MODELING AND SIMULATION OF REACTIVE DIVIDING WALL DISTILLATION COLUMN USING RATE BASED APPROACH

A DISSERTATION

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

MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Computer Aided Process Plant Design)

By#

RAJ KUMAR VERMA

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DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, ROORKEE
ROORKEE-247667 (INDIA)

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INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE
CANDIDATE'S DECLARATION

I hereby declare that the work being presented in the dissertation entitled "Modeling and Simulation of Reactive Dividing Wall Distillation Column using Rate Based Approach" in partial fulfillment of the requirements for the award of the degree of Master of Technology with specialization in Computer Aided Process Plant Design and submitted in the Department of Chemical Engineering of the Indian Institute of Technology Roorkee, Roorkee, is an authentic record of my own work carried out during the period from May 2013 to June 2014 under the supervision of Prof. I.M. Mishra, Department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute.

Date: Raj Kumar Verma

Place: Roorkee Enrolment No: 12514017

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

(Dr. I.M. Mishra)
Professor
Department of Chemical Engineering
Indian Institute of Technology Roorkee
Roorkee

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Raj Kumar Verma

Enrolment No: 12514017

ABSTRACT

Distillation is one of the most important separation technology adopted in the chemical process industries. All the petrochemicals units use at least one distillation column for the separation and purification of the products. However, the distillation process accounts for more than 50 % of the plant operating cost. Dividing wall distillation column (DWDC) is a powerful process intensification technology used in the distillation process. Using the reaction and separation within a DWDC makes the process intensification more alternative and thus resulted, reactive dividing wall distillation column (RDWDC). Since the reactions are time dependent and the RDWDC uses Sulzer- zx packing, the present work uses rate-based approach for modeling and simulation of a RDWDC. For easy group of the methodology and the analysis of the results, a case study has been adopted, as reported earlier by Mueller and Kenig (2007). This case study deals with the production and purification of Diethyl Carbonate (DEC) from the reaction of Dimethyl Carbonate (DMC) with ethanol. The input parameters for the reaction kinetics were taken from the work of Keller et al. (2011).

The analysis has been carried out using ASPEN Plus (Version: 6.0). The parameters reflux ratio (r), liquid split rate (l) and vapor split rate (v) were optimized by using the results obtained from simulation with the optimization software Design Expert (Version:6.0) using the Box-Behnken design under response surface methodology (RSM). Synthesis of the DEC in a RDWDC previously carried by Mueller and Kenig (2007). The reflux ratio obtained by them for the RDWDC was 11.67, which is very high. This requires 201342 Btu/hr of energy for the reboiler for the specified distillation operation. Using the optimization technique, the reflux ratio has been found to be 9.8. At this reflux ratio, the energy requirement is 173435 Btu/hr for the distillation operation as against 201342 Btu/hr for r=11.67. This means a reduction of 13.86 % in the reboiler duty has been effected by the optimization technique. However, it can be seen that the RDWDC can be operated in a wide range from 5.2 to 9.8. The composition and temperature profiles in the pre and post fractionator of the DWDC are found to be similar as those given by Mueller and Kenig (2007). This shows that the methodology adopted by the kinetics of the overall reaction as proposed works well with the case problem and that the proposed methodology for the RDWDC can be used with confidence.

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CHAPTER I

INTRODUCTION

1.1 Need of separation processes and their types

Separation is the most important operation associated with the chemical processing industries because this step is the building block of the quality and quantity of the products. Cost of the product is directly associated with the separation process used. This indicates that the separation processes should be energy efficient and cost effective. The different types of separations processes based on the energy used for separation is shown in the following Fig.1.1

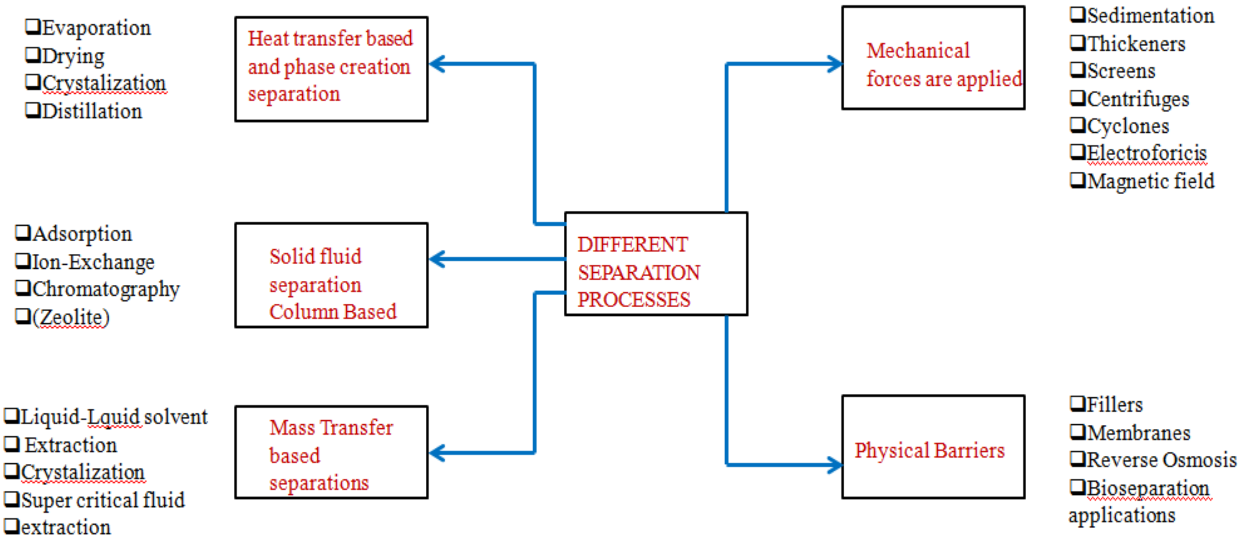


Fig.1.1 Different types of separation processes

Out of these processes distillation is the most important separation process widely used in petroleum and petrochemical industries, beverages industries, distilleries and organic process industries.

1.2 Distillation is the work horse of separation processes

Distillation is the method of separation of components from a liquid mixture in to its individual components based on the differences in the boiling point of the components of the liquid mixture. Distillation is generally performed in a column with internals like plates and their accessories or packing with a reboiler at the bottom and condenser at the top of the column. In the column a descending stream of condensate mixes with an ascending stream of hot vapor, the mixing of gas and liquid takes place and the temperature drop-up in the column cause the vapor to become more concentrated in the most volatile component towards the top of the column and collected in the form of distillate and the component that has the least volatility is removed from the bottoms of the column in the form of bottoms. Distillation can be done in many ways depending on the nature of the feed and its boiling point.

1.3 Distillation sequences: A mixture having more than two components is separated by using a battery or a sequence of distillation columns. There are three basic column sequences which are normally used for the separation of mixture of three components namely A, B and C. A being the more volatile component, B is the intermediate boiling component and C is the component having least boiling point.

1.3.1 Direct column sequence: In this configuration the most volatile component A is separated from the first column and then the mixture of other two components is separated in the second column. This arrangement is shown in the in the Fig.1.2.

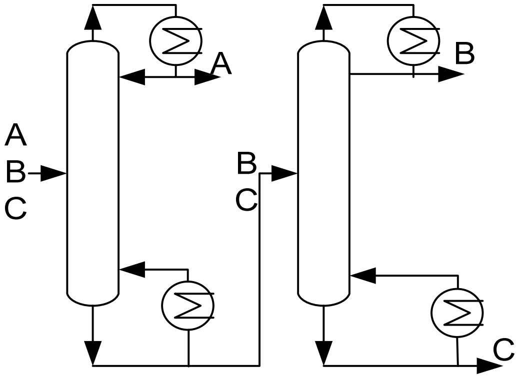


Fig.1.2 Direct column sequences

1.3.2 Indirect column sequence: In this type of column sequence the least volatile component C is separated from the first column and other two components, middle volatility and higher volatility components mixture is separated from the second column. This type of arrangement is shown in the Fig.1.3.

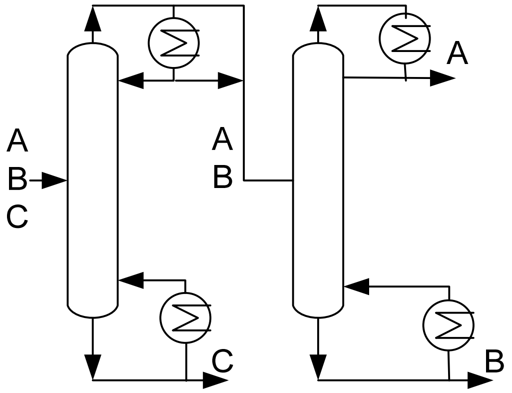


Fig.1.3 Indirect column sequences

1.3.3 Distributed column sequence: In this type of column sequence middle component B is distributed with the other two components A and B in first column and this mixture of two send in to two other columns where both components get separated. This shows that this type of separation uses an additional column for the separation. The following Fig.1.4 shows the three sequences arrangement.

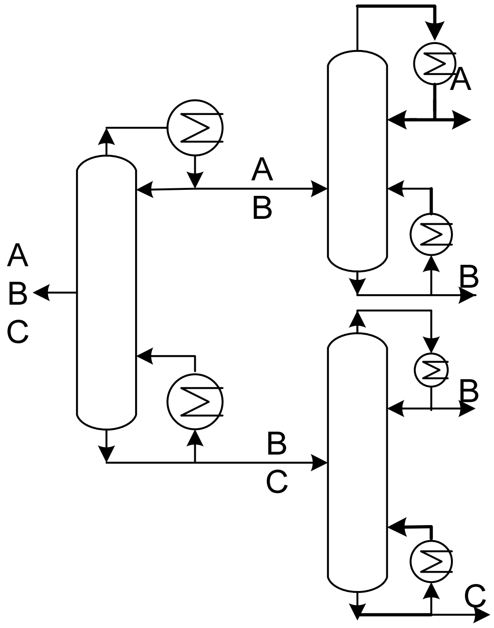


Fig.1.4 Distributed sequences

1.4 Process intensification technology in distillation process

Increase in production capacity within a given equipment volume and significant decrease in the energy consumption per ton of the product or even a marked cut in wastes or byproducts formation is the process intensification technology.

Past studies indicate that separation consumes about 50 % to 70 % of the capital and energy cost of a traditional chemical process. This shows that the chemical process industries are facing the challenges to provide green and energy efficient technology to maximize the production with less input and more output with a reduction in the total annual cost (TAC). In order to achieve this target, the optimal design and control of energy efficient distillation process is the need of the chemical process industries. Process intensification is the answer to this problem. This aims to decrease the physical size of the equipment leading to high production and decrease in capital and energy cost which result in a decrease in the total annual cost (TAC) of the separation process.

In in the distillation sequences, additional columns, reboiler and condensers are used. Therefore they account for additional capital and energy costs. To overcome this problem, Petlyuk (*Petlyuk, 1965*) used the concept of the process integration and linked different separation units together for the separation of a ternary mixture. He uses two thermally coupled distillation columns and connected them so that the condenser and the reboiler of the first columns are replaced by additional thermal links (vapor and liquid stream) with the main column which additionally result in decrease of capital as well as energy cost. The arrangement of the Petlyuk column is shown in the Fig. 1.5

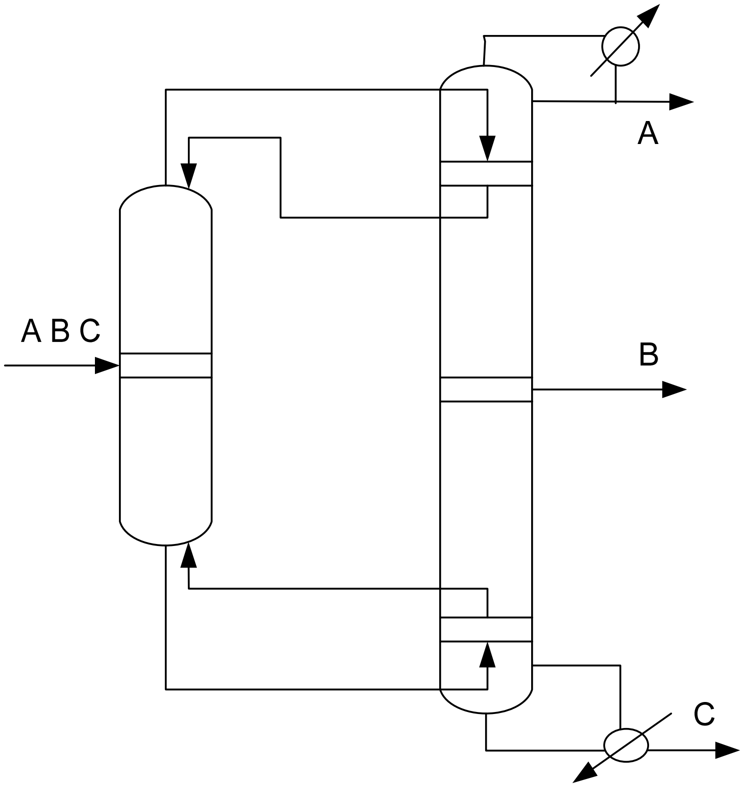


Fig.1.5 Schematic Representation of a Petlyuk Column

This shows that Petlyuk column is a primary step for process intensification. This Petlyuk column arrangement can be realized in a single column to yield dividing wall distillation column (DWDC)

1.5 Dividing wall distillation column (DWDC)

Dividing wall distillation column is the only known large scale process intensification technique available for distillation. This is an effective method for reducing both the capital and energy costs of the separation unit. Approximately 30 % reaction in the total cash can be effect in comparison to the traditional two column sequences. Later on, Wright [Wright, 1949] gave the concept of partitioning a column in two parts by placing a wall in the middle section of the column so that in the pre-fractionator (feed side) of the dividing section the feed is introduced and in the post-fractionator (side stream side) separation takes place. There is a provision to draw a side stream from the middle of the column in addition to the top and bottom products so that the third component can be separated from there. The dividing wall distillation column is shown in the Fig. 1.6

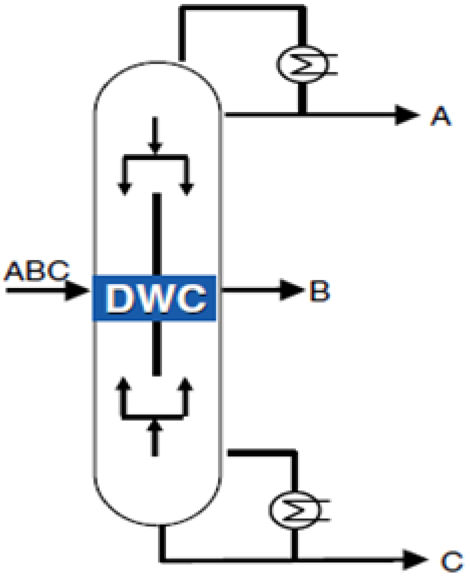


Fig. 1.6 Schematic representation of DWDC

1.6 Reactive dividing wall distillation column (RDWDC)

Reactive dividing wall distillation column is a highly integrated and energy efficient technology. This technology is the outcome of the integration of two integrated technology namely reactive distillation (Integration of Reaction-Separation) and the dividing wall distillation column (Integration of Separation-Separation). The key factor that allows such an integration of two columns in to one single unit is the similar pressure and temperature conditions in the stand alone columns. Reactive dividing wall distillation column (RDWDC) configuration consists of one condenser, one reboiler, a reactive zone, a pre-fractionator and the main column together in a single shell distillation setup. The development of the RDWDC from Distillation column can be best represented by the Fig.1.7.

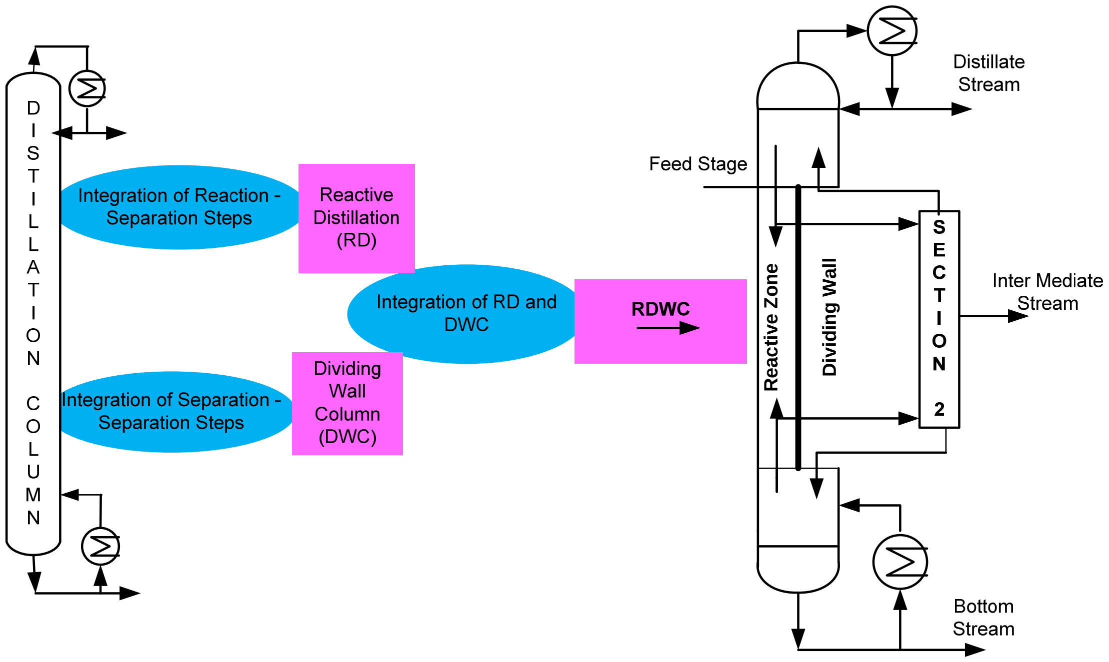


Fig.1.7 Application of process intensification technology on distillation

1.7 Advantages and of RDWDC

This technology provides advantages of both reactive distillations as well as of the dividing wall distillation columns RDWDC.

- Increases yield by reducing the chemical and thermodynamic limitations.
- Increases selectivity by suppressing the undesired consecutive reactions.
- Reduces energy consumption by integrating heat generated in case of exothermic reaction with reboiler duty and integrating heat required in case of endothermic reaction with heat released in condenser and this is the goal of the process intensification.
- Reduces the possibility of formation of hot-spots by simultaneous liquid evaporation
- Increases the ability to separate close boiling components by reactions.
- Gives high purity for all the three product streams in one single column.

- Gives thermodynamic efficiency than that for serial column sequence because of the reduced remixing effects with respect to the middle component.
- Shows a reduction in capital and energy cost by reducing the number of equipment units (*Kiss et al. 2009*).

1.8 Modeling of reactive dividing wall distillation column

The detail mathematical model equations involved in the modeling of the reactive dividing wall distillation column are given in Chapter IV. Modeling can be done by using two approaches.

- Equilibrium based approach
- Non- Equilibrium or Rate based approach.

1.8.1Equilibrium based approach

In Equilibrium approach, arrangement is made in such a way that the two phases when contacted with each other, they spend some time, during which there is a finite rate of mass transfer. However at the end, we have two leaving streams that are in equilibrium with each other.

Equilibrium staged model are very simple to design and elegant from the mathematical point of view. That is why, the basis chosen for many commercial columns is equilibrium approach. Model Equations which are used in modeling by using equilibrium approach are MESH equations. MESH is an acronym referring to different types of equations that are used in model.

- M stands for material balances
- E stands for equilibrium relationship (To express the assumption that the streams leaving the stage are in thermodynamic equilibrium
- S stands for summation equations
- H stands for Heat or Enthalpy balances.

1.8.2 Restrictions over Equilibrium modeling

The streams leaving from a real tray or a section of a packed column are not in equilibrium with each other and the separation achieved depends on the rates of mass transfer from the vapor to liquid phase. These rates are depending on the extent to which the vapor and liquid streams are deviates from the equilibrium.

The efficiency varies from stage to stage in a tray column and the Height Equivalent to Theoretical Plate (HETP) is a function of height in a packed column. Therefore the result obtained is deviates from the actual result. If a column is not at the steady state then efficiency varies with time as a result of changes in flow rates and the composition. Therefore equilibrium based model is not appropriate to model the dynamic behavior of a reactive dividing wall column. Rate based or non-equilibrium modeling can be used to overcome these problems [Taylor and Krisna, 2003].

1.8.3 Rate based or non-Equilibrium modeling

Non-Equilibrium modeling or rate based modeling is a standard procedure which is more accurate and gives more accurate results. This modeling approach is widely used in retrofitting and troubleshooting and is helpful in identifying what particular equipment design detail is responsible for a column failing to do for what it was designed. The assumptions of phase equilibrium are made only at the vapor liquid interface (Taylor and Krisna, 2003). Following are the areas where rate based modeling used.

- Packed Column
- Highly non-ideal systems
- Systems with trace components
- In columns with profiles that exhibit maxima and minima
- If efficiencies are unknown.

Model equations are complex equations, as a number of properties are needed to write the equations of the rate based models. In this type of modeling separate balance equations should be written for each phase. The main equations are

- Phase Mass Balance Equations
- Phase Energy Balance Equations
- Equilibrium Equations
- Summation Equations
- Mass Transfer in Vapor Phase
- Mass Transfer in Liquid Phase
- Energy Transfer Equations.

From the literature survey as given in Chapter II it is found that the RDWDC is a very powerful process intensification technology used in the distillation process. It is also found that RDWDC has been modelled and simulated using equilibrium approach by many authors. However work is available for RDWDC. This dissertation for modeling of RDWDC using the rate based approach for the calculation purpose, the production of diethyl carbonates (DEC) and methanol by the reaction of dimethyl carbonate (DMC) and ethanol has been taken as example.

Diethyl carbonate is an important compound generally used as a solvent in lithium ion batteries. Liquid electrolytes solutions play a key role in lithium ion batteries acting as a carrier of lithium ions between cathode and anode. At room temperature DEC is a clear liquid with a low flash point. The reaction is a pseudo homogeneous reaction as presented by the equation 1.1.

$$(CH_3)_2CO_3 + 2C_2H_5OH \rightleftarrows (C_2H_5)_2CO_3 + 2CH_3OH \qquad 1.1$$

In this reaction ethanol is used in excess and potassium carbonate (K_2CO_3) is used as the catalyst in the reaction. For the production the aforesaid compounds in a reactive dividing wall distillation column the data needed in simulation of the flow sheet with the ASPEN Plus software were taken from the paper Meuller et al. (2007) and additional data needed for the reaction is taken from the Kellar et al. (2011). Since the reaction and separation of the components taking place in a single column and there are more than three components Therefore RDWDC is found to be very effective process for this system.

1.9 PROBLEM STATEMENT

Development of the mathematical model for the RDWDC using rate based approach and determining the conditions for maximizing the compositions of various components in the distillate, bottoms and the side stream and minimizing the reboiler duty of the RDWDC.

1.10 AIMS AND OBJECTIVES

1. To carry out the rate based modeling of reactive dividing wall distillation column.
2. To simulate the flow sheet in the ASPEN Plus (2006.5) software.
3. To optimize the liquid split rate, vapor split rate and reflux ratio through the use of Design Expert (Version 7.0) Software with Box Behnken Design (BBD) under the Response Surface Methodology (RSM).
4. To check the purity of the DEC in the bottoms, methanol in the distillate and ethanol in the side stream under optimized conditions.
5. To validate the results by comparing with those available in literature.

CHAPTER II

LITERATURE REVIEW

2.1 Literature as shown by Scopus

Fig.2.2 shows the year wise analysis of the papers published so far on (DWDC and RDWDC. The trend shows that research in this area only a few research papers are published up to 2008 and there is a remarkable increase in since 2008 onwards.

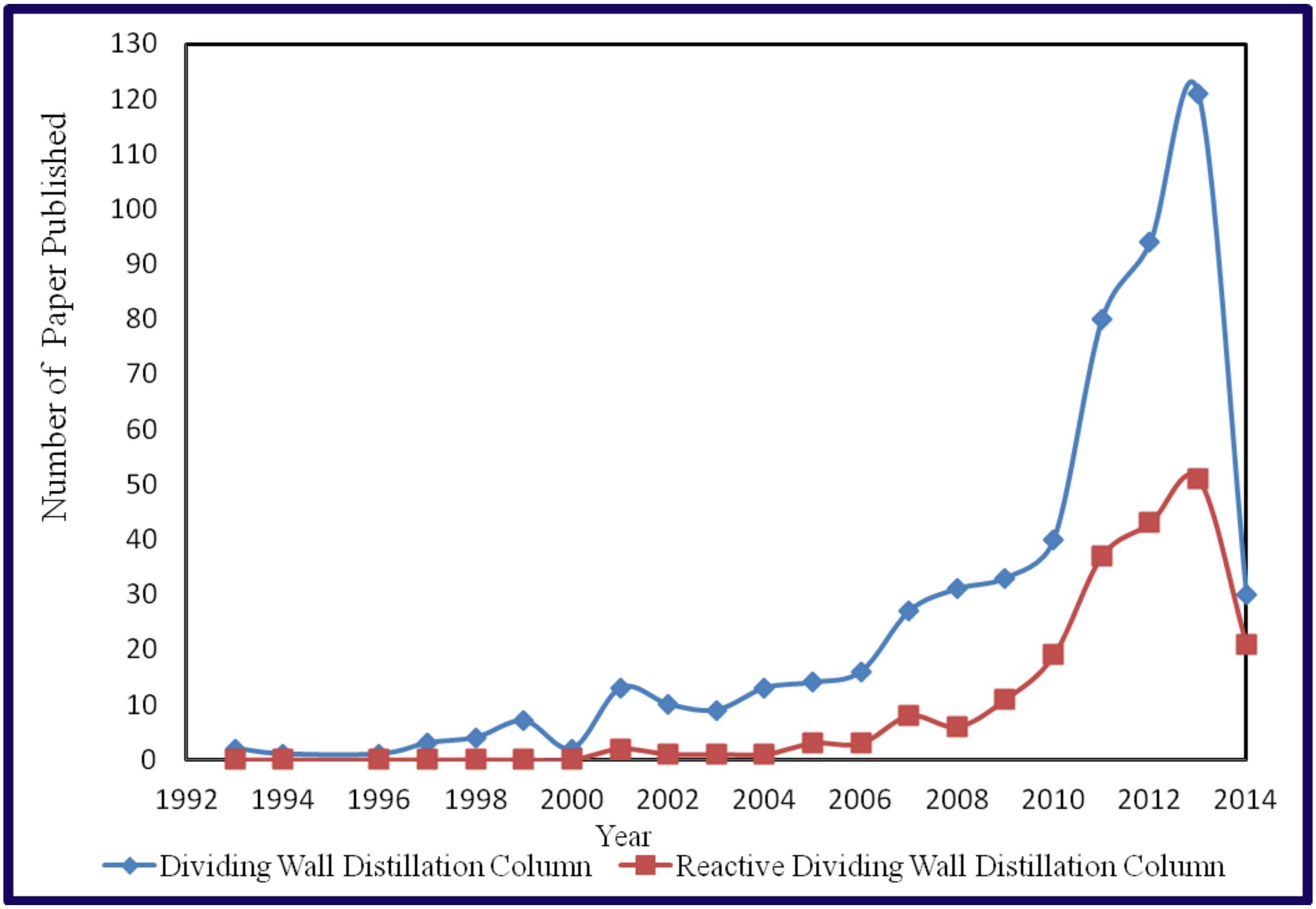


Fig. 2.1 Literature as shown by Scopus [http://www.scopus.com] (Keywords: Reactive Dividing Wall Distillation Column (RDWDC).

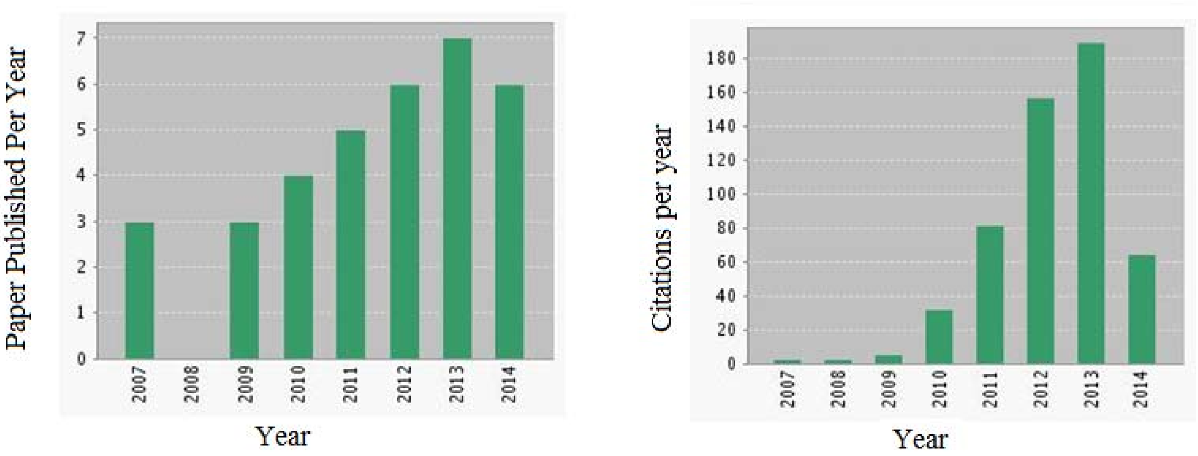


Fig 2.2 paper published per year and citation report as on web of science [http://apps.webofknowledge.com] (Keywords: Reactive Dividing Wall Distillation Column (RDWDC).

Fig. 2.2 shows the year wise analysis of the number of paper published per year and the citations per paper made over the year .Figure reflects that there is only a little work are done so far and also suggest that there is increasing interest in the study of reactive dividing wall distillation column. The detail literature review of the RDWDC presented in the following section 2.2

2.1.2 Detailed Literature Review

Huss et al. (1999) discussed about the computer aided tools for the conceptual design of a reactive distillation column to produce methyl acetate from methanol and acetic acid. The authors carried out the survey of available techniques and emphasized on the geometric methods for the design. They pointed out the opportunities for further research. In the geometric method, they used simple equilibrium model which acts as a starting point for the design of kinetically controlled reactive distillation process.

Patil et al. (2006) found that the RDWDC has been the prominent example of process intensification. RDWDC is the result of integration of the reactive distillation process with a dividing wall column. In their paper they used a novel approach for the design of RDWDC and the methodology of design is based on graphic based boundary value method (BVM). Reaction system is analyzed with four components in one reaction. Chemical equilibrium is assumed at each stage. They developed the cost function for the ranking of the design from several other designs which are proposed in the design procedures.

Alena et al. (2007) presented a methodology for modeling and simulation of the RDWDC by using commercial software available. ASPEN DISTIL ^{TM} and ASPEN HYSIS^{TM} Were used The feasibility of separation scheme is carried out using ASPEN DISTIL ^{TM} and simulation of flow sheet is performed using ASPEN HYSIS^{TM} with two columns model. The reaction zone in the pre fractionator section is assumed as two backflow CSTRs in series. They carried out a case study of isoamylenes etherification with ethanol to obtain tertiary-amyl ethyl ether in a reactive dividing wall distillation column with structured packing. According their result they recommend to place the reaction zone much closer to the pre fractionator top and to have feed inlet below the reaction zone, in order to increase the production of tertiary-amyl ethyl ether in reactive divided wall distillation column.

Mueller and Kenig (2007) expressed the need of the rate based modeling and simulation. They found that in taking the assumption that vapor liquid leaving from the tray are in equilibrium, does not provide the accurate result because separation achieved depends on the rate of mass transfer from the vapor to liquid phase and these rates further depend on the extent to which the vapor and liquid streams deviated from the equilibrium. To overcome this problem, generally efficiencies are used in the case of a tray columns and height equivalent to a theoretical plate (HETP) in the case of a packed column. Since the efficiency varies from tray to tray in a tray column and HETP varies with the height in a packed column therefore the calculated results deviate from the actual results in both the cases. Therefore the rate based approach is needed to model the RDWDC by earlier investigators. This model was applied to a non-reactive ternary alcohol mixture in a RDWDC and the results were successfully validated besides high conversion, the selectivity was found to be low. It was proved that this selectivity can be increased by integrating the dividing wall column with reactive distillation yielding the RDWDC.

Mueller and Kenig (2007) considered the transesterificatin of carbonates and modeled this system with rate based approach and carried out the simulation in ASPEN Custom Modeler simulation environment. They divided each packing section into smaller segments (stages), and each stage was described with film model. In their work they gave the special attention to both the heat transfer through the dividing wall and the vapor flow rate split below the wall. The results obtained are more accurate and clearly validate with the experiment result.

Rodrigo et al. (2008) designed and implemented a RDWDC by using Aspen plus and Aspen dynamics process simulator. In this arrangement, they used a reflux valve for controlling the composition of distillate and the temperature in the packed section. They also implement a reboiler in the lower section of the column for controlling composition in the bottom product and the temperature in the reboiler with heat duty supplied to it. This design is simulated by using steady state and dynamic simulation. They found that the minimum energy consumption is predicted more efficiently with the steady state simulation.

Gabriel et al. (2009) used multi objective genetic algorithm for optimized design of the RDWDC for the production of the biodiesel. Biodiesel production is carried out by esterification of laurie acid and methanol by using sulfuric acid as a catalyst. This catalyst is processed in thermally coupled distillation sequences with the side stripper. The result showed that the biodiesel obtained from above explained unit operation is high purity diesel oil, resulting in a drastic decrease in the energy consumption for the column.

Kiss et al. (2009) proposed "*How to get more with less resource?* In a DWDC and found that this could be done by the use of RDWDC. They carried out a case study in Akzo Nobel chemical industry and this was the first reported industrial application of RDWDC. The motive of their design was to decrease the production rate of the by product at the cost of the main product. They used a novel integrated design approach where two highly integrated steps were further integrated, yielding RDWDC leading reduced the capital investment by 35 % and the energy cost by 15 % as compared to base case design.

Satander et al. (2010) presented a novel process for the production of biodiesel from castor oil. Aspen Plus simulator and surface response methodology were used in the simulation. Performing various steps of experiments they found that the high yield in the transesterification reaction can be achieved using the following configuration: oil feed rate of 20.52 g/min, an ethanol oil molar ratio of 13, a molar reflux rate of 3.51 and a distillate-feed ethanol ratio of 0.84. The results showed that by using RDWDC the oil to ethanol molar ratio is reduced by 31.6 % as compared to standard conventional processes.

Delgado et al. (2011) conducted a review of the previous research of the RDWDC has been presented. They concluded that although in early 1949's much research is carried out on thermally coupled distillation column but the real application of this column was significantly reported in 1980's when reactive dividing wall column came in to existence. In the present work they carried out experiments for the production of ethyl acetate using RDWDC. The results obtained were being compared with simulation results of ASPEN ONE ASPEN plus simulator.

Gabriel et al. (2012) worked on a novel biodiesel production process with fatty acid methyl esters (FAMEs), in the reactive dividing-wall distillation column (RDWDC) that allows the use of only15% excess of methanol to completely convert the fatty acids feedstock. The design is a challenging global optimization problem with discrete and continuous decision variables. The optimal setup was established by using MATLAB, and coupled with rigorous simulations carried out in ASPEN Plus along with the FAME production. They showed that this design process reduces the energy requirement by 25% and using less equipment units than conventional processes.

Tavan and Hosseini (2013) studied the production of dimethyl ether from the dehydration of methanol in the RDWDC. With the help of ASPEN HYSYS software they analyzed the cost of the process and compared with the other processes available in the literature. They have shown that with the use of reactive dividing wall distillation column the operating cost is reduced by 44.53 % as compared to the conventional distillation column, while both schemes predict almost the same output specifications.

Ignat and Kiss (2013) produced the optimal design and worked on the dynamics and control of the RDWDC. They proposed an efficient control structure for a biodiesel process based on RDWDC technology. ASPEN Tech, ASPEN Plus and ASPEN Dynamics were used as computer aided process engineering (CAPE) tools to perform the rigorous steady-state and dynamic simulations and the optimization of the RDWDC for the biodiesel process. They also found that it was imperative to use a vapor feed of alcohol in order to reach the product specifications. Singular value decomposition (SVD) was effectively used to find the sensitive trays for inferential temperature control.

A brief summary of the literature review on RDWDC is given in Table 2.1. This table gives a synoptic view of the systems used, the parameters studied and the results which need highlighting.

Table 2.1 Brief Literature Summary of RDWDC

Authors and publication Year	**Column and arrangement used**	**Technique or Software used for the solution of model**	**System used**	**Parameters used**	**Remarks**
Huss et al. (1999)	Reactive distillation column	Computer aided tools and geometric methods	Methanol and acetic acid to produce methyl acetate	Kinetics of the reaction.	Equilibrium model is used which acts as a starting point for the design of kinetically controlled reactive distillation process.
Patil et al. (2006)	Reactive dividing wall distillation column	Graphically based boundary value method (BVM) is used	Reaction system is analyzed with four components carried out in one reaction	Assumption of Equilibrium at each stage.	They developed the cost function for the ranking of the design from several designs which are proposed in the design procedures

Alena et al. (2007)	Reactive dividing wall distillation column	The feasibility of separation scheme is carried out using ASPEN DISTIL ^{TM} and simulation of flow sheet is performed using ASPEN HYSIS^{TM}	Isoamylenes etherification with ethanol to obtain tertiary-amyl ethyl ether	Proper placement of Reaction zone and feed inlet	To increase the production, reaction zone should be placed much closer to the pre-fractionators top and the feed inlet to below the reaction zone.
Mueller and Kenig (2007)	Dividing wall distillation column	ASPEN Plus	Non-reactive ternary alcohol mixture	Heat transfer through the dividing wall of the dividing wall column	Separation achieved and the completely match with the experimental results.
Mueller and Kenig (2007)	Reactive Dividing wall distillation column	ASPEN Custom Modeler simulation environment	Non-reactive mixtures and idea about reactive system of transestrificatin of carbonates	Heat transfer through the dividing wall and the vapor flow rate split below the wall	Results obtained are more accurate. Successfully validated with the simulated results.

Rodrigoet al. (2008)	Reactive dividing wall distillation column	Aspen plus and Aspen dynamics process simulator	A comparison is made between steady state and dynamic modeling and simulation using ternary mixture.	Reflux valve and additional reboiler	Reflux valve for controlling the composition of distillate and temperature of the reboiler was used.
Gabriel et al. (2009)	Reactive dividing wall distillation column	Multi-objective genetic algorithm for optimization	Etherification of Laurie acid and methanol by using sulfuric acid as a catalyst to produce biodiesel	Catalyst is processed in thermally coupled distillation sequences with side stripper.	High purity diesel oil was produced in a drastic resulting in drastic decrease in energy of the column.
Kiss et al. (2009)	Reactive dividing wall distillation column	ASPEN Plus rigorous simulation is used.	Multi component separation process with aim, *How to*	The motive of the design was to decrease the production rate of by product at the consumption of main product.	RDWDC is reduces the capital investment by 35% and the energy cost by 15% as compared to base case design.

			Get More with Less Resources?		
Santander et al. (2010)	Reactive dividing wall distillation column	ASPEN Plus simulator and surface response methodology	Trans esterification reaction	Oil feed rate of 20.52 g/min, an ethanol oil molar ratio of 13, a molar Reflux rate of 3.51 and a distillate-feed ethanol ratio of 0.84	By using reactive dividing wall column oil to ethanol molar ratio is reduced by 31.6% as compared to standard conventional processes.
Delgado-Delgado et al., (2011)	Reactive dividing wall distillation column	ASPEN-ONE ASPEN plus simulator	Production of Ethyl acetate	Control of the column	Simulated results were successfully validated with the experimental data.
Gabriel et al., (2012)	Reactive dividing wall distillation column	MATLab, ASPEN Plus	Fatty acid methyl esters (FAMEs	Energy cost is taken as the optimizing parameter.	This design process reducesd the energy requirement by 25 % and used less equipment units than conventional processes.

Tavan and Hosseini (2013)	Reactive dividing wall distillation column	ASPEN HYSYS	Dehydration of methanol to produce dimethyl ether.	Comparison of the cost of process with conventional process.	This design process reduced the energy requirement by 44.5% and used less equipment units than conventional processes.
Ignat and kiss (2013)	Reactive dividing wall distillation column	ASPEN Tech, ASPEN Plus and ASPEN Dynamics	Biodiesel production.	Temperature control analysis.	This process is an efficient process in order to maintain the controllability of the process.

CHAPTER III

MATHEMATICAL MODELING

Mathematical modeling is an approach to quantify the material, energy and momentum output as a function of input parameters with the help of material, energy and momentum balance equations along with some constitutive relationships to describe the physical properties of the material as well as the system.

3.1Modeling of reactive dividing wall distillation column

Modeling of reactive dividing wall distillation column can be done by using the following two approaches:

I. Equilibrium based Approach
II. Non- Equilibrium or Rate based approach.

Equilibrium based Approach

The basic analysis can be shown by the following Fig 3.1

Fig. 3.1 Schematic representation of the first step to design a system

The functional relationship is written as

Output= f (Input)

This function f can be of several types such as:

I. Relation obtained by material, energy and momentum balance equations.
II. Constitutive relationships.
III. Empirical relationships.

A complete mathematical modeling of the reactive plus separation process requires material, energy and momentum balance equations along with the reaction rate equations for each individual tray of the column. Most of the existing models ignore momentum balances and try to model the system using material balance, equilibrium relationship, summation and heat balance equations. These equations are together known as basic MESH equations. For reaction and separation process to occur simultaneously, reaction rate equations are also included in the analysis and the equations together are called as MESHR equations.

Consider an equilibrium stage i as shown in the Fig.3.2 where several material and heat inputs and outputs are also shown. This is the basic diagram for mathematical modeling of a fractionating column.

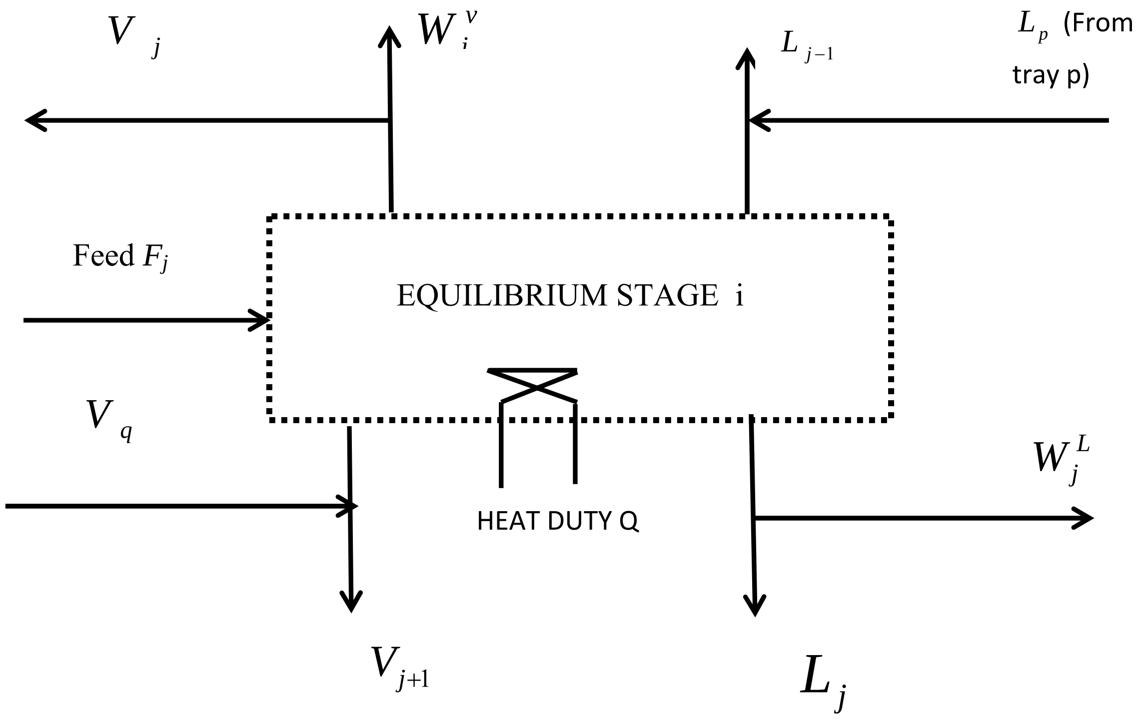


Fig.3.2 Schematic representation of an equilibrium stage

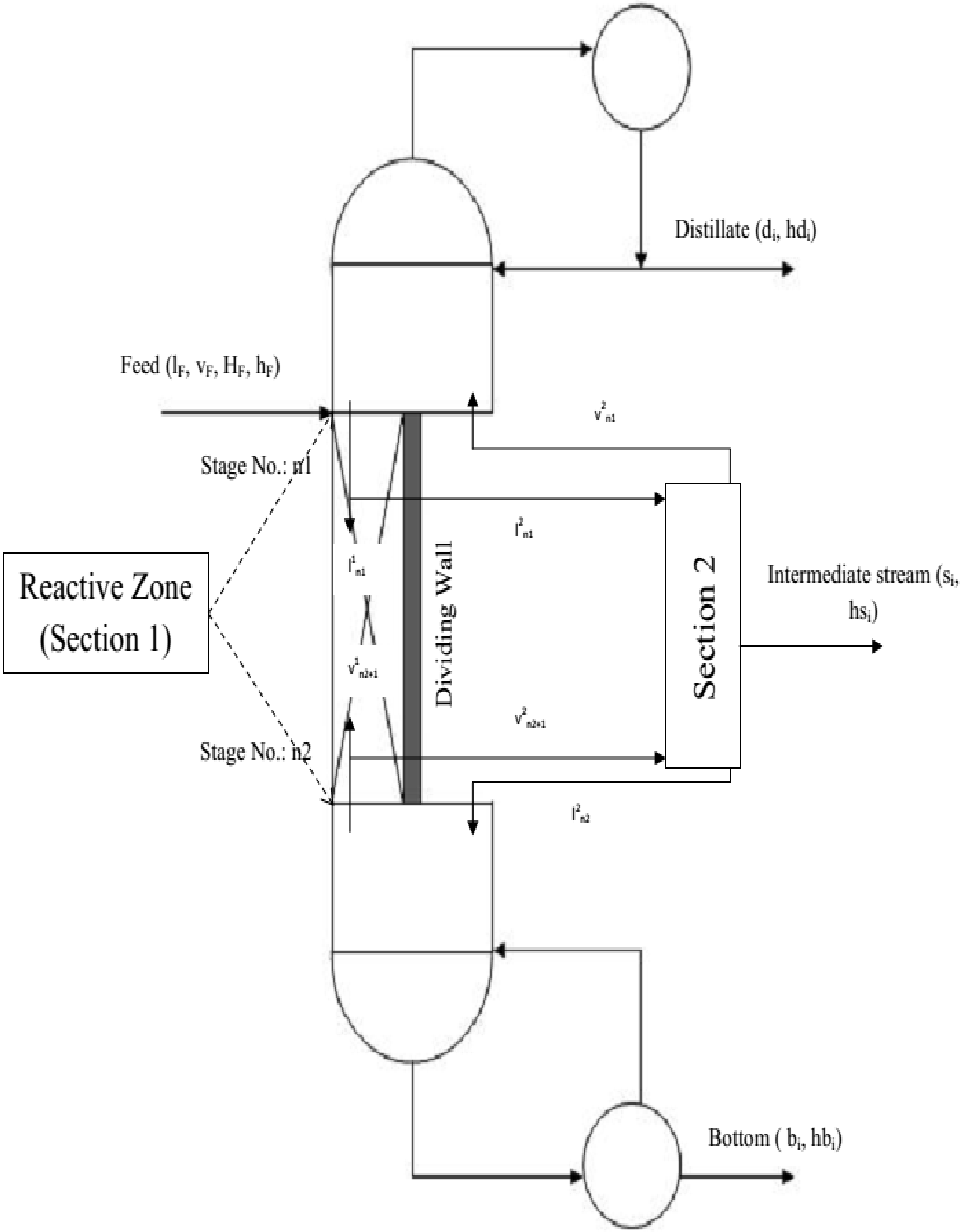


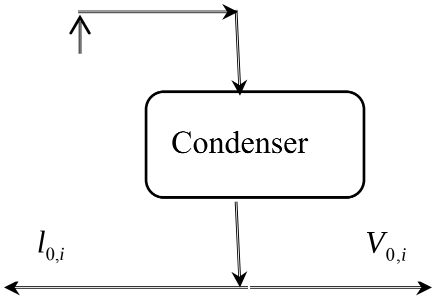
Fig 3.3 Schematic representation of the reactive dividing wall distillation column

Reactive DWC operates efficiently for ternary systems such as:

1) $A \longrightarrow B + C$ with moles of A in excess
2) $A + I \longrightarrow B + C$ with limited moles of A and inert added with the reactants
3) $A + B \longrightarrow C$ with both A and B in excess
4) $A + B \longrightarrow C + D$ with one of the reactants in excess

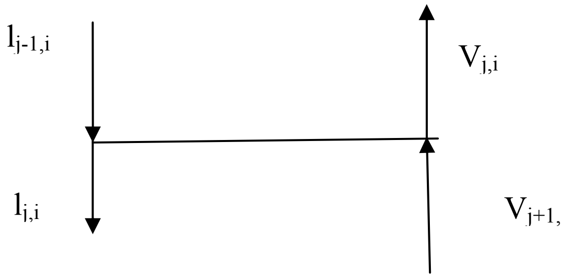
3.1(a) Material Balance:

For condenser



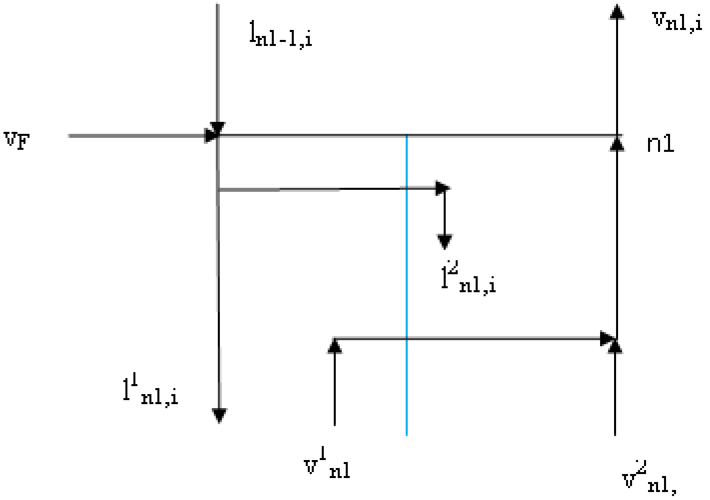
$V_{1,i} - l_{0,i} - V_{0,i} = 0$ .... for j=0 3.1

Material balance equation for above section of the dividing wall



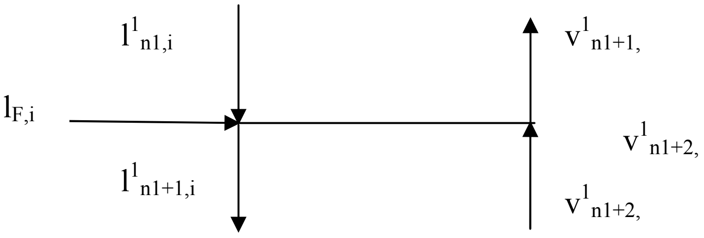
$V_{j+1,i} + l_{j-1,i} - V_{j,i} - l_{j,i} = 0 \ldots\ldots\ldots 1 \le j \le (n_1 - 1)$ 3.2

Material balance equation for 1st plate of the dividing section

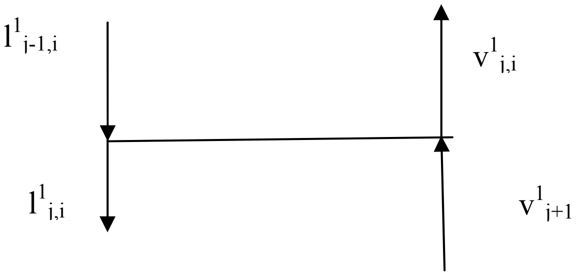


$v^1_{n1+1,i} + v^2_{n1+1,i} + l_{n1-1,i} - l^1_{n1,i} - l^2_{n1,i} - v_{n1,i} - v_{F,i} = 0$ ....for j = n1 3.3

Material balance equation for the reactive section (section-1)



$v^1_{n1+2,i} + l^1_{n1,i} - v^1_{n1+1,i} - l^1_{n1+1,i} \pm rV'^1_{n1+1} + l_{F,i} = 0$ ....for j=n1+1 3.4



$$v^{1}_{j+1,i} + l^{1}_{j-1,i} - v^{1}_{j,i} - l^{1}_{j,i} \pm rV^{'1}_{j} = 0 \text{ ....for n1+2} \le j \le n2-1 \tag{3.5}$$

Material balance equation for section-2 (similar to section 1)

$$v^{2}_{j+1,i} + l^{2}_{j-1,i} - v^{2}_{j,i} - l^{2}_{j,i} = 0 \text{ ....for } n1+1 \le j \le ns-2 \tag{3.6}$$

$$v^{2}_{ns,i} + l^{2}_{ns-2,i} - v^{2}_{ns-1,i} - l^{2}_{ns-1,i} - l_{s,i} = 0 \text{ ....for j=ns-1} \tag{3.7}$$

$$v^{2}_{ns+1,i} + l^{2}_{ns-1,i} - v^{2}_{ns,i} - l^{2}_{ns,i} - v_{s,i} = 0 \text{ ....for j=ns} \tag{3.8}$$

$$v^{2}_{j+1} + l^{2}_{j-1,i} - v^{2}_{j,i} - l^{2}_{j,i} = 0 \text{ ....for } ns+1 \le j \le n2-1 \tag{3.9}$$

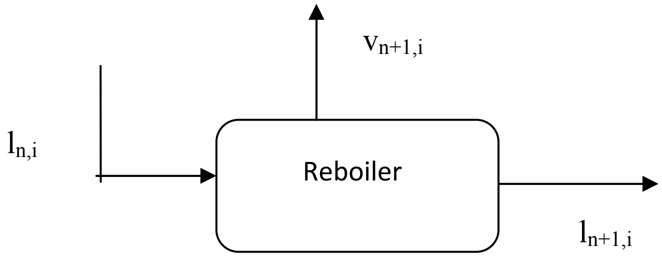
Material balance equation for the last plate of the dividing section

$$v^{1}_{n2+1,i} + v^{2}_{n2+1,i} + l^{1}_{n2-1,i} + l^{2}_{n2-1,i} - v^{1}_{n2,i} - v^{2}_{n2,i} - l^{1}_{n2,i} - l^{2}_{n2,i} \pm rV^{'1}_{n2,i} = 0 \text{ ....for j=n2} \tag{3.10}$$

Material balance equation for the column below the dividing section

$$v_{j+1,i} + l_{j-1,i} - v_{j,i} - l_{j,i} = 0 \text{ ....for } n2+1 \le j \le n \tag{3.11}$$

Material balance equation for reboiler



$$l_{n,i} - v_{n+1,i} - l_{n+1,i} = 0 \text{ ....for j=n+1} \tag{3.12}$$

3.1(b) Summation equation

$$L_j = \sum_{i=1}^{c} l_{j,i} \tag{3.13}$$

$$V_j = \sum_{i=1}^{c} v_{j,i} \tag{3.14}$$

3.1 (c) Equilibrium relationships

$$y_{j,i} = K_{j,i} x_{j,i} \qquad 3.15$$

$$K_{j,i} = f(T_{j,} P_j) \qquad 3.16$$

3.1 (d) Heat balance

For condenser

$$\sum_{i=1}^{c} v_{1,i} H_{1,i} - \sum_{i=1}^{c} l_{0,i} h_{0,i} - \sum_{i=1}^{c} v_{0,i} H_{0,i} - Q_c = 0 \qquad \text{For j=0} \qquad 3.17$$

Energy balance equation for above section of the dividing wall

$$\sum_{i=1}^{c} v_{j+1,i} H_{j+1,i} + \sum_{i=1}^{c} l_{j-,i} h_{j-1,i} - \sum_{i=1}^{c} v_{j,i} H_{j,i} - \sum_{i=1}^{c} l_{j,i} h_{j,i} = 0 \qquad 3.18$$

Energy balance equation for the 1st plate of the dividing

$$\sum_{i=1}^{c} v_{n1+1,i}^{1} H_{n1+1,i}^{1} + \sum_{i=1}^{c} v_{n1+1,i}^{2} H_{n1+1,i}^{2} + \sum_{i=1}^{c} l_{n1-1,i} h_{n1-1,i} - \sum_{i=1}^{c} l_{n1,i}^{1} h_{n1,i}^{1} -$$

$$\sum_{i=1}^{c} l_{n1,i}^{2} h_{n1,i}^{2} - \sum_{i=1}^{c} v_{n1,i} H_{n1,i} + \sum_{i=1}^{c} v_{F,i} H_{F,i} = 0 \qquad \text{..........for j=n1} \qquad 3.19$$

Energy balance equation for the reactive section (section-1)

$$\sum_{i=1}^{c} v_{n1+2,i}^{1} H_{n1+2,i}^{1} + \sum_{i=1}^{c} l_{n1,i}^{1} h_{n1,i}^{1} - \sum_{i=1}^{c} v_{n1+1,i}^{1} H_{n1+1,i}^{1} - \sum_{i=1}^{c} l_{n1+1,i}^{1} h_{n1+1,i}^{1} \pm r V_{n1+1,i}^{'1} \Delta H_{rn1+1} + \sum_{i=1}^{c} l_{F,i} h_{F,i} = 0 \text{ ....}$$

..for j=n1+1 3.20

$$\sum_{i=1}^{c} v_{j+1,i}^{1} H_{j+1,i}^{1} + \sum_{i=1}^{c} l_{j-1,i}^{1} h_{j-1,i}^{1} - \sum_{i=1}^{c} v_{j,i}^{1} H_{j,i}^{1} - \sum_{i=1}^{c} l_{j,i}^{1} h_{j,i}^{1} \pm r_i V_j^{'1} \Delta H_{r,j} = 0 \text{ ....for}$$

$$n1 + 2 \le j \le n2 - 1 \qquad 3.21$$

Energy balance equation for section-2

$$\sum_{i=1}^{c} v_{j+1,i}^{2} H_{j+1,i}^{2} + \sum_{i=1}^{c} l_{j-1,}^{2} h_{j-1,i}^{2} - \sum_{i=1}^{c} v_{j,i}^{2} H_{j,i}^{2} - \sum_{i=1}^{c} l_{j,i}^{2} h_{j,i}^{2} = 0 \text{ ....for } n1+1 \le j \le ns-2 \qquad 3.22$$

$$\sum_{i=1}^{c} v_{ns,i}^{2} H_{ns,i}^{2} + \sum_{i=1}^{c} l_{ns-2,i}^{2} h_{ns-2,i}^{2} - \sum_{i=1}^{c} v_{ns-1,i}^{2} H_{ns-1,ii=1}^{2} \sum^{c} l_{ns-1,i}^{2} h_{ns,i}^{2} - \sum_{i=1}^{c} l_{s,i} h_{s,i} = 0 \text{ ......for j=ns-1} \qquad 3.23$$

$$\sum_{i=1}^{c} v_{ns+1,i}^{2} H_{ns+1,i}^{2} + \sum_{i=1}^{c} l_{ns-1,i}^{2} h_{ns-1,i}^{2} \sum_{i=1}^{c} v_{ns,i}^{2} H_{ns,i}^{2} - \sum_{i=1}^{c} l_{ns,i}^{2} h_{ns,i}^{2} - \sum_{i=1}^{c} v_{s,i} H_{s,i} = 0 \text{ ....for j=ns} \qquad 3.24$$

$$\sum_{i=1}^{c} v_{j+1,i}^{2} H_{j+1,i}^{2} + \sum_{i=1}^{c} l_{j-1,i}^{2} h_{j-1,i}^{2} - \sum_{i=1}^{c} v_{j,i}^{2} H_{j,i}^{2} - \sum_{i=1}^{c} l_{j,i}^{2} h_{j,i}^{2} = 0 \text{ ....for } ns+1 \le j \le n2-1 \qquad 3.25$$

Energy balance equation for the last plate of the dividing section

$$\sum_{i=1}^{c} v_{n2+1,i}^{1} H_{n2+1,i}^{1} + \sum^{c} v_{n2+1,i}^{2} H_{n2+1,i}^{2} + \sum_{i=1}^{c} l_{n2-1,i}^{1} h_{n2-1,i}^{1} + \sum_{i=1}^{c} l_{n2-1,i}^{2} h_{n2-1,i}^{2} - \sum_{i=1}^{c} v_{n2,i}^{1} H_{n2,i}^{1} -$$

$$\sum_{i=1}^{c} v_{n2,i}^{2} H_{n2,i}^{2} - \sum_{i=1}^{c} l_{n2,i}^{1} h_{n2,i}^{1} - \sum_{i=1}^{c} l_{n2,i}^{2} h_{n2,i}^{2} \pm rV_{n2}^{'1} \Delta H_{rn2} = 0 \text{ .... for j= n2} \qquad 3.26$$

Energy balance equation for section below the dividing wall

$$\sum_{i=1}^{c} v_{j+1,i} H_{j+1,i} + \sum_{i=1}^{c} l_{j-1,i} h_{j-1,i} - \sum_{i=1}^{c} v_{j,i} H_{j,i} - \sum_{i=1}^{c} l_{j,i} h_{j,i} = 0 \text{ ..... for j=n+1} \qquad 3.27$$

Energy balance equation for reboiler

$$\sum_{i=1}^{c} l_{N,i} h_{N,i} - \sum_{i=1}^{c} v_{N+1,i} H_{N+1,i} - \sum_{i=1}^{c} l_{N+1,i} h_{N+1,i} = 0 \text{ .... for j=n+1} \qquad 3.28$$

$$r_i = f(C_{1,} C_2, C_3 \text{ ....} C_i \text{.................} C_c) \qquad 3.29$$

For several systems of RDC, the pressure at the plates are assumed to be constant as the operating pressure or the top condenser pressure, or it can be assumed to be constant pressure drop across each plate. In the present analysis, we have considered the pressure drop relation.

Here, the pressure drop is considered to comprise weir height pressure drop, over weir height pressure drop, dry plate pressure drop and residual head pressure drop. The equation is as shown below.

$$(P_j - P_{j-1}) - \rho_L g h_{t,j} = 0 \qquad \text{for j=1,2,3...................(n+1)} \qquad 3.30$$

Where $h_{t,j} = (h_w + h_{ow} + h_r)$ 3.31

htj denotes the liquid head between the j'th plate and (j-1)th plate, hw is the pressure head created by weir height, how is the pressure head created by over weir height, h_d is the dry plate pressure drop and hr is the residual head pressure drop.

These heads can be calculated by equations given below as presented by Lockett:

$$h_{ow} = f_1(L_j, W_L) \qquad 3.32$$

$$h_d = f_2(V_j, t_p, d_h) \qquad 3.33$$

$$h_r = f_3, \sigma_L, t_p, d_h) \qquad 3.34$$

Where WL is the weir length, dH is the hole diameter, tp is the plate thickness and σ_L is the surface tension of the liquid.

$$(P_{N+1} - P_N) - \Delta P_{\text{Re}} = 0 \qquad 3.35$$

Where ΔP_{re} is the reboiler pressure drop and is given by the following equation:

$$\Delta P_{re} = \frac{f^0 G_s^2 D_s (N_{pass} + 1)}{2 g \rho D_e \varphi} \qquad 3.36$$

Where f_o is the friction factor, D_s is the shell side diameter, Npass is the number of passes, ρ is the density, D_e is the equivalent diameter and φ_s is the ratio of viscosity of liquid to the viscosity of water.

3.2 Rate based Modeling

Assumptions

- The mass transfers resistances of all components are equal, this can be achieved by using HETP (Height equivalent to theoretical plate)
- No heat transfer occurs between the pre-fractionator and the main column through the dividing wall.
- Heterogeneously catalyzed reactions take place in the liquid bulk phase, treated as the Pseudo homogeneous reaction.
- Stage is described on the basis of the film model.
- Steady state operation

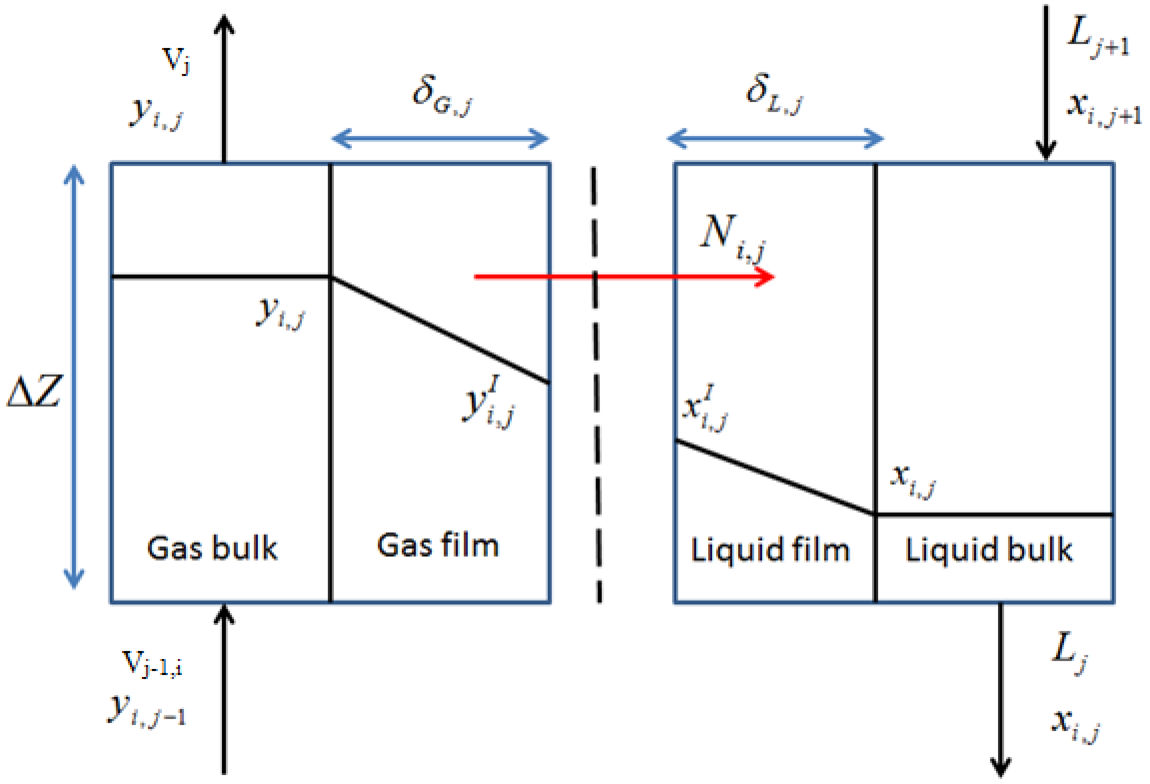


Fig.3.4 Representing a discrete stage with film model

3.2(a) Phase mass balance equations - In rate based modeling separate balance equations are needed for each phase. Following are the main mass balance equations.

Steady state component mass balance equation for vapor phase

$$V_{j-1}y_{i,j-1} - V_j y_{ij} - N_{ij} a_j A_j \Delta z_j = 0 \qquad 3.37$$

Steady state component mass balance for liquid phase

$$L_{j+1}x_{i,j+1} - L_j x_{i,j} + (N_{i,j} a_j + r_{i,j} \Psi_{cat} \rho_{cat}) A \Delta z_j \qquad 3.38$$

Where,

Ψ_{cat} = Catalyst volume fraction [$\frac{m^3}{m^3}$], N_{ij} = Molar flux [$mol/_{s.m^2}$],

Δz = Discrete stage height [m], a_j = Specific interfacial area [$\frac{m^2}{m^3}$]

A = Cross sectional area [m^2], δ = Film thickness [m]

Molar fluxes ($N_{i,j}$) are related to the diffusional fluxes by the following equations-

$$N_{i,j} = j^L{}_{i,j} + x_{i,j} \sum_{k=1}^{n} N_{i,j} = j^V{}_{i,j} + y_{i,j} \sum_{k=1}^{n} N_{k,j} \qquad \text{(for i = 1, 2, 3, 4…. n-1)} \qquad 3.39$$

3.2(b) Summation equation

$$\sum_{i=1}^{n} x_{i,j} = \sum_{i=1}^{n} y_{i,j} = 1 \qquad 3.40$$

Diffusional fluxes are further described based on the Fick's law as follows-

$$(j^L)_j = -c^{L,av}{}_{t,j} (k_L{}^{eff})(x - x^I)_j \quad \ldots \qquad 3.41\text{ a}$$

$$(j^L)_j = -c^{G,av}{}_{t,j} (k_G{}^{eff} (y^I - y\ )_j \qquad 3.41\text{ b}$$

3.2 (c) Phase Energy balance equations

The energy balances for the entire cross-section is sub divided on to the balances for the vapor and liquid phases as follows

Phase energy balance equation for Vapor Phase

$$V_{j-1}H_{G,,j-1} - V_j H_{G,j} - q^I{}_j a_j A_{col}\Delta z \ \underline{+}Q_{V,j}{}^{w} = 0 \qquad 3.42$$

Phase energy balance equation for Liquid Phase

$$L_{j+1}H_{L,,j+1} - L_j H_{L,j} - q^I{}_j a_j A_{col}\Delta z \ \underline{+}Q_{L,j}{}^{w} = 0 \qquad 3.43$$

In above equations "Q" is taken as positive for the pre-fractionator and negative for the main column. The heat flux across the vapor liquid interface consists of a convective component and a conductive component described by equation 3.44 and 3.45

$$q_j^I = \frac{\lambda_{V,j}}{\delta_{V,j}^{av}}(T_{V,j} - T_j^I) + \sum_{i=1}^{n} N_{i,j} H_{V,i,j} \qquad 3.44$$

$$q_j^I = \frac{\lambda_{L,j}}{\delta_{L,j}^{av}}(T_j^I - T_{L,j}) + \sum_{i=1}^{n} N_{i,j} H_{L,i,j} \ 4. \qquad 3.45$$

The average heat transfer film thickness (δ^{av}) for both phases liquid and vapor is needed to calculate the conductive interfacial heat transfer can be given by the equation 3.46

$$\delta_{L,j}^{av} = \sum_{i=1}^{n} x_{i,j}\delta_{L,i,j} = \sum_{i=1}^{n} x_{i,j}(D_{L,i,j}^{eff} / k_{L,i,j}^{eff}) \qquad 3.46$$

$$\delta_{G,j}^{av} = \sum_{i=1}^{n} y_{i,j}\delta_{G,i,j} = \sum_{i=1}^{n} y_{i,j}(D_{V,i,j}^{eff} / k_{V,i,j}^{eff}) \qquad 3.47$$

3.2 (d) Heat flow equations

Heat flow rate across the dividing wall (Q_j^W) is dependent on the phases that are adjacent to the wall. Equations

Energy balance equation for liquid phase

$$Q_{L,j}^{W} = k_j^{W} \Delta A^{W} (T_{L,j}^{PF} - T_{L,j}^{MC}) \quad 3.48$$

Energy balance equation for Vapor phase

$$Q_{V,j}^{W} = k_j^{W} \Delta A^{W} (T_{V,j}^{PF} - T_{V,j}^{MC}) \quad 3.49$$

Heat transfer coefficient (k_j^W) for stage j can be calculated using the heat transfer coefficient for the adjacent phases and the wall heat conduction coefficient, Can be estimated by the equation 3.50.

$$\frac{1}{k_j^{W}} = \frac{1}{\alpha_j^{W,Pf}} + \frac{S^{W}}{\lambda_j^{W}} + \frac{1}{\alpha_j^{W,MC}} \quad 3.50$$

3.2 (e) Liquid and vapor split-

Above the dividing wall the ascending vapor streams from the pre fractionator and the main column are mixed, while the liquid stream from the main column is split in to two stream which further flows along both side of the dividing wall. The scheme of the liquid and vapor split is shown in the Fig. 3.7

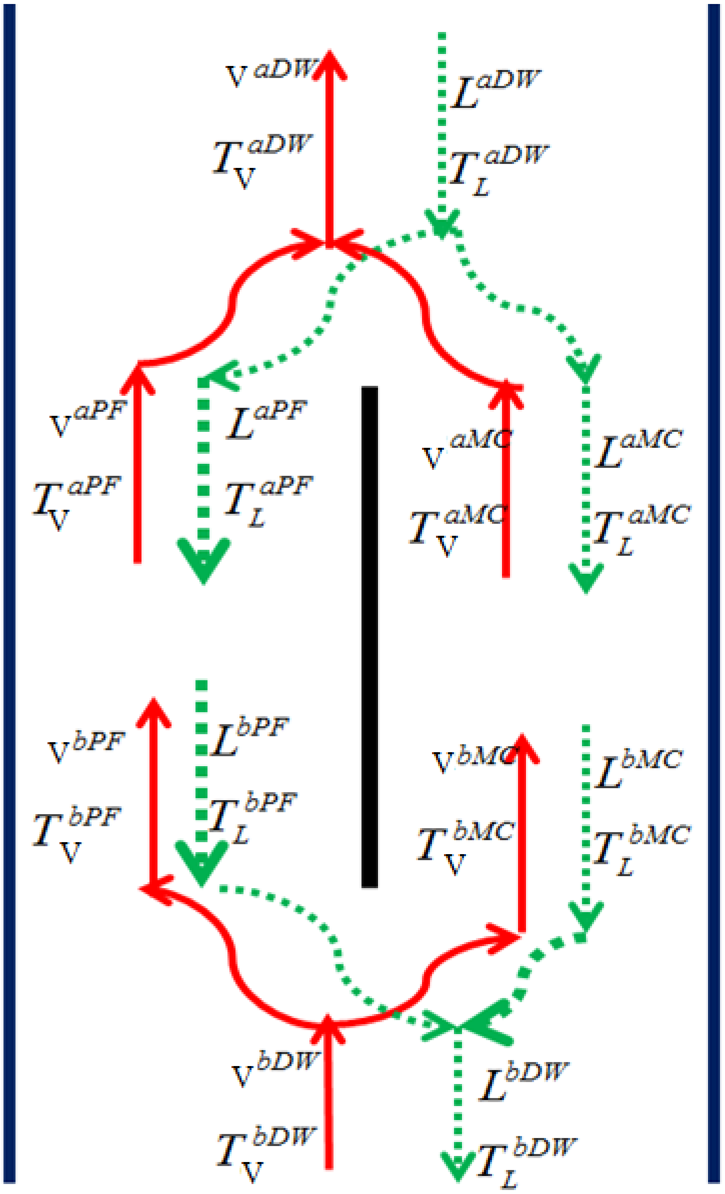


Fig. 3.5 Shows the liquid and vapor split patterns in a RDWDC

Mixing of down streaming liquid flows ($L^{b,MC}$) and (L^{bPF}) below the dividing wall to stream (L^{bDW}) is given by given by equation 3.51.

$$L^{bDW} x_i^{bDW} = L^{bMC} x_i^{bMC} + L^{bPF} x_i^{bPF} \ldots\ldots (\, for\,'i' = 1,2\ldots\ldots n\,) \qquad 3.51$$

The mixed stream (G^{aDW}) above the dividing wall (aDW) can be calculated by the equation 3.52

$$V^{aDW} y_i^{aDW} = V^{aMC} y_i^{aMC} + V^{aPF} y_i^{aPF} \quad \ldots.. \quad for' i' = 1,2......n) \qquad 3.52$$

Summation equations

$$\sum_{i=1}^{n} x_i^{bDW} = \sum_{i=1}^{n} y_i^{aDW} = 1 \qquad 3.53$$

Split ratios- Split ratios are defined as the ratio of the stream flow rate entering the pre-fractionator and the total stream flow rate. The split ratios are given by the equation 3.54 and 3.55 respectively.

Liquid split ratio-

$$\Phi_L = \frac{L^{aPF}}{L^{aDW}} \qquad 3.54$$

Vapor split ratio-

$$\Phi_G = \frac{V^{bPF}}{V^{bDW}} \qquad 3.55$$

In addition to the above equations, Balances of the flow rate are also required-

$$L^{aDW} = L^{aMC} + L^{aPF} \qquad 3.56$$

$$V^{bDW} = V^{bMC} + V^{bPF} \qquad 3.57$$

Both concentrations and temperatures remain unchanged for the split streams

This implies that

$$x_i^{aDW} = x_i^{aMC} = x_i^{aPF} \qquad (for' i' = 1,2......n) \qquad 3.58$$

$$y_i^{bDW} = y_i^{bMC} = y_i^{bPF} \qquad (for' i' = 1,2......n) \qquad 3.59$$

$$T_L^{aDW} = T_L^{aMC} = T_L^{aPF} \quad 3.60$$

$$T_V^{bDW} = T_V^{bMC} = T_V^{bPF} \quad 3.61$$

The liquid split ratio (Φ_L) can be used as an adjustable control parameter for the dividing wall column. However the vapor split ratio can't be easily controlled, rather it represents a self-adjusting parameter, because the vapor distribution in a reactive dividing wall distillation column must provide an equal pressure drop at both side of the dividing wall.

$$\Delta p^{MC} = \Delta p^{PF} \quad 3.62$$

The vapor split can set equal to the cross sectional are ratio, which can be defined as

$$\phi_{Area} = \frac{A^{PF}}{A_t} \quad 3.63$$

CHAPTER IV

METHODOLOGY

4.1 SIMUALTION SETUP

For the simulation set up, the following problem was used as discussed earlier in chapter- I (Problem statement and the Aims and Objectives). In the reaction of DMC with ethanol producing the DEC and methanol as represented by equation 2.1

$$(CH_3)_2CO_3 + 2C_2H_5OH \rightleftarrows (C_2H_5)_2CO_3 + 2CH_3OH \qquad 2.1$$

DEC has the least relative volatility among all of the compounds used in the reaction so DEC is collected from the bottoms and methanol has the higher relative volatility so it is collected from the distillate and ethanol is a compound having the intermediate relative volatility so it is collected from the side stream of the RDWDC. This section describe the simulation setup of transesterification of DMC with ethanol producing DEC and methanol which are industrially very important with the help of non-equilibrium modeling with ASPEN Plus software using Rate-Sep. Rate-Sep is a powerful tool in ASPEN Plus software which directly switch a Rad-Frac model into Rate-based and takes the account of mass and heat transfer limitations, liquid and vapor film diffusion, equipment hydrodynamics and chemical reaction mechanism, which occurs in equilibrium simulation. Rate-Sep uses Newton-based simultaneous correction approach for simulation, solution time increases with the square of the number of components. This simulates all types of multistage vapor liquid fractionation operation. This explicitly accounts for the underlying inter-phase mass and heat transfer processes to determine the degree of separation.

The most important feature of the Rate-Sep simulation process is that one can connect any number of columns by any number of connecting streams each connecting stream can have an associated heater and can draw any number of side products and can define pseudo-product streams to represent column internal flows connecting streams. The physical properties needed for simulation of rate based modeling are those same properties which are needed in equilibrium modeling and some extra properties are also required.

Properties needed for the simulation of Rate based modeling (Muller and Kenig, 2007) are

- Activity coefficient
- Fugacity coefficient
- Vapor pressure
- Density
- Enthalpy
- Diffusivity
- Viscosity
- Surface tension
- Thermal conductivity
- Mass transfer coefficient
- Heat transfer coefficient
- Interfacial area this simulation gives better results

The total number of stages in a RDWDC unit is taken to be 45 and is divided in to three sections as described below.

- Upper rectification zone.
- Middle reactive zone.
- Lower stripping section.

The reactive zone consists of stages from 10 to 34 these stages are a common stripping section consisting of stage 34 to 44 and a common rectifying zone (stage 1 to 10) counted from top to bottom with stage 1 as the condenser and stage 44 as the reboiler. Dimethyl carbonate is fed at stage 18 and ethanol is fed at stage 28. Dividing wall is placed at stage 10 and extends up to stage 34. The RDWDC is operating at 1.013 bar pressure. The DEC is obtained from column 1 as the bottom product .A mixture of unreacted DMC and methanol is recovered from the distillate and the excess ethanol is recovered from the side stream from stage 26 in the post fractionater. The reaction takes place in the liquid phase. For simulation the two thermally coupled RADFRAC units are used as a RDWDC system as described in Fig.4.1

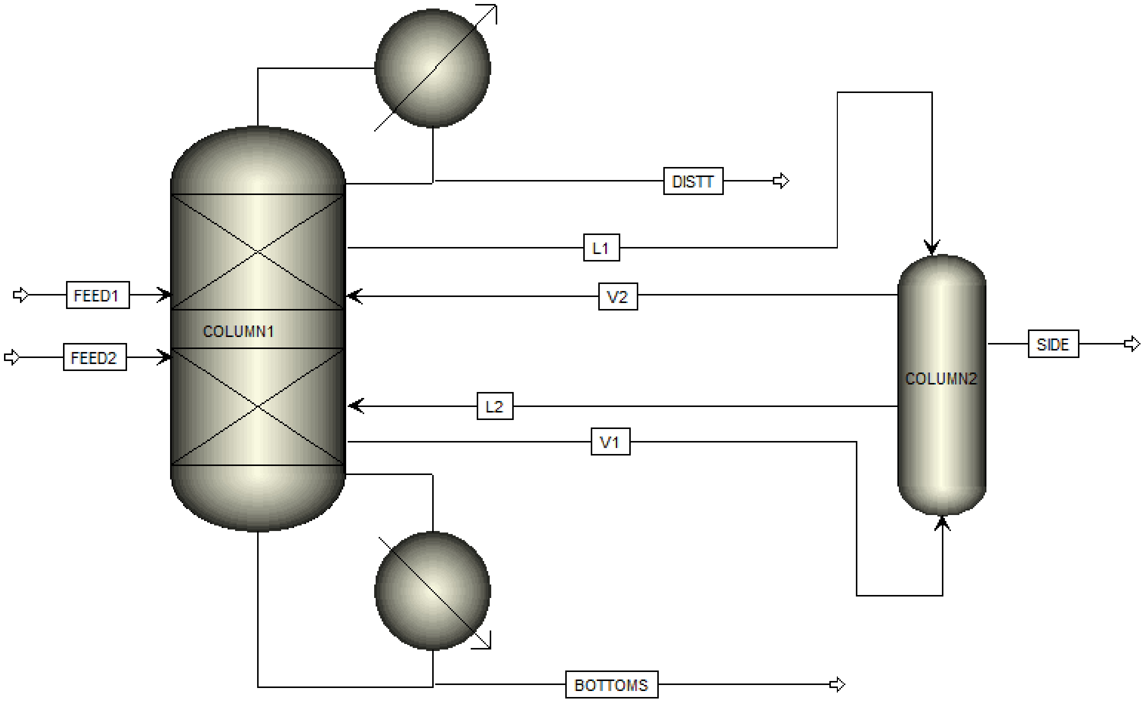
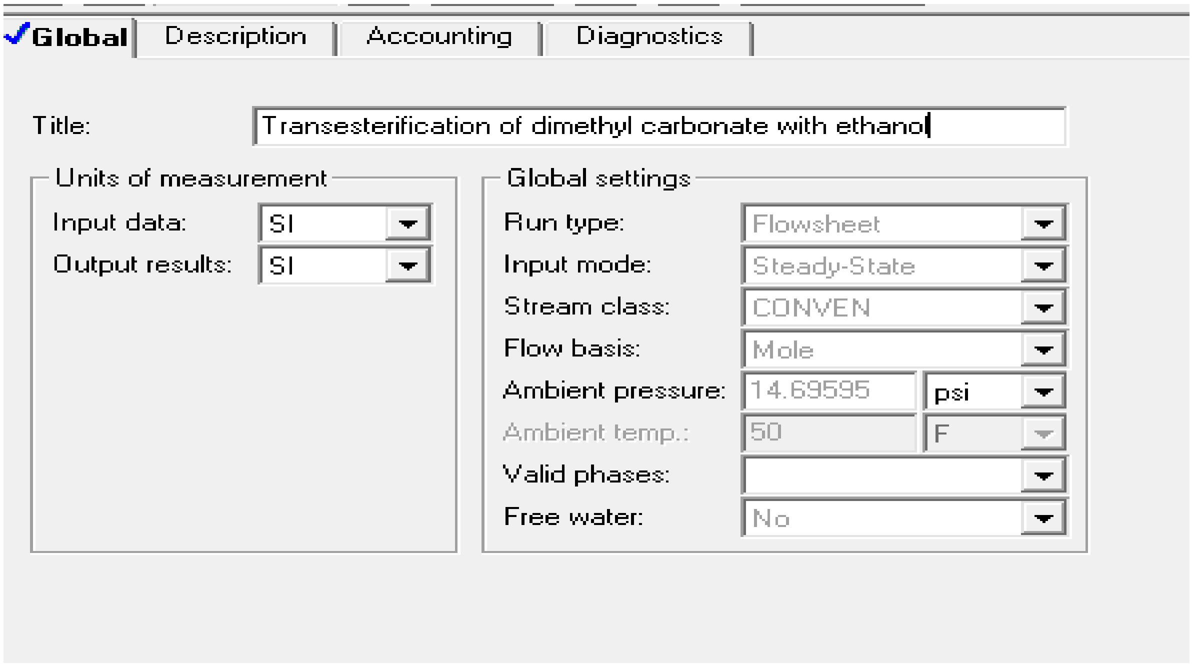


Fig.4.1 Two thermally coupled RADFRAC units acting as RDWDC

The title of the simulation and description is shown in the following Fig.4.2



Title: Transesterification of dimethyl carbonate with ethanol

Units of measurement

Input data: SI

Output results: SI

Global settings

Run type: Flowsheet

Input mode: Steady-State

Stream class: CONVEN

Flow basis: Mole

Ambient pressure: 14.69595 psi

Ambient temp.: 50 F

Valid phases:

Free water: No

Fig. 4.2 Aspen PLUS window to define title of the simulation and units

The UNIQAC method is used for physical properties.

UNIQUAC Activity Coefficient model:

The UNIQUAC model calculates liquid activity coefficient for the property methods: UNIQUAC, UNIQ-2, UNIQ-HOC, UNIQ-NTH, and UNIQ-RK. It is recommended for highly non-ideal chemical systems. The equation for the UNIQUAC model is as describe below

$$\ln\gamma_i = \ln\frac{\varphi_i}{x_i} + \frac{Z}{2}q_i^{'}\ln\frac{\theta_i}{\varphi_i} - q_i^{'}\ln t_i^{'} - q_i^{'}\sum\nolimits_j \frac{\theta_j^{'}\tau_{i,j}}{t_j^{'}} + l_j + q_i^{'} - \frac{\varphi_i}{x_i}\sum\nolimits_j x_j l_j \qquad 5.1$$

Where;

$$\theta_i = \frac{q_i x_i}{q_T}, \qquad q_T = \sum\nolimits_k q_k x_k \qquad 5.2$$

$$\theta_i^{'} = \frac{q_i^{'} x_i^{'}}{q_T^{'}}, \qquad q_k^{'} = \sum\nolimits_k q_k^{'} x_k^{'} \qquad 5.3$$

$$\varphi_i = \frac{r_i x_i}{r_T} \;; \qquad r_T = \sum\nolimits_k r_k x_k \qquad 5.4$$

$$l_i = \frac{z}{2}(r_i - q_i) + 1 - r_i \qquad 5.5$$

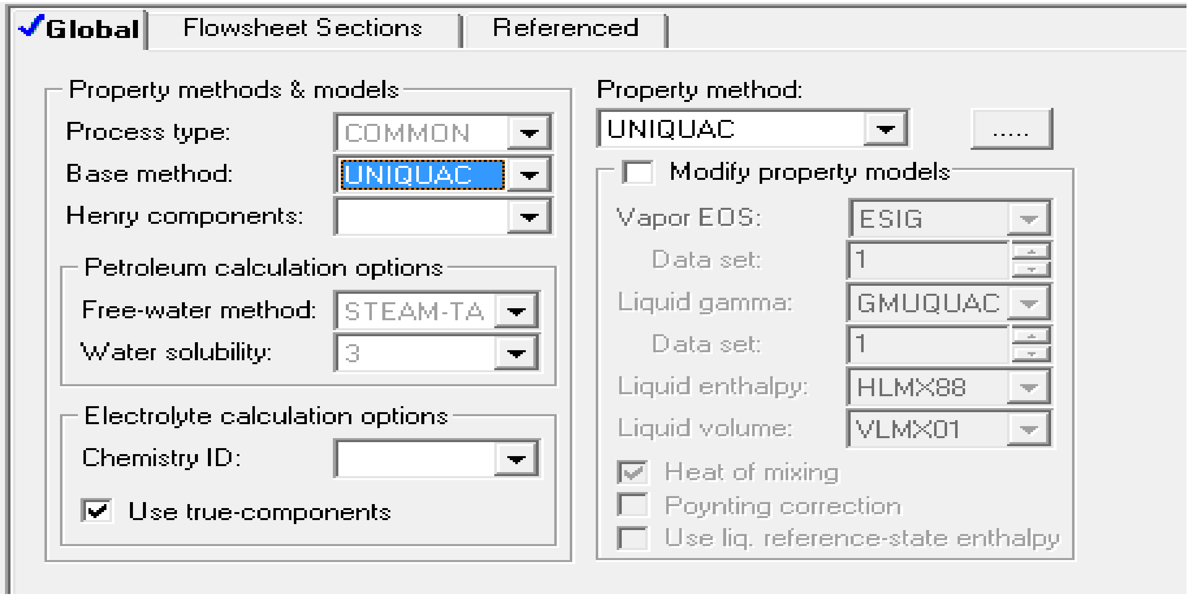
$$t_i^{'} = \sum\nolimits_k \theta_k^{'}\tau_{k,i} \qquad 5.6$$

$$\tau_{i,j} = \exp(a_{i,j} + \frac{b_{i,j}}{T} + C_{i,j}\ln T + \frac{e_{i,j}}{T^2}) \qquad 5.7$$

$$Z=10 \qquad 5.8$$

Here, a_{ij}, b_{ij}, c_{ij}, and d_{ij} are unsymmetrical. That is, a_{ij} may not be equal to a_{ji}, etc. Absolute temperature units are assumed for the binary parameters a_{ij}, b_{ij}, c_{ij}, d_{ij}, and e_{ij} can be determined from VLE and/or LLE data regression. The Aspen Physical Property System has a large number of built-in parameters for the UNIQUAC model. The binary parameters have been regressed.

The binary parameters for VLE applications were regressed using the ideal gas, Redlich-Kwong, and Hayden-O'Connell EOS. Aspen PLUS provides its own data bank which consists of several physical property data for different pure components at every temperature and pressure. During component specification, the chemical components that are to be used for simulation purposes are provided. The snapshot (Fig. 4.3) below clearly explains the situation.



Property methods & models

Process type: COMMON

Base method: UNIQUAC

Henry components:

Petroleum calculation options

Free-water method: STEAM-TA

Water solubility: 3

Electrolyte calculation options

Chemistry ID:

☑ Use true-components

Property method: UNIQUAC

☐ Modify property models

Vapor EOS: ESIG

Data set: 1

Liquid gamma: GMUQUAC

Data set: 1

Liquid enthalpy: HLMX88

Liquid volume: VLMX01

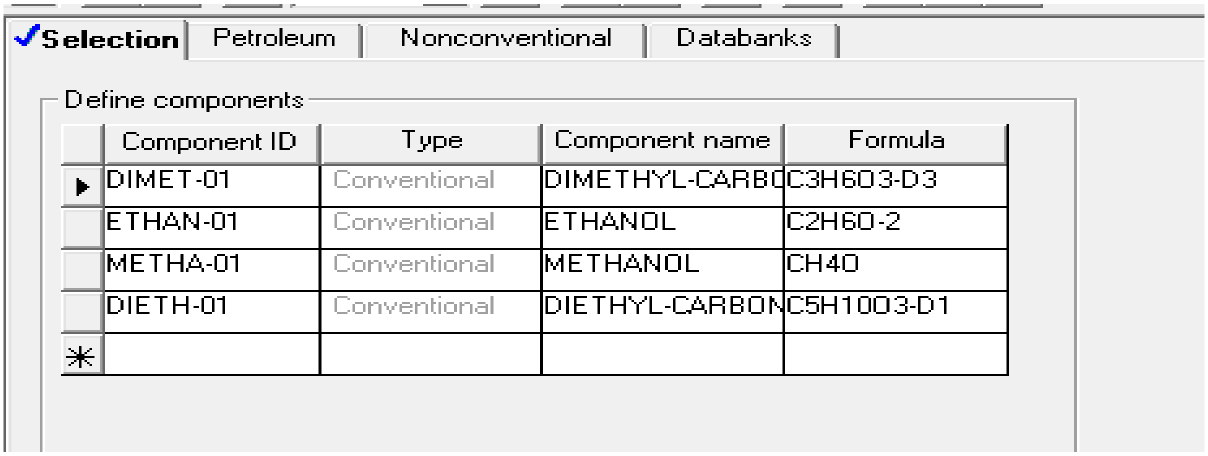
☑ Heat of mixing

☐ Poynting correction

☐ Use liq. reference-state enthalpy

Fig.4.3 Aspen PLUS window to define property method specifications

Aspen PLUS calculates itself the degrees of freedom for the process as given in the flow sheet (Fig. 4.4) and takes input to perform the simulation.

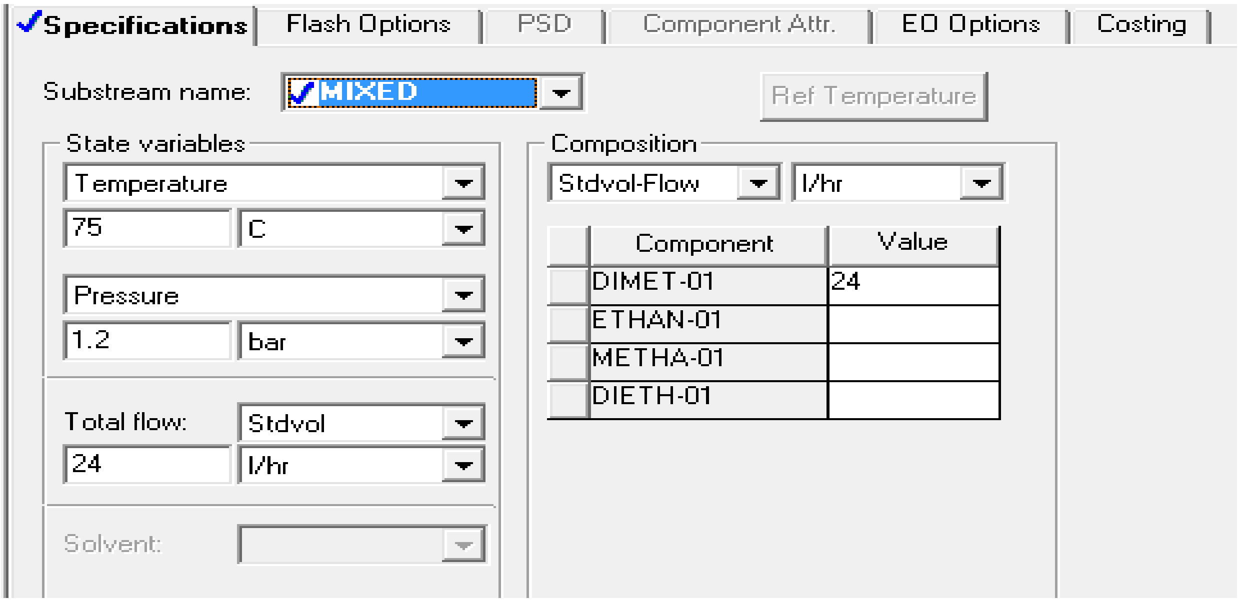


Define components

	Component ID	Type	Component name	Formula
▶	DIMET-01	Conventional	DIMETHYL-CARBO	C3H6O3-D3
	ETHAN-01	Conventional	ETHANOL	C2H6O-2
	METHA-01	Conventional	METHANOL	CH4O
	DIETH-01	Conventional	DIETHYL-CARBON	C5H10O3-D1
✳				

Fig. 4.4 Aspen PLUS window to define component specifications

For input to the column, the stream property is to be defined by us consisting of several inputs such as temperature, pressure, total flow and component flow or flow fraction. The snapshot below (Fig. 4.5) clearly explains the scenario.



Substream name: MIXED

State variables

Temperature: 75 C

Pressure: 1.2 bar

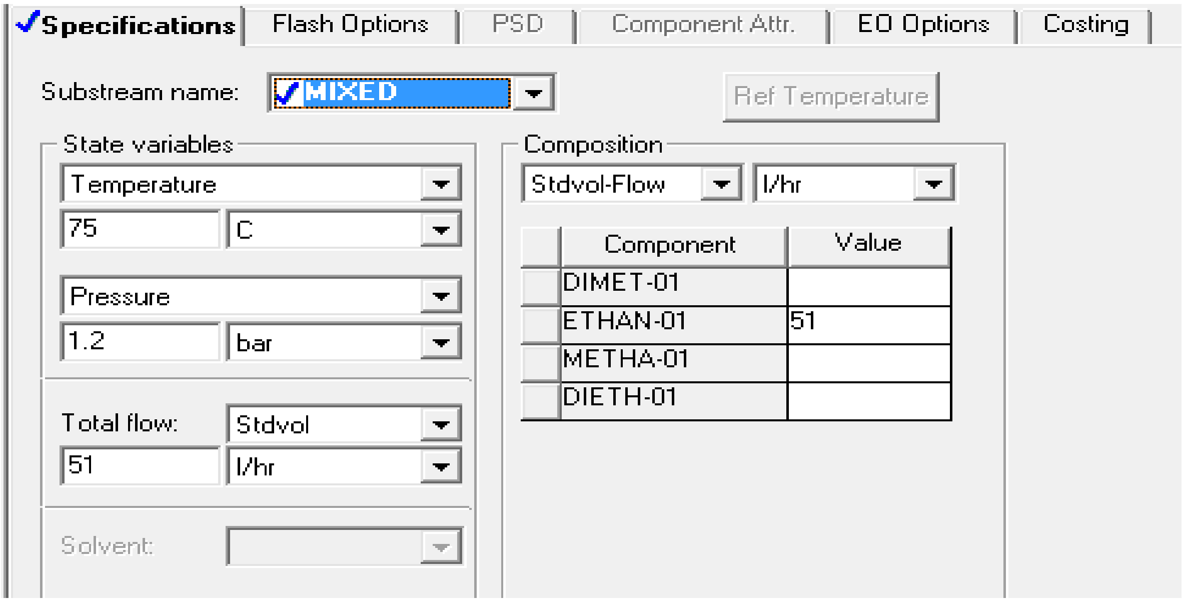
Total flow: Stdvol 24 l/hr

Solvent:

Composition: Stdvol-Flow l/hr

	Component	Value
	DIMET-01	24
	ETHAN-01	
	METHA-01	
	DIETH-01	

Fig. 4.5 (a) Aspen PLUS window shows input specifications of Feed1



Substream name: MIXED

State variables

Temperature: 75 C

Pressure: 1.2 bar

Total flow: Stdvol 51 l/hr

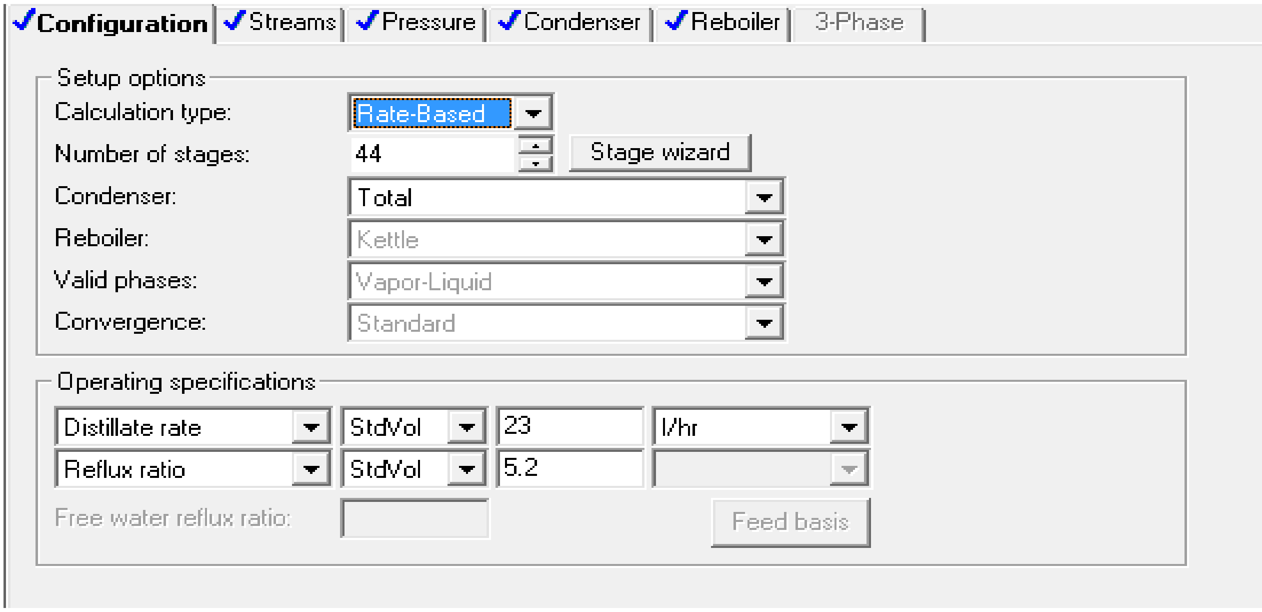
Solvent:

Composition: Stdvol-Flow l/hr

Component	Value
DIMET-01	
ETHAN-01	51
METHA-01	
DIETH-01	

Fig. 4.5 (b) Aspen PLUS window shows input specifications of Feed 2

The following Fig.4.6 shows the column 1 specification as number of trays and type of reboiler and condenser considered with distillate rate and reflux ratio.



Setup options

Calculation type: Rate-Based

Number of stages: 44

Condenser: Total

Reboiler: Kettle

Valid phases: Vapor-Liquid

Convergence: Standard

Operating specifications

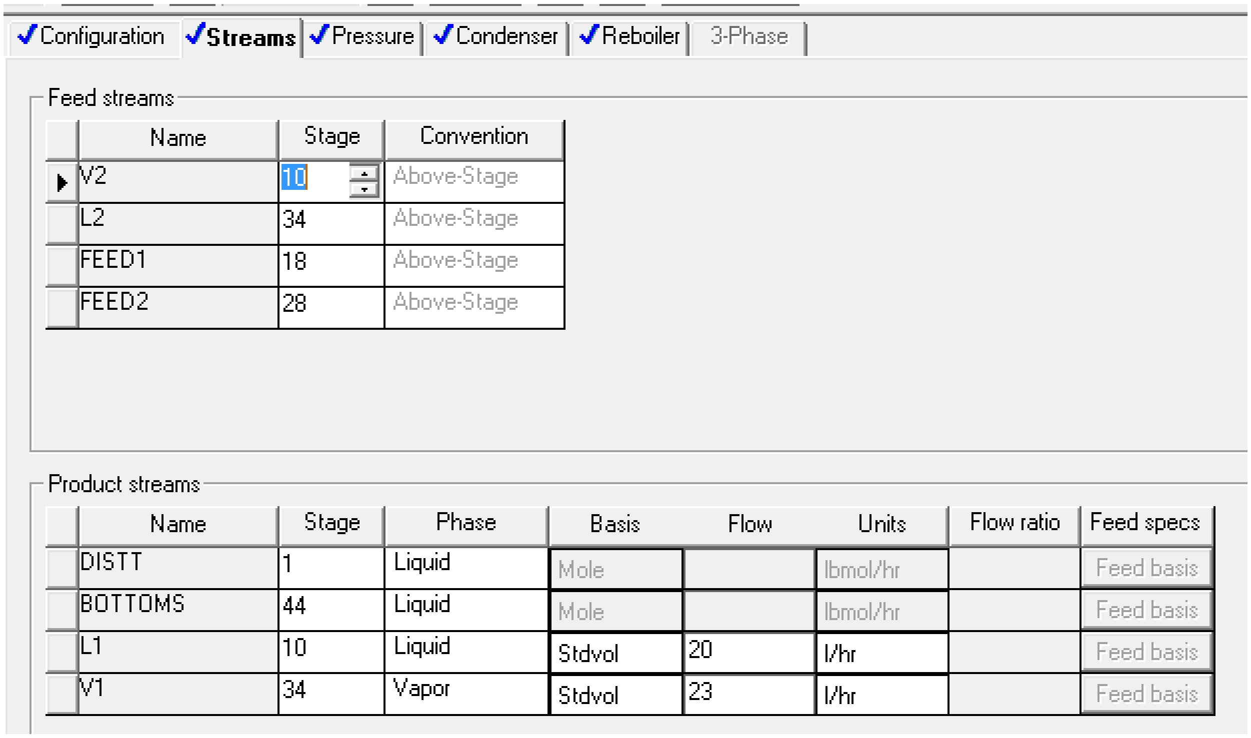
Distillate rate: StdVol 23 l/hr

Reflux ratio: StdVol 5.2

Free water reflux ratio:

Fig. 4.6 Aspen PLUS window to define column 1 specifications

Fig.4.7 shows the stages at which streams entering in the column1



Feed streams

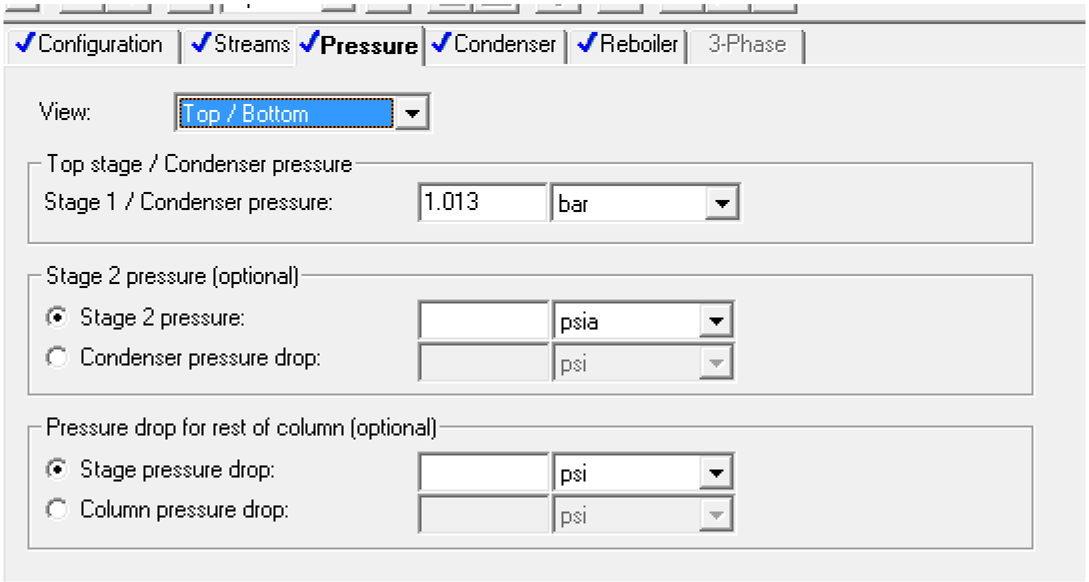
Name	Stage	Convention
V2	10	Above-Stage
L2	34	Above-Stage
FEED1	18	Above-Stage
FEED2	28	Above-Stage

Product streams

Name	Stage	Phase	Basis	Flow	Units	Flow ratio	Feed specs
DISTT	1	Liquid	Mole		lbmol/hr		Feed basis
BOTTOMS	44	Liquid	Mole		lbmol/hr		Feed basis
L1	10	Liquid	Stdvol	20	l/hr		Feed basis
V1	34	Vapor	Stdvol	23	l/hr		Feed basis

Fig. 4.7 Aspen PLUS window to define column 1 specifications

The condenser pressure is kept 1.013 bar and following Fig.4.8 shows the column pressure.



View: Top / Bottom

Top stage / Condenser pressure

Stage 1 / Condenser pressure: 1.013 bar

Stage 2 pressure (optional)

● Stage 2 pressure: psia

○ Condenser pressure drop: psi

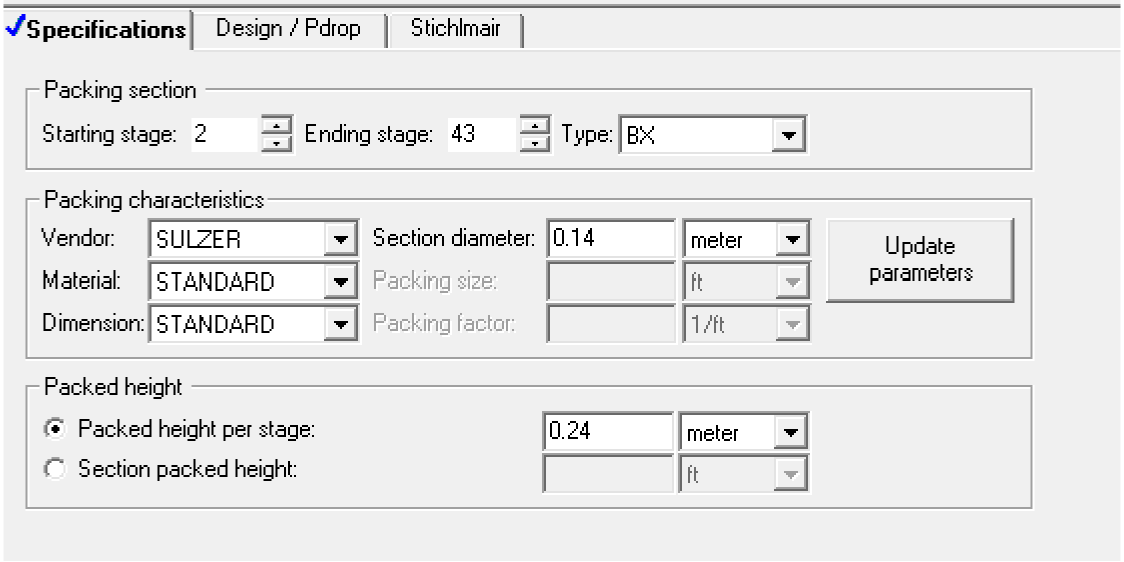
Pressure drop for rest of column (optional)

● Stage pressure drop: psi

○ Column pressure drop: psi

Fig. 4.8 Aspen PLUS window to define column 1 specifications

In reactive section (stage 10 to 34) packing of the potassium carbonate is done so that heterogeneous reaction takes place. And rest of the column is packed with the standard material as shown in the Fig.4.9 below.



Packing section

Starting stage: 2 Ending stage: 43 Type: BX

Packing characteristics

Vendor: SULZER

Material: STANDARD

Dimension: STANDARD

Section diameter: 0.14 meter

Packing size: ft

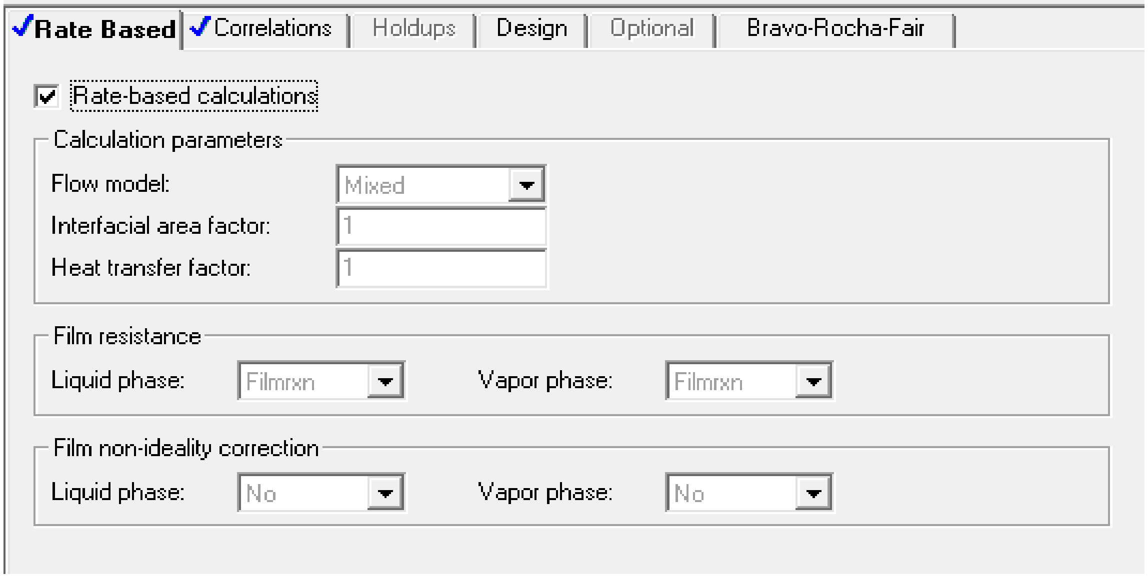
Packing factor: 1/ft

Packed height

● Packed height per stage: 0.24 meter

○ Section packed height: ft

Fig. 4.9 Aspen PLUS window to define packing specification of column 1



☑ Rate-based calculations

Calculation parameters

Flow model: Mixed

Interfacial area factor: 1

Heat transfer factor: 1

Film resistance

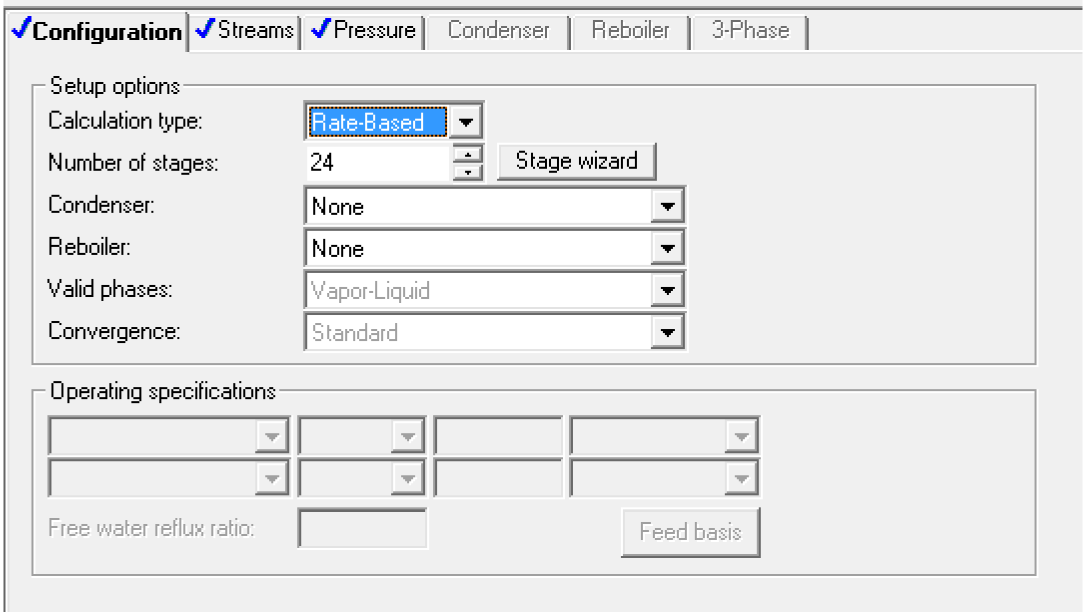
Liquid phase: Filmrxn Vapor phase: Filmrxn

Film non-ideality correction

Liquid phase: No Vapor phase: No

Fig. 4.10 Aspen PLUS window to define column 1 specifications

In this way the column 1specification is completed and now the column 2 specification is carried out. Following Fig.4.11 explains the exact situation.



Setup options

Calculation type: Rate-Based

Number of stages: 24

Condenser: None

Reboiler: None

Valid phases: Vapor-Liquid

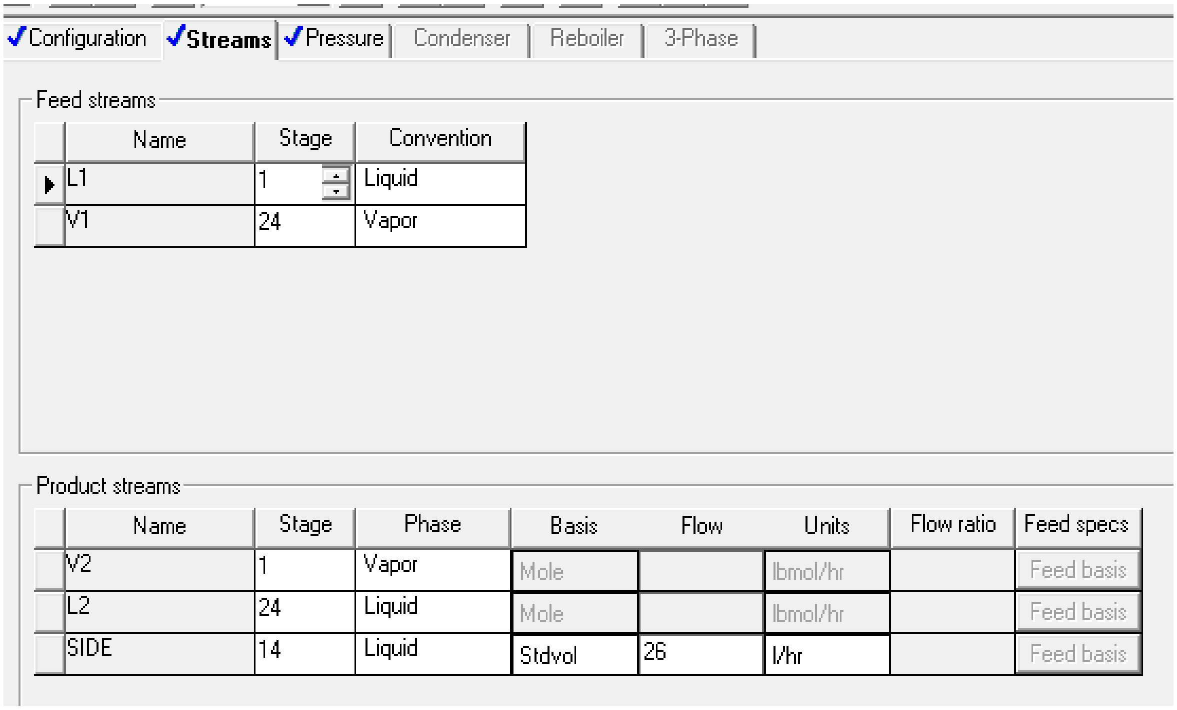
Convergence: Standard

Operating specifications

Free water reflux ratio:

Fig. 4.11 ASPEN PLUS window to define column 2 specifications

As sown in Fig. 4.11 there is no condenser and no reboiler so that this is a section of the RDWDC where separation takes place in this section no reaction taking place.



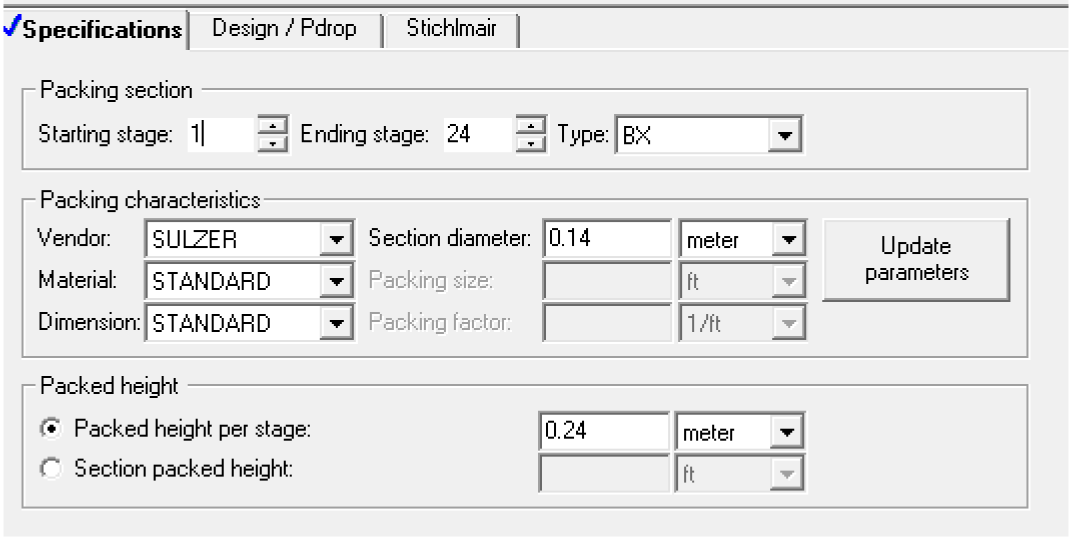
Feed streams

Name	Stage	Convention
L1	1	Liquid
V1	24	Vapor

Product streams

Name	Stage	Phase	Basis	Flow	Units	Flow ratio	Feed specs
V2	1	Vapor	Mole		lbmol/hr		Feed basis
L2	24	Liquid	Mole		lbmol/hr		Feed basis
SIDE	14	Liquid	Stdvol	26	l/hr		Feed basis

Fig. 4.12 Aspen PLUS window to define column 2 specifications



Packing section

Starting stage: 1 Ending stage: 24 Type: BX

Packing characteristics

Vendor: SULZER

Material: STANDARD

Dimension: STANDARD

Section diameter: 0.14 meter

Packing size: ft

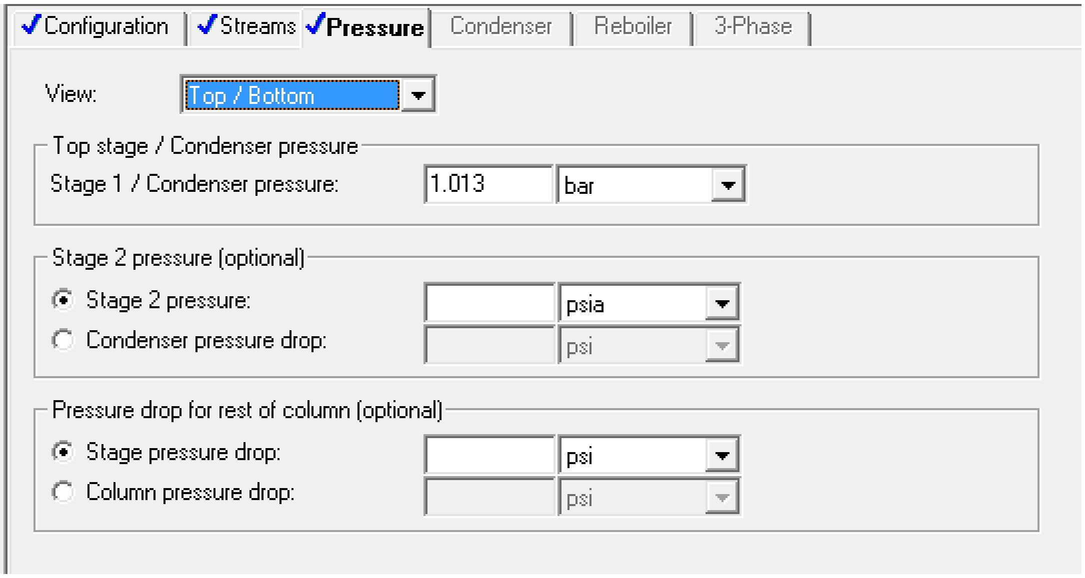
Packing factor: 1/ft

Packed height

● Packed height per stage: 0.24 meter

○ Section packed height: ft

Fig.4.13 Aspen PLUS window to define packing specification



View: Top / Bottom

Top stage / Condenser pressure

Stage 1 / Condenser pressure: 1.013 bar

Stage 2 pressure (optional)

● Stage 2 pressure: psia

○ Condenser pressure drop: psi

Pressure drop for rest of column (optional)

● Stage pressure drop: psi

○ Column pressure drop: psi

Fig. 4.14 Aspen PLUS window to define column 2 specifications

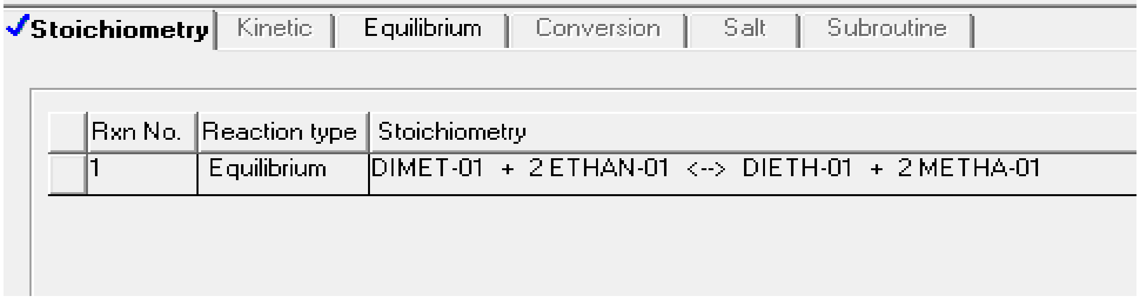
In Aspen PLUS, one can provide the reaction scheme to calculate its molar conversion such as the disappearance for the reactant and the formation of the products. The snapshots below show this situation.

	Name	Type	Status
	R-1	REAC-DIST	Input Complete

Fig. 4.15 Aspen PLUS window to define RD system

REAC-DIST specifies the RD process.

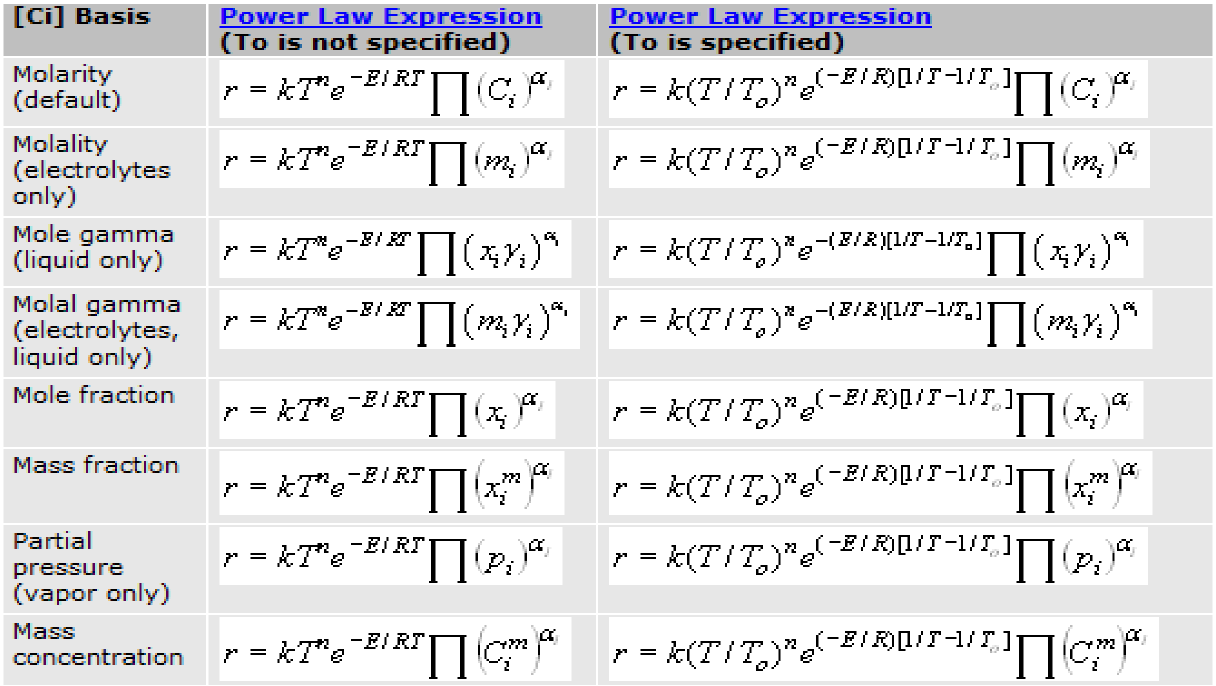
Since transesterification of DMC to produce the DEC and methanol takes place through two consecutive second order reactions following Fig. 4.16 shows the snap shots of both the reaction and kinetic parameter for the complete specification of the REAC- DIST.



	Rxn No.	Reaction type	Stoichiometry
	1	Equilibrium	DIMET-01 + 2 ETHAN-01 <--> DIETH-01 + 2 METHA-01

Fig. 4.16 Aspen PLUS window to reaction system

The built-in power law expression can be used to provide the kinetic parameters and the rate of formation of product for the reaction. In case the rate expression is quite complex, one has to use the kinetic subroutine for calculation of kinetic parameters or rate expression. The power law expression depends on the concentration basis one selects in the [Ci] Basis list box:

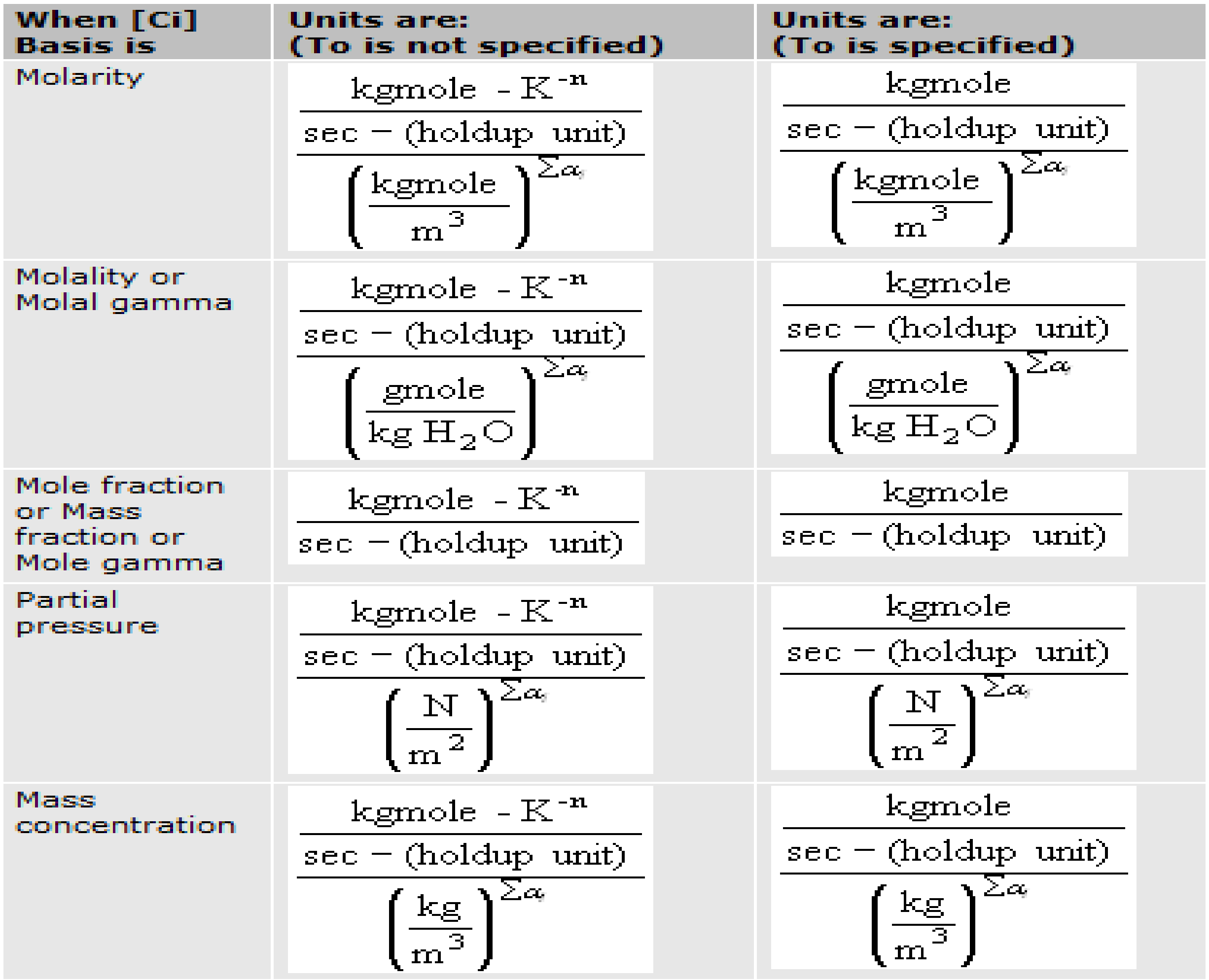


[Ci] Basis	Power Law Expression (To is not specified)	Power Law Expression (To is specified)
Molarity (default)	$r = kT^n e^{-E/RT} \prod (C_i)^{\alpha_i}$	$r = k(T/T_o)^n e^{(-E/R)[1/T - 1/T_o]} \prod (C_i)^{\alpha_i}$
Molality (electrolytes only)	$r = kT^n e^{-E/RT} \prod (m_i)^{\alpha_i}$	$r = k(T/T_o)^n e^{(-E/R)[1/T - 1/T_o]} \prod (m_i)^{\alpha_i}$
Mole gamma (liquid only)	$r = kT^n e^{-E/RT} \prod (x_i \gamma_i)^{\alpha_i}$	$r = k(T/T_o)^n e^{-(E/R)[1/T - 1/T_o]} \prod (x_i \gamma_i)^{\alpha_i}$
Molal gamma (electrolytes, liquid only)	$r = kT^n e^{-E/RT} \prod (m_i \gamma_i)^{\alpha_i}$	$r = k(T/T_o)^n e^{-(E/R)[1/T - 1/T_o]} \prod (m_i \gamma_i)^{\alpha_i}$
Mole fraction	$r = kT^n e^{-E/RT} \prod (x_i)^{\alpha_i}$	$r = k(T/T_o)^n e^{(-E/R)[1/T - 1/T_o]} \prod (x_i)^{\alpha_i}$
Mass fraction	$r = kT^n e^{-E/RT} \prod (x_i^m)^{\alpha_i}$	$r = k(T/T_o)^n e^{(-E/R)[1/T - 1/T_o]} \prod (x_i^m)^{\alpha_i}$
Partial pressure (vapor only)	$r = kT^n e^{-E/RT} \prod (p_i)^{\alpha_i}$	$r = k(T/T_o)^n e^{(-E/R)[1/T - 1/T_o]} \prod (p_i)^{\alpha_i}$
Mass concentration	$r = kT^n e^{-E/RT} \prod (C_i^m)^{\alpha_i}$	$r = k(T/T_o)^n e^{(-E/R)[1/T - 1/T_o]} \prod (C_i^m)^{\alpha_i}$

Fig.4.17 Aspen PLUS power law expressions used for the calculation

The units of the reaction rate and the pre-exponential factor depend on the following factors.

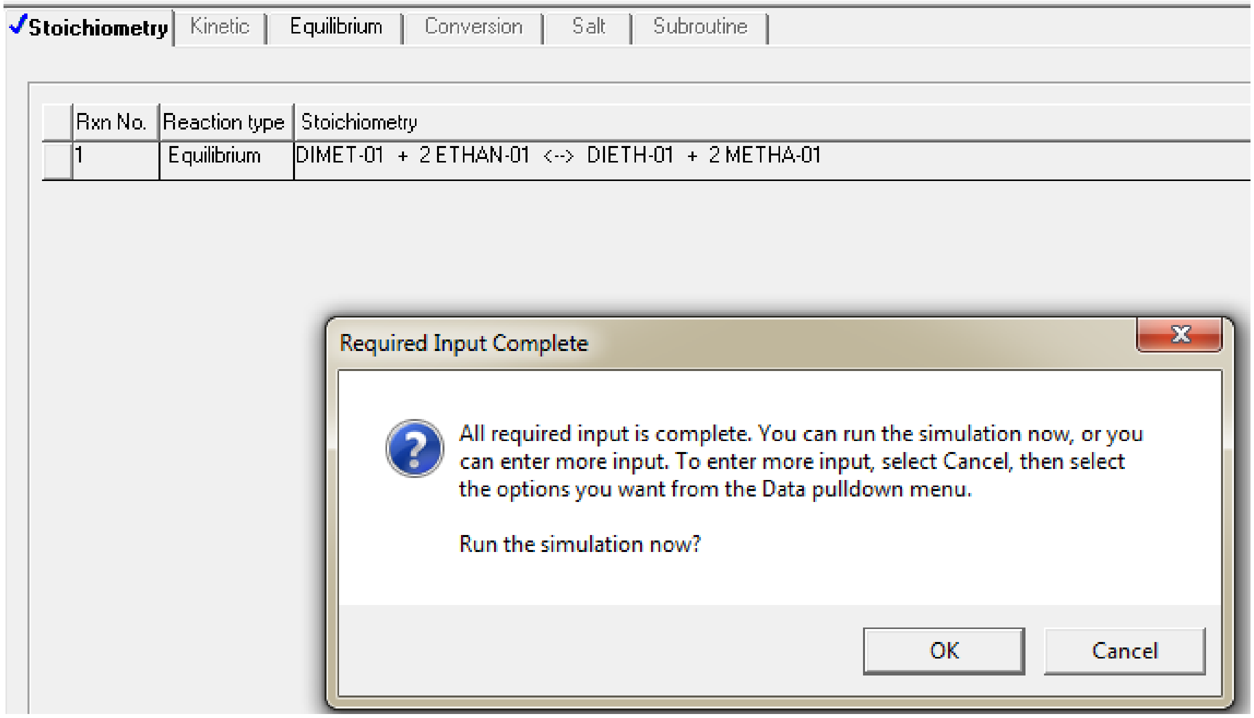
- Order of the reaction.
- Holdup basis used by the distillation block.
- Concentration basis selected in the [Ci] Basis list box.



When [Ci] Basis is	Units are: (To is not specified)	Units are: (To is specified)
Molarity	$\dfrac{\dfrac{\text{kgmole - K}^{-n}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{kgmole}}{\text{m}^3}\right)^{\Sigma\alpha_i}}$	$\dfrac{\dfrac{\text{kgmole}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{kgmole}}{\text{m}^3}\right)^{\Sigma\alpha_i}}$
Molality or Molal gamma	$\dfrac{\dfrac{\text{kgmole - K}^{-n}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{gmole}}{\text{kg H}_2\text{O}}\right)^{\Sigma\alpha_i}}$	$\dfrac{\dfrac{\text{kgmole}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{gmole}}{\text{kg H}_2\text{O}}\right)^{\Sigma\alpha_i}}$
Mole fraction or Mass fraction or Mole gamma	$\dfrac{\text{kgmole - K}^{-n}}{\text{sec} - (\text{holdup unit})}$	$\dfrac{\text{kgmole}}{\text{sec} - (\text{holdup unit})}$
Partial pressure	$\dfrac{\dfrac{\text{kgmole - K}^{-n}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{N}}{\text{m}^2}\right)^{\Sigma\alpha_i}}$	$\dfrac{\dfrac{\text{kgmole}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{N}}{\text{m}^2}\right)^{\Sigma\alpha_i}}$
Mass concentration	$\dfrac{\dfrac{\text{kgmole - K}^{-n}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{kg}}{\text{m}^3}\right)^{\Sigma\alpha_i}}$	$\dfrac{\dfrac{\text{kgmole}}{\text{sec} - (\text{holdup unit})}}{\left(\dfrac{\text{kg}}{\text{m}^3}\right)^{\Sigma\alpha_i}}$

Fig. 4.18 Aspen PLUS power law expression units

Now all the specifications are completed and the simulator is ready for run Fig. 4.19 shows the dialog box that appeared after the completion of the all input specifications.



Rxn No.	Reaction type	Stoichiometry
1	Equilibrium	DIMET-01 + 2 ETHAN-01 <--> DIETH-01 + 2 METHA-01

Required Input Complete

All required input is complete. You can run the simulation now, or you can enter more input. To enter more input, select Cancel, then select the options you want from the Data pulldown menu.

Run the simulation now?

Fig. 4.19 ASPEN PLUS window showing the completion of all input specifications

CHAPTER V

RESULTS AND DISCUSSIONS

5.1 Input Parameters

After performing several simulations using the RDWDC system as discussed in previous chapters, a number of results were obtained. The input parameters (Table 5.1) were taken from the work of Mueller (2007), and the additional data needed for the reaction system were taken from the Kellar et al. (2011) some process parameters were assumed as given in Table 5.1.

Table 5.1 Input parameters used during simulation

Parameters	Value	Unit	Ref.
Flow rate of feed stream 1	24	l/h	Mueller & Kenig (2007)
Flow rate of feed stream 2	51	l/h	Mueller & Kenig (2007)
Temperature of the feed stream	75	^{0}C	Mueller & Kenig (2007)
Pressure of the feed stream	1.2	bar	Mueller & Kenig (2007)
Number of stages	44	N/A	Mueller & Kenig (2007)
Stages of reactive zone (From/to Stage number)	10 to 34	N/A	Mueller & Kenig (2007)
Feed stage 1 number	18	N/A	Assumed
Feed stage 2 number	28	N/A	Assumed
Wall position (From/to Stage number)	10 to 34	N/A	Assumed
Distillate rate	23	l/h	Mueller & Kenig (2007)
Operating pressure	1.013	bar	Mueller & Kenig (2007)
Side draw Stage	12	N/A	Mueller & Kenig (2007)
Side stream flow rate	24	l/h	Mueller & Kenig (2007)
Activation Energy	4.5E+11	kJ/mol	Keller et al. (2011)

The following reversible reaction shows that the products diethyl carbonate (DEC) and methanol are formed by reaction between dimethyl carbonate (DMC) and ethanol as represented by the equation 5.1.

$$(CH_3)_2CO_3 + 2C_2H_5OH \rightleftarrows (C_2H_5)_2CO_3 + 2CH_3OH \qquad 5.1$$

The input parameters as given in Table 5.1 were applied in the ASPEN Plus (Version: 2006.5) software and the following results were obtained for the required composition of a DEC composition in the bottom product stream, methanol composition in the distillate and the ethanol composition in the side stream of the RDWDC with the variation of reflux ratio (r), vapor split rate (v) and liquid split rate (l). The minimum and maximum values of these variables were found by performing several simulations in the ASPEN Plus Software and these values are further used to define the maximum number of simulations with the help of Design Expert Software (Version: 6.0) for the maximization of the respective compositions in the bottoms, distillate and side streams and minimization of the reflux ratio for minimizing the reboiler duty of the column. The simulation results are presented in the Table 5.2. Table 5.3 shows the summary of key design parameters. Table 5.4 shows the minimum and maximum values of r, l and as deduced.

The following nomenclatures have been used in the analysis:

r: reflux ratio

l: liquid split (l/h)

v: vapor split (l/h)

D: Methanol mole fraction in the distillate

S: Ethanol mole fraction in the side draw

B: Diethyl Carbonate mole fraction in the bottoms

Q_b: reboiler duty (Btu/h)

Q_c: condenser duty (Btu/h)

Table 5.2 Results at several Inputs

Run	Reflux Ratio	Liquid Split (l/h)	Vapor Split (l/h)	Methanol Comp. in Distillate	Diethyl Carbonate Comp. in Bottoms	Ethanol Comp. in Side Stream	Reboiler Duty (Btu/h)	Condenser Duty (Btu/h)
	r	l	v	MeOH	DEC	EtOH	Qb	Qc
1	11.67	24	28	0.92	0.979	0.73	214532	-201683
2	5.2	28	23	0.89	0.962	0.68	155415	-152942
3	8.43	20	28	0.97	0.985	0.72	181025	-178153
4	8.43	28	28	0.87	0.989	0.71	116438	-114173
5	8.43	24	23	0.90	0.989	0.64	173435	-170714
6	5.2	24	18	0.89	0.949	0.65	116713	-114047
7	8.43	24	23	0.90	0.989	0.64	173435	-170714
8	8.43	28	18	0.96	0.974	0.63	168324	-161203
9	8.43	24	23	0.90	0.989	0.65	173435	-170714
10	11.67	24	18	0.91	0.969	0.68	153358	-151009
11	5.2	20	23	0.92	0.968	0.63	119115	-116306
12	5.2	24	28	0.93	0.953	0.77	155415	-152942
13	8.43	24	23	0.90	0.989	0.65	173435	-170714
14	8.43	24	23	0.90	0.989	0.65	173435	-170714
15	11.67	28	23	0.90	0.981	0.61	234498	-231859
16	11.67	20	23	0.91	0.989	0.71	201342	-201543
17	8.43	20	18	0.89	0.965	0.61	120166	-115399

Table 5.3 Key design summary

<table>
<tr><td>Study Type</td><td colspan="2">Response surface Methodology</td><td colspan="3" rowspan="3">No. of calculation runs=17
No. of Blocks=1</td></tr>
<tr><td>Initial Design</td><td colspan="2">Box Behnken</td></tr>
<tr><td>Design Model</td><td colspan="2">Quadratic and Linear</td></tr>
<tr><td>Response</td><td>Name</td><td>Unit</td><td>Minimum</td><td>Maximum</td><td>Model</td></tr>
<tr><td>Y1</td><td>D</td><td>-</td><td>0.913</td><td>0.982</td><td>Quadratic</td></tr>
<tr><td>Y2</td><td>B</td><td>-</td><td>0.899</td><td>0.989</td><td>Quadratic</td></tr>
<tr><td>Y3</td><td>S</td><td>-</td><td>0.618</td><td>0.777</td><td>Quadratic</td></tr>
<tr><td>Y4</td><td>Qb</td><td>Btu/h</td><td>116438</td><td>234498</td><td>Linear</td></tr>
<tr><td>Y5</td><td>Qc</td><td>Btu/h</td><td>-231859</td><td>-114047</td><td>Linear</td></tr>
</table>

Table 5.4 Maximum and minimum values of the variables

Factor	Name	Units	Type	Low Actual	High Actual	Low Coded	High Coded
A	r	-	Numeric	5.2	11.67	-1	+1
B	l	l/h	Numeric	20	28	-1	+1
C	v	l/h	Numeric	18	28	-1	+1

The model F- value defines the best fitting of the model. If F-value is greater than 5, it indicates that the model is significant. If the values of “Prob>F” is less than 0.05, then model terms are significant if these values are greater 0.1, indicate that the model terms. Adequate precision measures the signal to noise ratio (S/N), (S/N) ratio value greater than 4 is desirable since it is efficient in navigating the design space.

5.2.1 Composition of Methanol in distillate

Methanol has the highest relative volatility, along with that of DMC. However, DMC is almost fully converted and its concentration in various streams are almost- zero. Tables 5.5 presents the model results and Table 5.6 shows the model summary statics for methanol composition represents the models and on the basis of the suggested model analysis of variance is obtained and with Design Expert software.

Table 5.5 Model using methanol composition

Source Model	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F	Remarks
Mean	14.148	1	14.148	-	-	-
Linear	0.0008	3	0.00028	0.38	0.7643	Not suggested
2 Factor Interaction	0.0078	3	0.00261	14.17	0.0006	Suggested
Quadratic	0.0013	3	0.00044	6.18	0.0222	Suggested
Cubic	0.0005	3	0.00016	6366000	< 0.0001	Aliased
Residual	0	4	0			
Total	14.15	17	0.83290			

Table 5.6 Model Summary statistics for methanol composition

Source Model	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remarks
Linear	0.027	0.08	-0.13	-0.87	0.019	Not suggested
2FI	0.013	0.82	0.72	0.30	0.007	Suggested
Quadratic	0.008	0.95	0.89	0.23	0.008	Suggested
Cubic	0	1	1		+	Aliased

From these tables, it is found that the quadratic model fits the data well. Using these results, ANOVA was performed for distillate purity.

Table 5.7 ANOVA for distillate purity

Analysis of variance table [Partial sum of squares]						
Source	Sum of Squares	Degree of Freedom	Mean Square	F value	Prob>F	Remarks
Model	0.0092	7	0.001	20.92	< 0.0001	Significant
A-l	0.0006	1	0.0006	9.55	0.0129	Significant
B-v	0.0002	1	0.0002	2.94	0.1201	Not Significant
C-r	8E-06	1	8E-06	0.11	0.7392	Not Significant
AB	0.007	1	0.007	110.21	< 0.0001	Significant
BC	0.0002	1	0.0002	4.01	0.0761	Not Significant
A^2	0.0003	1	0.0003	4.52	0.0623	Not Sgnificant
B^2	0.0009	1	0.0009	14.05	0.0046	Significant
Residual	0.0006	9	6.7E-05			
Lack of Fit	0.0006	5	0.0001			
Pure Error	0	4	0			
Core Total	0.0105	16				

Std. Dev.	0.008	R-Squared	0.94
Mean	0.912	Adjusted R- Squared	0.89
C.V. %	0.902	Predicted R- Squared	0.51
PRESS	0.005	Adequate R-Squared	18.49

From ANOVA it is found that the quadratic model is significant for distillate purity. The equation for methanol purity is found to depend on the l, v and r as follows.

$$MeOH = 0.261 + 0.021\,l + 0.029\,v + 0.012\,r - 0.0021\,l\,v + 0.0005\,v\,r + 0.0005\,l^2 + 0.0006\,v^2 \qquad 5.2$$

where, [MeOH] is the methanol composition in the distillate. This equation is optimized by the Design Expert software and optimized 3 D results are presented in Fig. 5.2.

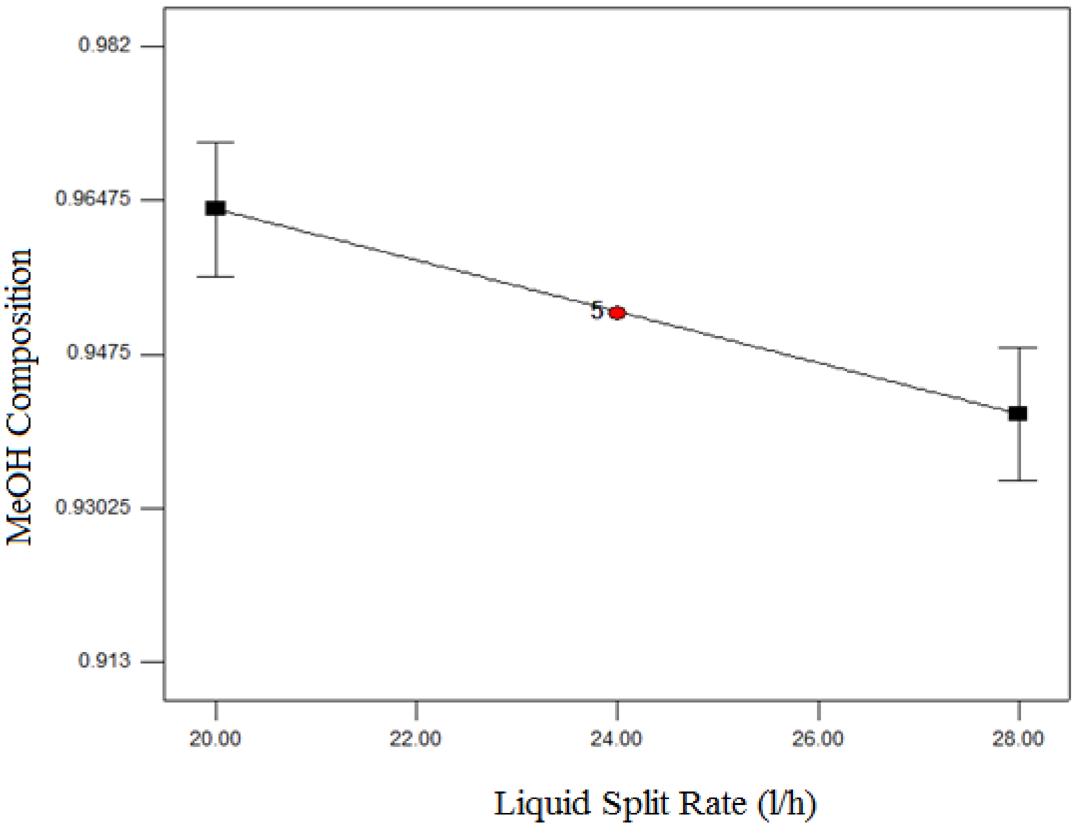


Fig. 5.1a Variation of methanol composition with liquid split rate

(For, v= 28 l/h and r=9.85).

Fig 5.1 (a,c) shows the one factor plot for the methanol composition with the liquid split rate. It is seen that the composition of methanol is decreases linearly with the liquid split rate while keeping the other factors constant as shown in this Figures and the reflux ratio, whereas the liquid split rate shows a dip in the MeOH concentration in between. It is seen that the improvement in the MeOH composition is in the range of 2-3 % while the values of l and r vary over a large range. The optimum values of l, v and r are found to be 20 l/h, 28 l/h and 5.20. However the vapor split rate hs least effect in the range of its values studied and even a value of 18l/h will not affect the MeOH composition to an appreciable extent. The combined impact of three parameters as the composition shows the intensive inter parametric effects as reflected in Fig. 5.2.

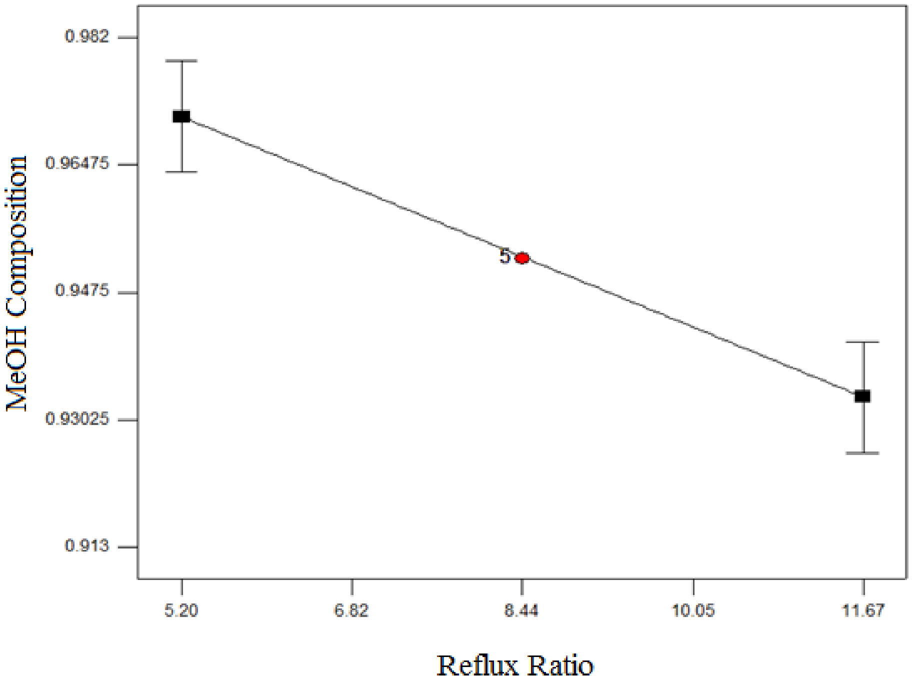


Fig. 5.1b Variation of methanol composition with reflux ratio (For l=20.2 l/h and v= 28 l/h)

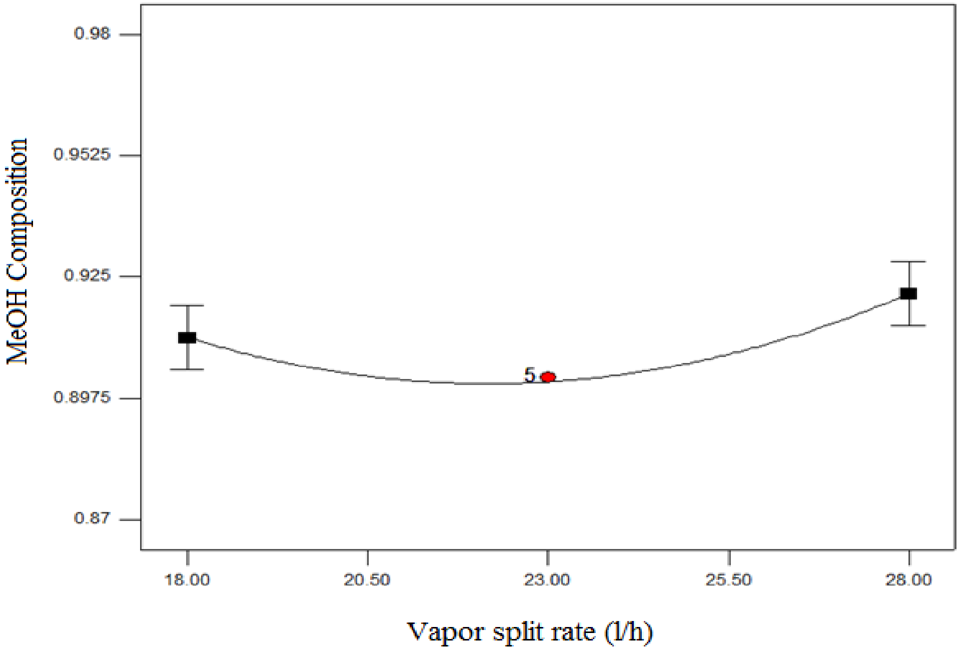


Fig.5.1c Variation of methanol composition with vapor split rate (For r=9.85 and l=20.2 l/h)

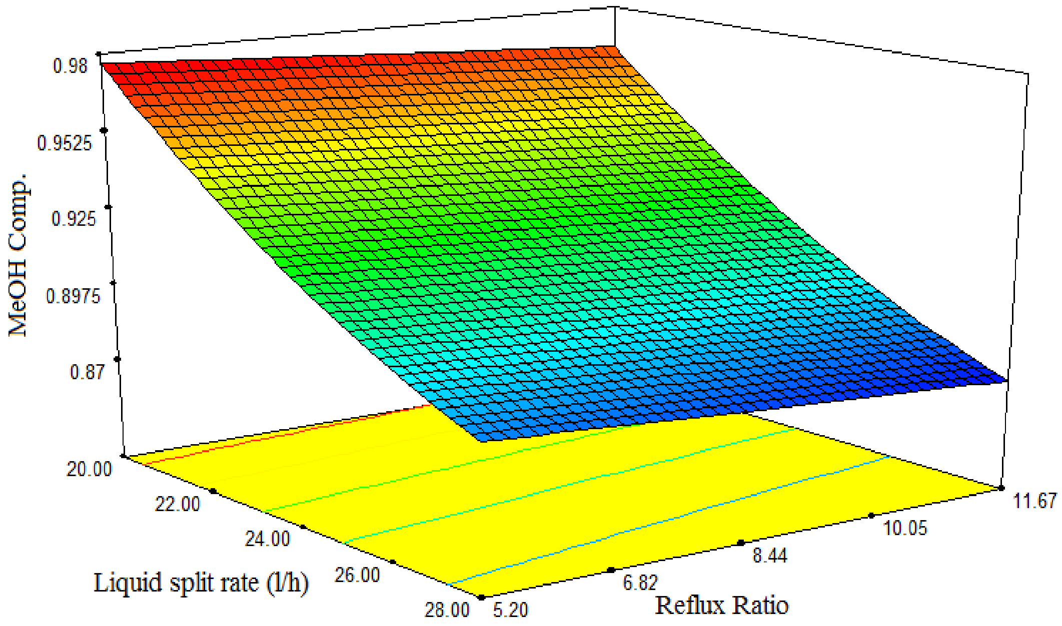


Fig.5.2 Optimized 3 D results for the distillate composition with liquid split rate and reflux ratio

Fig.5.2 represents the optimized results for the methanol composition with the liquid split rate and reflux ratio. The red portion of the 3 dimensional plot shows the optimum conditions for the maximization of the DEC composition in the bottoms stream of the RDWDC. The values of the optimum conditions are given later in the Table 5.20.

5.2.2 DEC composition in the bottoms

Diethyl carbonate has the least relative volatility so this is collected from the bottoms. Table 5.8 and 5.9 represent the models and on the basis of the suggested model, the analysis of variance is obtained and is represented in the Table 5.10.

Table 5.8 Results for response DEC composition in bottom stream

Source Model	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F	Remarks
Mean	16.22	1	16.22			
Linear	0.001	3	0.0004	3.03	0.0675	
2 Factor Interaction	1.6E-05	3	5.4E-06	0.031	0.9921	
Quadratic	0.001	3	0.0005	24.51	0.0004	Suggested
Cubic	0.0001	3	5.1E-05	63660000	< 0.0001	Aliased
Residual	0	4	0			
Total	16.22	17	0.95			

Table 5.9 Model summary statistics for DEC composition

Source Model	Stnd. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remarks
Linear	0.01	0.41	0.27	0.004	0.0029	
2FI	0.01	0.41	0.06	-1.01	0.008	
Quadratic	0.004	0.94	0.88	0.18	0.002	Suggested
Cubic	0	1	1		+	Aliased

Table 5.10 ANOVA for bottoms purity

Analysis of variance table [Partial sum of squares]						
Source	Sum of Squares	Degree of Freedom	Mean Square	F value	Prob>F	Remarks
Model	0.002	4	0.0007	49.39	< 0.0001	Significant
A-l	0.0003	1	0.0003	21.14	0.0006	
B-v	0.0009	1	0.0009	65.12	< 0.0001	
C-r	0.0005	1	0.0005	39.87	< 0.0001	
AB	0.0009	1	0.0009	65.40	< 0.0001	
BC	0.0001	12	1.4E-05			
A^2	0.0019	8	2.1E-05			
B^2	0	4	0			
Residual	0.002	16				
Lack of Fit	0.002	4	0.0007	49.39	< 0.0001	Significant
Pure Error	0.0003	1	0.0003	21.14	0.0006	
Cor Total	0.0009	1	0.0009	65.12	< 0.0001	

Std. Dev.	0.003	R-Squared	0.94
Mean	0.976	Adj R-Squared	0.92
C.V. %	0.385	Pred R-Squared	0.86
PRESS	0.003	Adeq Precision	21.18

The optimum results for the bottoms purity as obtained from the Design Expert software can be represented by Eq. 5.3. This equation shows that the bottoms purity depends on vapor split rate and the reflux ratio only.

$$DEC = 0.587 + 0.0022\,v + 0.0072\,r - 0.00046\,v^2 - 0.00141\,r^2 \qquad 5.3$$

This equation is optimized by the Design Expert software and optimized results are presented in in Fig. 5.3(a,b). Tables 5.11 and 5.12give the response analysis model satisfies for the optimization of DEC purity.

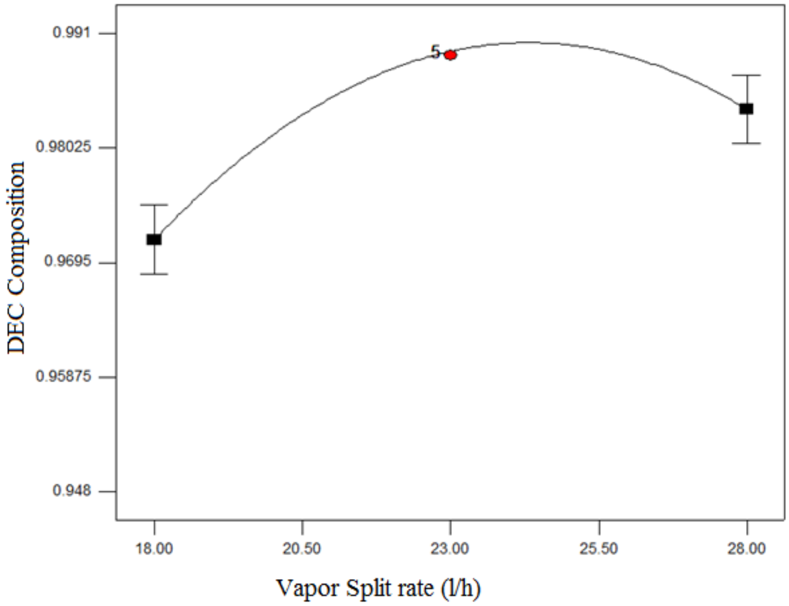


Fig.5.3a Variation of DEC composition with vapor split rate (For l=20.2 l/h and r=9.85)

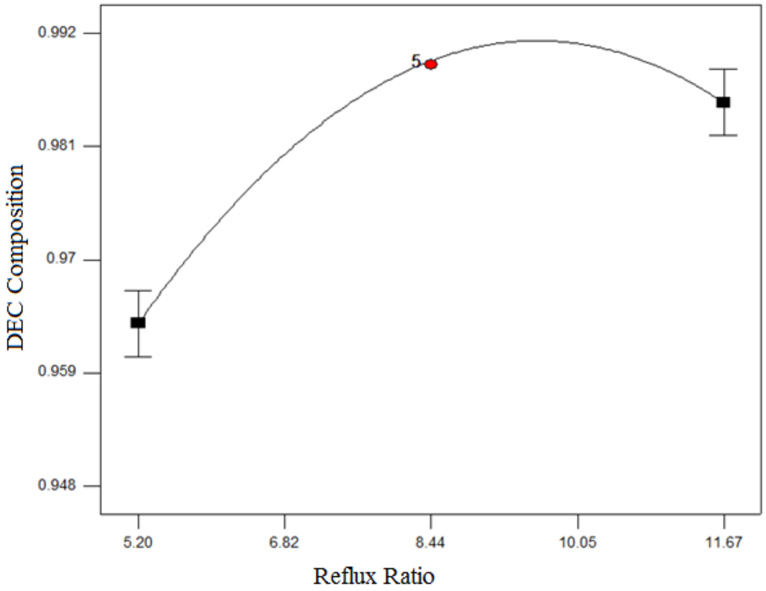


Fig.5.3b Variation of DEC composition with reflux ratio (F0r l=20.2 l/h and v=28 l/h)

The single factor plots for the effects of v and r on DEC composition in the bottoms (Fig. 5.3 (a-b)) shows that the purity improves by about 2 % over the entire range of v and r. Therefore, the optimum values of v and r to be used should be cost minimization.

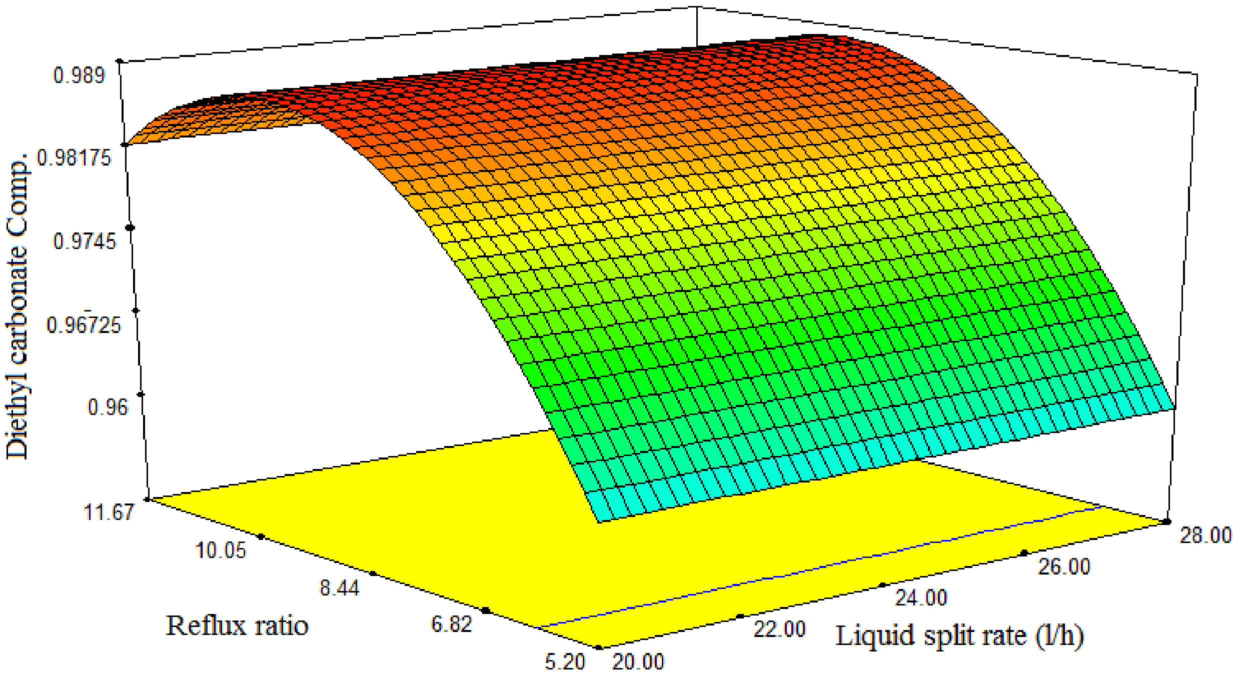


Fig.5.4 Optimized 3 D results for the DEC composition in the bottoms with liquid split rate and the reflux ratio

Fig.5.4 shows the optimized results of the DEC composition in bottoms with the liquid split rate and reflux ratio. The red portion of the 3 dimensional Fig. 5.4 is the optimum condition for the maximization of the DEC composition in the bottoms stream of the RDWDC.

5.2.3 Composition of Ethanol in the side stream

Ethanol has its relative volatility in between that of MeOH and DEC and is, therefore collected as the side stream of the RDWDC. Tables 5.11 and 5.12 represent the response and the summary statistics and Table 5.13 shows the ANNOVA based on the optimized concentration as represented by Eq. 5.4.

Table 5.11 Response analysis for ethanol composition

Source Model	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F	Remarks
Mean	7.57	1	7.57			
Linear	0.02	3	0.007	5.16	0.0144	
2 Factor Interaction	0.01	3	0.003	5.50	0.0171	
Quadratic	0.006	3	0.002	48.4	< 0.0001	Suggested
Cubic	0.0003	3	0.0001	63.66	< 0.0001	Aliased
Residual	0	4	0			
Total	7.61	17	0.44			

Table 5.12 Model summary statistics for ethanol composition

Source Model	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remarks
Linear	0.037	0.54	0.43	0.09	0.032	
2FI	0.026	0.81	0.72	0.30	0.027	
Quadratic	0.006	0.99	0.98	0.87	0.005	Suggested
Cubic	0	1	1		+	Aliased

Table 5.13 ANOVA for side stream purity

Analysis of variance table [Partial sum of squares]						
Source	Sum of Squares	Degree of Freedom	Mean Square	F value	Prob>F	Remarks
Model	0.0395	9	0.004	97.47	< 0.0001	significant
A-l	0.0001	1	0.0001	2.33	0.1707	Not significant
B-v	0.021	1	0.021	474.98	< 0.0001	significant
C-r	0.0002	1	0.0001	3.39	0.1080	Not significant
AB	0.0002	1	0.0002	5.67	0.0487	significant
BC	0.007	1	0.007	173.63	< 0.0001	significant
A^2	0.003	1	0.003	72.02	< 0.0001	significant
B^2	0.0004	1	0.0004	9.56	0.0175	significant
Residual	0.004	1	0.004	102.42	< 0.0001	significant
Lack of Fit	0.001	1	0.001	31.51	0.0008	
Pure Error	0.0003	7	4.5E-05			
Cor Total	0.0003	3	0.0001			

Std. Dev.	0.006	R-Squared	0.99
Mean	0.66	Adj R-Squared	0.98
C.V. %	1.006	Pred R-Squared	0.87
PRESS	0.005	Adeq Precision	31.86

Ethanol composition in the side stream is found to depend on the interactive effects of the variables (v, l and r) are also exhibited.

$$EtOH = -0.373 + 0.067\,l - 0.026\,v + 0.094\,r - 0.0004\,l\,v - 0.0034\,l\,r - 0.0017\,v\,r - 0.0063\,l^2 + 0.0013\,v^2 + 0.0017\,r^2 \qquad 5.4$$

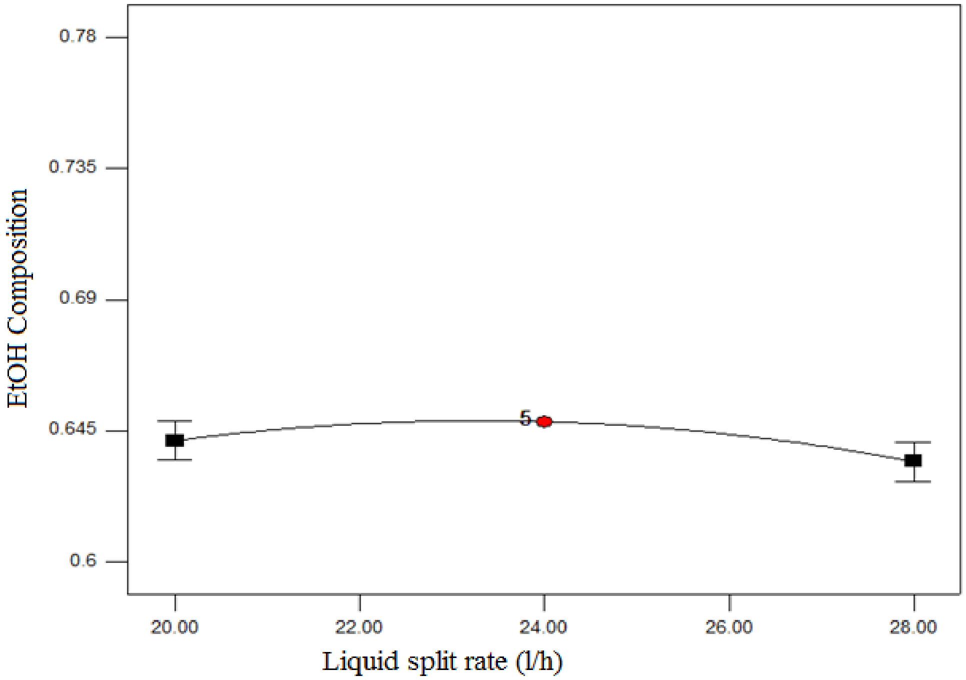


Fig.5.5a Variation of ethanol composition with liquid split rate (For v=28 l/h and r=9.85)

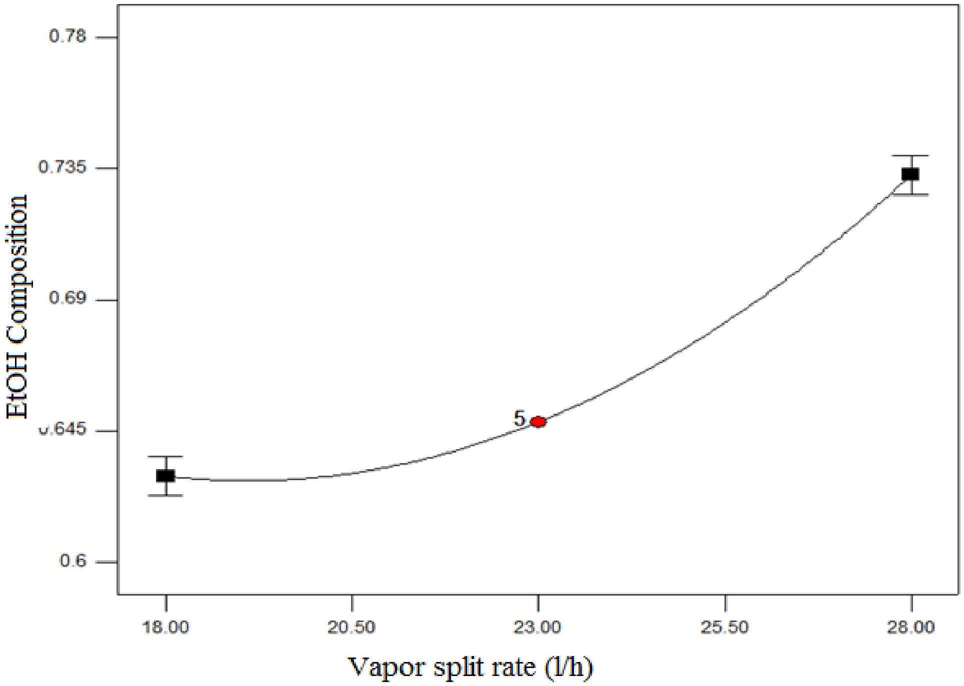


Fig.5.5b Variation of ethanol composition with vapor split rate (For l=20.2 andr=9.85)

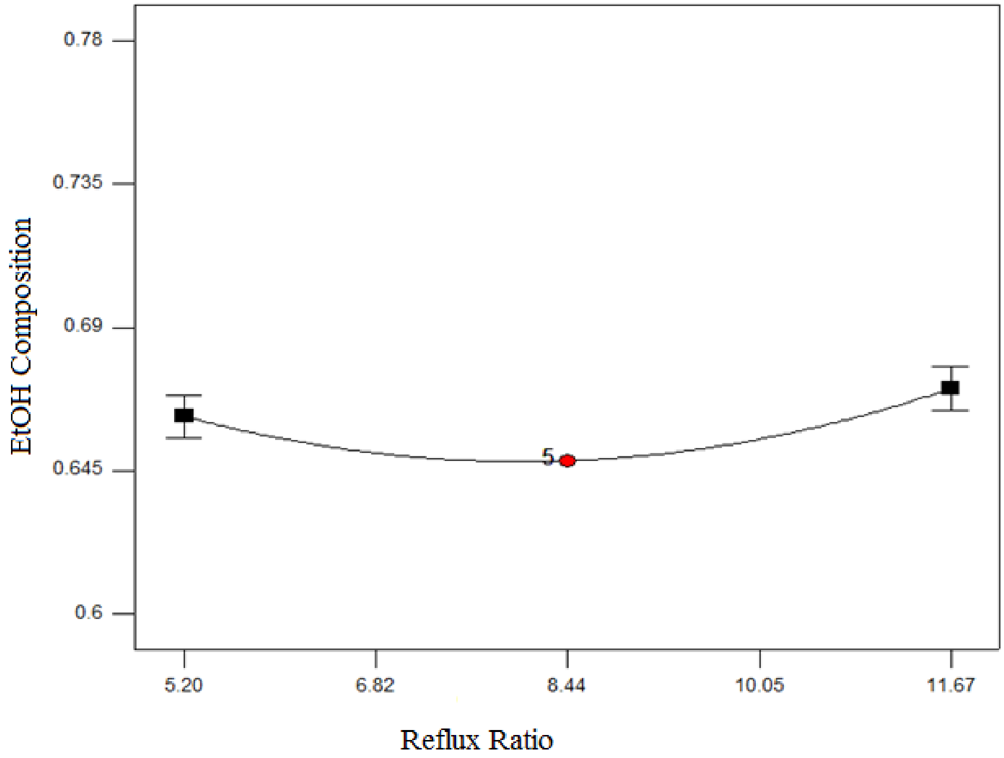


Fig.5.5c Variation of ethanol composition with liquid reflux ratio

Fig 5.5 (a,b,c) show the one factor plots for the ethanol composition with the liquid split rate, vapor split rate and the reflux ratio.. From the figures, it is observed that the vapor split rate has the maximum impact on the ethanol composition followed by that of the reflux ratio.

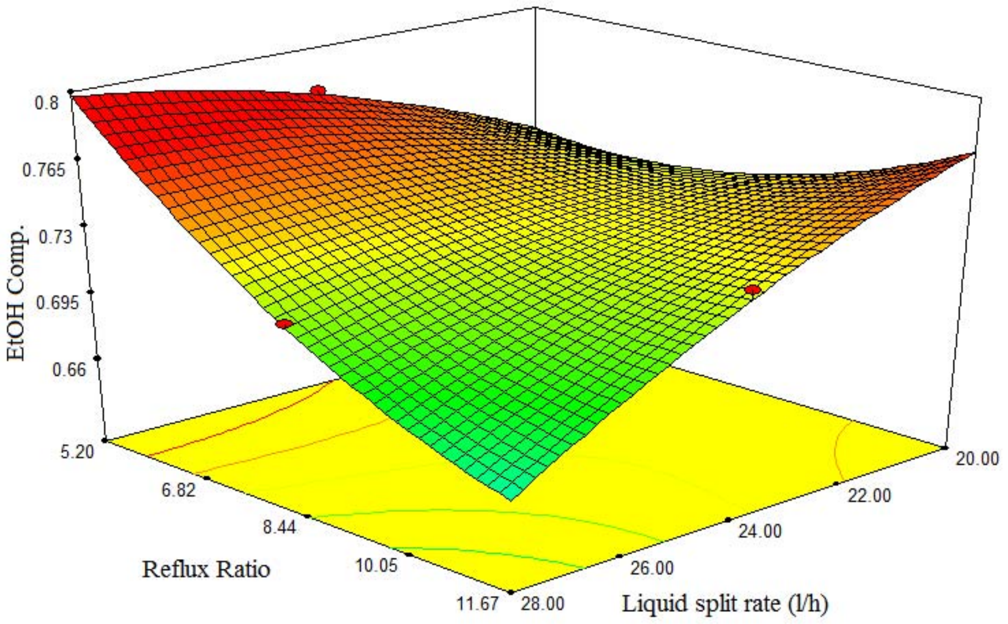


Fig.5.6 Optimized 3 D results for the side stream composition with liquid split rate and reflux ratio

Fig.5.6 shows the optimized results of the ethanol composition with the liquid split rate and reflux ratio. The red portion of the 3 dimensional figures shows the optimum conditions for the maximization of the ethanol composition in the side stream of the RDWDC.

5.2.4 Reboiler duty

As is known, the reflux ratio has maximum impact on the reboiler duty. Fig. 5.8 shows tis effect clearly. Tables 5.14 and 5.15 are obtained from the Design Expert software for the response and summary of the statistical analysis for the reboiler duty. The ANNOVA results are presented in Table 5.16.

Table 5.14 Response analysis for the reboiler duty, Qb

Source Model	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F	Remarks
Mean	4.6E+11	1	4.6E+11			
Linear	1.2E+10	3	3364416	5.29	0.0132	Suggested
2 Factor Interaction	3306577	3	1102192	2.22	0.1480	
Quadratic	246046	3	8201535	2.31	0.1637	
Cubic	249201	3	8306721	63.3	< 0.0001	Aliased
Residual	0	4	0			
Total	4.8E+11	17	2827577			

Table 5.15 Model summary statistics for response Qb

Source Model	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remarks
Linear	25205.39	0.54	0.44611908	0.07	16938	Suggested
2FI	22254.12	0.73	0.56823059	-0.30	23988	
Quadratic	18868.03	0.86	0.68962820	-1.17	39872	
Cubic	0	1	1		+	Aliased

Table 5.16 ANOVA for the reboiler duty, Qb

Analysis of variance table [Partial sum of squares]						
Source	Sum of Squares	Degree of Freedom	Mean Square	F value	Prob>F	Remarks
Model	8260751648	1	8260751648	12.27	0.0032	significant
A-l	8260751648	1	8260751648	12.27	0.0032	significant
B-v	1.0092E+10	15	672770008.9			
C-r	1.0092E+10	11	917413648.5			
AB	0	4	0			
BC	1.8352E+10	16				
A^2	8260751648	1	8260751648	12.27	0.0032	significant
B^2	8260751648	1	8260751648	12.28	0.0032	significant
Residual	1.0092E+10	15	672770008.9			
Lack of Fit	1.0092E+10	11	917413648.5			
Pure Error	0	4	0			
Cor Total	1.8352E+10	16				

Std. Dev.	25937.81	R-Squared	0.45
Mean	164912.70	Adjusted R-Squared	0.41
C.V. %	15.7282062	Predicted R-Squared	0.27
PRESS	1.3293E+10	Adequate Precision	7.22

Eq.5.5 shows the dependence of Qb on the reflux ratio. Fig. 5.7 shows the variation in reboiler duty with the reflux ratio.

$$Qb = 81125.90 + 9933.23 * r \tag{5.5}$$

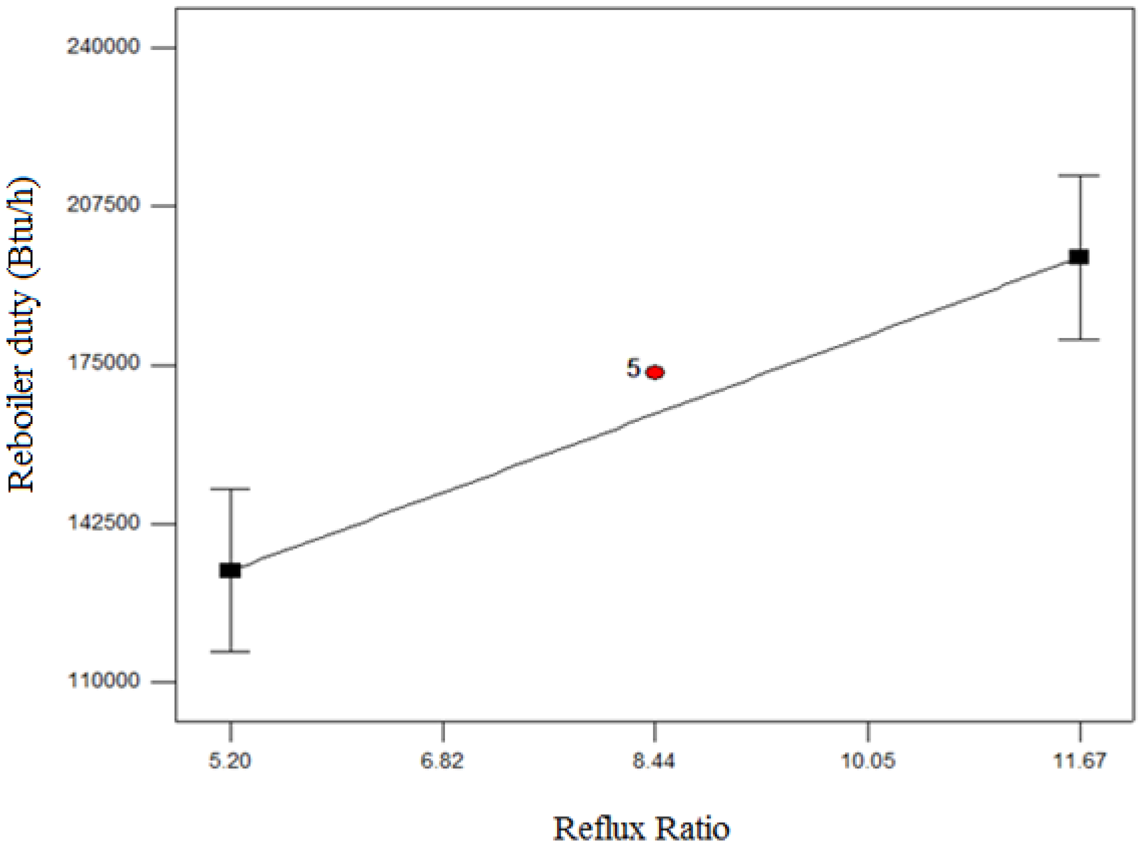


Fig.5.7 Variation of reboiler duty with reflux ratio (For l=20.2 l/h and v= 28 l/h)

5.2.5 Condenser duty

Tables 5.17 and 5.18 are obtained from the Design Expert software represents the models for the condenser duty. As is known, the condenser duty is affected by the reflux ratio. Therefore, a linear variation is expected in Qc with r. Table 5.19 shows the ANOVA results.

Table 5.17 Results for the response condenser duty, Qc

Source Model	Sum of Squares	Degree of Freedom	Mean Square	F Value	Prob>F	Remarks
Mean	4.4E+11	1	4.4E+11			
Linear	9.4E+11	3	3.1E+11	4.9E+11	0.0165	Suggested
2 Factor Interaction	3.5E+11	3	1.1E+11	1.9E+11	0.1865	
Quadratic	2.8E+11	3	9.6E+10	2.8E+11	0.1142	
Cubic	2.3E+11	3	7.8E+11	6.3E+11	< 0.0001	Aliased
Residual	0	4	0			
Total	4.6E+11	17	2.7E+11			

Table 5.18 Model summary statistics for response Qc

Source Model	Std. dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	Remarks
Linear	25267.14	0.53	0.42	0.046	1.7E+10	Suggested
2FI	22894.90	0.70	0.52	-0.41	2.5E+10	
Quadratic	18349.03	0.86	0.69	-1.12	3.7E+10	
Cubic	0	1	1		+	Aliased

Table 5.19 ANOVA for condenser duty Qc

Analysis of variance table [Partial sum of squares]						
Source	Sum of Squares	Degree of Freedom	Mean Square	F value	Prob>F	Remarks
Model	7803565056	1	7803565056	11.72	0.0038	significant
A-l	7803565056	1	7803565056	11.72	0.0038	significant
B-v	9982784060	15	665518937.3			
C-r	9982784060	11	907525823.6			
AB	0	4	0			
BC	17786349116	16				
A^2	7803565056	1	7803565056	11.72	0.0038	significant
B^2	7803565056	1	7803565056	11.72	0.0038	significant
Residual	9982784060	15	665518937.3			
Lack of Fit	9982784060	11	907525823.6			
Pure Error	0	4	0			
Core Total	17786349116	16				

Std. Dev.	25797.65372	R-Squared	0.43
Mean	-161460.529	Adj R-Squared	0.40
C.V. %	15.97768434	Pred R-Squared	0.29
PRESS	13100517667	Adeq Precision	7.05

The condenser duty can be calculated from the following equation

$$Qc = -80025.30 - 9654.44 * r \qquad 5.6$$

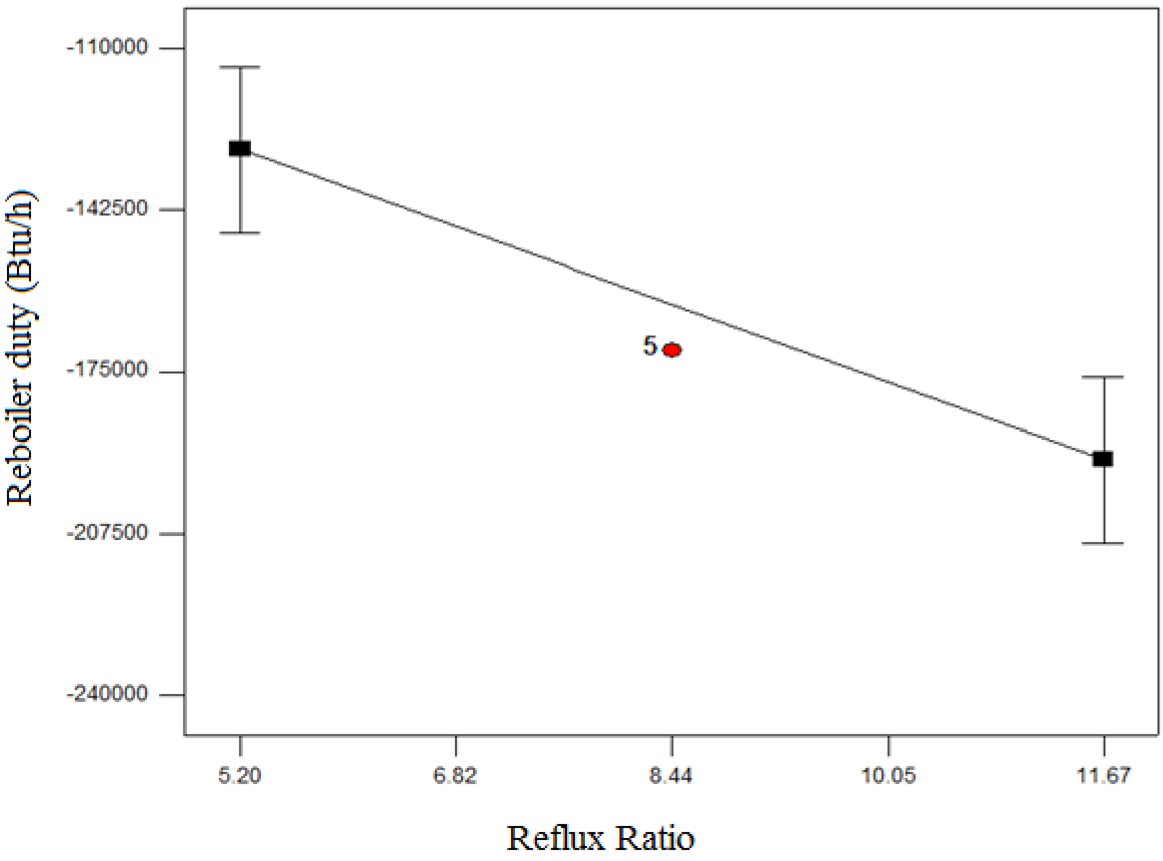


Fig. 5.8 Variation of condenser duty with reflux ratio

Table 5.20 Optimized solutions

No.	l(l/h)	v (l/h)	r	Methanol Comp. in D	DEC Comp. in B	Ethanol Comp. in S	Qb (Btu/h)	Qc (Btu/h)	Desirability
1	20	28	10.1	0.97	0.98	0.75	182309	-178369	0.71
2	20.5	28	10.1	0.97	0.98	0.75	182253	-178314	0.71
3	20	27.8	10.3	0.97	0.98	0.74	183579	-179604	0.71
4	20.2	28	9.85	0.97	0.98	0.74	179002	-175154	0.71
5	20	27.4	9.85	0.97	0.98	0.73	178810	-174968	0.70
6	20	27.5	9.14	0.97	0.98	0.72	171873	-168226	0.69
7	22.8	28	7.76	0.93	0.98	0.73	157910	-154655	0.61

Table 5.21 Optimized variables

Variables	Values
l(l/h)	20.2
v (l/h)	28
r	9.85

Based on the results, it is seen that the results in serial number 4 represent the optimum values for l, v and r, the purities of the distillate, bottoms and the side stream and the reboiler and condenser duties. These results are given in Table 5.21.

5.3 Results obtained from ASPEN Plus software with optimized variables

Using the optimized parametric variables as obtained by the Design Expert software for the simulation runs using ASPEN Plus Software we get the composition profiles in column 1 and column 2of the RDWDC as also the temperature variation in column 1 on various stages. For the simulation of the flow sheet with all other similar conditions as used in previous run. At these conditions we check the purity of the distillate, bottoms and side stream of the RDWDC for the production of the DEC.

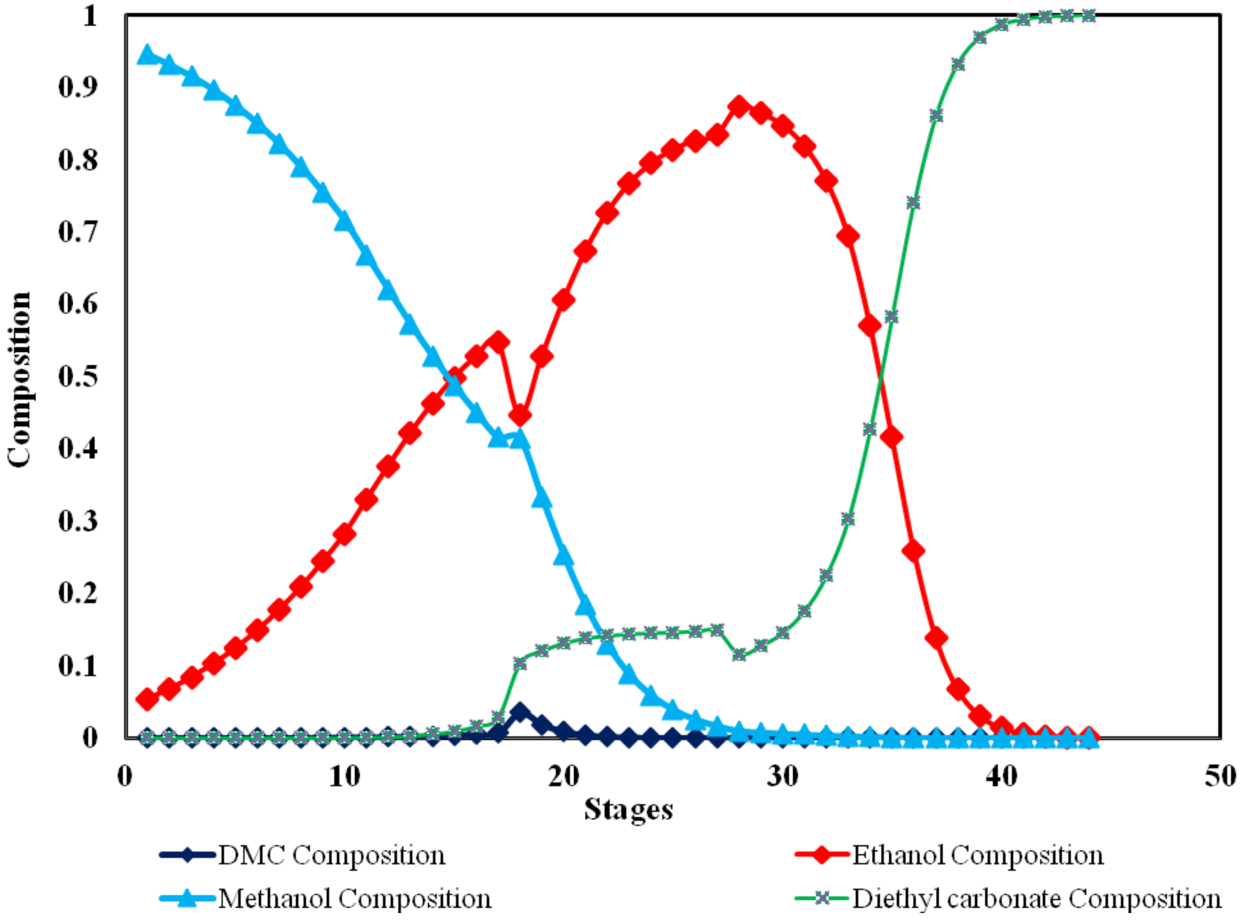


Fig. 5.9 Composition variation with stages in column1

Fig.5.9 shows the composition profiles of the pre-fractionator of the RDWDC. The purity of the distillate is 98.9 % and bottoms purity is 99.4 %.

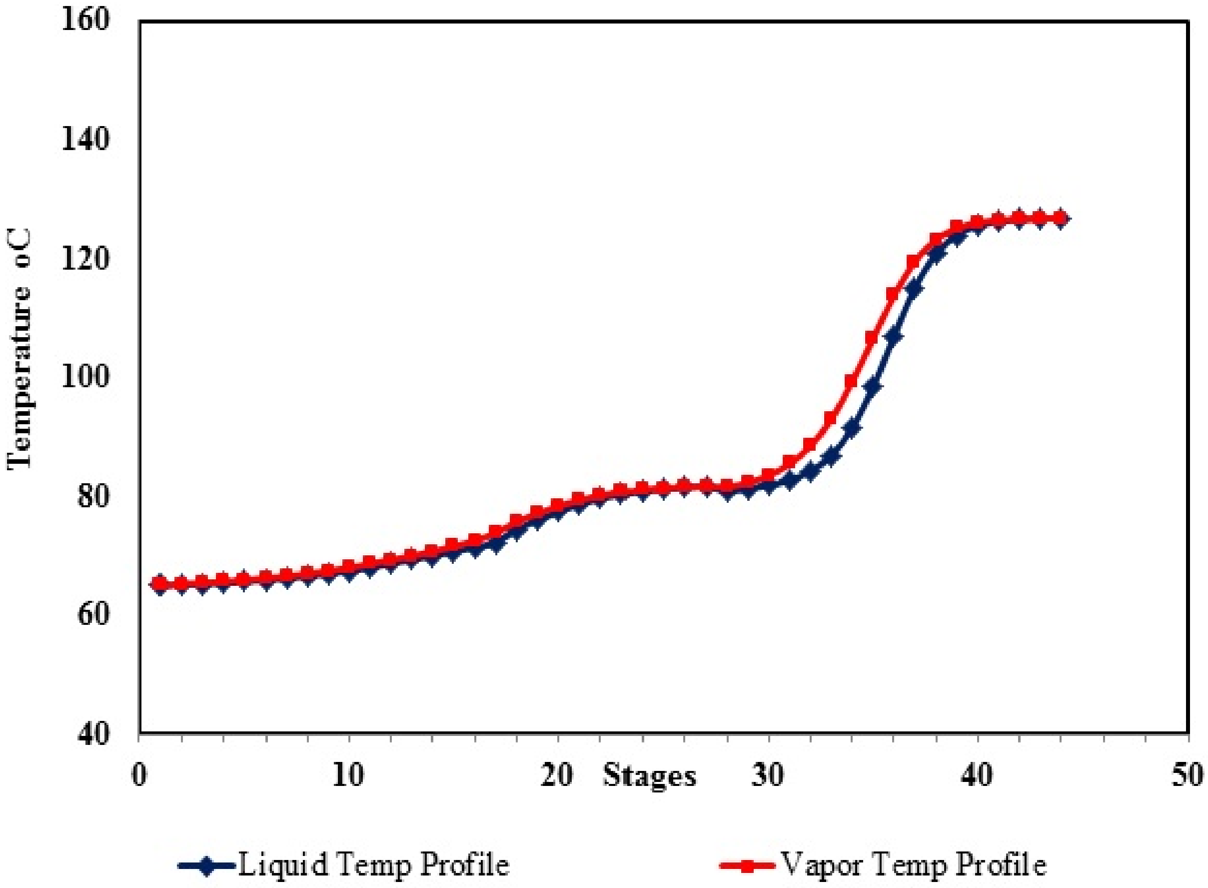


Fig. 5.10 Temperature variation with stages in column1

Fig.5.10 shows the temperature profile for the liquid and vapors in the RDWDC. The condenser temperature is 76 ^{0}C and the reboiler temperature is 127 ^{0}C. The trend shows that there is almost constant temperature up to 38th stage (reactive and rectifying) and in the stripping section temperature increases significantly from the 39th stage with the reboiler temperature being at 127 ^{0}C.

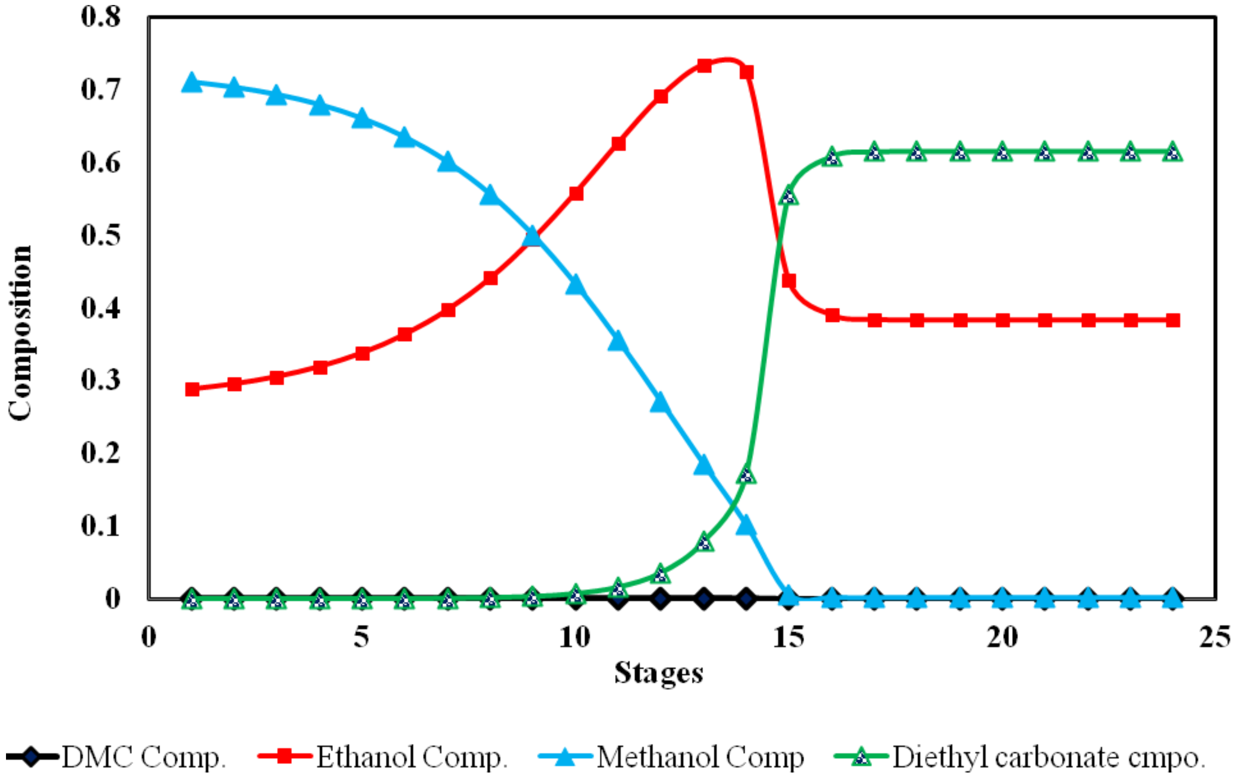


Fig. 5.11 Composition variation with stages in column 2

Fig.5.11 represents the composition profile of the side streams of RDWDC. Side stream is drawn from the 12th stage in the post fractionator side of the column and at this stage the purity of the side stream is 76.8 %, as seen from the figure.

5.4 Validation of the results

The values of the input parameters for the RDWDC operation as given in Table 5.1 were taken from the work of Mueller and Kenig (2007) By using the rate parameters for the overall reaction for the production of DEC, as given by Keller et al. (2011), we obtained the simulated results. These results are shown in Table 5.22. As can be seen, the optimization gave a much lower reflux ratio of 9.85 as against 11.67 obtained by Mueller and Kenig (2007). This reduction in v described the reboiler duty considerably, from 201342 Btu/h to173435 Btu/h. This shows a reduction of 13.8% energy, as in the Mueller Kenig (2007).

Table 5.22 Validation of the results

Parameters studied	Results in the present work	Results of Mueller and Kenig (2007)
Reflux Ratio	9.85	11.67
Distillate purity	98.99	99.89
Bottom Purity	99.45	99.98
Side stream Purity	76.86	79.67
Reboiler duty	Decreases significantly	More

Table 5.23 Energy duty at different reflux ratio

Reflux Ratio (r)	Reboiler Duty (Btu/h)	Condenser Duty (Btu/h)
5.2	119115	-116306
9.85	173435	-170714
11.67	201342	-201543

Table 5.23 shows that the reboiler duty decreases as the reflux ratio decreases from 11.67 to 5.2 Mueller and Kenig (2007) have shown that the optimum reflux ratio for the given problem was 11.67. Although, they have not reported the values of the reboiler and condenser duties, we have taken the value of the heat duties as calculated by using ASPEN Plus (2006.5). This is acceptable because the composition and temperature domain obtained thus, the optimized value of reflux ratio of 9.85 shows a reduction of 27907 Btu/h in the reboiler duty from that of the reflux ratio of 11.67. This means a 13.86% reduction can be termed as substantial heat economy for the reboiler.

CHAPTER VI

CONCLUSIONS AND RECCOMENDATIONS

6.1 Conclusions

In the present dissertation, the synthesis of DEC from DMC and ethanol has been presented along with the separation of the reactants and products in a RDWDC using a packed bed for vapor-liquid contacting. The RDWDC has been analyzed by using the ASPEN Plus software and the operating parameters have been optimized by using the Design Expert software. The optimized results were validated with that available in literature .For a similar case study, as reported, the analysis using the present methods showed that the reflux ratio used in the present case is much lower (r=9.85 as against a value of 11.67). Since the reaction and separation is taking place in a single column, this leads to a substantial reduction in the total annual cost (TAC). The bottom stream shows a DEC concentration of 99.45 %, (high purity) and the distillate stream gives methanol of 98.99% purity. The side streams give ethanol of 98.99% purity. Since the pressure of the column is 1.013 bar, it does not entail an additional cost to maintain the pressure in the two sides of the DWC. Since the reboiler and condenser duties increase as the reflux ratio increases, the operation of the reactive RDWDC at a lower reflux ratio reduces the energy requirement significantly. At this optimized reflux ratio energy demand for the distillation operation is decreases by 13.86 %.

6.2 Recommendations

From the present analysis of the reactive RDWDC along with the optimization of the operational variables, it is discerned that the following studies should be pursued in the future:

1. Rigorous cost analysis be done to determine the areas which need to be rationalized for the production of cost-effective production of DEC and methanol from dimethyl carbonate and ethanol in a reactive RDWDC.
2. The Conversion of the DMC into DEC and the selectivity of the catalyst should be studied.

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