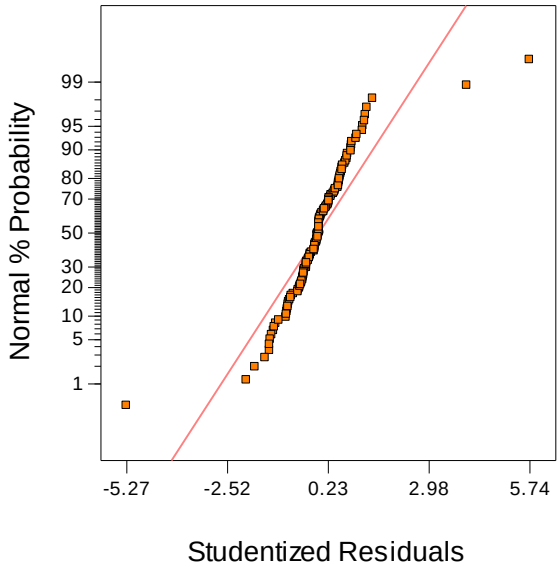

Figure 5.21: Normal% probabilities versus studentized residuals for the energy efficiency.

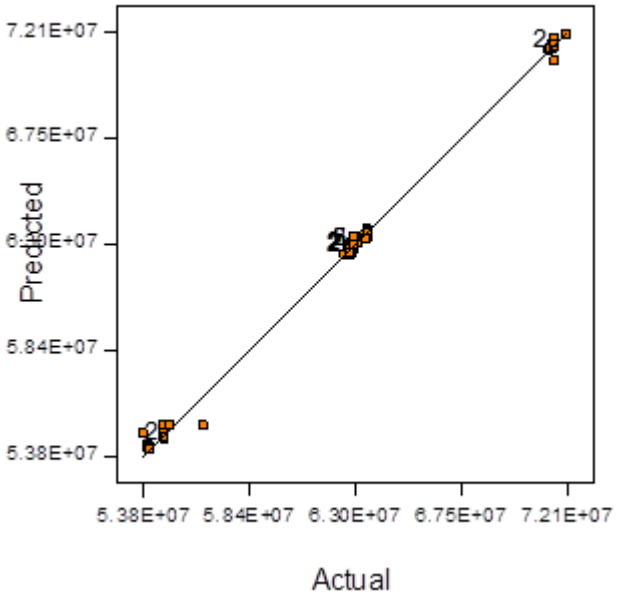

Figure 5.22: Scatter diagram for the predicted response versus actual response for the energy efficiency.

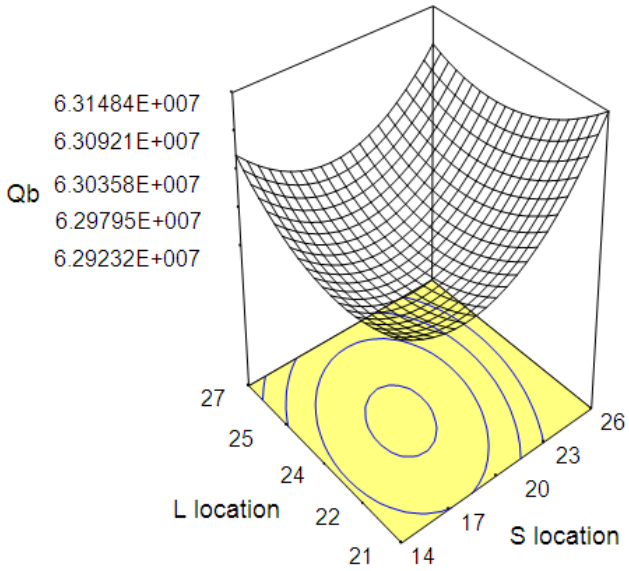

Figure 5.23: 3D response surface graph of side stream location versus liquid split location for the energy efficiency of a DWC.

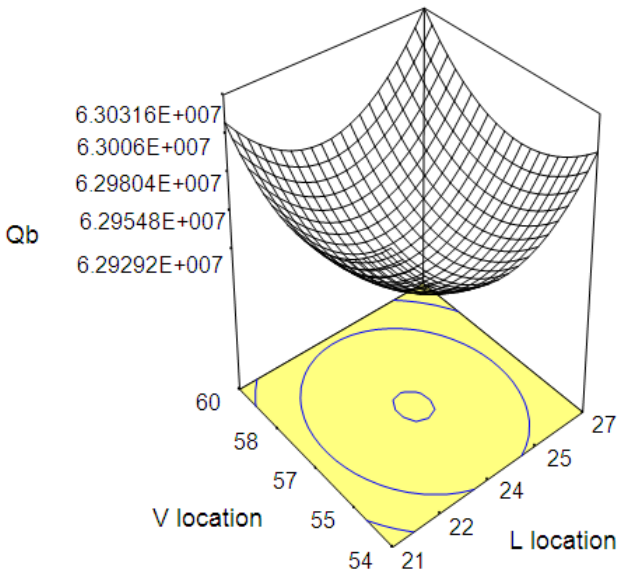

Figure 5.24: 3D response surface graph of vapour split location versus liquid split location for the energy efficiency of a DWC.

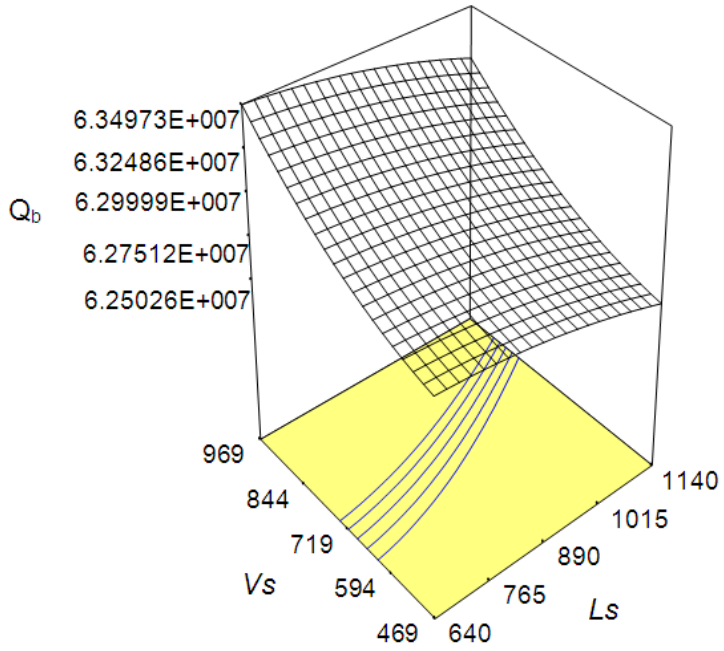

Figure 5.25: 3D response surface graph of vapour split versus liquid split for the energy efficiency of a DWC.

Before optimization, the locations for the feed stream, side stream, liquid split, and the vapour split in the main column were estimated to be 44th, 20th, 23rd and 57th tray, respectively. The number of trays in the main column before optimization was found to be 89. The stream flow rates (in kmol/h) were found to be: *Ls* = 643.15, *Vs* = 575.35 and *r* = 1500, and the energy requirement was 5.67×10^{7} Bth/h (16.6 MW).

Using the point prediction option in the software, the response of the validation simulations are predicted using the previously developed models. The optimum locations for the feed , side stream , liquid split and the vapour split in the main column, were found to be 49th, 23rd, 23rd and 59th tray, respectively. The optimized number of trays in the main column are found to be 85 which is less than that found earlier (i.e. 89) without optimization. The stream flow rates (in kmol/h) were found to be: *Ls*= 906, *Vs* = 612and *r* = 1400. The feed quality parameter was found to be *q*=0.30. The energy requirement after the optimization was found to be 5.4×10^{7} Bth/h (15.83 MW). Thus, the optimization of

the DWC by the present method leads to a saving of 2.63×10^6 Bth/h (~770 KW) of energy, i.e. a saving of 4.86 % of total energy. Table 5.29 shows the results for optimized parameters and validation simulation runs obtained for the process.

Table 5.29 Optimum and confirmative values of the process parameters of DWC: F Location=49, S Location = 23, L Location = 23, V Location = 59, N = 85, *Ls* = 906.05 kmol/h, *Vs* = 612.33 kmol/h, *r* = 1400.26 kmol/h and *q* = 0.30.

Process parameters	Optimized parameter (predicated value)	Confirmation simulation run
Distillate purity (mole fraction of benzene)	0.977	1.00
Side stream purity (mole fraction of toluene)	0.9008	0.9072
Bottom Product Purity (mole fraction of P-Xylene)	0.8879	0.8973
Condenser duty Q_c (BTU/h)	- 4.0536+07	- 4.0529+07
Energy efficiency [Reboiler duty Q_b + feed enthalpy (BTU/h)]	5.4353+07	5.4052+07
delta p (psi)	-3.58-006	0.02

Chapter –VI

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

From the present study the following conclusion are drawn:

1. Pressure difference plays an important role in deciding vapour and liquid flow rates across a tray (or trays), particularly in case of interconnected or divided wall distillation columns (DWCs). The tray hydraulics plays an important role in the DWC performance; therefore pressure drop calculations are unavoidable.
2. Considering the detailed mathematical model, which includes the MESHD (conventional MESH plus the pressure drop) equations, the degree of freedom for thermally coupled and divided wall distillation column (DWC) for steady state operation, with known feed and condenser pressure, is four. Thus, no extra degree of freedom is left to specify both the connecting streams between two columns simultaneously.
3. From the relation between 'natural' or 'feasible' vapour split ratio as a function of the reflux ratio and the liquid split ratio of a DWC, it is observed that only those values of vapour split (V_S) are feasible (at a given value of r or R and L_S or R_1), which give $\Delta(\Delta P)$, between the two divided sections, equal to zero.
4. Any arbitrary value of vapour split, Vs (or R_2), not only creates an imbalance in the pressure drop in the two sides of the DWC, but also severely distorts the concentration profile of the components.
5. The vapour split ratio, R_2, is almost independent of liquid split ratio, R_1, but is dependent on the reflux ratio, and to some extent, on feed superheat.

6. The composition of the middle product (side draw) can be regulated easily by controlling the liquid split ratio so as to maintain a constant V_S/L_S ratio in the product side of the DWC.
7. The feed quality influences the pressure drop across the divided wall as well as vapour split ratio. The vapour split ratio, $R_{2,}$ is almost independent of liquid split ratio, $R_{1,}$ and the reflux flow rate for sub-cooled and saturated liquid feeds. However, there is a very marginal effect for liquid-vapour mixture (two phase) feed. For saturated vapour and superheated vapour feed, the liquid split ratio has a major influence on the feasible vapour split ratio.
8. The variation in pressure drop with vapour flow rate is widely different in the two sections for two-phase, saturated vapour and superheated vapour feeds. This is observed even when the numbers of trays as well as the tray design are exactly the same in both the divided parts of a DWC. It is also observed that the equalization of pressure drop leads to nearly equal vapour flow rate on both the sides of the DWC for the sub-cooled and saturated liquid feeds.
9. If the DWC is operated with saturated liquid feed, the liquid split changes should not affect the vapour split. Therefore, operating a DWC with saturated liquid feed should provide some flexibility in changing the liquid split. However, if the column is operated with saturated vapour feed or superheated vapour feed, the vapour split will vary as the liquid split changes, thus offering no flexibility during the operation of a DWC. Also in the practical implementation of a DWC, liquid split can easily be manipulated.
10. For saturated liquid feed, there is no effect of liquid split and reflux rate on feasible vapour split. The middle product composition also varies with liquid split, reaching a maximum value at a certain value of liquid split. It is, therefore,

suggested that the DWC should be operated and easily controlled for a saturated liquid feed.

11. For the separation of C4-C6 normal paraffin mixture, the distillate and bottom products are 99% pure, while middle product is 97.9 % pure at the optimum values of the process parameters. The reboiler duty was found to be 487.58 KW which is comparable to the value (499.83 KW) reported by Gomez-Castro et al. (2008).
12. From the study of simultaneous optimization of structural and process parameters of a DWC, regression analysis showed good fit of the simulated data to the second order polynomial model with multiple correlation coefficient R^2= 0.99 for the energy efficiency.
13. The process parameters were found to be significant in affecting the energy efficiency of a DWC as compared to structural parameters.
14. The optimal energy requirement of a DWC for a specified BTX separation is found to be 15.83 MW, leading to a saving of ~770 KW of energy, The predictions from the BBD optimization agree well with the results of the rigorous simulation. The number of simulation runs also reduced significantly for the optimization of a DWC by BBD. The optimization by BBD under RSM vividly underscores the effects of different parameters and their interactions on the energy efficiency of a DWC.

6.2 Recommendations and Scope for Future Work

1. Several investigators, particularly those working on the control aspects of DWCs, have attempted to control two (or more) connecting streams and felt that the controllability of a DWC is difficult. Therefore, it is recommended that the control strategies for the DWC should be re-examined and splitting of vapour should be predicted using hydrodynamic correlations.

2. This study has reported on the steady state operation of a DWC in order to maximize the energy efficiency. A detailed controllability study is required for the combined composition control and minimum energy operation.
3. The main results presented in this thesis are developed for a single wall in a DWC. However, based on the new understanding, it is straightforward to develop simulation and optimization procedures for multiple dividing wall distillation columns.
4. Another important issue is the process integration within a large plant. Work should be initiated to incorporate the results on thermally coupled columns/DWCs in the process integration tool boxes.

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APPENDIX - I

Table A1 Selection of a satisfactory model for the purity of distillate (D)

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	276.64	1	276.64			
Linear	1.54	9	0.17	23.47	< 0.0001	
2FI	0.16	36	4.38E-03	0.51	0.986	
Quadratic	0.27	9	0.03	5.17	< 0.0001	suggested
Cubic	0.32	39	8.29E-03	2.53	0.0029	aliased
Residual	0.12	36	3.27E-03			
Total	279.05	130	2.15			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.085	0.6377	0.6105	0.572	1.03	
2FI	0.092	0.7032	0.5441	0.1631	2.02	
Quadratic	0.077	0.8169	0.685	0.5121	1.66	suggested
Cubic	0.057	0.9511	0.8247	-6.4021	17.82	aliased

Table A2 Selection of a satisfactory model for the purity of side stream (S)

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	105.57	1	105.57			
Linear	0.14	9	0.016	2.32	0.0189	
2FI	0.15	36	4.07E-03	0.5	0.989	
Quadratic	0.59	9	0.065	49.66	< 0.0001	suggested
Cubic	0.044	39	1.12E-03	0.74	0.8246	aliased
Residual	0.055	36	1.52E-03			
Total	106.55	130	0.82			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.083	0.1485	0.0846	0.0036	0.97	
2FI	0.09	0.2986	-0.0772	-0.8087	1.77	
Quadratic	0.036	0.8992	0.8266	0.6306	0.36	suggested
Cubic	0.039	0.9439	0.7991	-26.1905	26.53	aliased

Table A3 Selection of a satisfactory model for the purity of bottom product (B)

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	78.84	1	78.84			
Linear	0.62	9	0.069	2.17	0.029	
2FI	0.65	36	0.018	0.48	0.9919	
Quadratic	2.5	9	0.28	32.02	< 0.0001	suggested
Cubic	0.34	39	8.62E-03	0.99	0.5146	aliased
Residual	0.31	36	8.72E-03			
Total	83.25	130	0.64			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.18	0.1398	0.0753	-0.0055	4.44	
2FI	0.19	0.2869	-0.0951	-0.8254	8.06	
Quadratic	0.093	0.8527	0.7467	0.5728	2.33	suggested
Cubic	0.093	0.9289	0.7453	-24.0635	110.64	aliased

Table A4 Selection of a satisfactory model for the condenser duty (Q_c)

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	33383.85	1	33383.85			
Linear	49.96	9	5.55	48.05	< 0.0001	
2FI	1.21	36	0.033	0.22	1	
Quadratic	8.87	9	0.99	19.54	< 0.0001	suggested
Cubic	1.04	39	0.027	0.35	0.9992	aliased
Residual	2.75	36	0.076			
Total	33447.67	130	257.29			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	0.34	0.7828	0.7665	0.7426	16.43	
2FI	0.39	0.8017	0.6954	0.5089	31.34	
Quadratic	0.22	0.9407	0.898	0.8592	8.98	suggested
Cubic	0.28	0.9569	0.8457	0.4609	34.41	aliased

Table A5 Selection of a satisfactory model for pressure drop across the divided wall (ΔP)

Sequential Model Sum of Squares

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	Remark
Mean	113.7	1	113.7			
Linear	4209.17	9	467.69	281.64	< 0.0001	
2FI	65.55	36	1.82	1.14	0.3026	
Quadratic	64.14	9	7.13	7.68	< 0.0001	suggested
Cubic	27.54	39	0.71	0.6	0.937	aliased
Residual	42.04	36	1.17			
Total	4522.13	130	34.79			

Model Summary Statistics

Source	Std. Dev.	R-Squared	Adj. R^2	Pred. R^2	PRESS	Remark
Linear	1.29	0.9548	0.9514	0.9467	234.98	
2FI	1.26	0.9697	0.9534	0.9284	315.69	
Quadratic	0.96	0.9842	0.9729	0.9572	188.85	suggested
Cubic	1.08	0.9905	0.9658	0.4446	2448.6	aliased

Table A6 ANOVA for response surface quadratic model (for the purity of distillate D)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	1.97	54	0.036	6.19	< 0.0001	significant
F location	1.36E-03	1	1.36E-03	0.23	0.6323	
S location	0.011	1	0.011	1.92	0.1701	
L location	2.55E-05	1	2.55E-05	4.34E-03	0.9476	
V location	1.66E-03	1	1.66E-03	0.28	0.5968	
N	1.10E-03	1	1.10E-03	0.19	0.6668	
Ls	0.11	1	0.11	18.14	< 0.0001	Highly significant
Vs	0.63	1	0.63	107.81	< 0.0001	Highly significant
r	0.64	1	0.64	109.32	< 0.0001	Highly significant
q	0.14	1	0.14	23.26	< 0.0001	Highly significant
(F location)^2	2.35E-03	1	2.35E-03	0.4	0.5291	
(S location)^2	1.32E-03	1	1.32E-03	0.22	0.6373	
(L location)^2	3.83E-03	1	3.83E-03	0.65	0.422	
(V location)^2	5.58E-03	1	5.58E-03	0.95	0.333	
N^2	0.011	1	0.011	1.88	0.1743	
Ls^2	0.044	1	0.044	7.52	0.0076	
Vs^2	0.12	1	0.12	20.1	< 0.0001	Highly significant
r^2	0.082	1	0.082	13.99	0.0004	
q^2	0.026	1	0.026	4.36	0.0401	
F location * S location	1.16E-03	1	1.16E-03	0.2	0.6578	

F location * L location	1.18E-03	1	1.18E-03	0.2	0.6552	
F location * V location	1.95E-09	1	1.95E-09	3.32E-07	0.9995	
F location * N	6.29E-03	1	6.29E-03	1.07	0.3044	
F location * *Ls*	1.24E-03	1	1.24E-03	0.21	0.6472	
F location * *Vs*	7.80E-09	1	7.80E-09	1.33E-06	0.9991	
F location * *r*	1.24E-03	1	1.24E-03	0.21	0.6473	
F location * *q*	3.40E-03	1	3.40E-03	0.58	0.4496	
S location * L location	1.32E-03	1	1.32E-03	0.22	0.6373	
S location * V location	8.39E-03	1	8.39E-03	1.43	0.236	
S location * N	8.47E-03	1	8.47E-03	1.44	0.2337	
S location * *Ls*	2.44E-04	1	2.44E-04	0.041	0.8392	
S location * *Vs*	2.29E-04	1	2.29E-04	0.039	0.8443	
S location * *r*	8.12E-03	1	8.12E-03	1.38	0.2435	
S location * *q*	8.39E-03	1	8.39E-03	1.43	0.236	
L location * V location	2.31E-07	1	2.31E-07	3.93E-05	0.995	
L location * N	1.56E-10	1	1.56E-10	2.65E-08	0.9999	
L location * *Ls*	4.12E-04	1	4.12E-04	0.07	0.7919	
L location * *Vs*	2.64E-08	1	2.64E-08	4.49E-06	0.9983	
L location * *r*	4.10E-07	1	4.10E-07	6.97E-05	0.9934	
L location * *q*	2.48E-04	1	2.48E-04	0.042	0.8378	
V location * N	0	1	0	0	1	
V location * *Ls*	2.03E-06	1	2.03E-06	3.46E-04	0.9852	
V location * *Vs*	3.78E-08	1	3.78E-08	6.42E-06	0.998	
V location * *r*	4.27E-07	1	4.27E-07	7.26E-05	0.9932	
V location * *q*	8.39E-03	1	8.39E-03	1.43	0.236	
N * *Ls*	0	1	0	0	1	
N * *Vs*	0	1	0	0	1	
N * *r*	8.47E-03	1	8.47E-03	1.44	0.2338	
N * *q*	3.14E-03	1	3.14E-03	0.53	0.4671	
Ls * *Vs*	0.027	1	0.027	4.63	0.0346	
Ls * *r*	7.55E-03	1	7.55E-03	1.28	0.2606	
Ls * *q*	0.043	1	0.043	7.34	0.0084	
*Vs** *r*	3.35E-05	1	3.35E-05	5.70E-03	0.94	
Vs * *q*	1.83E-03	1	1.83E-03	0.31	0.5786	
*r** *q*	7.46E-03	1	7.46E-03	1.27	0.2635	
Residual	0.44	75	5.88E-03			
Lack of Fit	0.36	42	8.59E-03	3.54	0.0002	significant
Pure Error	0.08	33	2.43E-03			
Cor Total	2.41	129				

R^2=0. 0.8169, predicted R^2=0.5121, adjusted R^2= 0.685, adequate precision = 12.903.

Table A7 ANOVA for response surface quadratic model (for the purity of side stream S)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	0.88	54	0.016	12.39	< 0.0001	significant
F location	3.40E-04	1	3.40E-04	0.26	0.6123	
S location	6.31E-03	1	6.31E-03	4.81	0.0314	
L location	2.72E-05	1	2.72E-05	0.021	0.8858	
V location	2.87E-05	1	2.87E-05	0.022	0.8828	
N	7.23E-06	1	7.23E-06	5.51E-03	0.941	
Ls	2.63E-03	1	2.63E-03	2.01	0.1609	
Vs	8.27E-03	1	8.27E-03	6.31	0.0142	
r	0.066	1	0.066	50.04	< 0.0001	Highly significant
q	0.062	1	0.062	47.02	< 0.0001	Highly significant
(F location)^2	3.51E-03	1	3.51E-03	2.68	0.106	
(S location)^2	8.91E-03	1	8.91E-03	6.79	0.011	
(L location)^2	0.011	1	0.011	8.59	0.0045	
(V location)^2	7.49E-03	1	7.49E-03	5.71	0.0194	
N^2	8.26E-03	1	8.26E-03	6.3	0.0142	
Ls^2	0.42	1	0.42	322.6	< 0.0001	Highly significant
Vs^2	0.13	1	0.13	97.32	< 0.0001	Highly significant
r^2	0.015	1	0.015	11.55	0.0011	
q^2	4.41E-03	1	4.41E-03	3.36	0.0706	
F location * S location	2.29E-05	1	2.29E-05	0.017	0.8952	
F location * L location	2.00E-05	1	2.00E-05	0.015	0.9021	
F location * V location	1.72E-05	1	1.72E-05	0.013	0.9091	
F location * N	1.13E-03	1	1.13E-03	0.86	0.3569	
F location * *Ls*	3.55E-05	1	3.55E-05	0.027	0.8698	
F location * *Vs*	2.50E-05	1	2.50E-05	0.019	0.8906	
F location * *r*	6.01E-05	1	6.01E-05	0.046	0.8311	
F location * *q*	1.04E-03	1	1.04E-03	0.79	0.3771	
S location * L location	4.92E-04	1	4.92E-04	0.37	0.5422	
S location * V location	6.92E-06	1	6.92E-06	5.28E-03	0.9423	
S location * N	3.37E-04	1	3.37E-04	0.26	0.6139	
S location * *Ls*	4.91E-06	1	4.91E-06	3.75E-03	0.9514	
S location * *Vs*	1.89E-05	1	1.89E-05	0.014	0.9047	
S location * *r*	7.40E-04	1	7.40E-04	0.56	0.4548	
S location * *q*	4.25E-04	1	4.25E-04	0.32	0.5707	
L location * V location	1.20E-04	1	1.20E-04	0.091	0.7636	
L location * N	2.11E-09	1	2.11E-09	1.61E-06	0.999	
L location * *Ls*	4.65E-04	1	4.65E-04	0.35	0.5534	
L location * *Vs*	3.99E-06	1	3.99E-06	3.04E-03	0.9562	
L location * *r*	1.01E-05	1	1.01E-05	7.69E-03	0.9304	

L location * *q*	1.98E-03	1	1.98E-03	1.51	0.2229	
V location * N	3.13E-10	1	3.13E-10	2.38E-07	0.9996	
V location * *Ls*	3.61E-09	1	3.61E-09	2.76E-06	0.9987	
V location * *Vs*	4.87E-05	1	4.87E-05	0.037	0.8477	
V location * *r*	1.02E-05	1	1.02E-05	7.76E-03	0.9301	
V location * *q*	5.49E-04	1	5.49E-04	0.42	0.5197	
N * *Ls*	3.13E-10	1	3.13E-10	2.38E-07	0.9996	
N * *Vs*	3.13E-10	1	3.13E-10	2.38E-07	0.9996	
N * *r*	3.36E-04	1	3.36E-04	0.26	0.614	
N * *q*	1.01E-03	1	1.01E-03	0.77	0.382	
Ls * *Vs*	0.12	1	0.12	90.06	< 0.0001	Highly significant
Ls * *r*	2.08E-03	1	2.08E-03	1.58	0.2121	
Ls * *q*	8.02E-04	1	8.02E-04	0.61	0.4366	
*Vs** *r*	7.25E-03	1	7.25E-03	5.53	0.0213	
Vs * *q*	9.26E-03	1	9.26E-03	7.06	0.0096	
*r** *q*	7.50E-05	1	7.50E-05	0.057	0.8117	
Residual	0.098	75	1.31E-03			
Lack of Fit	0.084	42	2.01E-03	4.73	< 0.0001	significant
Pure Error	0.014	33	4.25E-04			
Cor Total	0.98	129				

R^2=0.8992, predicted R^2=0.6306, adjusted R^2= 0.8266, adequate precision = 15.89.

Table A8 ANOVA for response surface quadratic model (for the purity of bottom product B)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	3.76	54	0.07	8.04	< 0.0001	significant
F location	4.99E-04	1	4.99E-04	0.058	0.8111	
S location	7.21E-03	1	7.21E-03	0.83	0.3646	
L location	2.16E-03	1	2.16E-03	0.25	0.6189	
V location	2.85E-03	1	2.85E-03	0.33	0.5684	
N	1.02E-03	1	1.02E-03	0.12	0.7321	
Ls	0.015	1	0.015	1.78	0.1867	
Vs	0.043	1	0.043	4.95	0.0291	
r	0.16	1	0.16	18.53	< 0.0001	Highly significant
q	0.38	1	0.38	44.34	< 0.0001	Highly significant
(F location)^2	0.047	1	0.047	5.45	0.0223	
(S location)^2	0.08	1	0.08	9.27	0.0032	
(L location)^2	4.35E-03	1	4.35E-03	0.5	0.4808	
(V location)^2	0.045	1	0.045	5.19	0.0256	
N^2	0.058	1	0.058	6.69	0.0117	
Ls^2	1.49	1	1.49	171.99	< 0.0001	Highly significant
Vs^2	0.74	1	0.74	85.56	< 0.0001	Highly significant
r^2	0.086	1	0.086	9.93	0.0023	

q^2	0.13	1	0.13	15.28	0.0002	
F location * S location	5.89E-06	1	5.89E-06	6.79E-04	0.9793	
F location * L location	6.77E-06	1	6.77E-06	7.81E-04	0.9778	
F location * V location	3.34E-03	1	3.34E-03	0.38	0.5369	
F location * N	0.022	1	0.022	2.57	0.1133	
F location * *Ls*	1.82E-04	1	1.82E-04	0.021	0.8853	
F location * *Vs*	3.54E-03	1	3.54E-03	0.41	0.5248	
F location * *r*	3.04E-04	1	3.04E-04	0.035	0.852	
F location * *q*	3.08E-03	1	3.08E-03	0.36	0.553	
S location * L location	4.99E-03	1	4.99E-03	0.58	0.4504	
S location * V location	0.043	1	0.043	4.99	0.0285	
S location * N	1.69E-03	1	1.69E-03	0.19	0.6602	
S location * *Ls*	4.50E-06	1	4.50E-06	5.20E-04	0.9819	
S location * *Vs*	4.49E-06	1	4.49E-06	5.18E-04	0.9819	
S location * *r*	4.84E-04	1	4.84E-04	0.056	0.8139	
S location * *q*	7.66E-03	1	7.66E-03	0.88	0.3502	
L location * V location	7.54E-04	1	7.54E-04	0.087	0.7688	
L location * N	1.07E-08	1	1.07E-08	1.24E-06	0.9991	
L location * *Ls*	0.023	1	0.023	2.6	0.1107	
L location * *Vs*	2.08E-05	1	2.08E-05	2.40E-03	0.961	
L location * *r*	4.85E-05	1	4.85E-05	5.60E-03	0.9406	
L location * *q*	0.024	1	0.024	2.8	0.0987	
V location * N	9.30E-10	1	9.30E-10	1.07E-07	0.9997	
V location * *Ls*	1.33E-07	1	1.33E-07	1.53E-05	0.9969	
V location * *Vs*	1.16E-03	1	1.16E-03	0.13	0.7156	
V location * *r*	4.60E-05	1	4.60E-05	5.30E-03	0.9421	
V location * *q*	1.73E-03	1	1.73E-03	0.2	0.6566	
N * *Ls*	2.07E-09	1	2.07E-09	2.38E-07	0.9996	
N * *Vs*	0	1	0	0	1	
N * *r*	1.69E-03	1	1.69E-03	0.2	0.66	
N * *q*	0.017	1	0.017	1.94	0.1674	
Ls * *Vs*	0.43	1	0.43	49.59	< 0.0001	Highly significant
Ls * *r*	0.013	1	0.013	1.55	0.2174	
Ls * *q*	2.68E-04	1	2.68E-04	0.031	0.8609	
*Vs** *r*	0.032	1	0.032	3.71	0.0578	
Vs * *q*	0.014	1	0.014	1.59	0.2116	
*r** *q*	1.56E-04	1	1.56E-04	0.018	0.8936	
Residual	0.65	75	8.67E-03			
Lack of Fit	0.46	42	0.011	1.9	0.0296	significant
Pure Error	0.19	33	5.76E-03			
Cor Total	4.41	129				

R^2=0.8527, predicted R^2=0.5728, adjusted R^2= 0.7467, adequate precision = 12.693.

Table A9 ANOVA for response surface quadratic model (for condener duty Q_c)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	60.04	54	1.11	22.04	< 0.0001	significant
F location	7.66E-05	1	7.66E-05	1.52E-03	0.969	
S location	6.30E-04	1	6.30E-04	0.012	0.9113	
L location	0.14	1	0.14	2.68	0.1061	
V location	9.84E-05	1	9.84E-05	1.95E-03	0.9649	
N	1.02E-04	1	1.02E-04	2.02E-03	0.9643	
Ls	0.069	1	0.069	1.37	0.2458	
Vs	0.087	1	0.087	1.73	0.192	
r	49.39	1	49.39	979.02	< 0.0001	Highly significant
q	0.28	1	0.28	5.47	0.022	
(F location)^2	7.01E-04	1	7.01E-04	0.014	0.9065	
(S location)^2	1.11E-03	1	1.11E-03	0.022	0.8827	
(L location)^2	0.033	1	0.033	0.66	0.42	
(V location)^2	2.79E-03	1	2.79E-03	0.055	0.8147	
N^2	3.30E-03	1	3.30E-03	0.065	0.7987	
Ls^2	0.02	1	0.02	0.4	0.5293	
Vs^2	0.056	1	0.056	1.12	0.2934	
r^2	6.82	1	6.82	135.21	< 0.0001	Highly significant
q^2	0.018	1	0.018	0.36	0.5488	
F location * S location	1.06E-05	1	1.06E-05	2.10E-04	0.9885	
F location * L location	1.09E-05	1	1.09E-05	2.17E-04	0.9883	
F location * V location	5.15E-10	1	5.15E-10	1.02E-08	0.9999	
F location * N	1.78E-04	1	1.78E-04	3.53E-03	0.9528	
F location * *Ls*	4.75E-04	1	4.75E-04	9.41E-03	0.923	
F location * *Vs*	1.43E-09	1	1.43E-09	2.84E-08	0.9999	
F location * *r*	4.75E-04	1	4.75E-04	9.41E-03	0.923	
F location * *q*	1.58E-04	1	1.58E-04	3.14E-03	0.9555	
S location * L location	1.35E-05	1	1.35E-05	2.68E-04	0.987	
S location * V location	5.05E-04	1	5.05E-04	0.01	0.9206	
S location * N	6.18E-04	1	6.18E-04	0.012	0.9122	
S location * *Ls*	1.72E-05	1	1.72E-05	3.42E-04	0.9853	
S location * *Vs*	1.56E-05	1	1.56E-05	3.08E-04	0.986	
S location * *r*	5.97E-04	1	5.97E-04	0.012	0.9137	
S location * *q*	5.05E-04	1	5.05E-04	0.01	0.9206	
L location * V location	1.10E-08	1	1.10E-08	2.19E-07	0.9996	
L location * N	0	1	0	0	1	
L location * *Ls*	0.34	1	0.34	6.7	0.0116	
L location * *Vs*	7.95E-09	1	7.95E-09	1.58E-07	0.9997	
L location * *r*	2.03E-08	1	2.03E-08	4.03E-07	0.9995	
L location * *q*	0.33	1	0.33	6.64	0.0119	
V location * N	0	1	0	0	1	

V location * *Ls*	3.32E-07	1	3.32E-07	6.58E-06	0.998	
V location * *Vs*	9.67E-09	1	9.67E-09	1.92E-07	0.9997	
V location * *r*	2.03E-08	1	2.03E-08	4.03E-07	0.9995	
V location * *q*	5.05E-04	1	5.05E-04	0.01	0.9206	
N * *Ls*	0	1	0	0	1	
N * *Vs*	0	1	0	0	1	
N * *r*	6.18E-04	1	6.18E-04	0.012	0.9122	
N * *q*	1.58E-04	1	1.58E-04	3.13E-03	0.9555	
Ls * *Vs*	2.23E-03	1	2.23E-03	0.044	0.8342	
Ls * *r*	5.45E-06	1	5.45E-06	1.08E-04	0.9917	
Ls * *q*	0.42	1	0.42	8.37	0.005	
*Vs** *r*	0.033	1	0.033	0.65	0.4225	
Vs * *q*	0.031	1	0.031	0.61	0.4378	
*r** *q*	0.04	1	0.04	0.8	0.3734	
Residual	3.78	75	0.05			
Lack of Fit	1.1	42	0.026	0.32	0.9997	not significant
Pure Error	2.69	33	0.081			
Cor Total	63.82	129				

R^2=0.9407, predicted R^2=0.8592, adjusted R^2= 0.898, adequate precision = 18.77.

Table A10 ANOVA for response surface quadratic model ((for ΔP)

Source	Sum of Squares	d.f.	Mean - Square	F Value	P > F	Remarks
Model	4338.86	54	80.35	86.61	< 0.0001	significant
F location	27.47	1	27.47	29.61	< 0.0001	Highly significant
S location	0.26	1	0.26	0.28	0.5993	
L location	2.03	1	2.03	2.19	0.1428	
V location	5.01	1	5.01	5.4	0.0229	
N	0.1	1	0.1	0.11	0.7441	
Ls	6.57	1	6.57	7.09	0.0095	
Vs	2996.9	1	2996.9	3230.34	< 0.0001	Highly significant
r	1058.01	1	1058.01	1140.42	< 0.0001	Highly significant
q	112.81	1	112.81	121.59	< 0.0001	Highly significant
(F location)^2	0.36	1	0.36	0.39	0.5348	
(S location)^2	0.19	1	0.19	0.21	0.6517	
(L location)^2	1.82	1	1.82	1.97	0.165	
(V location)^2	2.27	1	2.27	2.45	0.1218	
N^2	0.52	1	0.52	0.56	0.4574	
Ls^2	4.28	1	4.28	4.62	0.0349	
Vs^2	0.21	1	0.21	0.22	0.637	
r^2	31.86	1	31.86	34.34	< 0.0001	Highly significant
q^2	26.95	1	26.95	29.05	< 0.0001	Highly significant
F location * S location	0.51	1	0.51	0.55	0.4597	

F location * L location	0.5	1	0.5	0.54	0.4655	
F location * V location	5.69E-05	1	5.69E-05	6.13E-05	0.9938	
F location * N	3.44E-04	1	3.44E-04	3.70E-04	0.9847	
F location * *Ls*	0.054	1	0.054	0.058	0.8099	
F location * *Vs*	3.2	1	3.2	3.45	0.0671	
F location * *r*	2.59	1	2.59	2.79	0.0989	
F location * *q*	2.43	1	2.43	2.61	0.1101	
S location * L location	0.49	1	0.49	0.53	0.4678	
S location * V location	4.49E-03	1	4.49E-03	4.84E-03	0.9447	
S location * N	0.05	1	0.05	0.054	0.8163	
S location * *Ls*	1.76E-04	1	1.76E-04	1.90E-04	0.9891	
S location * *Vs*	1.81E-03	1	1.81E-03	1.96E-03	0.9648	
S location * *r*	2.08E-03	1	2.08E-03	2.25E-03	0.9623	
S location * *q*	0.023	1	0.023	0.025	0.8758	
L location * V location	0.08	1	0.08	0.086	0.7695	
L location * N	1.33E-07	1	1.33E-07	1.43E-07	0.9997	
L location * *Ls*	3.44	1	3.44	3.71	0.058	
L location * *Vs*	6.35	1	6.35	6.85	0.0107	
L location * *r*	1.59	1	1.59	1.72	0.1939	
L location * *q*	5.31	1	5.31	5.73	0.0192	
V location * N	0.13	1	0.13	0.14	0.7053	
V location * *Ls*	0.26	1	0.26	0.28	0.6009	
V location * *Vs*	6.21	1	6.21	6.7	0.0116	
V location * *r*	0.63	1	0.63	0.68	0.4127	
V location * *q*	0.87	1	0.87	0.94	0.3358	
N * *Ls*	0.13	1	0.13	0.14	0.7055	
N * *Vs*	2.21E-07	1	2.21E-07	2.38E-07	0.9996	
N * *r*	0.051	1	0.051	0.055	0.8159	
N * *q*	4.00E-04	1	4.00E-04	4.32E-04	0.9835	
Ls * *Vs*	0.6	1	0.6	0.64	0.4253	
Ls * *r*	0.26	1	0.26	0.28	0.5957	
Ls * *q*	1.06	1	1.06	1.15	0.2879	
*Vs** *r*	17.09	1	17.09	18.42	< 0.0001	Highly significant
Vs * *q*	5.66	1	5.66	6.1	0.0158	
*r** *q*	5.96	1	5.96	6.42	0.0133	
Residual	69.58	75	0.93			
Lack of Fit	31.32	42	0.75	0.64	0.9119	not significant
Pure Error	38.26	33	1.16			
Cor Total	4408.44	129				

R^2=0.9842, predicted R^2=0.9572, adjusted R^2= 0.9729, adequate precision = 49.491.

Arc sin sqrt (D)

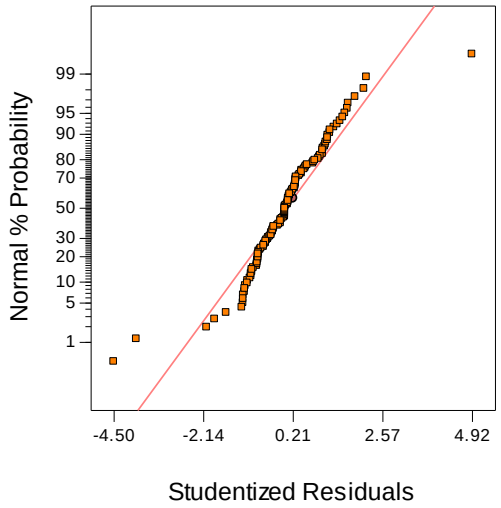

Figure A1: Normal% probabilities versus studentized residuals for the purity of distillate.

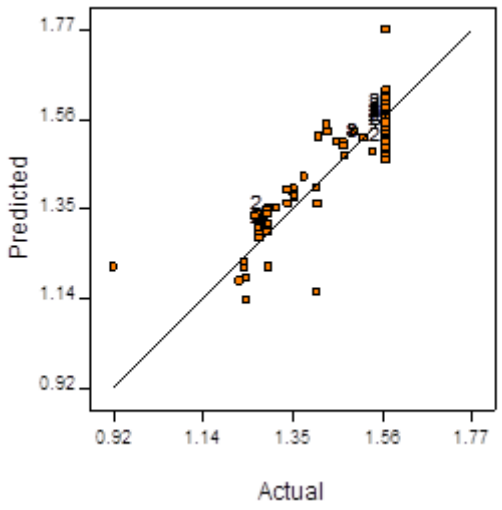

Figure A2: Scatter diagram for the predicted response versus actual response for the purity of distillate.

S

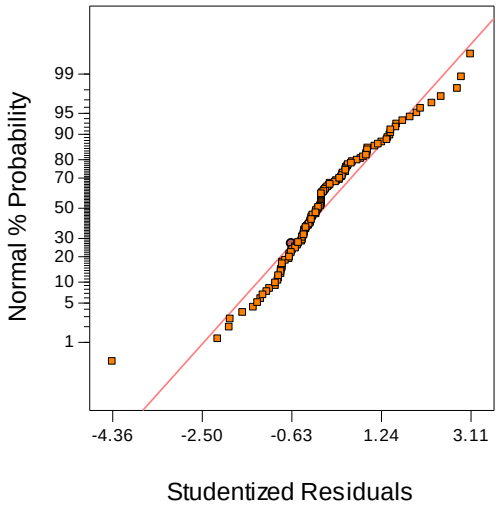

Figure A3: Normal% probabilities versus studentized residuals for the purity of side stream.

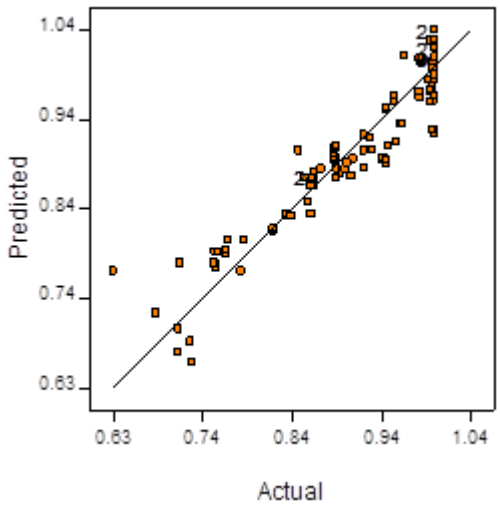

Figure A4: Scatter diagram for the predicted response versus actual response for the purity of side stream.

B^3

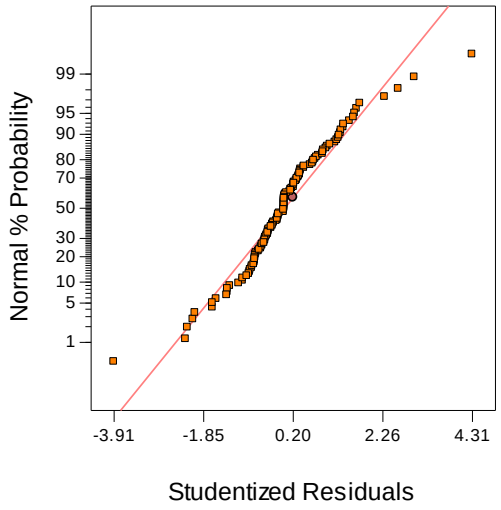

Figure A5: Normal% probabilities versus studentized residuals for the purity of bottom product.

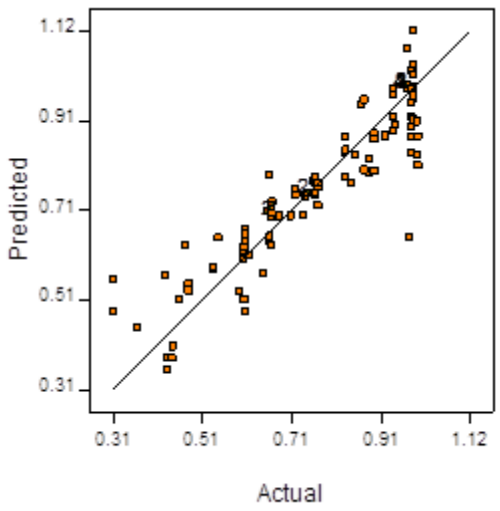

Figure A6: Scatter diagram for the predicted response versus actual response for the bottom product.

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Ln (Qc + 60000000.0)

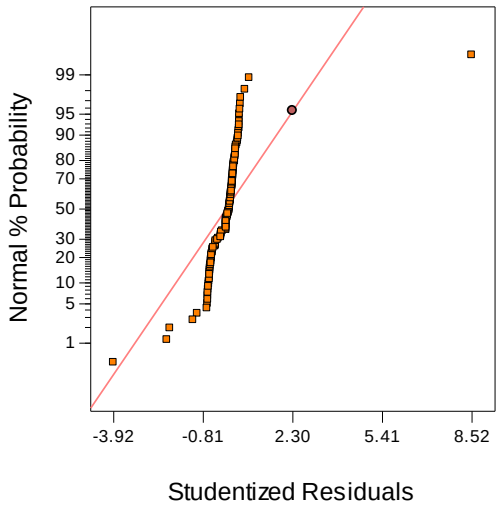

Figure A7: Normal% probabilities versus studentized residuals for the condenser duty.

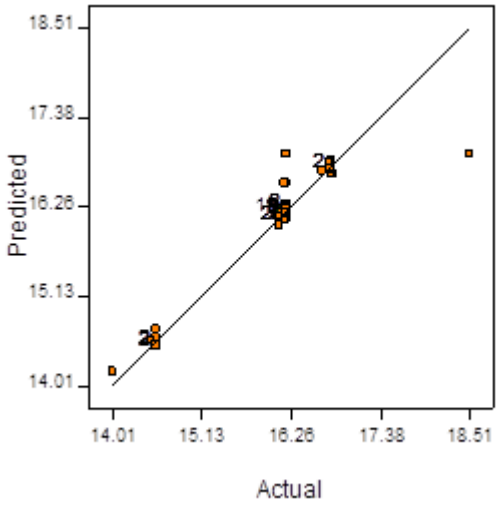

Figure A8: Scatter diagram for the predicted response versus actual response for condenser duty.

ΔP

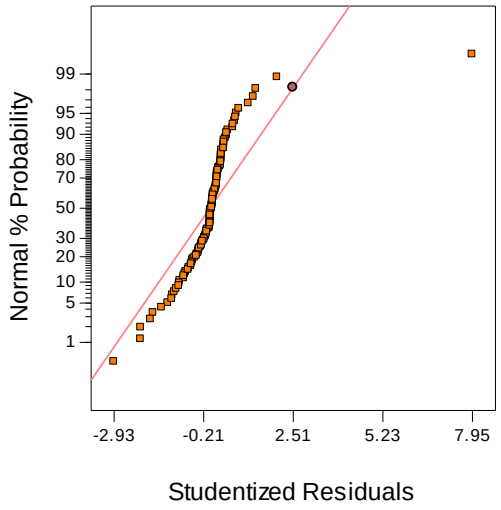

Figure A9: Normal% probabilities versus studentized residuals for the pressure drop across the divided wall.

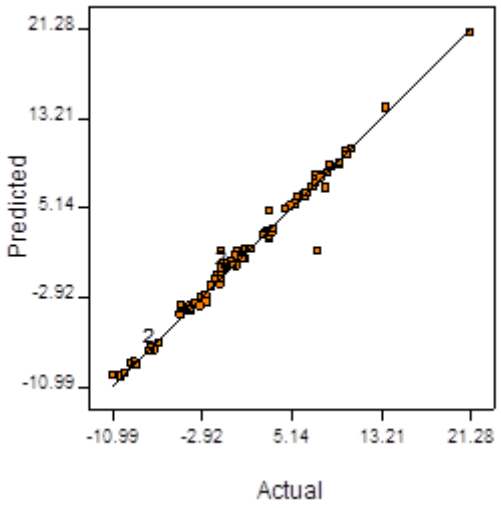

Figure A10: Scatter diagram for the predicted response versus actual response for the pressure drop across the divided wall.

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M. Tech. (Chemical Engg.)	2003	Ist Position	I. I. T. Roorkee

PUBLICATIONS FROM THESIS

Publications/communicated in journals

1. Sangal V. K., Kumar V., Mishra I. M., Divided wall distillation column: rationalization of degree of freedom analysis, *Theoretical Foundations of Chemical Engineerin*g, 2012, 46 (4), 319-328.
2. Sangal V. K., Bichalu L., Kumar V., Mishra I. M., Importance of pressure drop in divided wall distillation column, *Asia Pacific J. of Chemical Engineering*, (2012), DOI: 10.1002/apj.1633.
3. Sangal V. K., Kumar V., Mishra I. M., Optimization of structural and operational variables for the energy efficiency of a divided wall distillation column, *Computer & Chemical Engineering*, 40 (2012), 33-40.
4. Sangal V. K., Kumar V., Mishra I. M., Optimization of a divided wall column for the separation of C4-C6 normal paraffin mixture using Box-Behnken design, *Chemical Industry & Chemical Engineering Quarterly*, (2012), DOI: 10.2298/CICEQ121019047S.
5. Sangal V. K., Kumar V., Mishra I. M., Process parametric optimization of a divided wall distillation column, *Chemical Engineering Communication*, (Under revision).

Publications in conferences

1. Sangal V. K., Kumar V., Mishra I. M., Divided wall distillation column for the separation of light hydrocarbon mixtures, National Conference on Recent Advances in Chemical & Environmental Engineering, 20-21 January, 2012, NIT Rourkela, Odisha, India.