# Simulation studies of
# Extractive Divided Wall Distillation Columns

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**In**

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## DECLARATION

I hereby declare that dissertation entitled "Simulation studies of Extractive Divided Wall Distillation Column" is an authentic record of my own work carried out at as per requirement for the award of degree of M.Tech (Chemical Engineering) at Thapar University, Patiala, under the guidance of Dr. V.K.Sangal ( Assistant Professor, CHED) during July 2012 to June 2013.

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# ABSTRACT

Current environmental constraints require processes that are more energy efficient and lead to lesser greenhouse emissions. Distillation is the most working, but also the highly energy-intensive separation method being used in chemical process industry (CPI). Therefore, the efficient design of the distillation process is essential so as to diminish the energy requirement without compromising with the product quality. Various techniques have been tried and tested, the foremost being process intensification. 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. Extractive Divided Wall Column (EDWC) is a newest form of process integration, which eliminates the use of solvent recovery column required in extractive distillation. EDWC are just an extension of Divided Wall Column (DWC) for separating mixtures forming azeotropes, whose separation by ordinary distillation is not possible.

Simulation of an EDWC is a difficult task, as it involves several connecting streams making the problem highly non-linear. In the present work simulation studies of an EDWC were performed for the separation of water ethanol mixture. Water ethanol mixture form a minimum boiling azeotrope and its separation by ordinary distillation is not possible. The use of EDWC was proposed for the separation of this mixture and simulation studies were done using the rigorous Radfrac model available in ASEPN PLUS. Ethylene glycol was used as a solvent for separating water ethanol mixture. Conventionally, water ethanol mixture is separated by extractive distillation, requiring at least two columns, one for carrying out separation and other for solvent recovery. EDWC eliminates the use of solvent recovery column and performs the operation in just a single column.

The structural and process parameters of an EDWC are generally optimized separately and there are no reports in the literature on the simultaneous optimization of the structural and operating parameters of an EDWC. Box–Behnken design (BBD) under response surface methodology (RSM) was used for the optimization of the structural and operational parameters and to evaluate the effects of these parameters and their interactions on the energy efficiency of an EDWC.

The system has many structural variables and process variables including the location of the feed stage, the location of the side stream stage, and the number of stages in the pre-

fractionator and in the main column, location of the divided wall, number of stages in the divided wall section, reflux rate, liquid spilt, vapour split and the solvent flow rate. These variables were used for the optimization of the product purities and the reboiler duty and $CO_2$ emission. The main objective during optimization was to achieve maximum product purities of all the components and minimization of energy requirements and $CO_2$ emission.

It was found that the process variables are highly significant for the purity of distillate (ethanol) and energy efficiency of an EDWC. However the structural variable namely, the interaction of vapour split stage with number of stages in main column and the interaction of side product stage with vapour split stage were found to be significant for the purity of distillate (ethanol) and energy efficiency of an EDWC also. The energy requirements (reboiler duty) was 2369 kW and 1880 kW for the conventional extraction distillation and the EDWC respectively for the separation of water ethanol mixture, i.e. a saving of 20.6 % reboiler duty for an EDWC. 20% less $CO_2$ emissions was found for the EDWC as comparison of conventional process.

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# NORMENCLATURE AND ABBREVIATIONS

| | |
|---|---|
| CPI: | Chemical process industry |
| VLE: | Vapor liquid equibilirum |
| x: | Liquid phase mole fraction |
| y: | Vapor phase mole fraction |
| $T_{xy}$: | Variation of vapor liquid mole faction at constant temperature |
| $P_{xy}$: | Variation of vapor liquid mole faction at constant presseure |
| N: | Number of stages. |
| DWC: | Divided Wall Columns. |
| TCDS: | Thermally coupled distillation sequences. |
| F: | Feed flow rate |
| *s*: | Solvent flow rate |
| *l*: | liquid split |
| *v*: | vapor split |
| r: | reflux rate |
| L: | liquid split stage |
| V: | vapor split stage |
| N: | Number of stages in main column |
| W: | Side product stage. |
| D: | mole fraction of ethanol in distillate |
| S: | mole fraction of water in side product |
| B: | mole fraction of ethylene glycol at bottom |
| $Q_b$: | Reboiler Duty |
| M-V-IN: | Vapor entering from prefractionator to main column. |
| M-L-OUT: | Liquid entering from main column to prefractionator. |
| M-V-OUT: | Vapor entering from main column to prefractionator |
| M-L-IN: | Liquid entering from main column to prefractionator. |
| EDWC: | Extractive Divided Wall Columns |
| TCS: | Thermally coupled sequence |
| ESI: | Ease of separation index |
| FUG: | Fenske Underwood Gilliland |
| FUGK: | Fenske Underwood Gilliland Kirkbride |
| $V_{min}$: | Minimum vapor flow |
| TES: | Thermodynamically equivalent structures |
| CGCC: | Column grand composite curve |
| BBD: | Box Behnken Design |
| RSM: | Response surface methodology |
| BTX: | Benzene Toluene Xylene |

| | |
|---|---|
| SQP: | Sequential quadratic programming |
| PDC: | Pre concentration distillation column |
| SRC: | Solvent recovery column |
| EDC: | Extractive distillation column |
| NRTL: | Non Random two liquid model |
| NPSH: | Net positive suction head |
| H: | Height of column |
| Y: | Response |
| X: | Process and structural variables. |
| $R^2$: | Coefficient of regression |
| DF: | Degree of freedom |
| $d_i$: | Desirability |

# Chapter-1

## *Introduction*

Distillation is undoubtedly the most widely used separation process presently employed in the chemical process industry (CPI). It's a very mature process but one cannot ignore the fact that it is associated with tremendous amount of energy. It has been reported that distillation alone consumes more than 95% of the energy used by CPI worldwide (Vazquez-Castillo et al., 2009). Environmental regulations have forced CPI to come up with technologies that are more energy efficient and lead to lesser greenhouse emissions. Various researchers have tried and tested new things to come up with technologies that are more energy efficient, the foremost technique being process intensification. Process intensification aims to decrease the physical size of the equipment leading to high production and decrease in total annual cost.

Distillation is a method of separation of feed into its various constituents on the basis of difference in compositions between a liquid mixture and vapor formed form it. This composition difference is due to different vapor pressure or volatilities of the components of the liquid. When such a difference between vapor pressure or volatilities does not exist, separation by ordinary distillation process is not feasible.

Separations of close boiling mixtures and particularly those forming azeotropes are not feasible by ordinary distillation. Azeotropes are constant boiling mixtures and when a mixture reaches its azeotropic composition, liquid and vapor phase compositions become equal and the mixture cannot be separated by ordinary distillation. In these cases, a third component is added which increases the relative volatility of the two original components and make their separation feasible. Azeotropic mixtures are highly non ideal and are classified as maximum boiling azeotrope or azeotrope exhibiting negative deviation and minimum boiling azeotropes or azeotrope exhibiting positive deviation. Maximum boiling azeotropes are called so because at azeotropic composition the boiling point is greater than the boiling point of individual components and for minimum boiling azeotrope, at azeotropic composition the boiling point is lesser than that of individual component.

### 1.1 Vapor liquid equilibria

Separation of a mixture by distillation is based on the equilibrium distribution of components between the liquid and vapor phase therefore knowledge of vapor liquid equilibrium is essential for understanding the principles of distillation. The vapor liquid equilibrium relationships are given by Raoult's law and Henry's law. Raoult's law is valid at low to moderate pressure and for chemically similar substances and Henry's law is valid for any spices present at low concentration but at low to moderate pressure. Phase equilibrium diagrams are used for understanding the relationship between the mole fraction of a component in the vapor and liquid phases for varying temperature at constant pressure or for varying pressure at constant temperature.

### 1.2 Ideal Solutions

Ideal solutions are those in which the molecular interactions are identical to the interactions between molecules of different compounds and the compounds are of similar chemical nature. Vapor liquid equilibrium plots at constant temperature and constant pressure are shown in Figure 1.1 and 1.2 respectively. An ideal system of benzene toluene is taken and graphs are generated using the ASEPN PLUS software (Asepn technology, 2009).

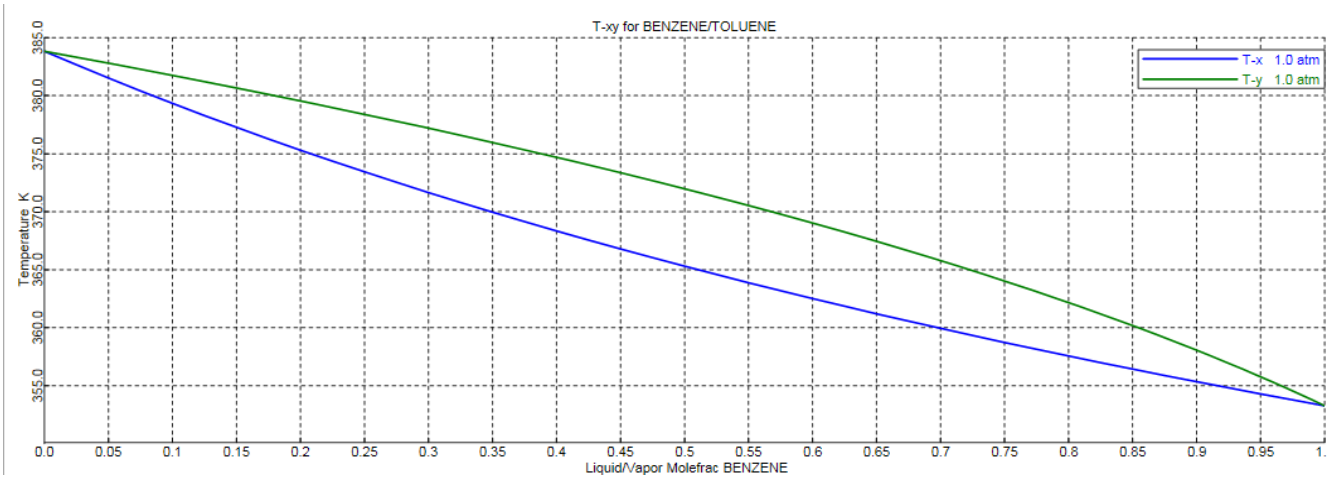


**Figure1.1 $T_{xy}$ plot of benzene toluene at constant pressure**

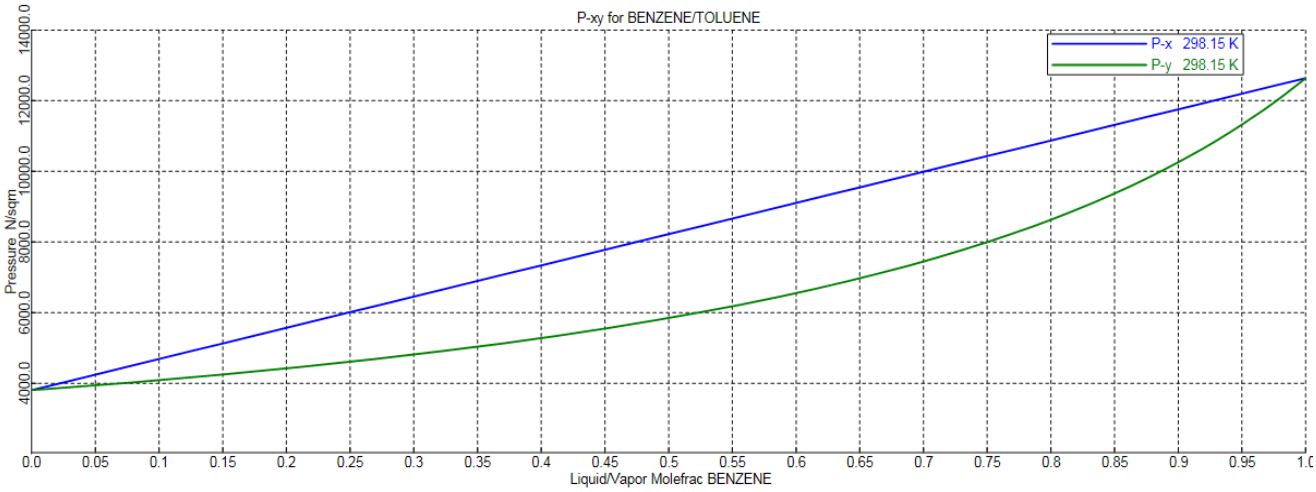


**Figure1.2 $P_{xy}$ plot of benzene toluene at constant temperature**

### 1.3 Non ideal solutions

Non ideal solutions are those in which the molecular interactions cannot be neglected and components are of dissimilar chemical nature. These solutions do not obey Raoult's law and exhibit a deviation known as negative (maximum boiling) and positive deviation (minimum boiling) from ideality.

#### 1.3.1 Minimum boiling azeotropes (positive deviation)

A liquid mixture exerting an equilibrium total vapor pressure more than that calculated by Raoult's law is said to exhibit a positive deviation from ideality, which directly means that the boiling point of the azeotropic composition will be less than the boiling point of individual components. A common example is of ethanol benzene mixture, ethanol has boiling point of 78.4°C while benzene has boiling point of 80°C and the mixture forms an azeotrope at 68.2°C at 1 atm and 67.6% weight benzene (Asepn Technology, 2009). Figure 1.3 and 1.4 represent VLE diagrams at constant temperature and constant pressure for solution exhibiting positive deviation.

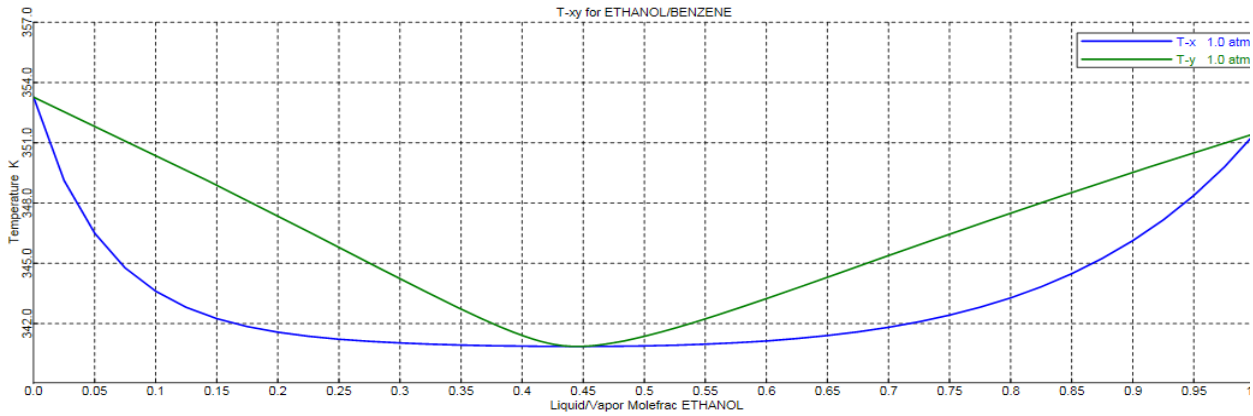


**Figure1.3 $T_{xy}$ plot for ethanol benzene mixture at constant pressure for minimum boiling azeotrope**

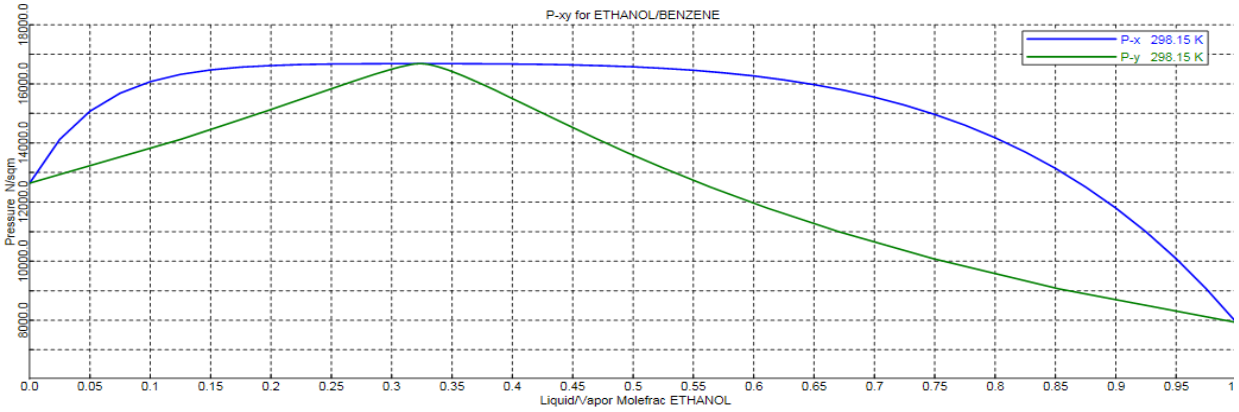


**Figure1.4 $P_{xy}$ plot for ethanol benzene mixture at constant temperature for minimum boiling azeotrope**

### 1.3.2 Maximum boiling azeotropes (Negative Deviation)

A liquid mixture exerting an equilibrium total vapor pressure less than that calculated by Raoult's law is said to exhibit a negative deviation from ideality, which directly means that the boiling point of the azeotropic composition will be greater than the boiling point of individual components. A common example is that of water and formic acid mixture, where the azeotropic temperature is 107.3°C and that of water and formic acid is 100°C and 100.8°C respectively at 1 atm and 77.5% weight formic acid composition.

### 1.4 Multicomponent Distillation

For separating N components is pure form by ordinary distillation we must have N-1 columns. For separating three component mixtures in pure form atleast two columns will be required. The two most common technique of separating three component mixtures are the direct and the indirect method. In direct method, the most volatile of the three components is taken as the top product from the first column and the remaining products are separated in another column according to their volatilities. In indirect method the heaviest fraction in feed is taken out as bottom product of first column and the two remaining products are further separated and taken out as top and bottom product according to their volatilities. Schematic diagrams of direct and in direct method for separating a three component mixture A, B, C are presented in figure 1.5(a) and (1.5b); A being the lightest and C being the heaviest.

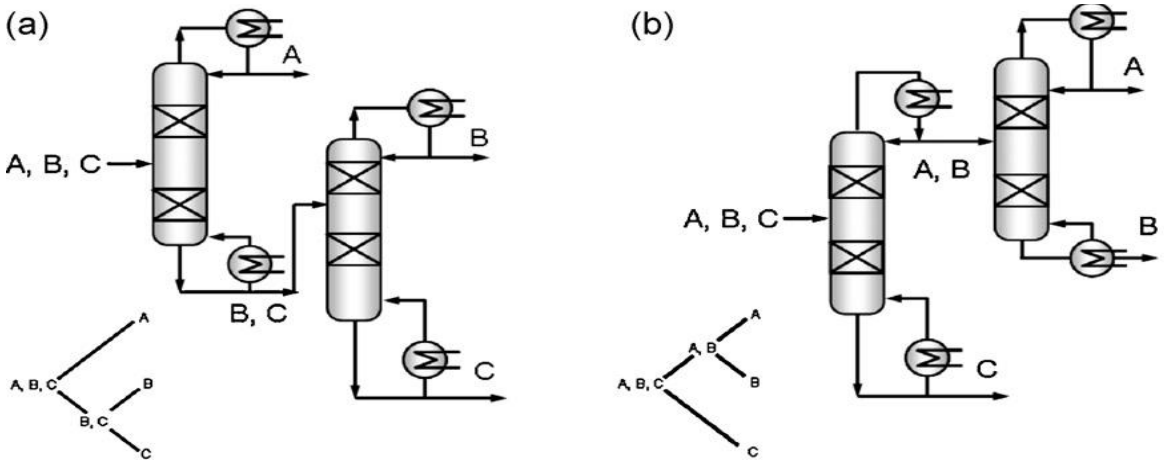


**Figure 1.5 (a) and (b) Direct and indirect sequences (Asprion and Kaibel, 2010)**

### 1.5 Divided wall columns

Dividing wall distillation column (DWC) is a breakthrough towards sustainable distillation, DWC allow separation of three components from a single column only. The concept of dividing wall has its emergence from fully thermally coupled distillation scheme (TCDS) or Petlyuk column, Petlyuk column consists of two column prefractionator and main column, thermal integration of process streams is there between these two columns.( Petlyuk et al,1965). The tertiary feed is introduced in the prefractionator, sharp splits between light key and heavy key are obtained in the prefractionator and stream from prefractionator top consisting predominately of

light key and middle key is fed to main column top, similarly stream from prefractionator bottom consisting predominately of middle key and heavy key is fed to main column bottom. From the main column top a stream of reflux liquid is fed to prefractionator top and from main column bottom a stream consisting of reboiler vapor is fed to prefractionator bottom. Thermal integration of process streams is same in DWC as in Petlyuk column, the only difference being that in the DWC both the prefractionator and the main column are in a single shell, both being separated by a dividing wall in the middle. Thermodynamically, a Petlyuk column is equivalent to DWC. Figures 1.6 and 1.7 represent schematic diagram of petlyuk column and DWC.

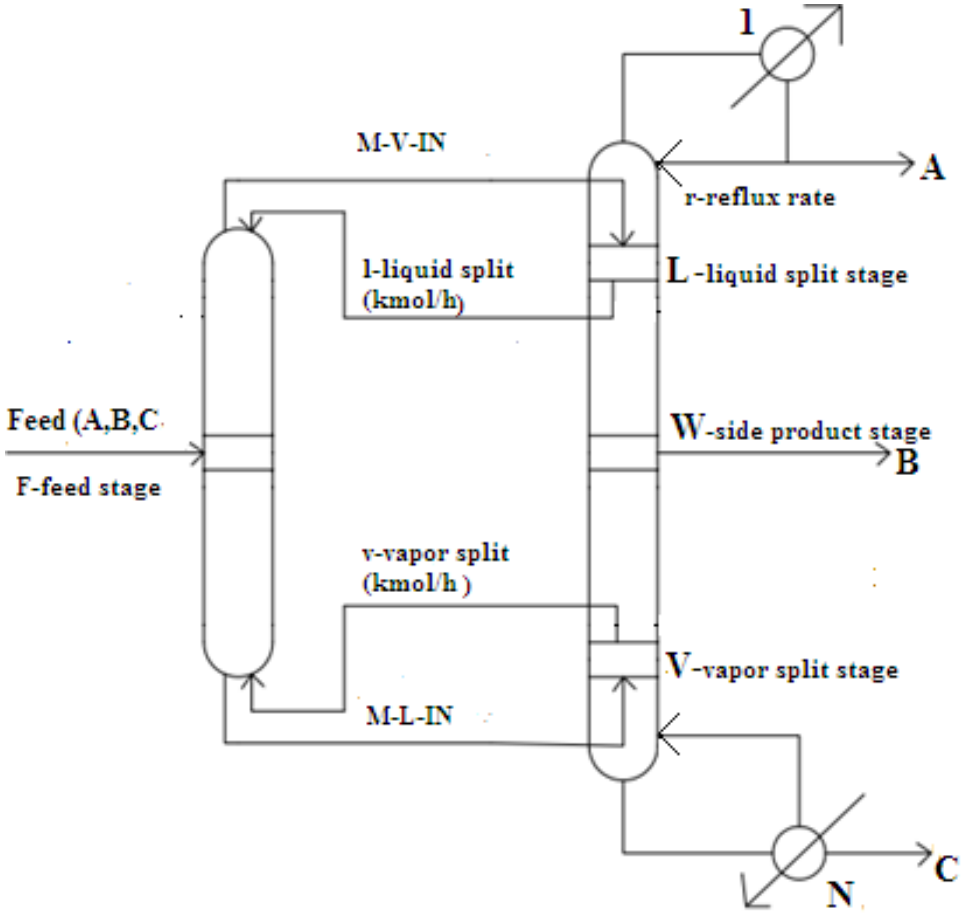


**Figure 1.6 Petlyuk column**

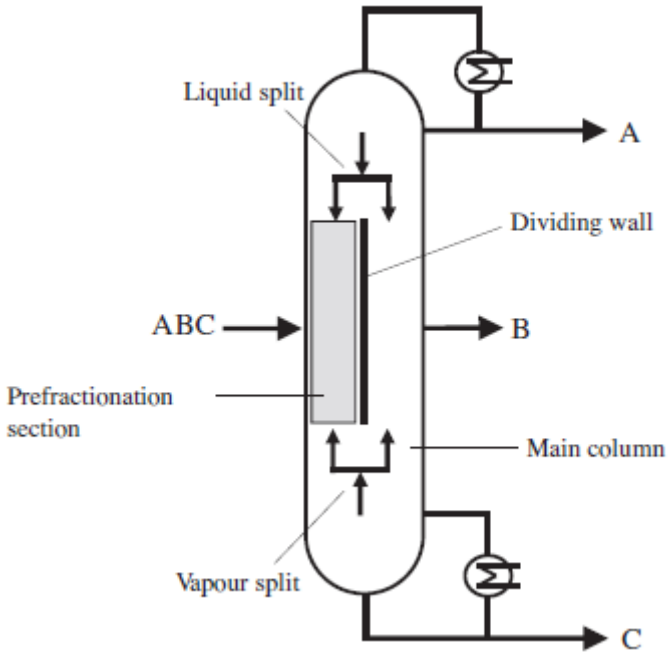


**Figure 1.7 Divided Wall Column (Yildirim et al., 2011)**

Concentration of middle key reaches a peak in the middle as the concentration of the middle key at the top and bottom has to be matched. So, a high purity middle component can be obtained from the middle section of the main column. As the bottom product form the prefractionator consists of no light key and similarly the top of the prefractionator consists of no heavy key, so this effectively reduces the contamination of the middle key drawn at other side of the column. Also because of the distribution of middle key with light key and heavy key at the top and bottom of prefractionator, the amount of remixing is reduced at feed tray location, because the feed can be introduced at the stage where feed composition matches with the tray location, so it provides a greater freedom to choose the feed stage location, (Rangaiah et al,. 2009). Overall efficiency of the divided wall column is further reduced by the thermal linking between the prefractionator and the main column. In fact, out of all the possible three component separation system, namely indirect, direct and DWC, DWC requires the least amount of rectifying liquid and stripped vapor because of the improved vapor liquid interaction in all sections of DWC.

### 1.6 Extractive Distillation

Extractive distillation separates close boiling mixtures by addition of third component which increases the relative volatility between two original components. This process is effective if the

two close boiling components are different in chemical nature. It cannot be successfully used for the separation of isomers because the third component added has almost the same effect on each component and as a result it cannot their relative volatility.

Extractive distillation unit consists of atleast of two columns: an extractive distillation column and a solvent recovery column. The extractive distillation columns consists of three sections the enriching and the stripping section same as the conventional column and a solvent recovery section which serve to concentrate the solvent for its recovery upto a level where solvent effectively extracts the specific substance in the section below the solvent feed plate. Accordingly, the solvent is always supplied to some plate over the feed plate. Also the solvent recovery section serves to prevent the solvent from contaminating the top product.

Extractive distillation is not applicable for separation of isomers but is well suited for separating materials that differ in polarity of hydrogen bonding tendency. Industrially it has it's use in separating aromatics from paraffins, for separation of diolefins from monoolefins. The solvents used in extractive distillation usually have polar or hydrogen bonding character and selectively decrease the volatility of more polar material relatively to the less polar material. Figure 1.8 represents the schematic diagram of Extractive Distillation.

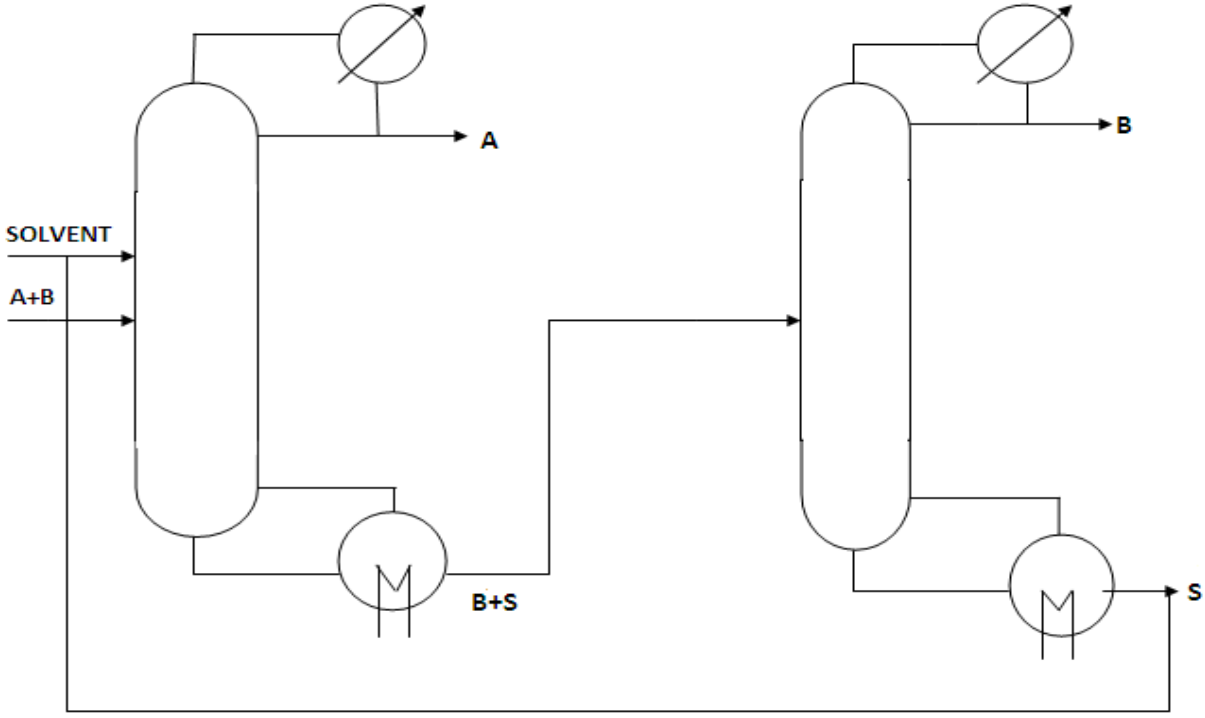


**Figure 1.8 Extractive Distillation**

### 1.7 Extractive Divided Wall Columns (EDWC)

Mixtures particularly those forming azeotropes can be separated by extractive distillation which requires atleast two columns one for separation and the other for solvent recovery, EDWC is a newest form of process integration which eliminates the use of extra column and performs the extraction and solvent recovery work in just a single column. It's basically performing the work of extractive distillation in a single column. The working and the interconnections of streams in EDWC will be exactly similar to DWC; the only thing extra is the additional solvent stream which will be entering in the prefractionator side of the DWC. All the advantages which DWC has to offer are accepted to be given by EDWC also. Figure 1.9 and 1.10 represent the schematic diagram of the proposed EDWC and its equivalent Petlyuk type configuration.

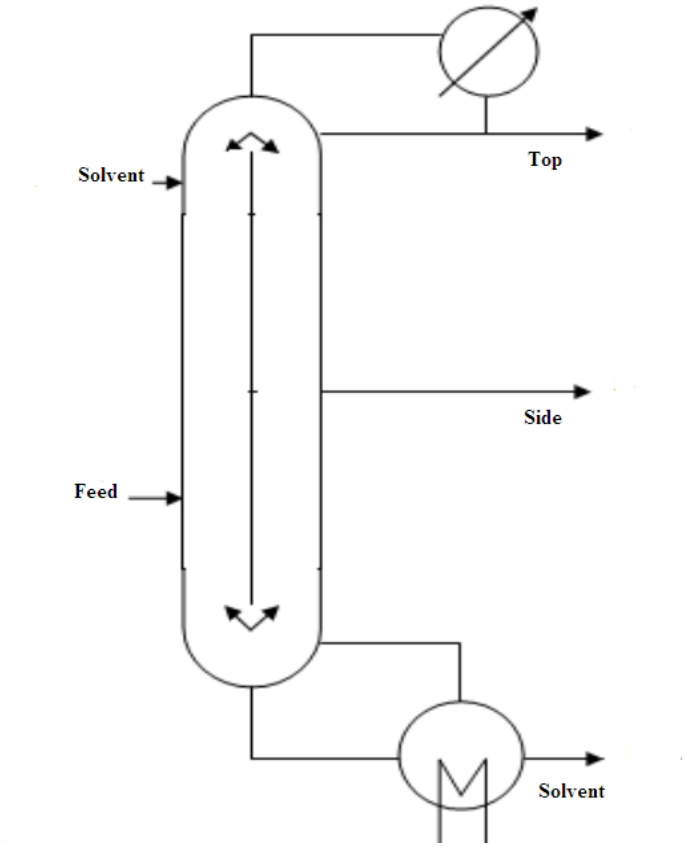


**Figure 1.9 Extractive Divided Wall Column**

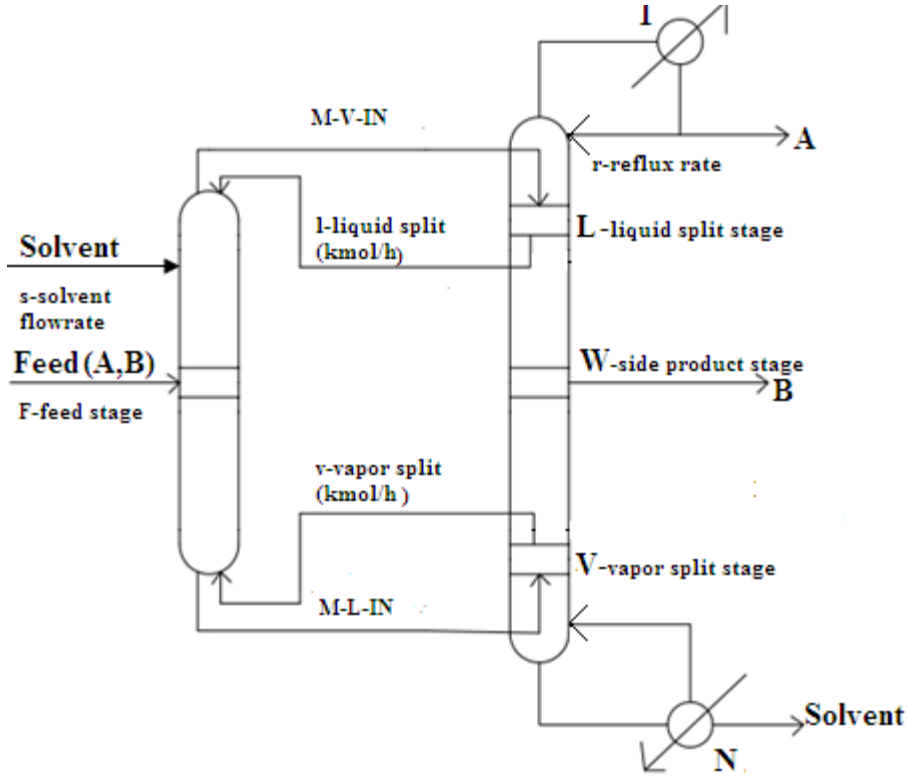


**Figure 1.10 EDWC in Petlyuk configuration**

Advantages which EDWC will offer over conventional distillation process are-

- Reduced capital investment due to the elimination of solvent recovery column.
- High purity of all three components in just a single column.
- High thermodynamic efficiency due to reduces remixing effects.
- Lesser energy requirement compared to conventional extractive distillation processes.

Despite of the numerous benefits which EDWC have to offer some disadvantages are also associated with its use.

- Lack of established design procedures and fear of control problems because of greater complexities as compared with the conventional methods.
- Temperature gap between the top and bottom of the column is far much greater as the entire refluxed liquid and reboiled vapor have to be provided by a single condenser and reboiler. So, a hotter heating utility and a colder cooling utility is required, (Rangaiah et al., 2009).

- To allow natural flow of vapor between the two sections the entire columns has to be operated at the same pressure, so it's possible that one of the splits may not be taking place at the optimum pressure and a greater reflux ratio may be required.

# Chapter-2

## *Literature Survey*

The very first idea about the use of partition wall in a column was given by Monroe in 1933. He suggested that the partition wall should be placed at the bottom of the column. Later on in 1949 R.O Wright was the first person who gave the design for separating a ternary feed mixture in a single column by using a partition wall in the middle of the column. The partition wall was installed exactly in the middle of the column and it was equidistant from the top and bottom of column. The feed was introduced in the middle of the column and the side product was also taken from the middle of the column. Figure 2.1 represents the schematic diagram of the design proposed by him.

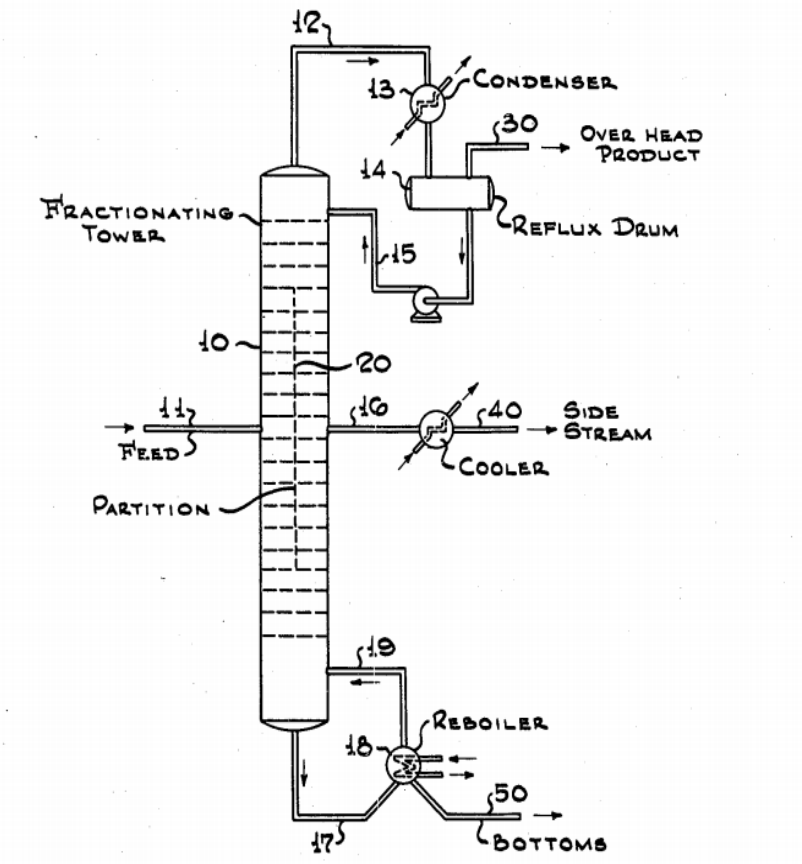


**Figure 2.1- Design proposed by Wright**

(Reference- US Patent No. 2,471,134)

Petlyuk et al (1965) came up with their design which involved a prefractionator and a main column for separation of ternary feed mixture. The basic idea of DWC goes to the Petlyuk configuration; the basic aim of this design was to prevent the thermodynamic losses from mixing of different streams at feed tray location.

Redder and Rudd (1978) presented a paper in which they had compared 8 different designs involving ternary components. They compared these 8 designs economically with a computer design model. They showed that the region of optimality i.e. minimum cost for various designs depends on the spices being separated; on the basis of their ESI i.e. ease of separation index. Changes in feed composition also had characteristics effects on the relative cost. It was concluded among all the factors vapor flow requirement of a tower where the most important.

Fidkowski and Krolikowski (1986) minimized the energy requirements of a thermally coupled system (TCS) provided that the ternary solution is idle. They also showed The TCS are energetically profitable in comparison with other sequences of distillation columns. They presented a analytical solution for the optimization of TCS and to compare the performance of TCS with other distillation sequences. It was also mentioned that incase of difficult separation vapor flow may not be the governing factor as far as minimization of cost is considered.

Kaibel (1987) presented a paper in which he discussed all the possible cases of using partition wall inside a column for the separating of a feed mixture into 3 or 4 pure fractions. For the first time the role of partitioned walls was extended to obtain 4 pure components. He emphasized on the fact that additional mixing must be avoided as far as possible in distillation by an appropriate design. The undesirable additional mixing would result in excess entropy to be removed and would require more exergy or more energy for the separation.

Triantafyllou and Smith (1992) presented a paper on design and optimization of thermally coupled distillation column. They presented a design method which provided a basis for investigating the degree of freedom to minimize energy consumption and number of plates. They came up with a design oriented method for separating a ternary mixture in DWC based on Fenske-Underwood-Gilliland-Kirkbride (FUKG) method. Assumption of constant relative volatility and constant molar overflow were made in their design procedures.

Lestak et al (1994) worked in the area of heat transfer across the dividing wall of DWC. He pointed out the shortcomings in the design method given by Triantafyllou and Smith and Kaibel

as they hadn't taken consideration of heat transfer across dividing wall. As the temperature was different in the two sides of DWC there must be some horizontal heat transfer across the divided wall. He identified the beneficial and the non beneficial heat transfer areas across the dividing by using the combined stage versus enthalpy and stage versus temperature profiles. He took four cases studies to examine the beneficial and non beneficial areas and concluded that 5-10% energy can be saved on proper insulation of the non beneficial areas. The figures of the cases studied by him are given below.

Hernandez and Jimenez (1996) presented a paper on design of thermally coupled distillation system using a dynamic model. The objective of their design of thermally coupled distillations systems was the minimization of total heat duty required for the separation. They performed their research on both direct and indirect methods for separating ternary mixtures. They also concluded that the control of TCDS was not as complicated as perceived in comparison to conventional sequences.

Christiansen et al (1997) extended the Petlyuk idea for separation of four components. He considered all the possible cases of arrangements available in the literature. He introduced the noble idea of the use of triangular wall to overcome some limitations of the DWC with regard to flexibility. The diagrams of the set up considered by him for separation of four components mixtures are represented in the figure below.

Mutalib and Smith (1998) presented their paper on operation and control of DWC. They investigated the degrees of freedom of DWC and the effect of liquid and vapor split on the operation and control of DWC. They further suggested that it was impractical to manipulate the vapor split and the vapor split was fixed by the position of wall. They provided the result of simulation and pilot plant study conducted by them. In their pilot plant instead of using the unreliable composition control they used the temperature control.

Agarwal and Fidkowski (1998) calculated and compared the thermodynamic efficiency of five different distillation configurations for ternary mixtures. He suggested that fully thermally coupled columns i.e. Petlyuk configuration which is known to require least energy for ternary distillation is the most thermodynamic efficient only for recent range of values of feed compositions and relative volatilities.

Amminudin et al (2001) came up with a new design and optimization methodology that was semi rigorous method which was based on equilibrium stage composition concept developed for design of azeotropic distillation system. 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 vapor flow criteria. They gave some improvements in the design procedure suggested by Triantafyllou and Smith and also suggested that the shortcut method using FUG (Frenske Underwood Gilliland) was unreliable for initialization of rigorous simulation. They possibility about the use of DWC in retrofit has been discussed. It was reported that instead of using DWC, the use of thermodynamically equivalent arrangements, such as the prefractionator arrangement and the Petlyuk column, can prove beneficial, not only in terms of achieving energy savings or capacity improvement, but also in the ability to exploit the existing hardware to the maximum.

Muralikrishna et al (2002) performed his work on finding a design space for the design of DWC. As the DWC have large number of design variables then a conventional column, so it will be desirable to find a design space over which all the design of the DWC will lie. An attempt was made in this paper to address this problem through graphical representation of all possible DWC designs for a specified separation of ternary feed.

Halvorsen and Skogestad (2003) presented their study on minimum energy consumption in ternary and multicomponent distillation on the basis of $V_{min}$ diagram. They also used the three column set up used by Muralikrishna for the explanation of their study. They provided an analytical solution for columns with an infinite number of stages, assuming constant relative volatilities and constant molar flows. The $V_{min}$ diagram was based on feed data only. Their study concluded on the basis of $V_{min}$ diagram and suggested that if the peaks in the $V_{min}$ diagram are of similar height, Petlyuk arrangement will be the most attractive in terms of vapor flow and separation work.

Abad-Zarate et al (2006) performed their study on steady state behavior of a Petlyuk distillation column by using a non-equilibrium stage model. Rigorous simulations were done using the RATEFRAC module in ASEPN PLUS. A comparison was also done between equilibrium and non-equilibrium stage models for sieve, valve and bubble cap trays. It was reported that both stage models predicted energy savings and equilibrium stage models required lesser energy as

compared to the non-equilibrium stage models. The energy consumption depended strongly on liquid and vapor split.

Rong and Turunen (2006) presented a new method for synthesis of thermodynamically equivalent structures (TES) for the Petlyuk arrangement. He studied all the possible TES and reported that all TES have the same minimum energy consumption as the original Petlyuk arrangement. He reported that TES's can produce more operable configurations in terms of vapor transfers between columns. Also the optimal design of the Petlyuk arrangement among all of the TESs can not only ensure savings on energy and capital costs, but also improve the equipment design and hydraulic performance.

Suphanit et al (2007) presented their work on exergy loss analysis of heat transfer across the DWC. It is reported by many authors that if heat transfer across the DWC is considered better control may be obtained. He reported that the effects of heat transfer across the dividing wall can be analyzed by using the column grand composite curve (CGCC). In this work, the exergy analysis is applied to the dividing-wall column in order to determine whether heat should be added or rejected at any particular stage. The minimum exergy loss value in the column is set as the criterion for determining the heat load targets at any stage.

Rangaiah et al (2009) gave a simplified procedure for quick design of Dividing Wall Column. The main objective of this study is to develop general procedures for simulation and optimization of DWCs for industrial applications. They took six industrial examples and then examined the relative importance of various design variables through rigorous simulations with help of process simulator ASEPN HYSUS. Their study also showed that liquid and vapor splits have significant impact on the energy requirements of DWC although there effect on reboiler and condenser duty is less pronounced within the optimal region. Their studies also showed that while optimizing DWC variation in number of stages was not required as its effect on the total annual cost is small.

Barroso-Munoz et al (2010) presented his work on experimental studies on effect on pressure drop in DWC. Several different values of liquid and gas velocities were tested in order measure pressure drops and identify operational regions. According to the result the experimental DWC operated at turbulent regimes showed better mass transfer. The diameter and height of the packed bed of the experimental dividing wall distillation column were 0.17 m and 2 m, respectively, a

packing with external diameter of 20 mm was fabricated using Teflon hollow tubes. The experimental set up used by them is given in the figure below.

Norbert Asprion and Gerd Kaibel (2010) presented a paper on recent advances and use of DWC in industry. He reported that currently in industry close to 90 columns are operating. He highlighted the fact that for temperature sensitive products the thermal stress is reduced since the product is reboiled just only once. The main disadvantage highlighted by him was that in comparison to conventional configurations, where for each column an own pressure range can be chosen, here only one pressure range is possible. This results in a larger temperature difference between reboiler and condenser and the use of DWC generally requires a column of greater height as compared to conventional column.

Bravo et al (2010) presented a mutiobjective stochastic procedure to obtain optimal design of EDWC. The approach is based on the use of genetic algorithms to determine the design that minimizes energy consumption and total annualized cost. They took 4 case studies to show the feasibility of performing extractive separations in dividing wall distillation columns. Their design had four objective functions the minimization of number of stages across both sides of wall, solvent flow and reboiler duty.

Kiss and Rewagad (2011) presented their work on energy efficient control of BTX in a divided wall column. The control structures proposed in their paper were based on PID controllers in multiloop framework in which they were able to maintain product purities and minimize energy requirement. The strategy proposed by them to control the heavy component composition at the top of the prefractionator side of the DWC by manipulating the liquid split ratio.

Sangal et al (2012a) presented his studies on degree of freedom analysis of DWC for steady state by using detailed mathematical model which consisted of MESHD equation (conventional MESH equation plus the pressure drop equation). They reported in their paper that pressure drop played an important role in DWC in deciding the vapor and liquid flow rates in divided section of DWC. They also reported that the degree of freedom in DWC or Petlyuk column operating under steady state was four unlike three in conventional distillation column with three product streams.

Sangal et al (2012b) optimized structural and process parameters of DWC for energy efficiency. Box Behnken Design (BBD) under response surface methodology (RSM) was used for the

optimization of parameters and to study the effect of these parameters and their interactions with other on the energy efficiency of DWC. They also reported that process variables had a significant effect on energy efficiency as compared to structural variables. Predictions from the BBD optimization agreed well with the results of rigorous simulations.

Sangal et al (2013a) carried out studies to find a relation between natural or feasible vapor split ratio as a function of reflux ratio and liquid split ratio for a DWC. The multifrac module of ASEPN PLUS was used for the simulation of DWC for BTX mixture. They reported that in case of columns such as DWC where interlinking of streams is involved, consideration of pressure drop becomes necessary as vapor split cannot be maintained at desirable valve and is completely determined by vapor phase hydrodynamics of the column.

Sangal et al (2013 b) presented their work on process parametric optimization of DWC. Rigorous simulations were done using the Multifrac model of ASEPN PLUS. Box Behnken Design (BBD) was used for the optimization of three process variables reflux rate, vapor split and liquid split. A comparison of the product purities for the C4, C5 and C6 mixture obtained by him in comparison to other researchers was presented.

**EDWC and thermally coupled Extractive Distillation Sequences**

Salvador Hernández (2008) compared three process of thermally coupled extractive distillation to separate water ethanol mixture, the three thermally coupled extractive distillation process involved the use of a side rectifier, side stripper, and fully thermally coupled columns. It was reported that out of the three processes studied the fully thermally coupled process required the least amount of energy for separating water ethanol azeotropic mixture.

Gutiérrez-Guerra et al (2009) presented design and optimization procedure for conventional extractive distillation sequence and a thermally coupled extractive distillation scheme. The design objective was minimization of energy consumption, leading to lesser $CO_2$ emissions. He also reported that the thermally coupled extractive distillation scheme outperformed the conventional extractive distillation in terms of operating cost, greenhouse emissions, control properties and thermodynamic efficiency.

Bravo et al (2010) presented a mutiobjective stochastic procedure to obtain optimal design of EDWC. The approach is based on the use of genetic algorithms to determine the design that

minimizes energy consumption and total annualized cost. They took 4 case studies to show the feasibility of performing extractive separations in dividing wall distillation columns. Their design had four objective functions the minimization of number of stages across both sides of wall, solvent flow and reboiler duty.

Kiss and Suszwalak (2012) extended the use of DWC to azeotropic and extractive distillation for bioethanol dehydration. Ethylene glycol and pentane were used as the mass separating agent. Comparison between conventional and the alternative DWC processes was presented. The results reported by him suggest that DWC saved 10-20% energy in comparison with conventional process and also the two novel process integration required lesser space.

Ignat and kiss (2012) presented their work on use of EDWC for bioethanol. Their process involved the use of just a single shell that was able to concentrate and dehydrate bioethanol in just a single step. They also presented a comparison between conventional method employed for bioethanol production and use of EDWC for the same. The results reported by them showed that EDWC was way ahead of conventional process in terms of both operating as well as investment cost.The rigorous simulations were carried out in Aspen Plus, and for a fair comparison all alternatives were optimized using the reliable sequential quadratic programming (SQP) method.

Li and Bai (2012) presented a new operation strategy for separation of ethanol–water by extractive distillation. A new extractive distillation strategy with three columns is suggested to produce anhydrous ethanol. The operation process and the column configurations were investigated by using process simulator ASEPN PLUS. The influence of the most important operational parameters was studied through sensitivity analysis. The results provided the optimal parameters to obtain an eligible ethanol product with minimum energy consumption.

Based on the review of the literature, the objectives of this study are set as (i) the simulation of EDWC for the separation of ethanol water mixture using ethylene glycol as a solvent and commercial simulation software ASPEN Plus (ii) investigation of the effect of structure and operational variables on the energy efficiency and product purities; and (iii) to propose a method based on relative importance of variables, for the optimization of an EDWC that will be fast and will require less number of simulation runs for optimization.

# Chapter-3

# *Problem Formulation and Solution Techniques*

Simulation of water ethanol mixture using ethylene glycol as solvent was carried out using ASEPN PLUS process simulator. Simulation of EDWC was a very challenging and tedious task as it involved a number of variables.

## 3.1 Problem Definition

Ethanol is without a shadow of doubt one of the most promising and sustainable biofuel alternatives to fossil fuels, being readily usable in the existing car engines and conveniently distributed within the current infrastructure. The present industrial scale production of ethanol relies on several processes, such as: corn-to-ethanol, sugarcane-to-ethanol, basic and integrated lignocellulosic biomass to ethanol. All these processes produce diluted ethanol in the range of 5-12% wt ethanol, which needs to be concentrated to 99-99.8% wt ethanol in order to meet the current international standards (ASTM D 4806 and EN 15376) for its use as a fuel. Due to the formation of the homogenous minimum boiling binary water ethanol azeotrope at 95.63% wt ethanol, the separation becomes highly complex in order to achieve the target purity. Generally, the first step involves the use of a pre concentrator in which ethanol concentration are raised from 5-12% wt to 92-93% wt and then in the second step bioethanol is dehydrated up to higher concentration above the water ethanol azeotrope concentration by the use of mass separating agent (MSA) or solvent. The steps mentioned above are carried out in sequence in three different distillation columns- a pre concentration distillation column (PDC), an extractive distillation column (EDC), a solvent recovery column (SRC). The use of these three different distillation columns will require huge amount of energy requirements and investment. A solution to overcome the high energy demands of conventional distillation is by using process intensification and integration techniques, such as thermally coupled distillation columns or dividing-wall columns (DWC). DWC is one of the best examples of proven process intensification technology in distillation, as it allows significantly lower investment and operating costs. As the $CO_2$ emissions are directly linked to the energy requirement DWC will contribute to lesser $CO_2$ emissions in environment. (Gadalla et al., 2006)

It has been reported in literature by various authors that use of DWC is not limited to separation of ternary mixtures, but DWC can also be used in azeotropic separations, extractive distillation and even reactive distillation.

In the present study use of Extractive Divided Wall Columns (EDWC) is presented for separating water ethanol mixture using ethylene glycol as the solvent. Conventionally water ethanol mixture is separated via extractive distillation requiring at least two columns a preconcentrator and a solvent recovery column. EDWC eliminates the use of extra column and performs water ethanol separation in just a single column.

### 3.2 Simulation of an EDWC

ASEPN PLUS, process simulator was used to carry out the steady state simulation of EDWC. Some initial estimates were required in order to carry out the rigorous simulation, so shortcut simulation was done first using the easy to use DSTWU models.

#### 3.2.1 Shortcut simulation of EDWC

Shortcut simulations for obtaining initial estimates for rigorous simulations were done using the DSTWU model available in the ASEPN PLUS library. DSTWU performs shortcut design calculations for two product distillation column. For specified recovery of light and heavy key components DSTWU estimate the minimum reflux ratio or the minimum number of stages. The feed and solvent conditions are given in Table 3.1.

**Table -3.1 Feed and solvent condition for shortcut simulation**

| | Total (kmol/h) | Components | Mole fraction | Temperature (°C) | Pressure (atm) | Fluid Package |
|---|---|---|---|---|---|---|
| Feed | 100 | Ethanol | 0.5 | 79 | 1 | NRTL |
| | | Water | 0.5 | | | |
| Solvent | 50 | Ethylene glycol | 1 | 25 | 1 | |

Figure 3.1 and Table 3.2 shows the schematic diagram of shortcut simulation and the result of the shortcut simulation respectively.

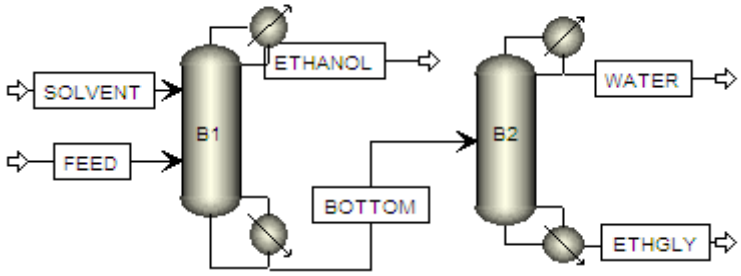


**Figure 3.1 Flow sheet of shortcut simulation**

**Table 3.2 Output of shortcut simulation**

| | Column 1 | Column 2 |
|---|---|---|
| No of stages | 20 | 25 |
| Reflux ratio | 3 | 1.5 |

### 3.2.2 Rigorous Simulation using RADFRAC

Rigorous simulation was done using the RADFRAC module available in ASEPN Plus. RADFRAC is the simulating model available in ASEPN Plus which is used for simulating all types of multi stage vapor-liquid separation operation. The operation in which RADFRAC module can be applied include

- Absorption
- Stripping
- Simple distillation
- Extractive distillation

Due to the non availability of DWC set up in the ASEPN Plus equipment library, a two column structure equivalent to the operation of DWC was implemented using the RADFRAC module of ASEPN Plus. The structure chosen from RADFRAC module were absorber and a distillation column. The structure implemented in ASEPN Plus for EDWC looked exactly as the petlyuk configuration as already shown in Figure 1.10. The absorber served as prefractionator and the distillation column as the main column. The schematic diagram of EDWC implemented in ASEPN Plus is given in Figure 3.2.

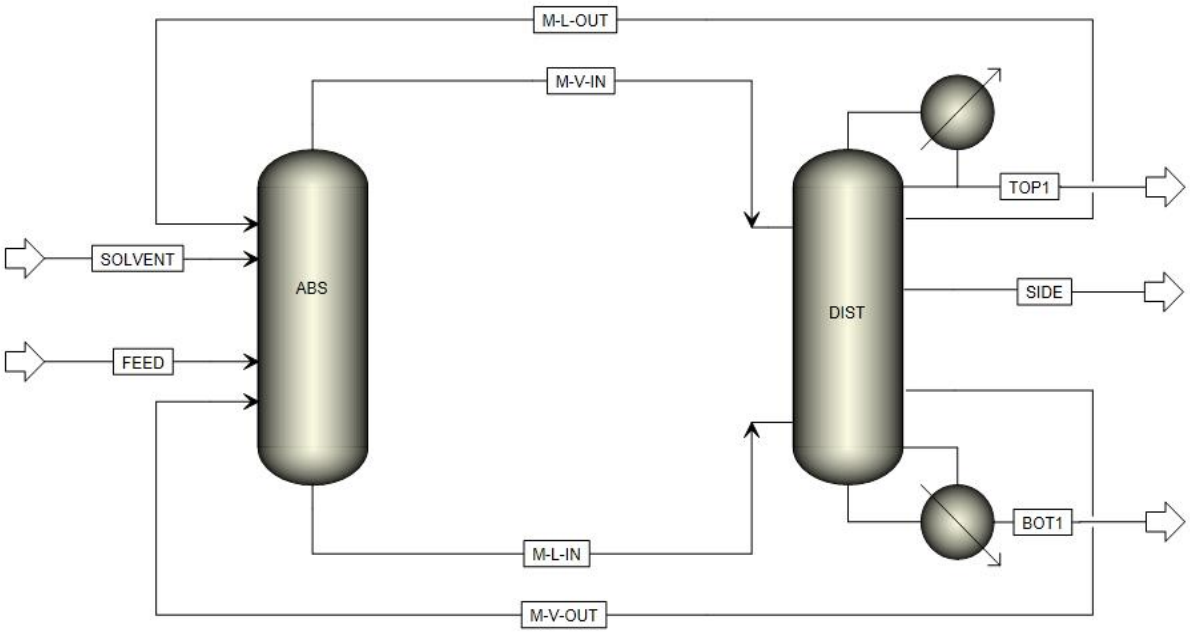


**Figure 3.2 Flow sheet of EDWC in two columns set up**

### 3.2.3 Specification sheets for Rigorous Simulation

The feed conditions were the same as used in shortcut simulation. The specification sheet indicating the temperature, pressure and feed distribution is shown in Figure 3.3.

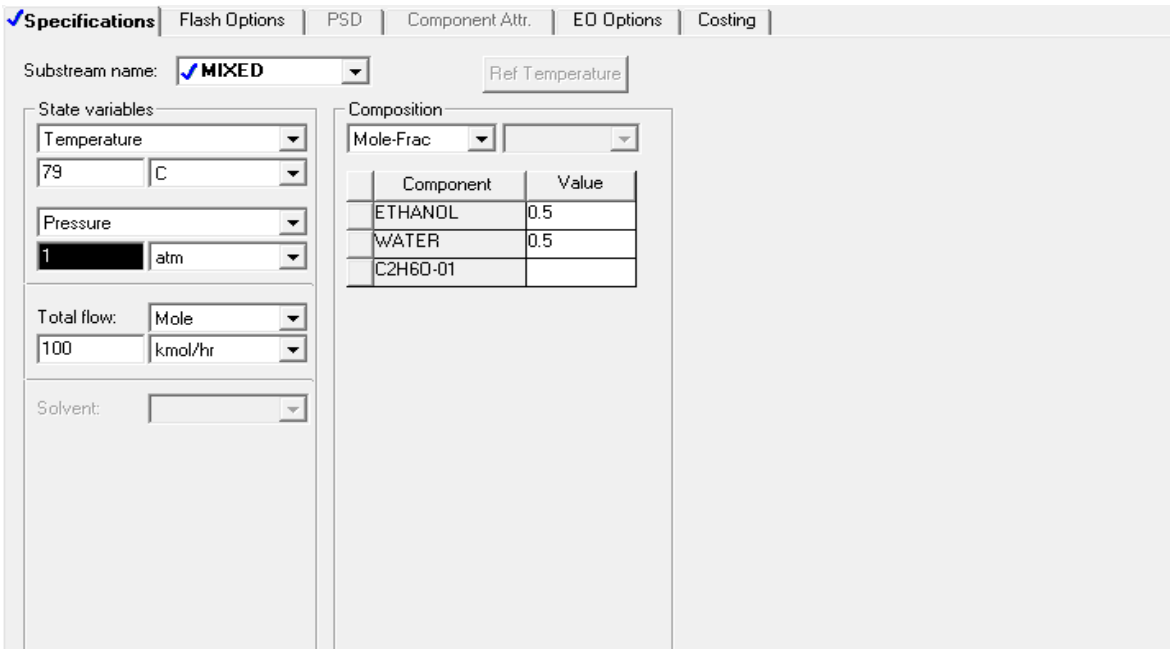


**Figure 3.3 Specification sheet for feed conditions**

Specification sheet indicating the solvent entering temperature and pressure is shown in Figure 3.4

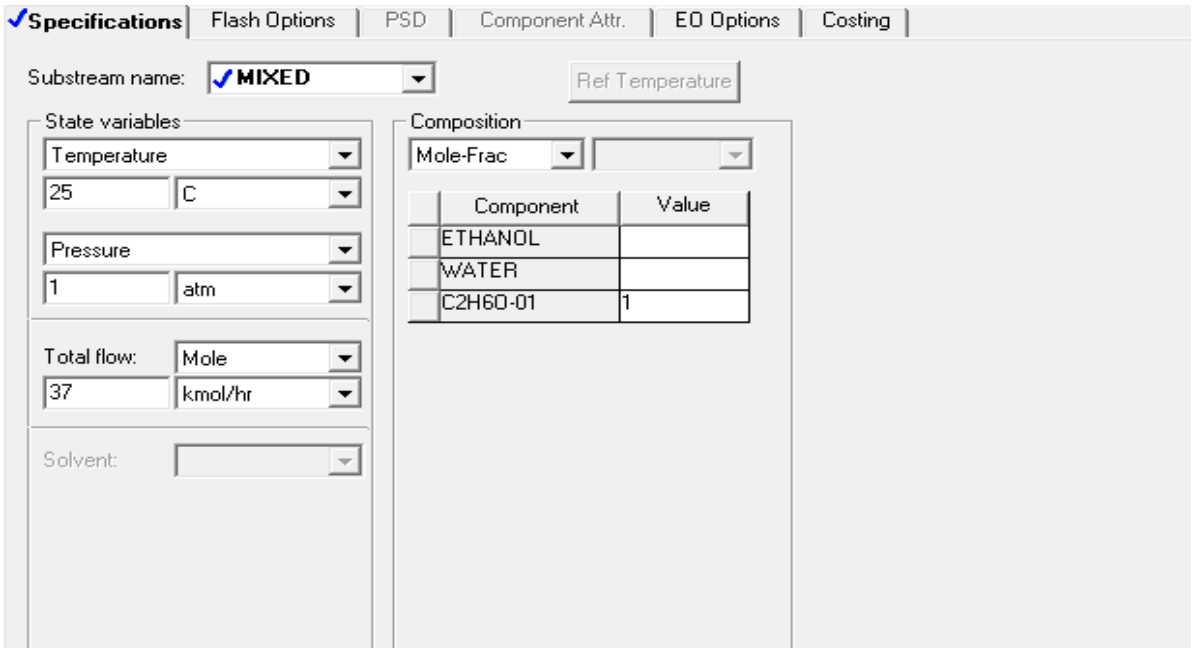


**Figure 3.4 Specification sheet for solvent**

**Prefractionator**- The absorber column taken from the RADFRAC module served as a prefractionator by selecting the condenser and reboiler options as none. The number of stages as

25 and calculation type as equilibrium was entered on the configuration tab obtained by double clicking on the absorber column. Figure 3.5 and 3.6 indicate the data entered on the configuration sheet and stream sheet of the prefractionator column respectively.

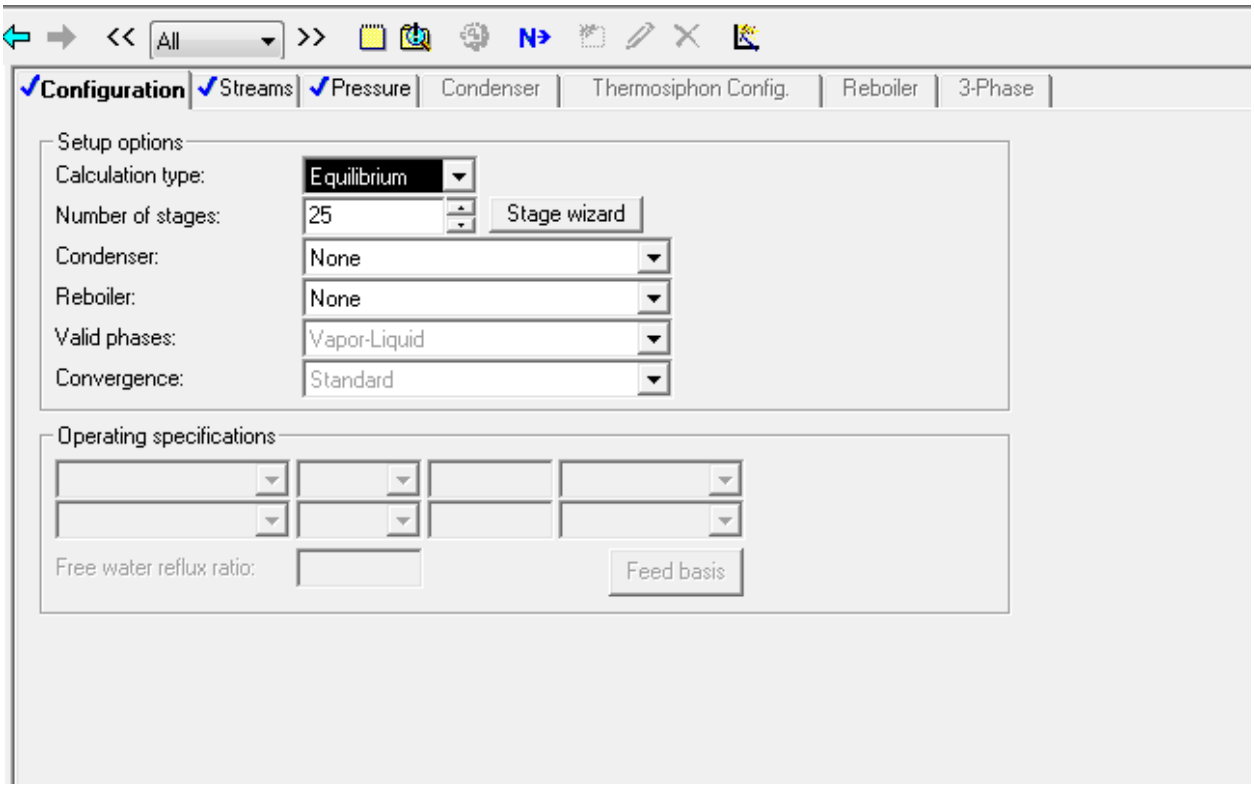


**Figure 3.5-Specification sheet for prefractionator (set up)**

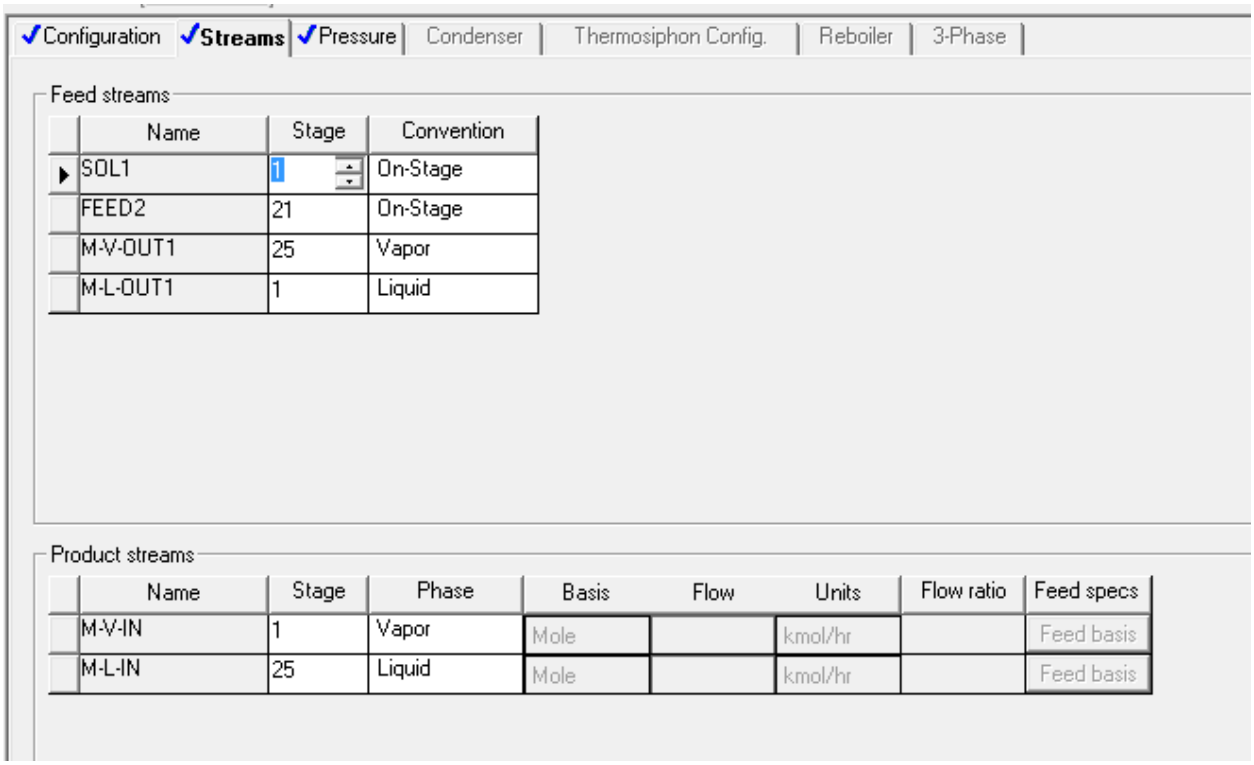


**Figure 3.6 Specification sheet for prefractionator (streams)**

**Main column**- The fractionator set up available in the RADFRAC module was chosen to represent the main column. Condenser type as total and reboiler type as kettle was selected in the configuration sheet of main column. Figure 3.7 and 3.8 indicate the data entered in the configuration sheet and stream sheet respectively.

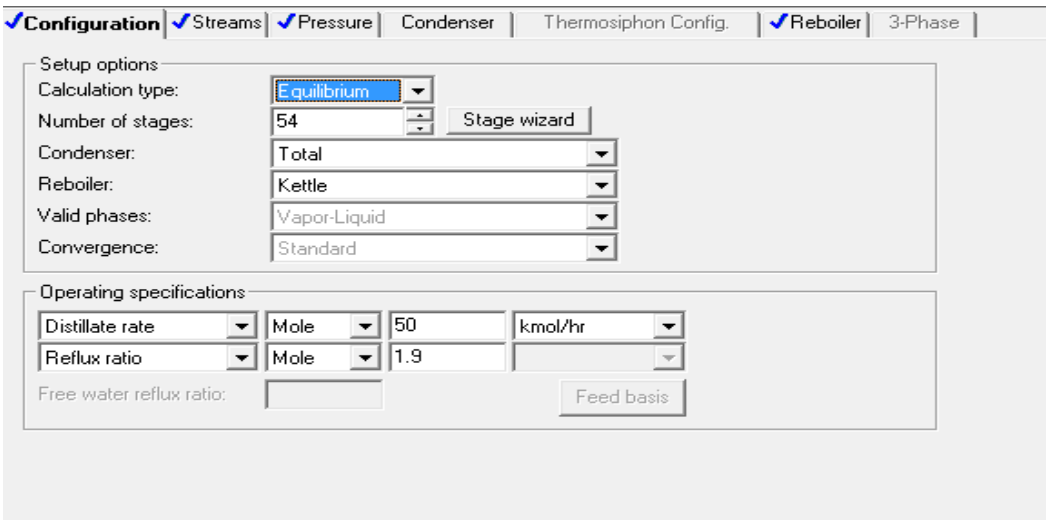


**Figure 3.7-Specification sheet for main column (set up)**

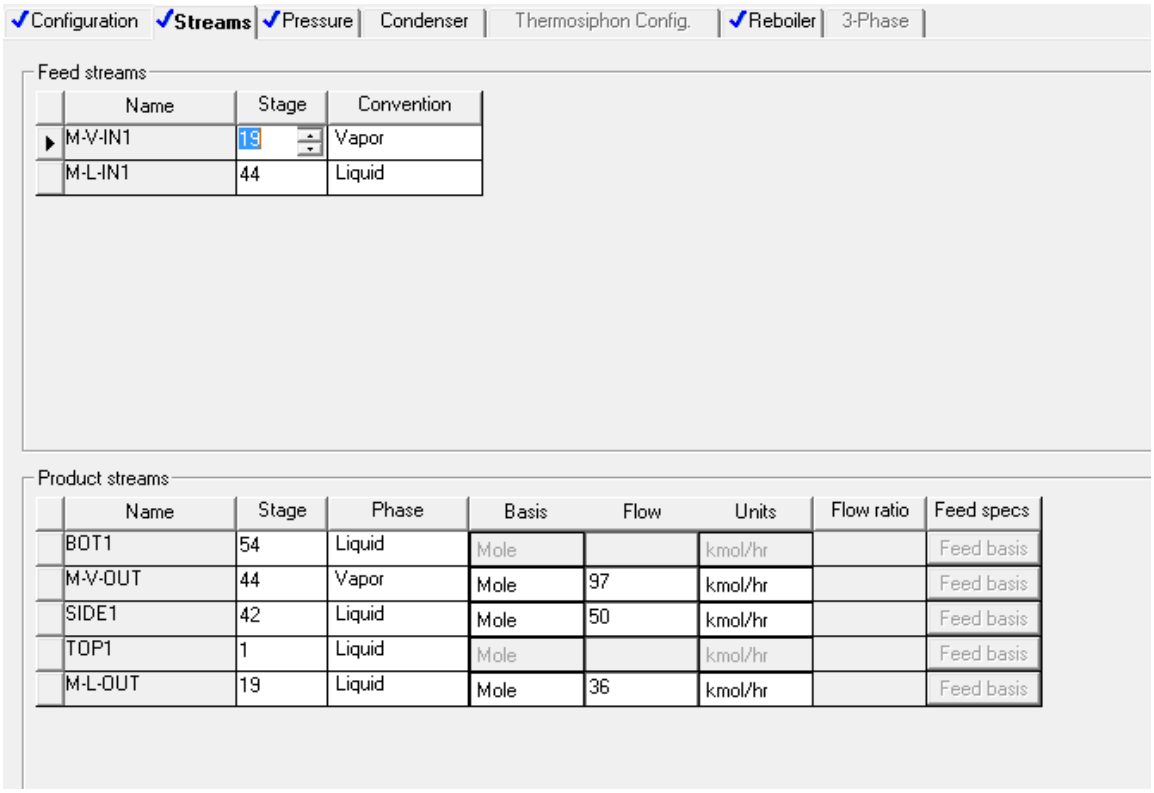


**Figure 3.8- Specification sheet for main column (streams)**

## 3.3 Equipment Sizing

### 3.3.1 Length

The tray spacing was chosen as 0.61m (2 ft). Height of the tower can be calculated if the numbers of trays are known. If the calculated number of stages are N, the number of stages is N+2, one for reboiler and the other for reflux drum. In addition to the space needed to accommodate the number of trays some space is needed at top where reflux enters the vessel and some space at column bottom for liquid hold up and to provide enough head to satisfy net positive suction head NPSH requirements of pump. A feasible design procedure is to provide 20% more length in addition to the length required to accommodate the number of trays.

$$H= 1.2*(0.61)*(N-2)$$

where H is the height of the column in metres. Table 3.3 reports the stages and height of prefractionator and main column.

**Table 3.3 Height of prefractionator and main column**

| Block | Stages | Height (metres) |
|---|---|---|
| Prefractionator | 25 | 16.8 |
| Main column | 54 | 38 |

### 3.3.2 Diameter

ASEPN PLUS has an easy to use tray sizing feature which was used to calculate the diameter of the column. The simulation steps involved for calculating the diameter are as follows. Firstly tray sizing feature is selected from the input library of column, then type of trays, tray spacing and number of trays are selected. After entering this data simulation is runned and diameter of column is reported by the software. The diameters reported for prefractionator and main columns are reported in the Table3.4. Steps followed while using the tray sizing feature of ASEPN PLUS are shown in Figure 3.9 and 3.10.

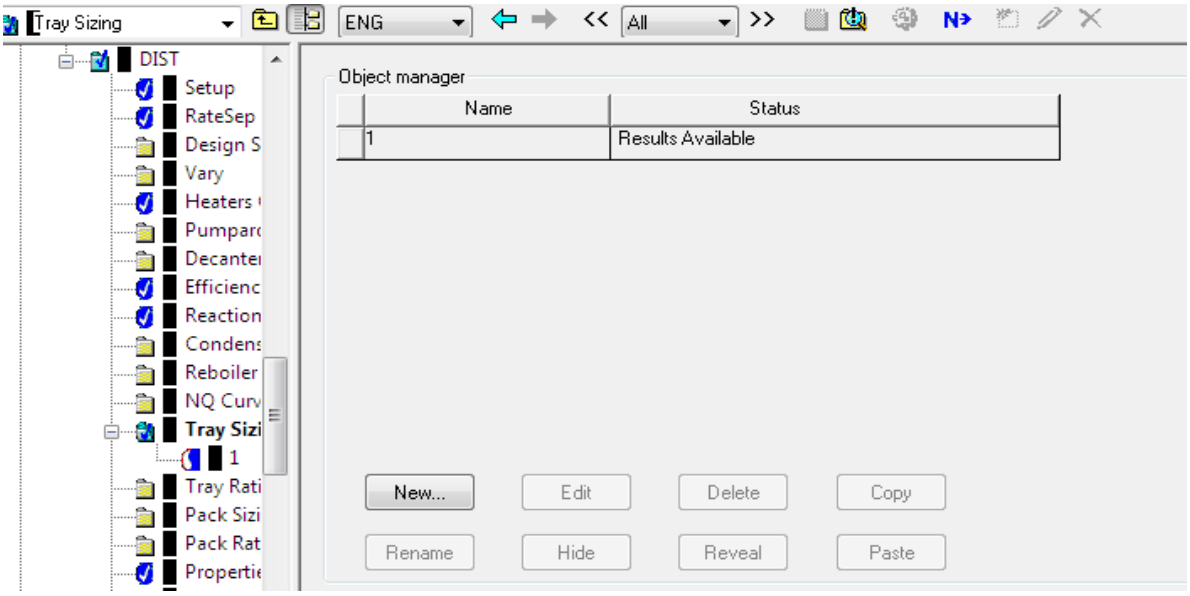


**Figure 3.9- Specification sheet for tray sizing (Main column)**

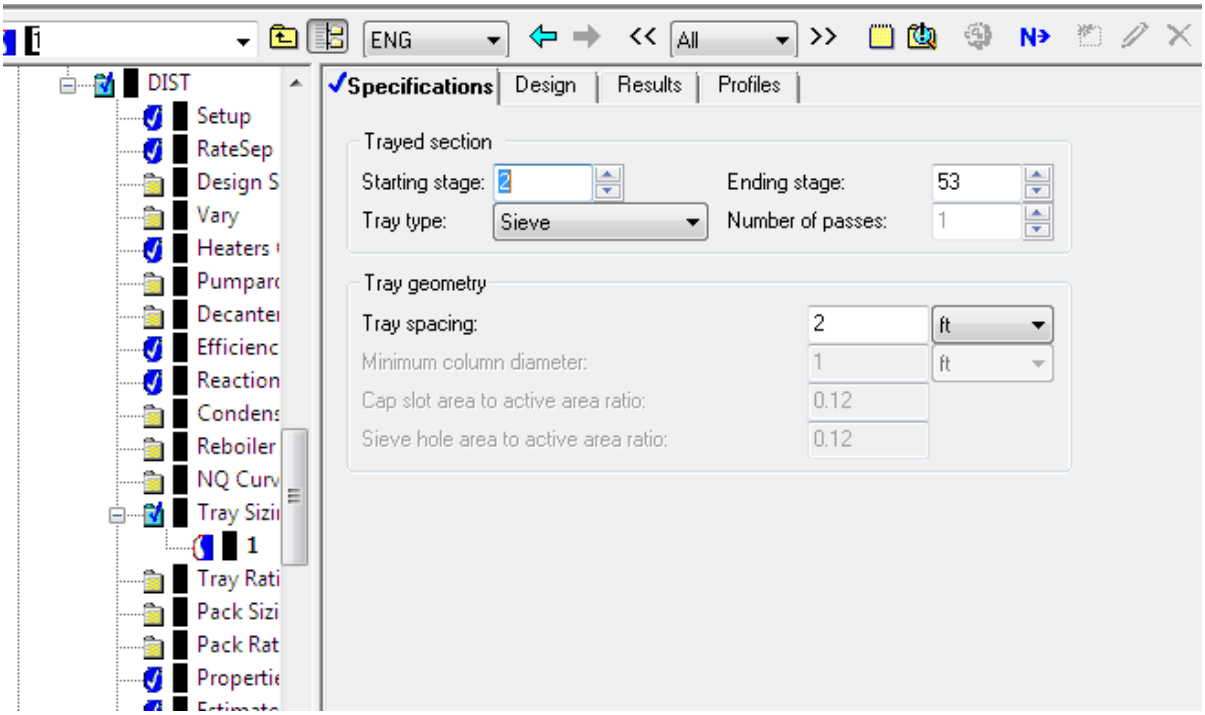


**Figure 3.10- Specification sheet tray sizing (type of tray)**

On the basis of tray spacing and tray type chosen, ASEPN PLUS calculates the diameter. The calculated diameters of prefractionator and main column are reported in Table 3.4.

**Table 3.4 Diameters of prefractionator and main column**

| Block | Diameter(metres) |
|---|---|
| Prefractionator | 0.71 |
| Main Column | 0.93 |

## 3.4 Optimization

Box–Behnken design (BBD) under response surface methodology (RSM) was used for the optimization of the process and structural parameters and to evaluate the effects of these parameters and their interactions on the energy efficiency of an EDWC.

### 3.4.1 Box- Behnken design

The best performance of a BBD depends on some prior information of the system being optimized. The BBD can optimize number of simulations or experimental runs which are

essential to be carried out to determine the possible inter-parametric interactions and their effects on the product quality and the energy efficiency of an EDWC. The BBD requires a simulation or experimental run according to $N = k^2 + k + c_p$, where, k is the factor number and $c_p$ is the replicate number of the central point (Ferreira et al., 2004). BBD is a spherical, revolving design; having a central point and the middle points of the boundaries of the cube circumscribed on the sphere.

To analyze a process or a system having a response X, where X depends on the input factors: $y_1$, $y_2$. . . $y_k$, the relationship between the response and the input process parameters is described as:

$X=f(y_1, y_2, \ldots\ldots, y_k) \pm\varepsilon$

where $f$ is the unknown but real response function with its format being unidentified, and ε is the residual error which describes the differentiation that can be included by the function $f$. Since the relationship between the response and the input parameters can be described as a surface of the $y_1$, $y_2$, . . ., $y_k$ coordinates in the graphical sense, the study of these relationships is named as the response surface methodology (RSM).

A second order polynomial Eq. (1) was used through non-linear regression to fit the simulated data and to recognize the relevant model terms. Considering all the linear terms, square terms and the linear by linear interaction terms, the quadratic response model can be described as:

$X=\beta_0+\Sigma\beta_i y_i+\Sigma\beta_{ii} y_i^2+\Sigma\Sigma_{i<j}\beta_{ij} y_i y_j+ \varepsilon$ ---------- (1)

where $\beta_0$ is the constant, $\beta_i$ the slope or linear effect of the input factor $y_i$, $\beta_{ij}$ the linear by linear interaction effect between the input factors $y_i$ and $y_j$, and $\beta_{ii}$ is the quadratic effect of input factor $y_i$ (Box and Hunter, 1957).

Five responses were being considered namely, purity of ethanol in distillate, purity of water in side product, purity of ethylene glycol at bottom, reboiler duty and $CO_2$ emissions. Since there were five responses being considered, multi-response process optimization by desirability function approach was used for the optimization of structural and process parameters of EDWC for the energy efficiency. The desirability function approach is one of the most extensively used methods in industry for the optimization of multiple response processes (Derringer and Suich, 1980).

One-sided desirability $d_i$ is given by:

$$d_i = \begin{cases} 0 & if \quad X_i \le X_{i-\min} \\ \left[\dfrac{X_i - X_{i-\min}}{X_{i-\max} - X_{i-\min}}\right]^r & if \quad X_{i-\min} < X_i < X_{i-\max} \\ 1 & if \quad X_i \ge X_{i-\max} \end{cases}$$

Where, $X_i$ is response values, $X_{i\text{-}min}$ and $X_{i\text{-}max}$ is minimum and maximum acceptable values of response *i*, and *r* is a weight and a positive constant, used to determine scale of desirability. The desirability, $d_i$ lies between 0 and 1 representing the nearness of a response to its ideal value.

In the multi-response process optimization, desirability function transforms each response to a corresponding desirability value between 0 and 1. All the desirability functions are joint to form a composite desirability function which converts multi-responses into a one single response. The individual desirability functions are combined in order to get the overall desirability De, as follows:

$$D_e = (d_1 \times d_2 \times d_3 \ldots\ldots)^{\frac{1}{m}}$$

Where, $0 \le D_e \le 1$and 'm' is the number of responses.

If all of the quality characteristics reach their ideal values, the desirability $d_i$ is 1 for all *i*. Consequently, the total desirability is also 1. If any one of the responses does not approach its ideal value, the desirability $d_i$ is less than 1 for that response and the total desirability is less than 1 (Sangal et al, 2013).

# Chapter –4

## *Results and Discussion*

This chapter presents the results and discussions of the simulation and optimization studies carried out for an EDWC using ethanol-water mixture as case studies. The main objective of the simulation studies was to maximize the purities of ethanol, water and ethylene glycol in top, side and bottom stream respectively and minimize the reboiler duty.

### 4.1 Simulation of an EDWC

The steady state simulation converged and then a number of simulation runs were performed to achieve the maximized purities. The operating condition of feed and result of the first simulation run using the initial estimates of the shortcut simulation are presented in the Table 4.1 and 4.2.

**Table 4.1- Operating parameters and feed conditions**

| **Parameters** | **Specification** |
|---|---|
| Feed pressure | 1 atm(saturated liquid) |
| Feed flowrate<br>Feed Composition(Mole fraction)<br>Feed entering stage | 100 kmol/h<br>Ethanol 0.5;Water 0.5;<br>17 |
| Solvent flow rate<br>Solvent entering stage | 50 kmol/h<br>1 |
| Stages in prefractionator | 20 |
| Stages in main column | 25 |
| Liquid split<br>Liquid split stage in main column | 30 kmol/h<br>3 |
| Vapor split<br>Vapor split stage in main column | 110 kmol/h<br>22 |
| Side product stage | 20 |
| Distillate flow rate | 50 kmol/h |
| Side product flowrate | 50 kmol/h |

**Table 4.2-Data obtained using initial estimates**

| | |
|---|---|
| Product purities | Ethanol (top) -0.82<br>Water (side) -0.81<br>Ethylene Glycol (bottom)-0.99 |
| Reboiler Duty | 1979 kW |
| Condenser Duty | 1580 kW |

The purities of ethanol water mixture obtained using the initial estimates was not sufficient according to industrial standards. The industrial standards require purity of ethanol to the extent of 99-99.8 %wt (Ignat and Kiss, 2012). A number of simulation runs were then performed in order to minimize reboiler duty and achieve maximum purity of product streams.

### 4.2 Optimization of an EDWC

A common difficulty related with rigorous simulation for optimization of an EDWC is the number of process and structural variables. These variables interact with each other and need to be optimized simultaneously for optimal operation and design. The optimization of an EDWC is a mixed integer non-linear programming problem, which cannot be solved with the existing commercial simulation software. The problem can be tackled only with the pairing of an external sub-routine/software for optimization with process simulators. In the present work, the structural and process parameters of an EDWC have been optimized simultaneously for the separation of a water ethanol mixture using ethylene glycol as solvent. The Aspen Plus software in combination with an external optimization technique (i.e., BBD under RSM) has been used to optimize total energy requirement of an EDWC.

A three level-nine factor BBD was used to estimate the effect of the structural and process parameters on the energy efficiency of an EDWC. Various ranges of values of structural and process variables were taken as the variables input parameters. In all a total of nine variables were taken five structural namely feed stage (F), side product stage (W), stages in main column (N), stage of liquid split (L), stage of vapor split (V) and four process variables namely solvent flowrate (*s*), reflux rate (*r*), liquid split (*l*) and vapor split (*v*). Extreme ranges of these nine variables were taken upto which the simulator showed converged simulation. A schematic

representation indicating the location of these nine variables on the EDWC set up implemented in ASEPN Plus in Petlyuk configuration is shown in Figure 4.1.

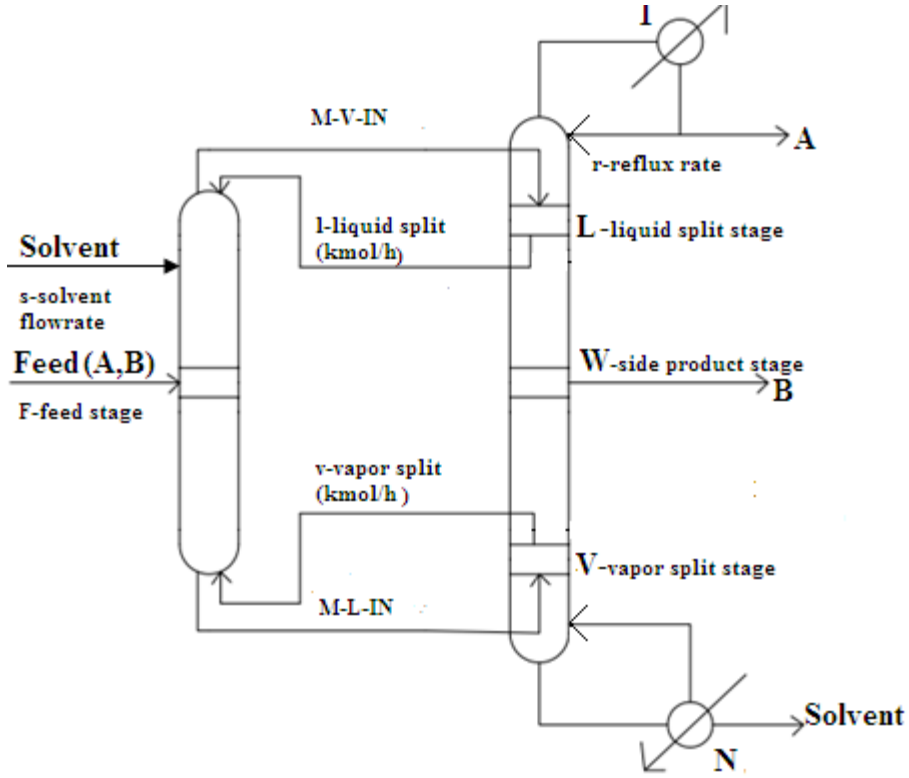


**Figure 4.1 Representation of variables on EDWC in Petlyuk Configuration**

Table 4.3 lists the experimental design levels of nine variables chosen.

**Table 4.3-Experimental design levels of chosen variables**

| **Variables** | **Low level(-1)** | **Middle level(0)** | **High level(+1)** |
|---|---|---|---|
| Feed stage location (F) | 17 | 22 | 27 |
| Side product location (W) | 34 | 39 | 44 |
| Liquid split stage (L) | 14 | 19 | 24 |
| Vapor split stage (V) | 45 | 48 | 51 |
| Stages in main column (N) | 52 | 57 | 62 |
| Liquid split (*l* kmol/h) | 28 | 34 | 40 |
| Vapor split (*v* kmol/h) | 85 | 105 | 125 |
| Reflux rate (*r* kmol/h) | 95 | 160 | 225 |
| Solvent Flow (*s* kmol/h) | 30 | 50 | 70 |

### 4.3 Model Fitting and Statistical Analysis

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

Simulations were done according to the design matrix obtained from Design software for further analysis. Five responses ethanol mole fraction at top (D), water mole fraction in side (W), ethylene glycol mole fraction at bottom (B), reboiler duty ($Q_b$), $CO_2$ emissions ($CO_2$) were noted for all simulations runs. Table 4.4 lists the simulation runs for the values of design matrix generated by Design Expert.

**Table 4.4-Simulation runs of values of design matrix**

| | | Variables y | | | | | | | | | Responses X | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Structural Variables | | | | | Process Variables | | | | | | | | |
| Std | Run | F | W | L | V | N | *l* | *v* | *r* | *s* | D | S | B | $Q_b$ | $CO_2$ |
| | | | | | | | | | | | | | | | |
| 7 | 1 | 17 | 39 | 19 | 51 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2692 | 306.8 |
| 15 | 2 | 22 | 34 | 19 | 48 | 62 | 34 | 105 | 225 | 50 | 0.9 | 0.9 | 0.99 | 3399 | 387.4 |
| 79 | 3 | 17 | 39 | 19 | 48 | 57 | 40 | 105 | 95 | 50 | 0.98 | 0.97 | 0.98 | 1977 | 225.3 |
| 37 | 4 | 22 | 39 | 19 | 45 | 52 | 40 | 105 | 160 | 50 | 0.97 | 0.97 | 0.99 | 2691 | 306.7 |
| 63 | 5 | 22 | 39 | 14 | 45 | 57 | 34 | 105 | 225 | 50 | 0.91 | 0.91 | 0.99 | 3398 | 387.2 |
| 31 | 6 | 17 | 34 | 24 | 48 | 57 | 34 | 105 | 160 | 50 | 0.9 | 0.9 | 0.99 | 2691 | 306.7 |
| 127 | 7 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 104 | 8 | 27 | 39 | 19 | 45 | 57 | 34 | 85 | 160 | 50 | 0.92 | 0.92 | 0.99 | 2690 | 306.6 |
| 49 | 9 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 66 | 10 | 22 | 39 | 24 | 51 | 57 | 34 | 105 | 225 | 50 | 0.9 | 0.9 | 0.99 | 3399 | 387.4 |
| 65 | 11 | 22 | 39 | 14 | 51 | 57 | 34 | 105 | 225 | 50 | 0.91 | 0.91 | 0.99 | 3398 | 387.2 |
| 44 | 12 | 22 | 39 | 19 | 48 | 57 | 34 | 125 | 225 | 30 | 0.86 | 0.86 | 0.99 | 3242 | 369.5 |
| 12 | 13 | 22 | 44 | 19 | 48 | 62 | 34 | 105 | 95 | 50 | 0.91 | 0.91 | 0.99 | 1980 | 225.6 |
| 101 | 14 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 121 | 15 | 22 | 39 | 14 | 48 | 57 | 40 | 105 | 160 | 30 | 0.89 | 0.89 | 0.99 | 2531 | 288.4 |
| 110 | 16 | 27 | 39 | 19 | 51 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2692 | 306.8 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 115 | 17 | 22 | 34 | 19 | 48 | 52 | 34 | 105 | 225 | 50 | 0.9 | 0.9 | 0.99 | 3399 | 387.4 |
| 70 | 18 | 22 | 44 | 19 | 48 | 57 | 40 | 85 | 160 | 50 | 0.96 | 0.96 | 0.99 | 2692 | 306.8 |
| 120 | 19 | 22 | 39 | 24 | 48 | 57 | 28 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2534 | 288.8 |
| 52 | 20 | 27 | 39 | 19 | 48 | 52 | 34 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2533 | 288.7 |
| 117 | 21 | 22 | 34 | 19 | 48 | 62 | 34 | 105 | 225 | 50 | 0.9 | 0.9 | 0.99 | 3399 | 387.4 |
| 128 | 22 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 39 | 23 | 22 | 39 | 19 | 45 | 62 | 40 | 105 | 160 | 50 | 0.97 | 0.97 | 0.99 | 2691 | 306.7 |
| 19 | 24 | 22 | 39 | 14 | 48 | 57 | 40 | 105 | 160 | 30 | 0.89 | 0.89 | 0.99 | 2531 | 288.4 |
| 58 | 25 | 27 | 39 | 19 | 48 | 62 | 34 | 105 | 160 | 70 | 0.97 | 0.97 | 0.99 | 2852 | 325 |
| 8 | 26 | 27 | 39 | 19 | 51 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2692 | 306.8 |
| 4 | 27 | 27 | 39 | 19 | 51 | 57 | 34 | 85 | 160 | 50 | 0.96 | 0.96 | 0.99 | 2690 | 306.6 |
| 50 | 28 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 42 | 29 | 22 | 39 | 19 | 48 | 57 | 34 | 125 | 95 | 30 | 0.83 | 0.82 | 0.98 | 1820 | 207.4 |
| 67 | 30 | 22 | 34 | 19 | 48 | 57 | 28 | 85 | 160 | 50 | 0.96 | 0.95 | 0.99 | 2690 | 306.6 |
| 73 | 31 | 22 | 34 | 19 | 48 | 57 | 40 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2693 | 306.9 |
| 69 | 32 | 22 | 34 | 19 | 48 | 57 | 40 | 85 | 160 | 50 | 0.95 | 0.94 | 0.99 | 2690 | 306.6 |
| 38 | 33 | 22 | 39 | 19 | 51 | 52 | 40 | 105 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2693 | 306.9 |
| 27 | 34 | 17 | 34 | 14 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 84 | 35 | 27 | 39 | 19 | 48 | 57 | 40 | 105 | 225 | 50 | 0.96 | 0.96 | 0.99 | 3395 | 386.9 |
| 105 | 36 | 17 | 39 | 19 | 51 | 57 | 34 | 85 | 160 | 50 | 0.96 | 0.96 | 0.99 | 2690 | 306.6 |
| 107 | 37 | 17 | 39 | 19 | 45 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2692 | 306.8 |
| 111 | 38 | 22 | 34 | 19 | 48 | 52 | 34 | 105 | 95 | 50 | 0.91 | 0.9 | 0.99 | 1980 | 225.6 |
| 94 | 39 | 22 | 39 | 24 | 48 | 52 | 34 | 85 | 160 | 50 | 0.95 | 0.95 | 0.99 | 2690 | 306.6 |
| 62 | 40 | 22 | 39 | 24 | 51 | 57 | 34 | 105 | 95 | 50 | 0.91 | 0.9 | 0.99 | 1980 | 225.6 |
| 77 | 41 | 17 | 39 | 19 | 48 | 57 | 28 | 105 | 95 | 50 | 0.86 | 0.85 | 0.99 | 1981 | 225.8 |
| 71 | 42 | 22 | 34 | 19 | 48 | 57 | 28 | 125 | 160 | 50 | 0.85 | 0.84 | 0.99 | 2690 | 306.6 |
| 6 | 43 | 27 | 39 | 19 | 45 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.84 | 0.99 | 2690 | 306.6 |
| 56 | 44 | 27 | 39 | 19 | 48 | 52 | 34 | 105 | 160 | 70 | 0.97 | 0.97 | 0.99 | 2852 | 325 |
| 80 | 45 | 27 | 39 | 19 | 48 | 57 | 40 | 105 | 95 | 50 | 0.99 | 0.97 | 0.98 | 1978 | 225.4 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 116 | 46 | 22 | 44 | 19 | 48 | 52 | 34 | 105 | 225 | 50 | 0.91 | 0.91 | 0.99 | 3398 | 387.2 |
| 11 | 47 | 22 | 34 | 19 | 48 | 62 | 34 | 105 | 95 | 50 | 0.91 | 0.9 | 0.99 | 1980 | 225.6 |
| 96 | 48 | 22 | 39 | 24 | 48 | 62 | 34 | 85 | 160 | 50 | 0.95 | 0.95 | 0.99 | 2690 | 306.6 |
| 108 | 49 | 27 | 39 | 19 | 45 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.84 | 0.99 | 2690 | 306.6 |
| 92 | 50 | 22 | 44 | 19 | 51 | 57 | 34 | 105 | 160 | 70 | 0.98 | 0.97 | 0.99 | 2852 | 325 |
| 83 | 51 | 17 | 39 | 19 | 48 | 57 | 40 | 105 | 225 | 50 | 0.96 | 0.96 | 0.99 | 3395 | 386.9 |
| 61 | 52 | 22 | 39 | 14 | 51 | 57 | 34 | 105 | 95 | 50 | 0.91 | 0.91 | 0.99 | 1980 | 225.6 |
| 59 | 53 | 22 | 39 | 14 | 45 | 57 | 34 | 105 | 95 | 50 | 0.91 | 0.91 | 0.99 | 1980 | 225.6 |
| 97 | 54 | 22 | 39 | 14 | 48 | 52 | 34 | 125 | 160 | 50 | 0.84 | 0.84 | 0.99 | 2693 | 306.9 |
| 9 | 55 | 22 | 34 | 19 | 48 | 52 | 34 | 105 | 95 | 50 | 0.91 | 0.9 | 0.99 | 1980 | 225.6 |
| 10 | 56 | 22 | 44 | 19 | 48 | 52 | 34 | 105 | 95 | 50 | 0.91 | 0.91 | 0.99 | 1980 | 225.6 |
| 1 | 57 | 17 | 39 | 19 | 45 | 57 | 34 | 85 | 160 | 50 | 0.96 | 0.96 | 0.99 | 2690 | 306.6 |
| 22 | 58 | 22 | 39 | 24 | 48 | 57 | 28 | 105 | 160 | 70 | 0.93 | 0.92 | 0.99 | 2850 | 324.8 |
| 2 | 59 | 27 | 39 | 19 | 45 | 57 | 34 | 85 | 160 | 50 | 0.92 | 0.92 | 0.99 | 2690 | 306.6 |
| 51 | 60 | 17 | 39 | 19 | 48 | 52 | 34 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2533 | 288.7 |
| 119 | 61 | 22 | 39 | 14 | 48 | 57 | 28 | 105 | 160 | 30 | 0.85 | 0.85 | 0.99 | 2534 | 288.8 |
| 123 | 62 | 22 | 39 | 14 | 48 | 57 | 28 | 105 | 160 | 70 | 0.94 | 0.94 | 0.99 | 2850 | 324.8 |
| 125 | 63 | 22 | 39 | 14 | 48 | 57 | 40 | 105 | 160 | 70 | 0.98 | 0.97 | 0.99 | 2852 | 325 |
| 100 | 64 | 22 | 39 | 24 | 48 | 62 | 34 | 125 | 160 | 50 | 0.86 | 0.85 | 0.99 | 2691 | 306.7 |
| 35 | 65 | 22 | 39 | 19 | 45 | 62 | 28 | 105 | 160 | 50 | 0.87 | 0.86 | 0.99 | 2693 | 306.9 |
| 106 | 66 | 27 | 39 | 19 | 51 | 57 | 34 | 85 | 160 | 50 | 0.96 | 0.96 | 0.99 | 2690 | 306.6 |
| 122 | 67 | 22 | 39 | 24 | 48 | 57 | 40 | 105 | 160 | 30 | 0.89 | 0.89 | 0.99 | 2531 | 288.4 |
| 40 | 68 | 22 | 39 | 19 | 51 | 62 | 40 | 105 | 160 | 50 | 0.97 | 0.97 | 0.99 | 2691 | 306.7 |
| 45 | 69 | 22 | 39 | 19 | 48 | 57 | 34 | 85 | 95 | 70 | 0.96 | 0.96 | 0.99 | 2144 | 244.3 |
| 21 | 70 | 22 | 39 | 14 | 48 | 57 | 28 | 105 | 160 | 70 | 0.94 | 0.94 | 0.99 | 2850 | 324.8 |
| 87 | 71 | 22 | 34 | 19 | 51 | 57 | 34 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2533 | 288.7 |
| 91 | 72 | 22 | 34 | 19 | 51 | 57 | 34 | 105 | 160 | 70 | 0.96 | 0.96 | 0.99 | 2851 | 324.9 |
| 124 | 73 | 22 | 39 | 24 | 48 | 57 | 28 | 105 | 160 | 70 | 0.93 | 0.92 | 0.99 | 2850 | 324.8 |
| 72 | 74 | 22 | 44 | 19 | 48 | 57 | 28 | 125 | 160 | 50 | 0.85 | 0.84 | 0.99 | 2690 | 306.6 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 23 | 75 | 22 | 39 | 14 | 48 | 57 | 40 | 105 | 160 | 70 | 0.98 | 0.97 | 0.99 | 2852 | 325 |
| 48 | 76 | 22 | 39 | 19 | 48 | 57 | 34 | 125 | 225 | 70 | 0.87 | 0.86 | 0.99 | 3563 | 406 |
| 24 | 77 | 22 | 39 | 24 | 48 | 57 | 40 | 105 | 160 | 70 | 0.96 | 0.96 | 0.99 | 2851 | 324.9 |
| 16 | 78 | 22 | 44 | 19 | 48 | 62 | 34 | 105 | 225 | 50 | 0.91 | 0.91 | 0.99 | 3398 | 387.2 |
| 33 | 79 | 22 | 39 | 19 | 45 | 52 | 28 | 105 | 160 | 50 | 0.87 | 0.86 | 0.99 | 2693 | 306.9 |
| 29 | 80 | 17 | 44 | 14 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 30 | 81 | 27 | 44 | 14 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 57 | 82 | 17 | 39 | 19 | 48 | 62 | 34 | 105 | 160 | 70 | 0.97 | 0.97 | 0.99 | 2852 | 325 |
| 102 | 83 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 28 | 84 | 27 | 34 | 14 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 109 | 85 | 17 | 39 | 19 | 51 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2692 | 306.8 |
| 114 | 86 | 22 | 44 | 19 | 48 | 62 | 34 | 105 | 95 | 50 | 0.91 | 0.91 | 0.99 | 1980 | 225.6 |
| 95 | 87 | 22 | 39 | 14 | 48 | 62 | 34 | 85 | 160 | 50 | 0.97 | 0.83 | 0.99 | 2683 | 305.8 |
| 126 | 88 | 22 | 39 | 24 | 48 | 57 | 40 | 105 | 160 | 70 | 0.96 | 0.96 | 0.99 | 2851 | 324.9 |
| 3 | 89 | 17 | 39 | 19 | 51 | 57 | 34 | 85 | 160 | 50 | 0.96 | 0.96 | 0.99 | 2690 | 306.6 |
| 34 | 90 | 22 | 39 | 19 | 51 | 52 | 28 | 105 | 160 | 50 | 0.85 | 0.84 | 0.99 | 2691 | 306.7 |
| 14 | 91 | 22 | 44 | 19 | 48 | 52 | 34 | 105 | 225 | 50 | 0.91 | 0.91 | 0.99 | 3399 | 387.4 |
| 55 | 92 | 17 | 39 | 19 | 48 | 52 | 34 | 105 | 160 | 70 | 0.97 | 0.97 | 0.99 | 2852 | 325 |
| 26 | 93 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 78 | 94 | 27 | 39 | 19 | 48 | 57 | 28 | 105 | 95 | 50 | 0.86 | 0.85 | 0.99 | 1981 | 225.8 |
| 17 | 95 | 22 | 39 | 14 | 48 | 57 | 28 | 105 | 160 | 30 | 0.85 | 0.85 | 0.99 | 2534 | 288.8 |
| 74 | 96 | 22 | 44 | 19 | 48 | 57 | 40 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2693 | 306.9 |
| 113 | 97 | 22 | 34 | 19 | 48 | 62 | 34 | 105 | 95 | 50 | 0.91 | 0.9 | 0.99 | 1980 | 225.6 |
| 81 | 98 | 17 | 39 | 19 | 48 | 57 | 28 | 105 | 225 | 50 | 0.88 | 0.87 | 0.99 | 3402 | 387.7 |
| 103 | 99 | 17 | 39 | 19 | 45 | 57 | 34 | 85 | 160 | 50 | 0.96 | 0.96 | 0.99 | 2690 | 306.6 |
| 86 | 100 | 22 | 44 | 19 | 45 | 57 | 34 | 105 | 160 | 30 | 0.88 | 0.87 | 0.99 | 2529 | 288.2 |
| 82 | 101 | 27 | 39 | 19 | 48 | 57 | 28 | 105 | 225 | 50 | 0.88 | 0.87 | 0.99 | 3402 | 387.7 |
| 85 | 102 | 22 | 34 | 19 | 45 | 57 | 34 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2533 | 288.7 |
| 20 | 103 | 22 | 39 | 24 | 48 | 57 | 40 | 105 | 160 | 30 | 0.89 | 0.88 | 0.99 | 2531 | 288.4 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 68 | 104 | 22 | 44 | 19 | 48 | 57 | 28 | 85 | 160 | 50 | 0.97 | 0.97 | 0.99 | 2691 | 306.7 |
| 75 | 105 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 18 | 106 | 22 | 39 | 24 | 48 | 57 | 28 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2533 | 288.7 |
| 53 | 107 | 17 | 39 | 19 | 48 | 62 | 34 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2534 | 288.8 |
| 118 | 108 | 22 | 44 | 19 | 48 | 62 | 34 | 105 | 225 | 50 | 0.91 | 0.91 | 0.99 | 3399 | 387.4 |
| 93 | 109 | 22 | 39 | 14 | 48 | 52 | 34 | 85 | 160 | 50 | 0.97 | 0.96 | 0.99 | 2690 | 306.6 |
| 13 | 110 | 22 | 34 | 19 | 48 | 52 | 34 | 105 | 225 | 50 | 0.9 | 0.9 | 0.99 | 3399 | 387.4 |
| 32 | 111 | 17 | 44 | 24 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 64 | 112 | 22 | 39 | 24 | 45 | 57 | 34 | 105 | 225 | 50 | 0.87 | 0.86 | 0.99 | 3402 | 387.7 |
| 25 | 113 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 54 | 114 | 27 | 39 | 19 | 48 | 62 | 34 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2534 | 288.8 |
| 41 | 115 | 22 | 39 | 19 | 48 | 57 | 34 | 85 | 95 | 30 | 0.98 | 0.97 | 0.99 | 1824 | 207.9 |
| 60 | 116 | 22 | 39 | 24 | 45 | 57 | 34 | 105 | 95 | 50 | 0.84 | 0.83 | 0.99 | 1982 | 225.9 |
| 89 | 117 | 22 | 34 | 19 | 45 | 57 | 34 | 105 | 160 | 70 | 0.96 | 0.96 | 0.99 | 2851 | 324.9 |
| 98 | 118 | 22 | 39 | 24 | 48 | 52 | 34 | 125 | 160 | 50 | 0.86 | 0.85 | 0.99 | 2691 | 306.7 |
| 88 | 119 | 22 | 44 | 19 | 51 | 57 | 34 | 105 | 160 | 30 | 0.86 | 0.86 | 0.99 | 2534 | 288.8 |
| 43 | 120 | 22 | 39 | 19 | 48 | 57 | 34 | 85 | 225 | 30 | 0.95 | 0.95 | 0.99 | 3234 | 368.5 |
| 46 | 121 | 22 | 39 | 19 | 48 | 57 | 34 | 125 | 95 | 70 | 0.83 | 0.82 | 0.99 | 2138 | 243.6 |
| 90 | 122 | 22 | 44 | 19 | 45 | 57 | 34 | 105 | 160 | 70 | 0.98 | 0.97 | 0.99 | 2843 | 324 |
| 76 | 123 | 22 | 39 | 19 | 48 | 57 | 34 | 105 | 160 | 50 | 0.91 | 0.91 | 0.99 | 2690 | 306.6 |
| 36 | 124 | 22 | 39 | 19 | 51 | 62 | 28 | 105 | 160 | 50 | 0.87 | 0.86 | 0.99 | 2693 | 306.9 |
| 99 | 125 | 22 | 39 | 14 | 48 | 62 | 34 | 125 | 160 | 50 | 0.84 | 0.84 | 0.99 | 2693 | 306.9 |
| 5 | 126 | 17 | 39 | 19 | 45 | 57 | 34 | 125 | 160 | 50 | 0.85 | 0.85 | 0.99 | 2692 | 306.8 |
| 47 | 127 | 22 | 39 | 19 | 48 | 57 | 34 | 85 | 225 | 70 | 0.94 | 0.94 | 0.99 | 3558 | 405.5 |
| 112 | 128 | 22 | 44 | 19 | 48 | 52 | 34 | 105 | 95 | 50 | 0.91 | 0.91 | 0.99 | 1980 | 225.6 |

*F-feed stage, W-side product stage, L- liquid split stage, V- vapor split stage, N-Number of stages in main column, *l*- liquid split(kmol/h), *v*- vapor split(kmol/h), *r*-reflux rate(kmol/h), *s*-moles of solvent(kmol/h).

*D- mole fraction of ethanol in distillate, S- mole fraction of water in side product, B- mole fraction of ethylene glycol in bottom product, $Q_b$- reboiler Duty (kW), $CO_2$- Carbon dioxide emissions (kg/h).

The simulated data were fitted to the second-order polynomial, Eq (1) using a manual repression method and the significant model terms were recognized. For selecting the best model, the sequential F-test and other adequacy measures were used (Muthukumar et al., 2003).

The p values for all the regressions were found to be less than 0.01. This means that at least one of the terms in the regression equation had a significant correlation with the response variable. Two different tests, as sequential model sum of squares and model summary statistics were carried out to determine the adequacy of the model for product quality and the energy efficiency of an EDWC.

The model F values for D, S, B, $Q_b$ and $CO_2$ were 6.65, 5.54, 1.8, 81049.15and 172225.60 respectively which implied that the models were significant. The value of adequate precision for D, S, B, $Q_b$, $CO_2$ were 12.96, 12.068, 8.137, 1206, 1762 and adequate precision ratios above 4 were reported for all models, indicating adequate model efficacy and model can be used to navigate design space. Coefficient of regression ($R^2$) for D, S, B, $Q_b$, and $CO_2$ were 0.83, 0.80, 0.77, 0.99 and0.99 respectively. Table 4.5 and 4.6 show the sequential model sum of squares and model summary statistics test for $Q_b$ (reboiler duty).

**Table 4.5 Sequential Model Sum of Squares for Reboiler Duty**

| Sequential Model Sum of Squares | | | | | | |
|---|---|---|---|---|---|---|
| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
| Mean | 342387.6 | 1 | 342387.6 | | | |
| Linear | 2000.913 | 9 | 222.3236 | 4023.104 | < 0.0001 | |
| 2FI | 0.370125 | 36 | 0.010281 | 0.137066 | 1.0000 | |
| Quadratic | 6.117275 | 9 | 0.679697 | 1481.917 | < 0.0001 | Suggested |
| Cubic | 0.031332 | 38 | 0.000825 | 13.42394 | < 0.0001 | Aliased |
| Residual | 0.00215 | 35 | 6.14E-05 | | | |
| Total | 344395 | 128 | 2690.586 | | | |

**Table 4.6- Model summary statics for Reboiler Duty**

| Source | Std. Dev. | R-Squared | Adjusted R-Squared | Predicted R-Squared | PRESS | | |
|---|---|---|---|---|---|---|---|
| Linear | 0.235078 | 0.996752 | 0.996504 | 0.996148 | 7.73240351 | | |
| 2FI | 0.273878 | 0.996936 | 0.995255 | 0.99128 | 17.5047201 | | |
| Quadratic | 0.021416 | 0.999983 | 0.999971 | 0.999922 | 0.15735568 | Suggested | |
| Cubic | 0.007837 | 0.999999 | 0.999996 | | | Aliased | |

ANOVA for mole fraction of ethanol in distillate i.e. Response D, Mole fraction of water in side product i.e. Response S, for reboiler duty i.e. Response $Q_b$ and $CO_2$ emissions i.e. Response $CO_2$ are presented in Table 4.7-4.10 respectively.

**Table 4.7 ANOVA for response surface quadratic model (For mole fraction of ethanol in distillate)**

| | Sum of | | Mean | F | | |
|---|---|---|---|---|---|---|
| Source | Squares | DF | Square | Value | Prob > F | |
| Model | 0.209166558 | 54 | 0.003873455 | 6.648485481 | < 0.0001 | Significant |
| F | 0.000117523 | 1 | 0.000117523 | 0.20171921 | 0.6547 | |
| W | 0.000469444 | 1 | 0.000469444 | 0.805765075 | 0.3723 | |
| L | 0.000749136 | 1 | 0.000749136 | 1.2858339 | 0.2605 | |
| V | 1E-05 | 1 | 1E-05 | 0.017164226 | 0.8961 | |
| N | 0.00049 | 1 | 0.00049 | 0.841047096 | 0.3621 | |
| *L* | 0.0235225 | 1 | 0.0235225 | 40.37455167 | < 0.0001 | Highly significant |
| *v* | 0.11236 | 1 | 0.11236 | 192.8572484 | < 0.0001 | Highly significant |
| *r* | 2.5E-06 | 1 | 2.5E-06 | 0.004291057 | 0.9480 | |
| *s* | 0.05476 | 1 | 0.05476 | 93.99130406 | < 0.0001 | Highly significant |

| | | | | | | |
|---|---|---|---|---|---|---|
| $F^2$ | 0.000255447 | 1 | 0.000255447 | 0.438454767 | 0.5100 | |
| $W^2$ | 4.24776E-05 | 1 | 4.24776E-05 | 0.072909466 | 0.7879 | |
| $L^2$ | 0.000399406 | 1 | 0.000399406 | 0.685549331 | 0.4104 | |
| $V^2$ | 0.00079413 | 1 | 0.00079413 | 1.363063148 | 0.2468 | |
| $N^2$ | 2.11891E-05 | 1 | 2.11891E-05 | 0.036369409 | 0.8493 | |
| $l^2$ | 0.000171079 | 1 | 0.000171079 | 0.293643495 | 0.5895 | |
| $v^2$ | 0.001031042 | 1 | 0.001031042 | 1.769703866 | 0.1876 | |
| $r^2$ | 0.000110196 | 1 | 0.000110196 | 0.189143645 | 0.6649 | |
| $s^2$ | 0.000524571 | 1 | 0.000524571 | 0.900386279 | 0.3458 | |
| FW | 1.5873E-06 | 1 | 1.5873E-06 | 0.00272448 | 0.9585 | |
| FL | 3.73754E-07 | 1 | 3.73754E-07 | 0.00064152 | 0.9799 | |
| FV | 0.0004 | 1 | 0.0004 | 0.686569058 | 0.4100 | |
| FN | 0 | 1 | 0 | 0 | 1.0000 | |
| F*l* | 1.25E-05 | 1 | 1.25E-05 | 0.021455283 | 0.8839 | |
| F*v* | 0.0004 | 1 | 0.0004 | 0.686569058 | 0.4100 | |
| F*r* | 1.25E-05 | 1 | 1.25E-05 | 0.021455283 | 0.8839 | |
| F*s* | 0 | 1 | 0 | 0 | 1.0000 | |
| WL | 4.80159E-05 | 1 | 4.80159E-05 | 0.082415532 | 0.7749 | |
| WV | 5E-05 | 1 | 5E-05 | 0.085821132 | 0.7704 | |
| WN | 0 | 1 | 0 | 0 | 1.0000 | |
| W*l* | 0 | 1 | 0 | 0 | 1.0000 | |
| W*v* | 5E-05 | 1 | 5E-05 | 0.085821132 | 0.7704 | |
| W*r* | 1E-04 | 1 | 1E-04 | 0.171642265 | 0.6799 | |
| W*s* | 5E-05 | 1 | 5E-05 | 0.085821132 | 0.7704 | |
| LV | 0.00125 | 1 | 0.00125 | 2.145528307 | 0.1473 | |
| LN | 0 | 1 | 0 | 0 | 1.0000 | |
| L*l* | 1E-04 | 1 | 1E-04 | 0.171642265 | 0.6799 | |
| L*v* | 0.0008 | 1 | 0.0008 | 1.373138116 | 0.2451 | |
| L*r* | 5E-05 | 1 | 5E-05 | 0.085821132 | 0.7704 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| L*s* | 0.0004 | 1 | 0.0004 | 0.686569058 | 0.4100 | |
| VN | 0.00245 | 1 | 0.00245 | 4.205235481 | 0.0439 | Significant |
| V*l* | 0.00125 | 1 | 0.00125 | 2.145528307 | 0.1473 | |
| V*v* | 0.0004 | 1 | 0.0004 | 0.686569058 | 0.4100 | |
| V*r* | 0.0002 | 1 | 0.0002 | 0.343284529 | 0.5597 | |
| V*s* | 5E-05 | 1 | 5E-05 | 0.085821132 | 0.7704 | |
| N*l* | 0.00125 | 1 | 0.00125 | 2.145528307 | 0.1473 | |
| N*v* | 0 | 1 | 0 | 0 | 1.0000 | |
| N*r* | 0 | 1 | 0 | 0 | 1.0000 | |
| N*s* | 0 | 1 | 0 | 0 | 1.0000 | |
| *lv* | 5E-05 | 1 | 5E-05 | 0.085821132 | 0.7704 | |
| *lr* | 0.0010125 | 1 | 0.0010125 | 1.737877928 | 0.1915 | |
| *ls* | 0 | 1 | 0 | 0 | 1.0000 | |
| *vr* | 0.0018 | 1 | 0.0018 | 3.089560762 | 0.0830 | |
| *vs* | 0.0002 | 1 | 0.0002 | 0.343284529 | 0.5597 | |
| *rs* | 5E-05 | 1 | 5E-05 | 0.085821132 | 0.7704 | |
| Residual | 0.042530317 | 73 | 0.000582607 | | | |
| Lack of Fit | 0.042530317 | 40 | 0.001063258 | | | |
| Pure Error | 0 | 33 | 0 | | | |
| Cor Total | 0.251696875 | 127 | | | | |

From the ANOVA test it was found that the variables *l* (liquid split), *v* (vapor split), *s* (solvent flow rate) were highly significant model terms and VN (interaction of vapor split stage with total number of stages in main column) was significant model term for the purity of ethanol.

**Table 4.8 ANOVA for response surface quadratic model (For purity of side stream)**

| | Sum of | | Mean | F | | |
|---|---|---|---|---|---|---|
| Source | Squares | DF | Square | Value | Prob > F | |
| Model | 0.207735 | 54 | 0.003847 | 5.444227 | < 0.0001 | significant |
| F | 0.000227 | 1 | 0.000227 | 0.321849 | 0.5722 | |
| W | 0.000711 | 1 | 0.000711 | 1.006368 | 0.3191 | |
| L | 0.000184 | 1 | 0.000184 | 0.260904 | 0.6110 | |
| V | 9E-05 | 1 | 9E-05 | 0.127369 | 0.7222 | |
| N | 2.5E-06 | 1 | 2.5E-06 | 0.003538 | 0.9527 | |
| *l* | 0.026523 | 1 | 0.026523 | 37.53479 | < 0.0001 | Highly significant |
| *v* | 0.103023 | 1 | 0.103023 | 145.798 | < 0.0001 | Highly significant |
| *r* | 0.000202 | 1 | 0.000202 | 0.286579 | 0.5940 | |
| *s* | 0.05184 | 1 | 0.05184 | 73.36426 | < 0.0001 | Highly significant |
| $F^2$ | 0.000594 | 1 | 0.000594 | 0.840534 | 0.3623 | |
| $W^2$ | 0.000169 | 1 | 0.000169 | 0.239627 | 0.6259 | |
| $L^2$ | 0.001525 | 1 | 0.001525 | 2.157641 | 0.1462 | |
| $V^2$ | 0.000662 | 1 | 0.000662 | 0.936162 | 0.3365 | |
| $N^2$ | 0.000662 | 1 | 0.000662 | 0.936162 | 0.3365 | |
| $l^2$ | 7.67E-06 | 1 | 7.67E-06 | 0.010854 | 0.9173 | |
| $v^2$ | 0.003495 | 1 | 0.003495 | 4.946501 | 0.0292 | significant |
| $r^2$ | 0.000319 | 1 | 0.000319 | 0.451454 | 0.5038 | |
| $s^2$ | 0.000802 | 1 | 0.000802 | 1.134329 | 0.2904 | |
| FW | 4.86E-06 | 1 | 4.86E-06 | 0.006879 | 0.9341 | |
| FL | 1.04E-08 | 1 | 1.04E-08 | 1.47E-05 | 0.9970 | |
| FV | 0.000625 | 1 | 0.000625 | 0.884504 | 0.3501 | |
| FN | 0 | 1 | 0 | 0 | 1.0000 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| F*l* | 0 | 1 | 0 | 0 | 1.0000 | |
| F*v* | 0.000225 | 1 | 0.000225 | 0.318421 | 0.5743 | |
| F*r* | 0 | 1 | 0 | 0 | 1.0000 | |
| F*s* | 0 | 1 | 0 | 0 | 1.0000 | |
| WL | 6.2E-05 | 1 | 6.2E-05 | 0.087748 | 0.7679 | |
| WV | 1.25E-05 | 1 | 1.25E-05 | 0.01769 | 0.8946 | |
| WN | 0 | 1 | 0 | 0 | 1.0000 | |
| W*l* | 0 | 1 | 0 | 0 | 1.0000 | |
| W*v* | 0.0002 | 1 | 0.0002 | 0.283041 | 0.5963 | |
| W*r* | 0 | 1 | 0 | 0 | 1.0000 | |
| W*s* | 1.25E-05 | 1 | 1.25E-05 | 0.01769 | 0.8946 | |
| LV | 0.001513 | 1 | 0.001513 | 2.140499 | 0.1477 | |
| LN | 0.002113 | 1 | 0.002113 | 2.989622 | 0.0880 | |
| L*l* | 6.25E-06 | 1 | 6.25E-06 | 0.008845 | 0.9253 | |
| L*v* | 0.001013 | 1 | 0.001013 | 1.432896 | 0.2352 | |
| L*r* | 0.000112 | 1 | 0.000112 | 0.159211 | 0.6910 | |
| L*s* | 0.000306 | 1 | 0.000306 | 0.433407 | 0.5124 | |
| VN | 0.00245 | 1 | 0.00245 | 3.467254 | 0.0666 | |
| V*l* | 0.00125 | 1 | 0.00125 | 1.769007 | 0.1876 | |
| V*v* | 0.000225 | 1 | 0.000225 | 0.318421 | 0.5743 | |
| V*r* | 0.000113 | 1 | 0.000113 | 0.159211 | 0.6910 | |
| V*s* | 1.25E-05 | 1 | 1.25E-05 | 0.01769 | 0.8946 | |
| N*l* | 0.00125 | 1 | 0.00125 | 1.769007 | 0.1876 | |
| N*v* | 0.002113 | 1 | 0.002113 | 2.989622 | 0.0880 | |
| N*r* | 0 | 1 | 0 | 0 | 1.0000 | |
| N*s* | 0 | 1 | 0 | 0 | 1.0000 | |
| *lv* | 0.0002 | 1 | 0.0002 | 0.283041 | 0.5963 | |
| *lr* | 0.00045 | 1 | 0.00045 | 0.636843 | 0.4274 | |
| *ls* | 6.25E-06 | 1 | 6.25E-06 | 0.008845 | 0.9253 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| *vr* | 0.0018 | 1 | 0.0018 | 2.54737 | 0.1148 | |
| *vs* | 5E-05 | 1 | 5E-05 | 0.07076 | 0.7910 | |
| *rs* | 0 | 1 | 0 | 0 | 1.0000 | |
| Residual | 0.051583 | 73 | 0.000707 | | | |
| Lack of Fit | 0.051533 | 40 | 0.001288 | 850.2881 | < 0.0001 | significant |
| Pure Error | 0.00005 | 33 | 1.52E-06 | | | |
| Cor Total | 0.259318 | 127 | | | | |

From the ANOVA test it was found that the variables *l* (liquid split), *v* (vapor split), s (solvent flowrate) were highly significant model terms and $v^2$ (interaction of vapor split with itself) was significant model terms for the purity of side streams. Similar results were obtained by Sangal et al., (2013 b) for purity of side stream for DWC.

**Table 4.9- ANOVA for response surface quadratic model (For reboiler duty)**

| Source | Sum of Squares | DF | Mean Square | F Value | Prob > F | |
|---|---|---|---|---|---|---|
| Model | 2007.4 | 54 | 37.17408 | 81049.15 | < 0.0001 | significant |
| F | 3.34E-05 | 1 | 3.34E-05 | 0.072909 | 0.7879 | |
| W | 0.000242 | 1 | 0.000242 | 0.527193 | 0.4701 | |
| L | 0.000123 | 1 | 0.000123 | 0.267918 | 0.6063 | |
| V | 0.000387 | 1 | 0.000387 | 0.843256 | 0.3615 | |
| N | 5.68E-05 | 1 | 5.68E-05 | 0.123806 | 0.7260 | |
| *l* | 0.001243 | 1 | 0.001243 | 2.709048 | 0.1041 | |
| *v* | 0.002098 | 1 | 0.002098 | 4.574685 | 0.0358 | significant |
| *r* | 1905.512 | 1 | 1905.512 | 4154512 | < 0.0001 | Highly significant |
| *s* | 95.39225 | 1 | 95.39225 | 207979.9 | < 0.0001 | Highly significant |
| $F^2$ | 7.07E-05 | 1 | 7.07E-05 | 0.154211 | 0.6957 | |
| $W^2$ | 4.92E-05 | 1 | 4.92E-05 | 0.107358 | 0.7441 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| $L^2$ | 6.44E-06 | 1 | 6.44E-06 | 0.014046 | 0.9060 | |
| $V^2$ | 0.000553 | 1 | 0.000553 | 1.206677 | 0.2756 | |
| $N^2$ | 0.001316 | 1 | 0.001316 | 2.868569 | 0.0946 | |
| $l^2$ | 0.000632 | 1 | 0.000632 | 1.376967 | 0.2444 | |
| $v^2$ | 1.39E-05 | 1 | 1.39E-05 | 0.03034 | 0.8622 | |
| $r^2$ | 4.973846 | 1 | 4.973846 | 10844.28 | < 0.0001 | Highly significant |
| $s^2$ | 0.003211 | 1 | 0.003211 | 7.001632 | 0.0100 | significant |
| FW | 4.25E-08 | 1 | 4.25E-08 | 9.26E-05 | 0.9923 | |
| FL | 1.02E-05 | 1 | 1.02E-05 | 0.022151 | 0.8821 | |
| FV | 9.29E-05 | 1 | 9.29E-05 | 0.202551 | 0.6540 | |
| FN | 0 | 1 | 0 | 0 | 1.0000 | |
| F*l* | 1.58E-05 | 1 | 1.58E-05 | 0.034454 | 0.8533 | |
| F*v* | 9.29E-05 | 1 | 9.29E-05 | 0.202551 | 0.6540 | |
| F*r* | 1.58E-05 | 1 | 1.58E-05 | 0.034454 | 0.8533 | |
| F*s* | 0 | 1 | 0 | 0 | 1.0000 | |
| WL | 3.22E-05 | 1 | 3.22E-05 | 0.070123 | 0.7919 | |
| WV | 0.002245 | 1 | 0.002245 | 4.894886 | 0.0301 | significant |
| WN | 0 | 1 | 0 | 0 | 1.0000 | |
| W*l* | 1.16E-05 | 1 | 1.16E-05 | 0.025314 | 0.8740 | |
| W*v* | 0.000105 | 1 | 0.000105 | 0.227884 | 0.6345 | |
| W*r* | 1.84E-05 | 1 | 1.84E-05 | 0.040096 | 0.8418 | |
| W*s* | 0.00016 | 1 | 0.00016 | 0.348944 | 0.5565 | |
| LV | 0.00029 | 1 | 0.00029 | 0.63291 | 0.4289 | |
| LN | 0.00057 | 1 | 0.00057 | 1.242704 | 0.2686 | |
| L*l* | 4.83E-06 | 1 | 4.83E-06 | 0.010536 | 0.9185 | |
| L*v* | 0.001406 | 1 | 0.001406 | 3.066437 | 0.0841 | |
| L*r* | 5.21E-05 | 1 | 5.21E-05 | 0.113516 | 0.7371 | |
| L*s* | 4.83E-06 | 1 | 4.83E-06 | 0.010536 | 0.9185 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| VN | 0 | 1 | 0 | 0 | 1.0000 | |
| V*l* | 0.000186 | 1 | 0.000186 | 0.404952 | 0.5265 | |
| V*v* | 9.29E-05 | 1 | 9.29E-05 | 0.202551 | 0.6540 | |
| V*r* | 1.32E-06 | 1 | 1.32E-06 | 0.002888 | 0.9573 | |
| V*s* | 0.00015 | 1 | 0.00015 | 0.327054 | 0.5692 | |
| N*l* | 0.000186 | 1 | 0.000186 | 0.404952 | 0.5265 | |
| N*v* | 0.00057 | 1 | 0.00057 | 1.242704 | 0.2686 | |
| N*r* | 0 | 1 | 0 | 0 | 1.0000 | |
| N*s* | 4.93E-05 | 1 | 4.93E-05 | 0.107572 | 0.7439 | |
| *lv* | 0.00029 | 1 | 0.00029 | 0.632855 | 0.4289 | |
| *lr* | 0.000214 | 1 | 0.000214 | 0.467183 | 0.4964 | |
| *ls* | 0.001711 | 1 | 0.001711 | 3.7315 | 0.0573 | |
| *vr* | 0.006265 | 1 | 0.006265 | 13.66021 | 0.0004 | significant |
| *vs* | 0.000269 | 1 | 0.000269 | 0.586193 | 0.4464 | |
| *rs* | 0.335822 | 1 | 0.335822 | 732.1789 | < 0.0001 | Highly significant |
| Residual | 0.033482 | 73 | 0.000459 | | | |
| Lack of Fit | 0.033359 | 40 | 0.000834 | 223.9324 | < 0.0001 | Significant |
| Pure Error | 0.000123 | 33 | 3.72E-06 | | | |
| Cor Total | 2007.434 | 127 | | | | |

From the ANOVA test for reboiler duty it was found that variables *r* (reflux rate), *s* (solvent flow rate), $r^2$ (interaction of reflux rate with itself), *rs* (interaction between reflux rate and solvent flow rate) were highly significant model terms and *v* (vapor split), $s^2$ (interaction of solvent flowrate with itself), *vr* (interaction between vapor split and reflux rate) and WV (interaction between side product stage and vapor split stage) were significant model terms.

From Table 4.9, it is clear that the process variables are highly significant as compared to structural variables for energy efficiency of EDWC. For the case of DWC, Sangal et al., (2012 b)

also found that the process variables are highly significant as compared to structural variables for energy efficiency.

**Table 4.10 ANOVA for response surface quadratic model (For $CO_2$ emissions)**

| | Sum of | | Mean | F | | |
|---|---|---|---|---|---|---|
| Source | Squares | DF | Square | Value | Prob > F | |
| Model | 274556.5 | 54 | 5084.38 | 172225.6 | < 0.0001 | Significant |
| F | 0.005844 | 1 | 0.005844 | 0.197972 | 0.6577 | |
| W | 0.036075 | 1 | 0.036075 | 1.221974 | 0.2726 | |
| L | 0.016653 | 1 | 0.016653 | 0.564092 | 0.4550 | |
| V | 0.05487 | 1 | 0.05487 | 1.858623 | 0.1770 | |
| N | 0.008117 | 1 | 0.008117 | 0.274944 | 0.6016 | |
| *l* | 0.171752 | 1 | 0.171752 | 5.817819 | 0.0184 | Significant |
| *v* | 0.353568 | 1 | 0.353568 | 11.97657 | 0.0009 | Significant |
| *r* | 261369.8 | 1 | 261369.8 | 8853502 | < 0.0001 | Highly significant |
| *s* | 13182.46 | 1 | 13182.46 | 446535.6 | < 0.0001 | Highly significant |
| $F^2$ | 0.008052 | 1 | 0.008052 | 0.272755 | 0.6031 | |
| $W^2$ | 0.010904 | 1 | 0.010904 | 0.369371 | 0.5452 | |
| $L^2$ | 0.002549 | 1 | 0.002549 | 0.086356 | 0.7697 | |
| $V^2$ | 0.067736 | 1 | 0.067736 | 2.294468 | 0.1342 | |
| $N^2$ | 0.173885 | 1 | 0.173885 | 5.890091 | 0.0177 | significant |
| $l^2$ | 0.086347 | 1 | 0.086347 | 2.924858 | 0.0915 | significant |
| $v^2$ | 0.006583 | 1 | 0.006583 | 0.223006 | 0.6382 | |
| $r^2$ | 0.375726 | 1 | 0.375726 | 12.72714 | 0.0006 | significant |
| $s^2$ | 0.396528 | 1 | 0.396528 | 13.43177 | 0.0005 | significant |
| FW | 1.29E-05 | 1 | 1.29E-05 | 0.000436 | 0.9834 | |
| FL | 0.002267 | 1 | 0.002267 | 0.076774 | 0.7825 | |
| FV | 0.012987 | 1 | 0.012987 | 0.439911 | 0.5093 | |
| FN | 0 | 1 | 0 | 0 | 1.0000 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| F*l* | 0.001623 | 1 | 0.001623 | 0.054989 | 0.8153 | |
| F*v* | 0.012987 | 1 | 0.012987 | 0.439911 | 0.5093 | |
| F*r* | 0.001623 | 1 | 0.001623 | 0.054989 | 0.8153 | |
| F*s* | 0 | 1 | 0 | 0 | 1.0000 | |
| WL | 0.004651 | 1 | 0.004651 | 0.157547 | 0.6926 | |
| WV | 0.318179 | 1 | 0.318179 | 10.77781 | 0.0016 | significant |
| WN | 0 | 1 | 0 | 0 | 1.0000 | |
| W*l* | 0.001623 | 1 | 0.001623 | 0.054989 | 0.8153 | |
| W*v* | 0.01461 | 1 | 0.01461 | 0.4949 | 0.4840 | |
| W*r* | 0.003247 | 1 | 0.003247 | 0.109978 | 0.7411 | |
| W*s* | 0.025974 | 1 | 0.025974 | 0.879821 | 0.3513 | |
| LV | 0.040584 | 1 | 0.040584 | 1.374721 | 0.2448 | |
| LN | 0.079545 | 1 | 0.079545 | 2.694453 | 0.1050 | |
| L*l* | 0.000812 | 1 | 0.000812 | 0.027494 | 0.8688 | |
| L*v* | 0.196427 | 1 | 0.196427 | 6.65365 | 0.0119 | significant |
| L*r* | 0.01461 | 1 | 0.01461 | 0.4949 | 0.4840 | |
| L*s* | 0.000812 | 1 | 0.000812 | 0.027494 | 0.8688 | |
| VN | 0 | 1 | 0 | 0 | 1.0000 | |
| V*l* | 0.025974 | 1 | 0.025974 | 0.879821 | 0.3513 | |
| V*v* | 0.012987 | 1 | 0.012987 | 0.439911 | 0.5093 | |
| V*r* | 0.001623 | 1 | 0.001623 | 0.054989 | 0.8153 | |
| V*s* | 0.025974 | 1 | 0.025974 | 0.879821 | 0.3513 | |
| N*l* | 0.025974 | 1 | 0.025974 | 0.879821 | 0.3513 | |
| N*v* | 0.079545 | 1 | 0.079545 | 2.694453 | 0.1050 | |
| N*r* | 0 | 1 | 0 | 0 | 1.0000 | |
| N*s* | 0.006493 | 1 | 0.006493 | 0.219955 | 0.6405 | |
| *lv* | 0.040584 | 1 | 0.040584 | 1.374721 | 0.2448 | |
| *lr* | 0.079545 | 1 | 0.079545 | 2.694453 | 0.1050 | |
| *ls* | 0.234576 | 1 | 0.234576 | 7.945888 | 0.0062 | significant |

| | | | | | | |
|---|---|---|---|---|---|---|
| *vr* | 0.858758 | 1 | 0.858758 | 29.0891 | < 0.0001 | significant |
| *vs* | 0.040584 | 1 | 0.040584 | 1.374721 | 0.2448 | |
| *rs* | 0.079545 | 1 | 0.079545 | 2.694453 | 0.1050 | |
| Residual | 2.155079 | 73 | 0.029522 | | | |
| Lack of Fit | 2.135599 | 40 | 0.05339 | 90.44352 | < 0.0001 | significant |
| Pure Error | 0.01948 | 33 | 0.00059 | | | |
| Cor Total | 274558.7 | 127 | | | | |

Form the Table 4.10 it was found that the variables *r* (reflux rate), *s* (solvent flow rate) were highly significant model terms and *l* (liquid split), *v* (vapor split), $N^2$ (interaction of stages in main column with itself), $l^2$ (interaction of liquid split with itself), $r^2$ (interaction of reflux rate with itself), $s^2$ (interaction of solvent flowrate with itself), WV (interaction between side product stage and vapor split stage), L*v* (interaction between liquid split stage and vapor split), *ls* (interaction between liquid split and solvent flowrate), *vr* (interaction between vapor split and reflux rate) were significant model terms.

A normal probability plot and a dot diagram of the residuals are shown in Figure 4.2- 4.5 for the reboiler duty, distillate purity, side product purity and $CO_2$emissions. The data points on these plots lie reasonably close to a straight line, signifying that the underlying assumptions of the analysis were satisfied.

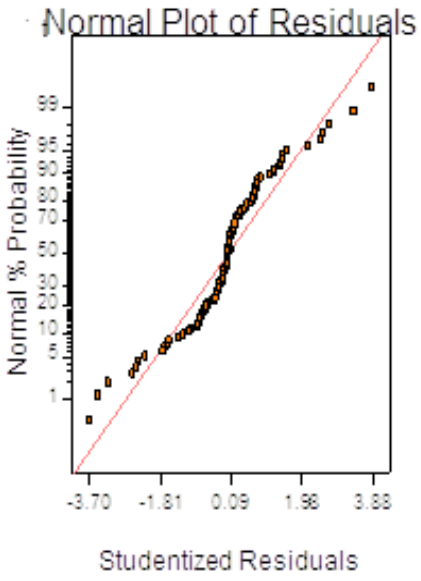


**Figure 4.2 Residual plot for reboiler duty**

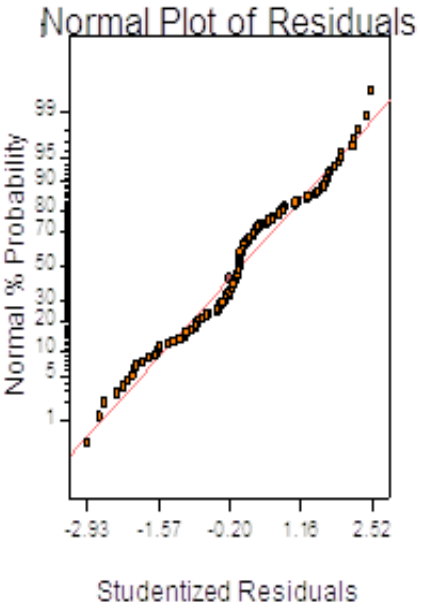


**Figure 4.3 Residual plot for distillate purity**

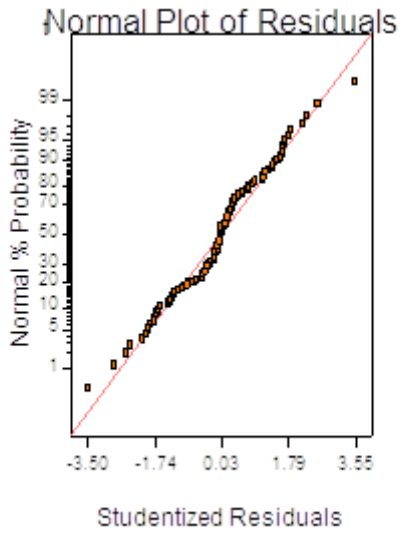


**Figure 4.4 Residual plot for side purity**

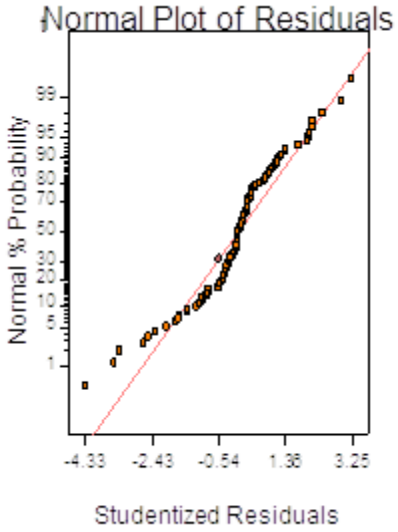


**Figure 4.5 Residual plot for $CO_2$ emissions**

Figure 4.6 - 4.9 shows the relationship between the actual and predicted values of reboiler duty, distillate purity, side product purity and $CO_2$ emissions. It can be seen from 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.

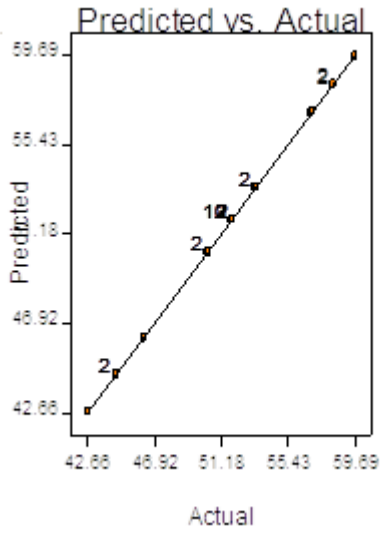


**Figure 4.6 Predicted vs Actual for reboiler duty**

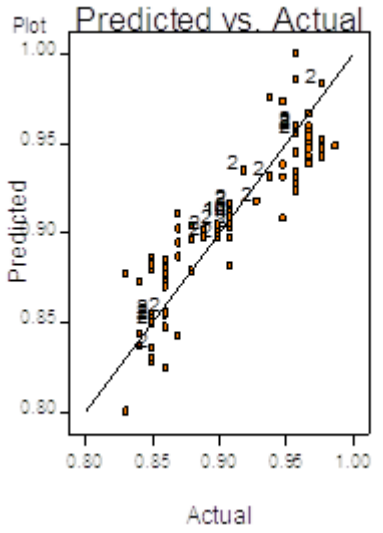


**Figure 4.7 Predicted vs Actual for distillate purity**

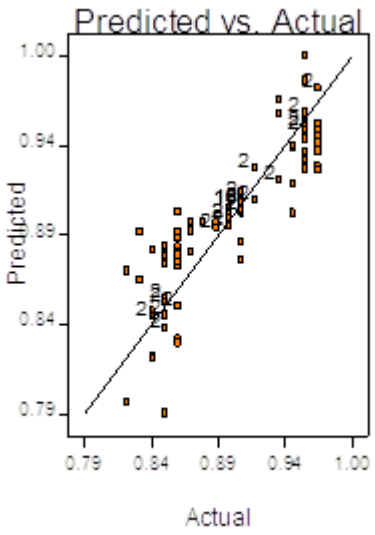


**Figure 4.8 Predicted vs Actual for side purity**

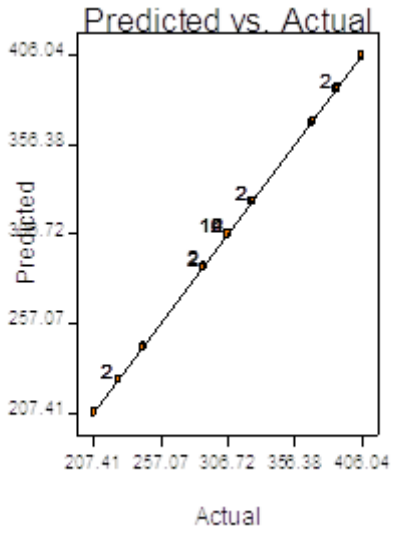


**Figure 4.9 Predicted vs Actual for $CO_2$ emissions**

3-D response curves for ethanol purity in distillate are presented in Figures 4.10-4.17

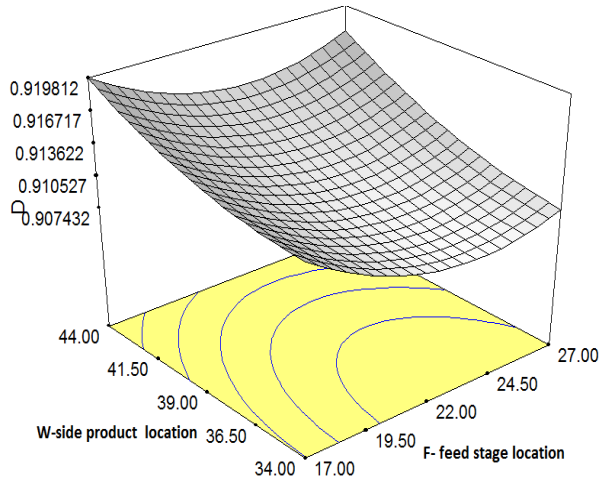


**Figure 4.10 Feed stage location versus side Product stage location for ethanol purity in distillate**

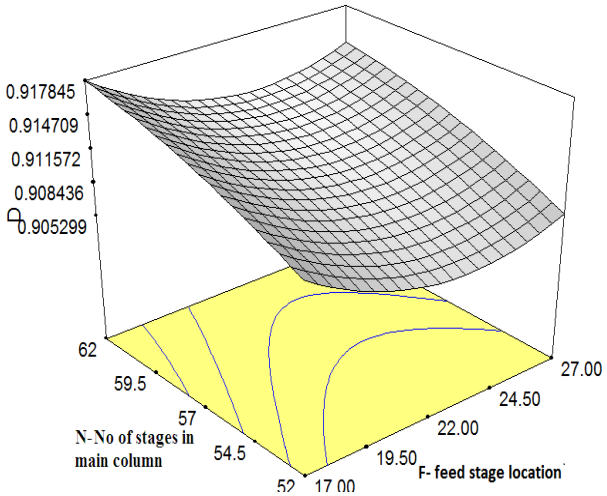


**Figure 4.11 Feed stage location versus stages in column for ethanol purity in distillate**

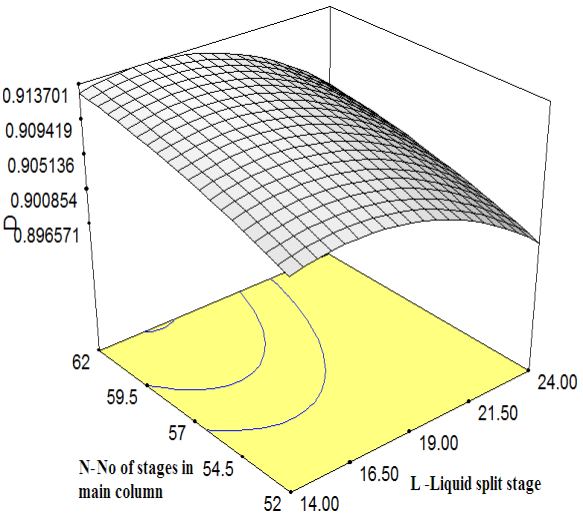


**Figure 4.12 Liquid split stage versus number of stages in column for ethanol purity in distillate**

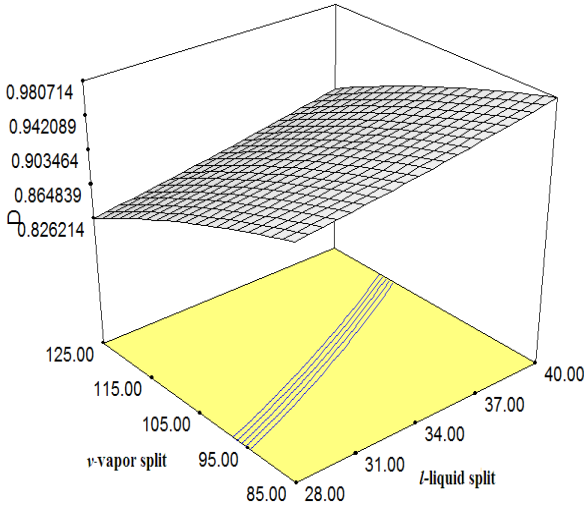


**Figure 4.13 Liquid split versus vapor split for ethanol purity in distillate.**

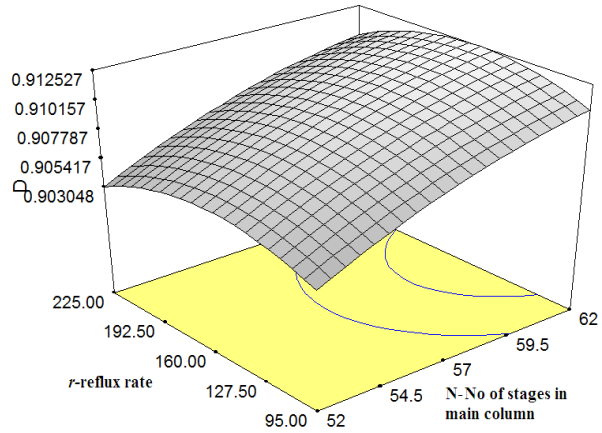


**Figure 4.14 Stages in column versus reflux rate for ethanol purity in distillate**

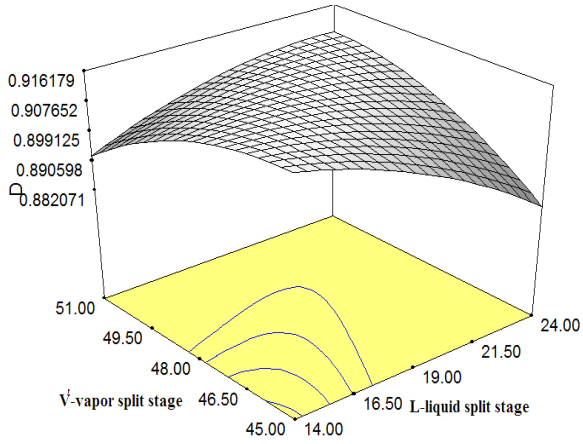


**Figure 4.15- Liquid split stage versus vapor split stage for ethanol purity in distillate**

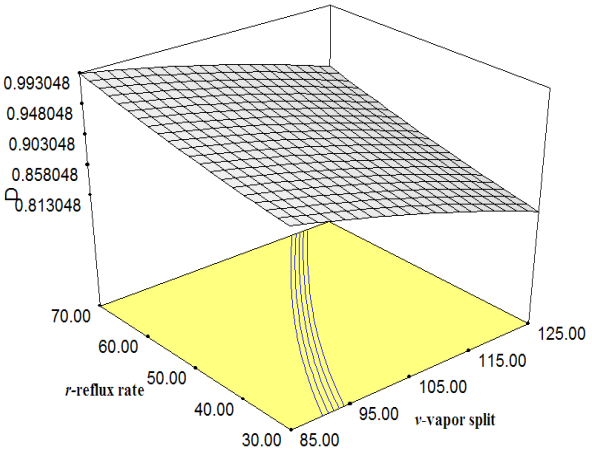


**Figure 4.16 Vapor split versus reflux rate for Ethanol purity in distillate.**

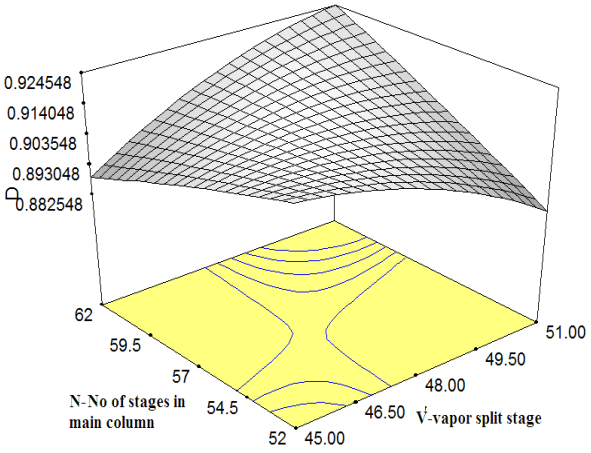


**Figure 4.17 Vapor split stage versus number stages in column for ethanol purity in distillate**

3D response curve for purity of water in side product are represented in Figures 4.18-4.21.

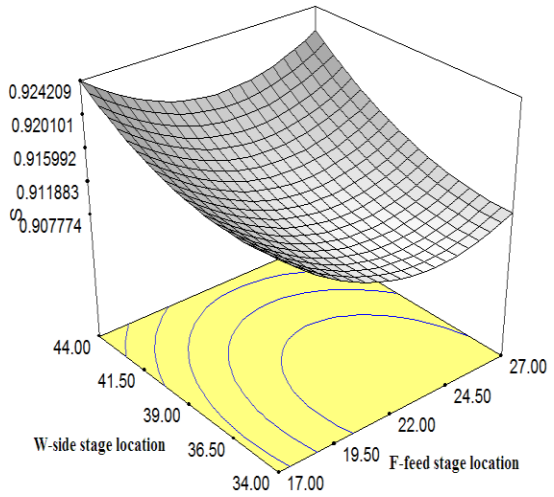


**Figure 4.18 Feed stage location versus side Product stage location for purity of water In side product**

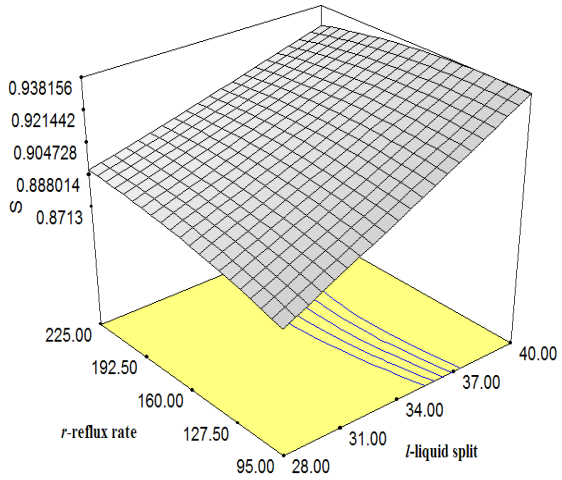


**Figure 4.19 Liquid split versus reflux rate for purity of water in side product.**

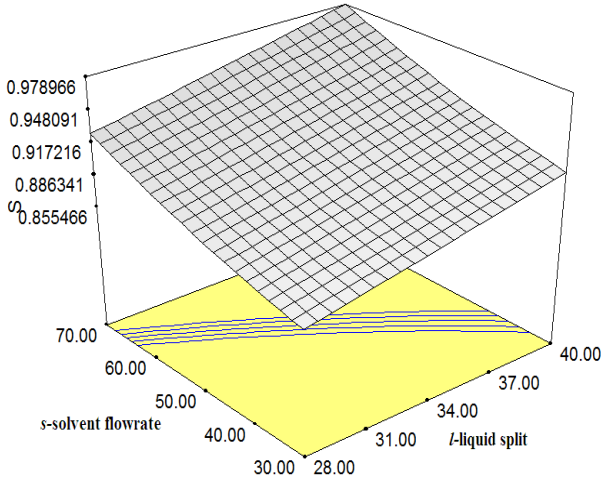


**Figure 4.20 Liquid split versus solvent flow rate For purity of water in side product**

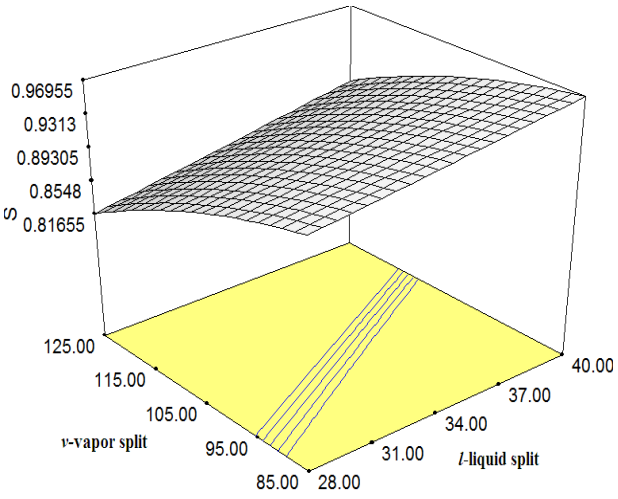


**Figure 4.21 Liquid split versus vapor split for purity of water in side product.**

3D response surface graphs for purity of ethylene glycol in bottom product are presented in Figures 4.22-4.27.

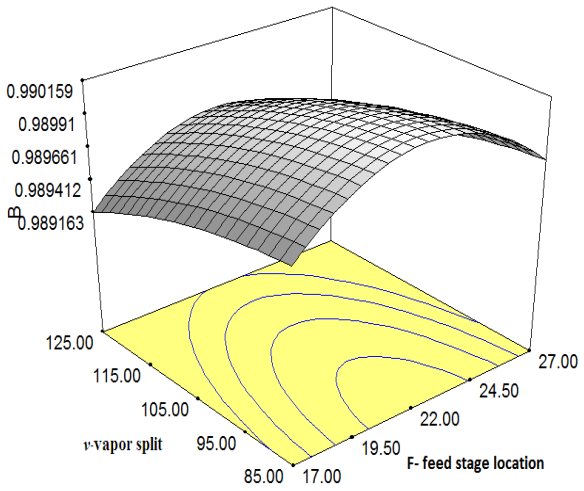


**Figure 4.22 Feed stage location versus vapor split for purity of ethylene glycol in bottom product**

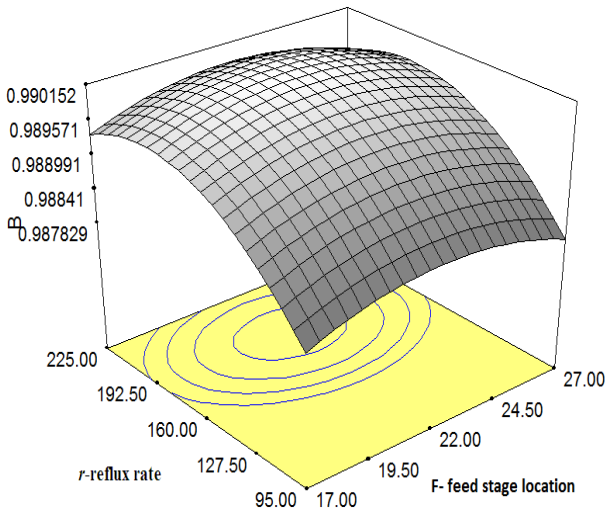


**Figure 4.23 Feed stage location versus reflux rate for purity of ethylene glycol in bottom product**

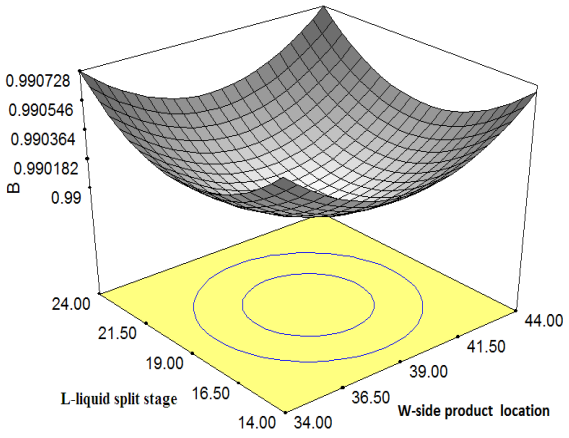


**Figure 4.24 Side product stage location versus liquid split stage for purity of ethylene glycol in bottom product**

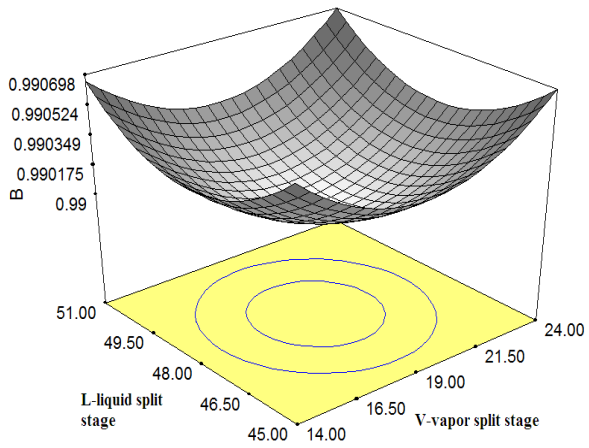


**Figure 4.25 Vapor split stage versus liquid split stage for purity of ethylene glycol in bottom product.**

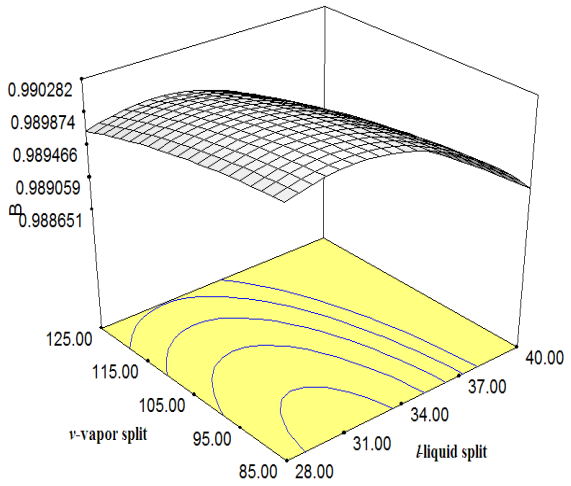


**Figure 4.26 Liquid split versus vapor split for purity of ethylene glycol in bottom product**

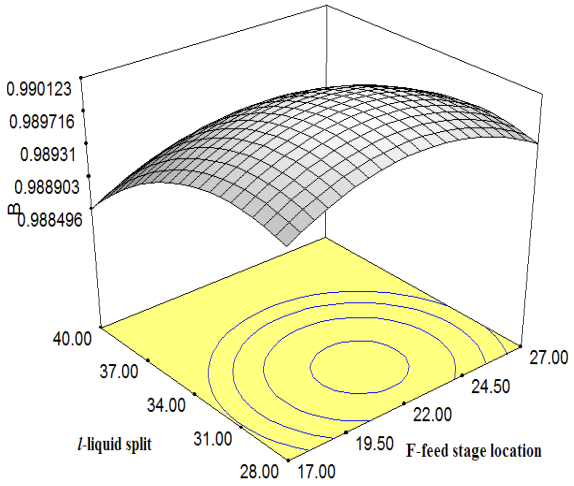


**Figure 4.27 Feed stage location versus liquid split for purity of ethylene glycol in bottom product.**

3D response surface graphs of reboiler duty are presented in Figure 4.28-4.30.

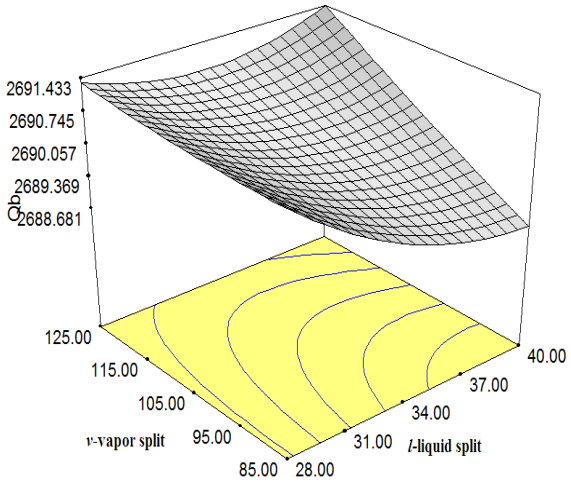


**Figure 4.28 Liquid split versus vapor split for reboiler duty**

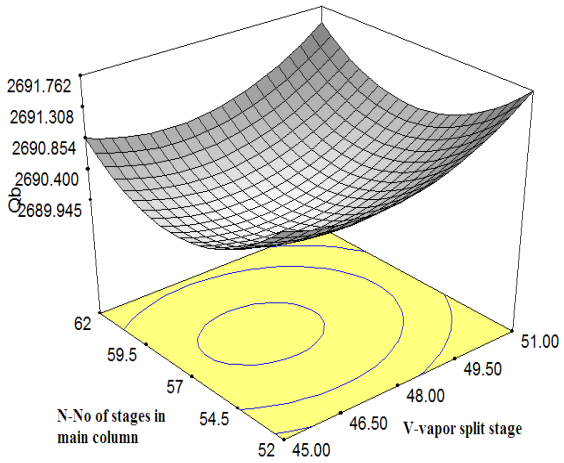


**Figure 4.29 Vapor split stage versus number of stages in column for reboiler duty.**

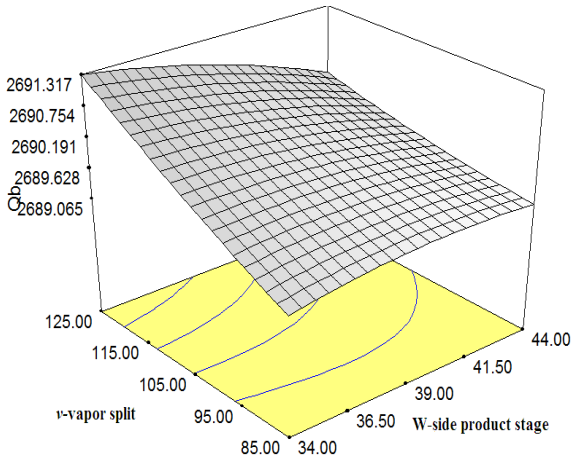


**Figure 4.30 Side product stage versus vapor split for reboiler duty**

3D response surface graphs for $CO_2$ emissions are presented in Figures 4.31-4.33

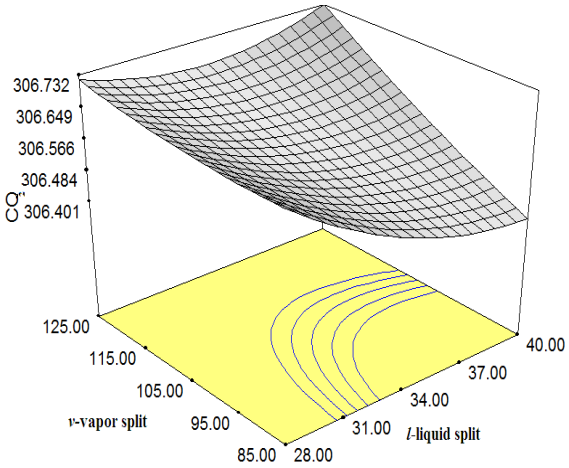


**Figure 4.31 Liquid split versus vapor split for $CO_2$ emissions.**

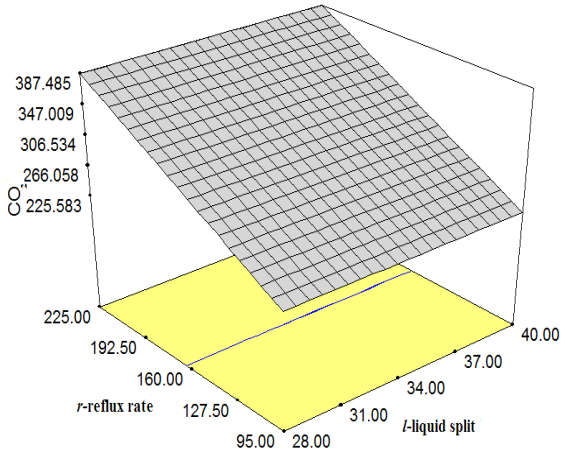


**Figure 4.32 Liquid split versus reflux rate for $CO_2$ emissions**

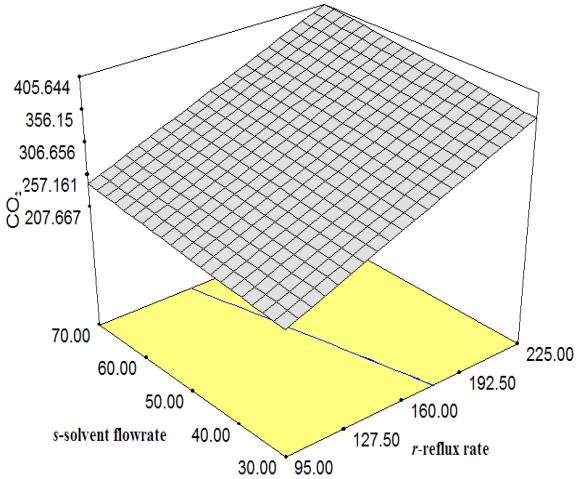


**Figure 4.33 Reflux rate versus solvent flowrate for $CO_2$ emissions**

Using the point prediction option in the software, the optimized values of structural and process variables are given in Table 4.11.

**Table-4.11 Optimized values of Variables**

| Variable | Optimized Value |
|---|---|
| Feed Stage | 21 |
| Stages in main column | 54 |
| Liquid split stage | 19 |
| Vapor split stage | 44 |
| Side product stage | 42 |
| Liquid split | 36 kmol/h |
| Vapor split | 97 kmol/h |
| Reflux rate | 95 kmol/h |
| Solvent flow | 37 kmol/h |

A comparison of predicted value and confirmed simulation run obtained when all the optimized variables were used as inputs for the simulation is given in Table 4.12.

**Table 4.12- Optimum and confirmative value of the response of EDWC**

| | Optimized parameter (predicted value) | Confirmation simulation run |
|---|---|---|
| Reboiler duty | 1886 kW | 1880 kW |
| $CO_2$ emissions | 214.8 kg/hr | 214 kg/hr |
| Product purities | Ethanol -0.990<br>Water -0.975<br>Ethylene Glycol-0.987 | Ethanol -0.99<br>Water -0.98<br>Ethylene Glycol-0.99 |

Simulations done with optimized variables reported a reboiler duty of 1880 kW and purity of ethanol in distillate as 0.99 and that of water in side product as 0.98, while a reboiler duty of 1979 kW and ethanol and water purities of 0.83 and .081 were reported when simulations were

done using variables obtained from shortcut simulations (Table 4.2) i.e. better recoveries of top and side products was obtained when simulations were performed using optimized variables.

The pressure drop across the divided wall was calculated by using the TRAY RATING feature available in ASEPN PLUS. The value of pressure drop across the divided wall came out to 0.19 atm.

### 4.4 Composition and temperature profile in prefractionator and main column

ASEPN PLUS has a very easy to use graphical tool which tells about the composition and temperature profiles in both prefractionator and main column. At the optimum condition, the temperature and composition profiles in prefractionator and main column are shown in Figures 4.34 and 4.35.

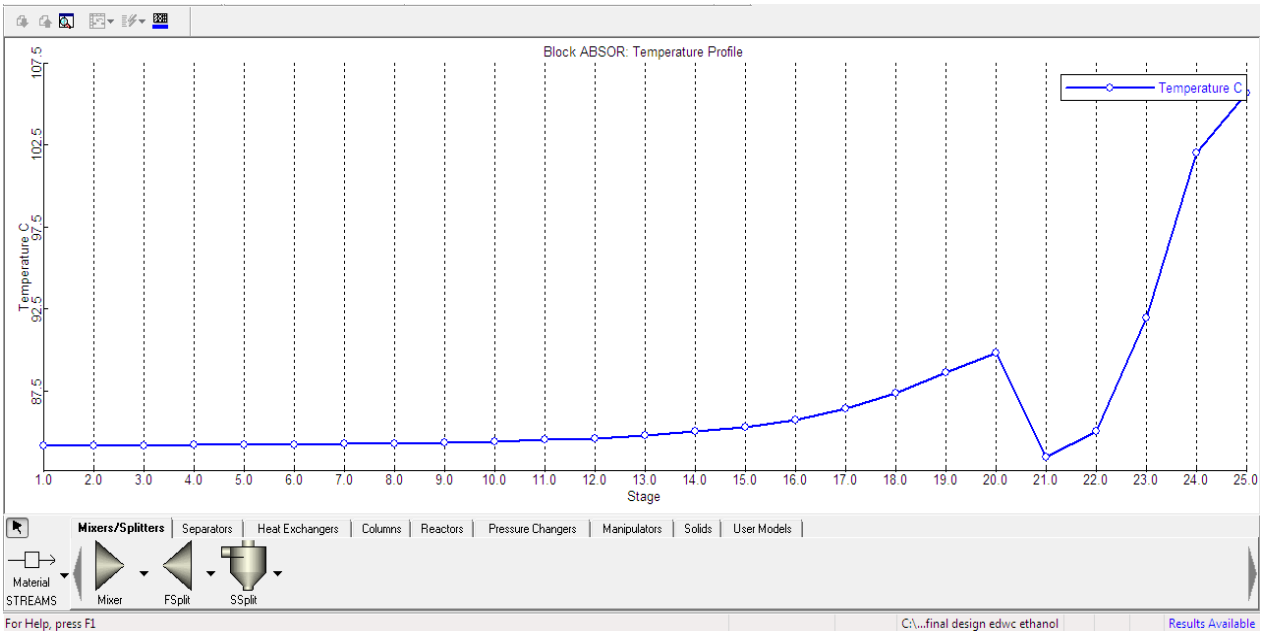


**Figure 4.34- Temperature profile in prefractionator**

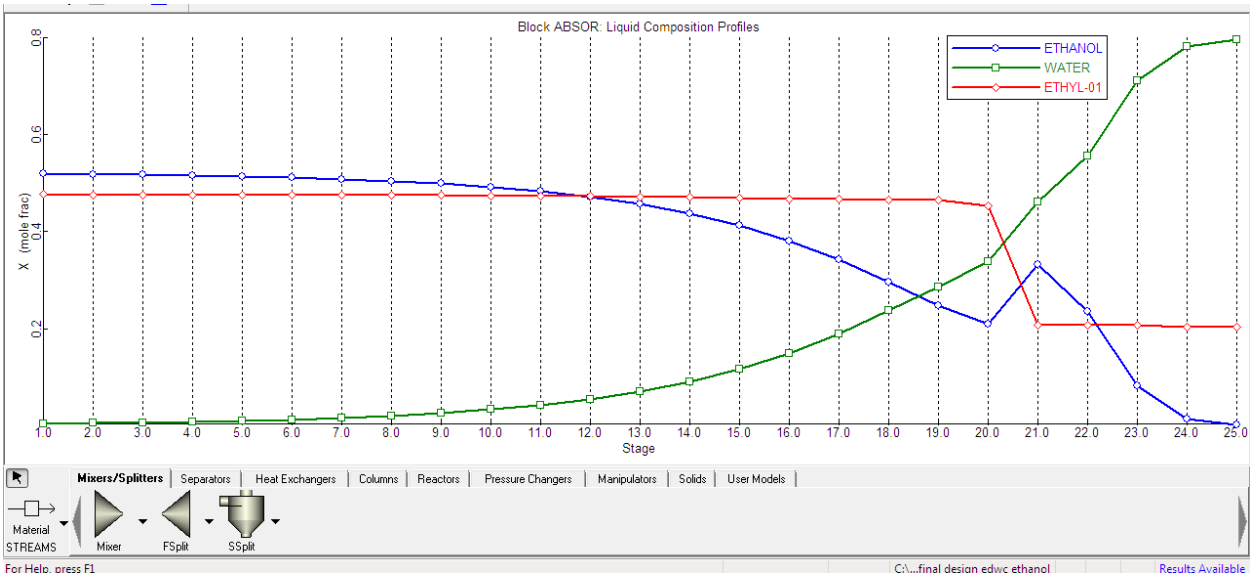


**Figure 4.35- Composition profile in prefractionator**

The temperature and composition profile in the main column are reported in Figure 4.36 and 4.37.

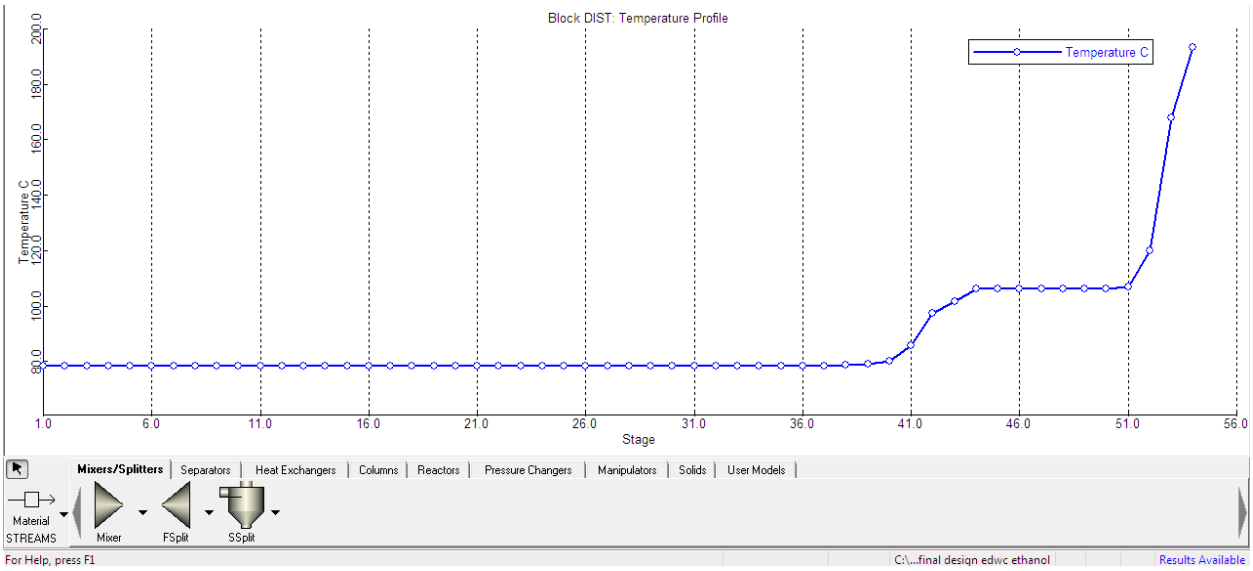


**Figure 4.36- Temperature profile in main column**

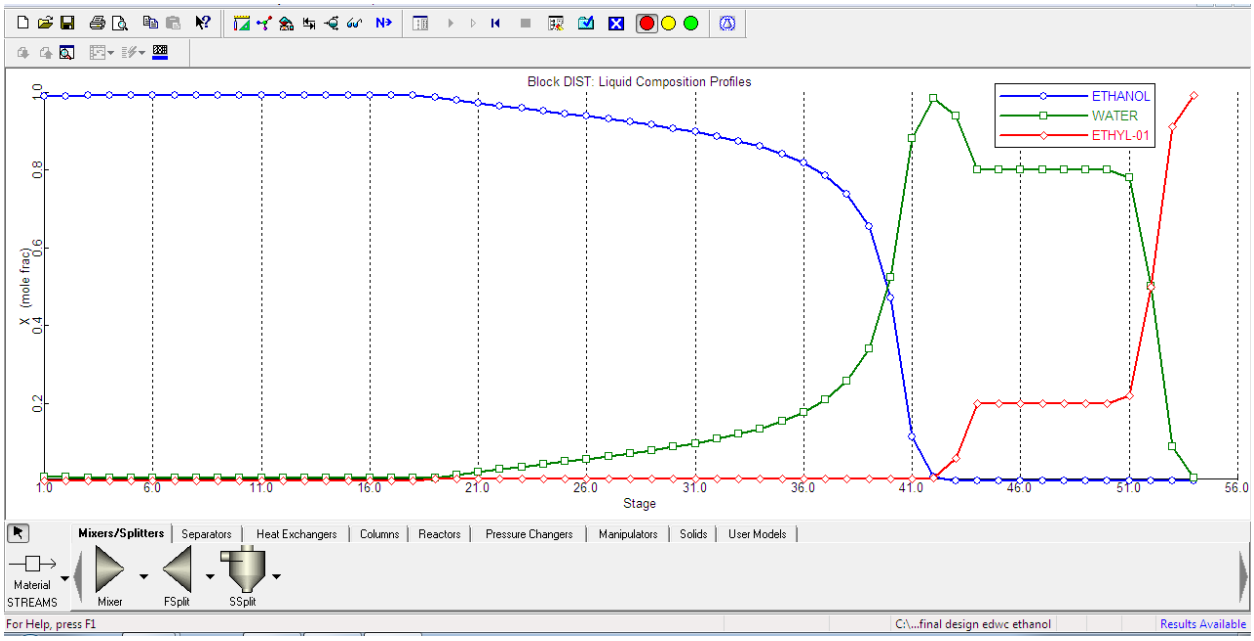


**Figure 4.37- Composition profile in main column**

### 4.5 Comparison of EDWC with the conventional extractive distillation process

A comparison of separating water ethanol mixture by proposed EDWC and the conventional extractive distillation was carried out using the ASEPN Plus process simulator. The feed conditions for the conventional were taken same as that of EDWC. The schematic diagram of conventional extractive distillation set up used in ASEPN Plus is shown in Figure 4.38. Table 4.13 shows the comparison of conventional extractive distillation and EDWC for the separation of ethanol-water mixture using ethylene glycol as a solvent.

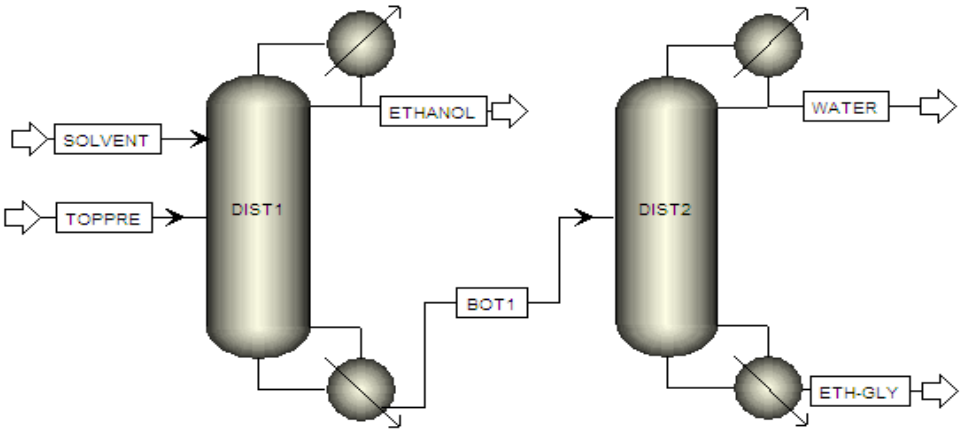


**Figure 4.38 -Conventional extractive distillation sequence implemented in ASEPN Plus**

**Table 4.13- Results of the Conventional extractive distillation process**

| | Extractive Distillation | EDWC |
|---|---|---|
| Product purities | Ethanol (top) -0.99<br>Water (side) -0.98<br>Ethylene Glycol (bottom)-0.99 | Ethanol (top) -0.99<br>Water (side) -0.98<br>Ethylene Glycol (bottom)-0.99 |
| Reboiler Duty | 2369 kW | 1880 kW |
| $CO_2$ emission | 270 kg/h | 214 kg/h |
| Condenser Duty | 2043 kW | 1569 kW |
| No of stages in column (a) | 25 | 25 |
| No of stages in column (b) | 20 | 54 |
| Solvent required | 37 kmol/h | 37 kmol/h |

From Table 4.13 it is clear that for carrying the same separation EDWC saved 20.6% reboiler duty in comparison to extractive distillation. In terms of $CO_2$ emissions also EDWC was mush ahead of extractive distillation process causing 20% less $CO_2$ emissions in environment. The $CO_2$ emissions were calculated by method suggested by (Gadalla et al., 2006).

# Chapter-5

## *Conclusion and future recommendations*

The following conclusions are drawn from this study:

1) For minimizing the energy requirement and maximizing the product purities the optimum feed stage location, stages in main column, side product stage, liquid split stage and vapour split stage are 21, 54, 42, 19 and 42 respectively, for the separation of ethanol water mixture through EDWC.

2) The optimum values of the process variables such as liquid split flow rate, vapour split flow rate, reflux rate and solvent flow rate are 36, 97, 95 and 37 kmol/h respectively.

3) At the optimum condition the ethanol and recovered solvent purity is 99%.

4) At the optimum condition the energy requirement and $CO_2$ emission is 1880 kW and 214 kg/h respectively.

5) The structural variables such as feed stage location, side product stage location, liquid split stage, vapor split stage, number of stages in main column do not have a significant effect on ethanol purity in distillate, only the interaction effect between vapor split stage and number of stages in main column was significant for ethanol purity. On the other hand the process variables such as solvent flowrate, liquid split and vapor split were highly significant for ethanol purity.

6) The process variables such as liquid split, vapor split and solvent flowrate are highly significant for side stream purity. None of the structural variables are significant for side stream purity.

7) For reboiler duty the process variables such as reflux rate, solvent flowrate, vapor split, interaction between reflux rate and solvent flowrate, interaction effect between vapor split and reflux rate were found to be significant. Only one structural variable namely the interaction effect between side product stage and vapor split stage had a significant effect on reboiler duty.

8) The purity of streams and energy efficiency of EDWC is highly dependent on process variables as comparison to structural variables.

9) EDWC saved 20.6% reboiler duty as compared to conventional extractive distillation for the separation of water ethanol mixture.

10) As compared to conventional extractive distillation the EDWC reduced the 20% $CO_2$ emission for the separation of water ethanol mixture.

**Recommendations and future scope:**

1) The present case demonstrated the use of EDWC for separating minimum boiling homogenous azeotropes. The EDWC will be a viable option for separating the mixtures forming maximum boiling azeotropes.

2) The EDWC can also be used for separating mixtures which from azeotrope in two phases.

3) For complete analysis of an EDWC the dynamic simulation study will also required.

**References**

Agarwal, R., Fidkowski, Z., T., Are thermally coupled distillation columns always thermodynamically more efficient for ternary distillations, *Ind. Eng. Chem. Res.*, 1998, *37*, 3444-3454.

Amminudin, K. A., Smith, R., Thong, D. Y. C., Towler, G. P., Design and optimization of fully thermally coupled distillation columns Part 1: Preliminary design and optimization methodology, *Trans IChemE*, 2001, 79, 701-715

.

Amminudin, K. A., Smith, R., Thong, D. Y. C., Towler, G. P., Design and optimization of fully thermally coupled distillation columns Part 2: Application of dividing wall columns in retrofit, *Trans IChemE*, 2001, 79, 716-724

Asprion, N., Kaibel, G., Dividing wall columns: Fundamentals and recent advances, *Chem. Eng. Process Intensification*, 2010, 49, 139-146.

Box, G., E., P., Hunter, J., S., Multi factor experimental designs for exploring response surfaces. *Annals of Mathematical Statistics*, 1957, 28, 195–241

.

Barroso-Munoz, F., O., Hernandez, S., Hernandez-Escoto, H., Segovia-Hernandez, J., G., Rico-Ramirez, V., Chavez, R., H., Experimental study on pressure drops in a dividing wall distillation column, *Chem. Eng. and Processing*, 2010.

Bravo-Bravo, C., Segovia-Hernandez, J., G., Gutierrez-Antonio, C., Duran, A., L., Bonilla-Petriciolet, A., Briones-Ramirez, A., Extractive Dividing Wall Column: Design and Optimization**,** *Ind. Eng. Chem. Res.*, 2010**,** 49, 3672–3688.

Derringer, G., Suich, R., Simultaneous Optimization of Several Response Variables, *J. of Quality Technol.*, 1980, 12, 214-219.

Ferreira, S., L., C., Doehlert Matrix: A chemometric tool for analytical chemistry—Review, *Talanta*, 2004, 63, 1061–1067

Fidowski, Z.T., Krolikowski, L., Thermally coupled system of distillation columns: optimization procedure, *AIChE Journal*, 1986, 32,537.

Gadalla, M., Olujic, Z., De Rijkeb, A., & Jansens, P. J., Reducing CO2 emissions of internally heat-integrated distillation columns for separation of close boiling mixtures, *Energy*, 2006, 31, 2409–2417.

Gutiérrez-Guerra, R., Segovia-Hernández, J., G., Hernández, S., Reducing energy consumption and $CO_2$ emissions in extractive distillation, *Chemical Engineering Research and Design*, 2009, 87, 145–152.

Halvorsen, I., J., Skogestad, S., Minimum Energy Consumption in Multicomponent Distillation. 2. Three-Product Petlyuk Arrangements**,** *Ind. Eng. Chem. Res.*, 2003**,** *42*, 605-615

Hernández, S., Analysis of Energy-Efficient Complex distillation options to purify bioethanol**,** *Chem. Eng. Technol.*, 2008, *31*(4), 597–603

Ignat, R., M., Kiss, A.,A., Integrated Bioethanol Separation and Dehydration in a Novel Extractive DWC, *Chemical Engineering Transactions*, 2012, 29, 619-624.

Kaibel, B., Distillation columns with vertical partitions, *Chem. Eng. Tech.*,1987, 10(2), 92-98.

Kiss, A., A., Rewagad, R., R., Energy efficient control of a BTX dividing-wall column, *Computers and Chemical Engineering*, 2011, 29, 1555-1559.

Kiss A., A., D. Suszwalak, D., J-P., C., Efficient bioethanol dehydration in azeotropic and extractive dividing-wall columns, *Procedia Engineering*, 2012, 42, 566 – 572

Lestak, F., Smith, R. and Dhole, V.R., Heat transfer across the wall of dividing wall column, *Trans IChemE*, 1994, 72, 639-644.

Mutalib, M., I., A., Smith, R., Operation and control of dividing wall distillation columns Part 1: Degrees of Freedom and Dynamic Simulation, *Trans IChemE*, 1998, 76, 308-311.

Mutalib, M., I., A., Smith, R., Operation and control of dividing wall distillation columns Part 2: Degrees of Freedom and Dynamic Simulation, *Trans IChemE*, 1998, Simulation and Pilot Plant Studies Using temperature Control, 76, 319-334.

Muralikrishna V, K., Madhavan, P., Shah, S. S., Development of dividing wall distillation column design space for a specified separation, *Trans IChemE*, 2002, 80, 155-166.

Muthukumar, M., Mohan, D., Rajendran, M., Optimization of mix proportions of mineral aggregates using Box–Behnken design of experiments, *Cement and Concrete Composites*, 2003, 25, 751–758.

Omer Yildirim, O., Kiss, A., A., Kenig, E., Y., Dividing wall columns in chemical process industry: A review on current activities, *Separation and Purification Technology*, 2011, 80, 403–417.

Petlyuk, F.B., Platonov, V.M., Slavinskii, D.M., Thermodynamically optimal method for separating multicomponent mixtures, *Int. Chem. Eng*, 1965, 5, 555–561.

Rangaiah, G.P., Ooi, E.L., Premkumar, R., A simplified procedure for quick design of dividing-wall columns for industrial applications, *Chemical Product and Process Modelling*, 2009, 4(1), Article7.

Rong, B., G., Turunen, I., A new method for synthesis of thermodynamically equivalent structures for petlyuk arrangements, *Trans IChemE*, 2006, 84(A12), 1095–1116.

Sangal, V., K., Kumar, V., Mishra, I., M., Divided Wall Distillation Column: rationalization of degree of freedom analysis, *Theoretical Foundations of Chemical Engineering*, 2012a, 46(4), 319-328.

Sangal, V., K., Kumar, V., Mishra, I., M., Optimization of structural and operational variables for the energy efficiency of a divided wall distillation column, *Computers and Chemical Engineering*, 2012b, 40, 33– 40.

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*, 2013a, 8, 85-92.

Sangal, V., K., Kumar, V., Mishra, I., M., Process Parametric Optimization of a Divided Wall Distillation Column, *Chemical Engineering Communications*, 2013b, DOI:10.1080/00986445.2012.762625.

Suphanit, B., Bischert, A., Narataruksa, P., Exergy loss analysis of heat transfer across the wall of the dividing-wall distillation column, *Energy*, 32, 2007, 2121–2134.

Tedder, D.W., Rudd, D.F., Parametric studies in industrial distillation: Part 1 Design comparison, *AIChE Journal*, 1978, 24, 30

Triantafyllou, C., Smith, R., The design and optimisation of fully thermally coupled distillation columns, *TransIChemE*, 1992, 70, 118–132

Wright, R.O., Fractionation apparatus, 1948, US Patent No. 2,471,134

Vazquez-Castillo, J. A., Venegas-Sanchez, J. A., Segovia-Hernandez, J. G., Hernandez- Escoto, H., Hernandez, S., Gutierrez-Antonio, C., et al., Design and optimization, using genetic algorithms, of intensified distillation systems for a class of quaternary mixtures, *Computers and Chemical Engineering*, 2009, 33, 1841–1850.