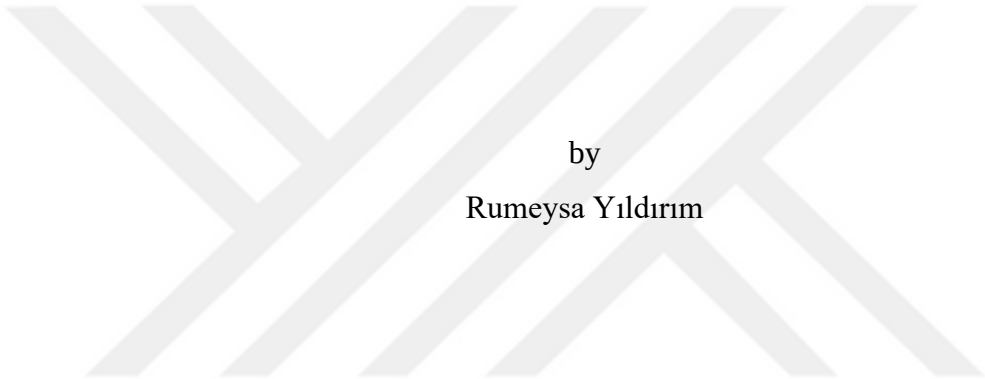


EXTRACTIVE DISTILLATION OF ISOBUTYL ALCOHOL-ISOBUTYL ACETATE
MIXTURE USING DIMETHYL SULFOXIDE: PROCESS DESIGN AND
INTENSIFICATION



by
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MIXTURE USING DIMETHYL SULFOXIDE: PROCESS DESIGN AND
INTENSIFICATION

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ABSTRACT

EXTRACTIVE DISTILLATION OF ISOBUTYL ALCOHOL-ISOBUTYL ACETATE MIXTURE USING DIMETHYL SULFOXIDE: PROCESS DESIGN AND INTENSIFICATION

Separation process of isobutyl alcohol and isobutyl acetate mixture is designed using conventional extractive distillation and extractive dividing-wall column (E-DWC) distillation methods. Due to the existence of pressure-sensitive minimum boiling azeotrope in the binary system, thermodynamic analyses based on the NRTL activity coefficient model are carried out. Compared to the atmospheric pressure, operating at vacuum pressures has resulted in less energy consumption when dimethyl sulfoxide (DMSO) is used as the solvent. The distillation column parameters are optimized for economic objective using sensitivity analysis and successive quadratic programming techniques. Environmental performances of the distillation processes are also evaluated. For a product purity of 99.9 mole %, the E-DWC process has resulted in 10.5 % and 9.9 % reductions in the total annual cost and CO₂ emission rates respectively compared to the conventional method.

ÖZET

İZOBÜTİL ALKOL-İZOBÜTİL ASETAT KARIŞIMININ DİMETİL SÜLFOKSİT İLE ÖZÜTLEMELİ DAMITILMASI: SÜREÇ TASARIMI VE YOĞUNLAŞTIRILMASI

İzobütil alkol-izobütil asetat karışımının geleneksel ekstraktif distilasyon ve ekstraktif-bölme duvarlı kolon (E-DWC) yöntemleri kullanılarak ayırma prosesi tasarlanmıştır. Basınca duyarlı minimum kaynama noktası azeotropu oluşması sebebi ile, NRTL aktivite katsayısı modeli baz alınarak ikili systemin termodinamik analizi gerçekleştirilmiştir. Dimetil sülfoksitin (DMSO) çözücü olarak kullanılması durumunda, vakum basınç altında çalışmanın atmosferik basınçla karşılaştırıldığında daha az enerji gerektirdiği görülmüştür. Distilasyon kolon parametreleri, ekonomik koşulları belirlemek amacı ile hassasiyet analizi ve sıralı ikinci dereceden programlama teknikleri kullanılarak optimize edilmiştir. Ayrıca, distilasyon proseslerinin çevresel performansları değerlendirilmiştir. %99.9 saflıkta ürün elde edilen ayırma proseslerinde, E-DWC yönteminin geleneksel ekstraktif distilasyona kıyasla yıllık toplam maliyette %10.5 ve CO₂ emisyon oranlarında %9.9 azalma sağladığı görülmüştür.

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LIST OF SYMBOLS/ABBREVIATIONS

D	Diameter
T	Temperature
x	Liquid mole fraction
y	Vapor mole fraction
α	Relative volatility
α_{ji}	Non-randomness parameter
G_{ji}	Gibbs energy
τ_{ji}	Binary interaction parameter
AD	Azeotropic distillation
BUP	Butyl propionate
CEPCI	Chemical engineering plant cost index
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DWC	Dividing wall column
EC	Extractive column
ED	Extractive distillation
E-DWC	Extractive-dividing wall column
EHS	Environmental health and safety
FCI	Fixed capital investment
F_s	Solvent rate
HEX	Heat exchanger
IBA	Isobutyl alcohol
IBAc	Isobutyl acetate
NS_{C1}	Stage number of extractive column
NS_{C2}	Stage number of solvent recovery column
NT_F	Binary mixture feed tray number
NT_{F2}	Feed tray number in solvent recovery column
NT_S	Solvent feed tray number
OC	Operational cost

PI	Process intensification
PSD	Pressure swing distillation
RCM	Residue curve map
RHD	Reboiler heat duty
SQP	Successive Quadratic Programming
SRC	Solvent recovery column
TAC	Total annual cost
VLE	Vapor liquid equilibrium



1. INTRODUCTION

Engineers focus on the design of sustainable processes due to the growing environmental awareness in recent decades. Since massive amounts of solvents are used in the industry, selecting solvents that have no toxicity, least environmental effect and low energy demand is crucial. Isobutyl alcohol (IBA) and isobutyl acetate (IBAc) are reported as recommended solvents based on health, safety and environment scores [1]. They have desired features such as biodegradability, miscibility with common organic solvents and low solubility in water [2].

IBA and IBAc are commonly used in various fields such as coatings, cosmetics, pharmaceutical and industrial cleaning products. Isobutyl alcohol can be obtained from different bio-sources, but is mainly produced by hydrogenation of isobutyraldehyde. On the other hand, isobutyl acetate is produced via esterification of acetic acid with isobutyl alcohol. However, the equilibrium conversion is limited to 70% in the reversible esterification reaction. The resulting IBA-IBAc mixture requires complex separation techniques due to the existence of minimum boiling point azeotrope in the system [2-5].

Pressure swing distillation (PSD), azeotropic distillation (AD) and extractive distillation (ED) methods have been the subject of many studies for separation of azeotropic mixtures. Pressure swing distillation is a widely utilized technique when the azeotropic composition is sensitive to pressure. In PSD method, it is aimed to obtain high purity products by applying pressure alteration [6]. Azeotropic distillation and extractive distillation separation methods are based on the common principle of adding a third component to the system to change the relative volatility of components. The solvent selection is a key issue in both the AD and ED systems. Extractive distillation and azeotropic distillation differ from each other because they have different column sequences and feasibility rules. There is an extractive section in ED while the mixture and solvent are fed to the tower at the same stage in AD [7].

Process intensification techniques attract significant attention due to the disadvantage of excessive energy consumption in the conventional distillation method. Different technologies have been employed in process design to reduce operational cost and increase efficiency. It is reported that vapor recompression strategy provides higher thermal efficiency in distillation systems and utility cost can be decreased with heat integration [8,9].

In this method, overhead vapor stream is compressed to a higher pressure to be used as utility in the reboiler. On the other hand, dividing wall columns (DWCs) are widely preferred in process intensification applications to reduce the total annual cost. Here, the conventional ED sequence which consists of two columns is reduced to a single column with the addition of a partition wall.

The separation process design of IBA+IBAc mixture has been investigated in several studies. Munoz et al. separated the IBA-IBAc system by using extractive distillation and pressure-swing distillation techniques. They evaluated the performance of the solvents, butyl-propionate (BUP), 1-hexanol, N, N-Dimethyl formamide (DMF). Their results showed that PSD was more economical compared to the ED [10]. Luo et al. performed design and control of fully heat-integrated pressure swing distillation for separating isobutyl alcohol and isobutyl acetate and found that reboiler heat duty can be decreased with heat integration [11]. Heat pump technology was used in PSD by Wang et al. [12] Hybrid PSD was performed by Miao et al. [13]. Also, extractive distillation with thermally coupled heat pump technology was applied for the separation of IBA-IBAc system using DMF and BUP as solvents [14,15].

In this study, we have designed a separation process for isobutyl alcohol and isobutyl acetate mixture using the extractive distillation method. Dimethyl sulfoxide (DMSO) is evaluated as a solvent and NRTL equation is used as the thermodynamic model. Estimation of the thermodynamic model parameters is performed using the vapor-liquid equilibrium data reported by Liu et al. [16]. Both conventional extractive distillation and extractive-dividing wall column processes are built in ChemCAD and comparison of methods is carried out. The economic and environmental evaluation of systems are presented on the basis of the total annual cost and CO₂ emission rate calculation.

In this thesis, a comprehensive literature review on azeotropy, separation methods of azeotropic mixtures and thermodynamic analyses of distillation systems are presented in Chapter 2. This chapter also comprises information about process intensification and dividing-wall column technique. In Chapter 3, thermodynamic, economic and environmental evaluation methods of extractive distillation systems are defined and vapor-liquid equilibrium diagrams, residue curve maps are discussed. Furthermore, conventional extractive distillation, dividing wall column simulations results and optimization procedure are explained in Chapter 4. In addition, comparison of alternative systems is presented with

economic and environmental aspects. Finally, conclusions and recommendations are elaborated in Chapter 5.



2. THEORETICAL BACKGROUND

In this chapter, it is aimed to give detailed information about distillation, azeotropy and special distillation methods used for azeotropic mixtures.

2.1. DISTILLATION

Simple distillation is a separation technique based on the volatility difference of components in a mixture. In this process, liquid and vapour phases are formed by heating liquid mixture until it begins to boil. Hot vapour is collected in the upside of tower and condensed. Thus, top product which is rich in the most volatile component is obtained, while the heavy component is withdrawn as the bottom product. The main condition in the distillation process is that the compositions of vapor and liquid phases in equilibrium are different [17].

Figure 2.1 illustrates a typical simple distillation system which consists of various equipment that provides heat and mass transfer; the column where the separation takes place; the reboiler for evaporation, and the condenser for the collected vapor streams. The column can be designed with trays or packing materials. The section of the tower above the feed stream location is called the rectifying section and the lower part is the stripping section. Simple distillation technique is used for separation of two or more component mixtures.

The history of distillation dates back to ancient times and has been applied for thousands of years. In 1813, the first continuous distillation column was invented by Cellier-Blumenthal in France. The first industrial tar distillation plants were built in Britain, in 1822. Othmer group reported the first reactive distillation application for esterification of dibutyl phthalate from butanol and phthalic acid in 1948. Since old times, distillation has been used in chemical industry as one of the major separation methods [18].

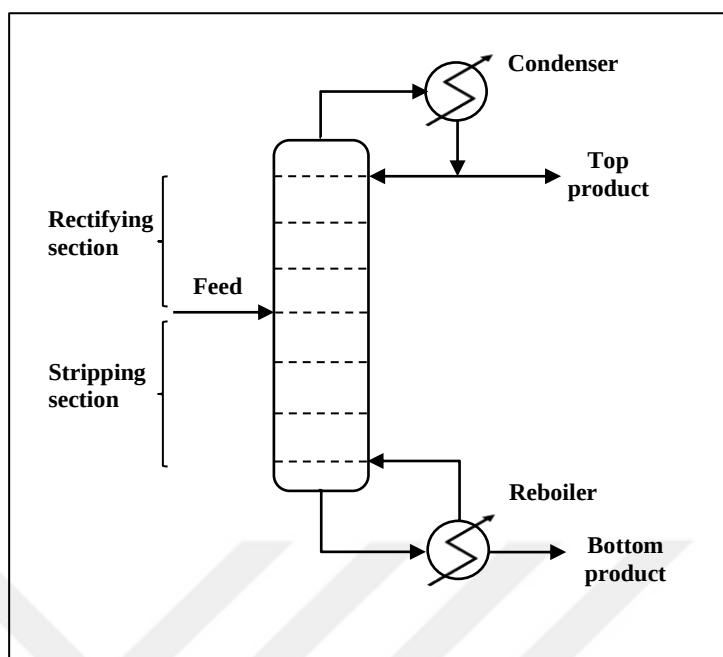


Figure 2.1 Simple distillation column

2.2 AZEOTROPIC MIXTURES

An azeotropic mixture has liquid and vapor phases of the same composition at a certain pressure. The formation of the azeotrope depends on the interaction of molecular forces between the components. Ideal mixtures obey Raoult's law, while azeotropic mixtures show deviation from Raoult's law either negatively or positively [19].

If an azeotropic mixture is homogeneous at the equilibrium temperature, the azeotrope is called a homoazeotrope, and when two separate liquid phases exist, it is referred to as a heteroazeotrope. Azeotropes, can also be examined in two groups; minimum boiling and maximum boiling azeotropes. The boiling point of the azeotrope being lower than the boiling points of pure components of mixture is called as a minimum-boiling azeotrope. If the boiling point of the azeotrope is higher than the boiling points of pure components of mixture, then it is a maximum-boiling azeotrope. Examples of azeotropic behavior are shown in Figure 2.2 [20].

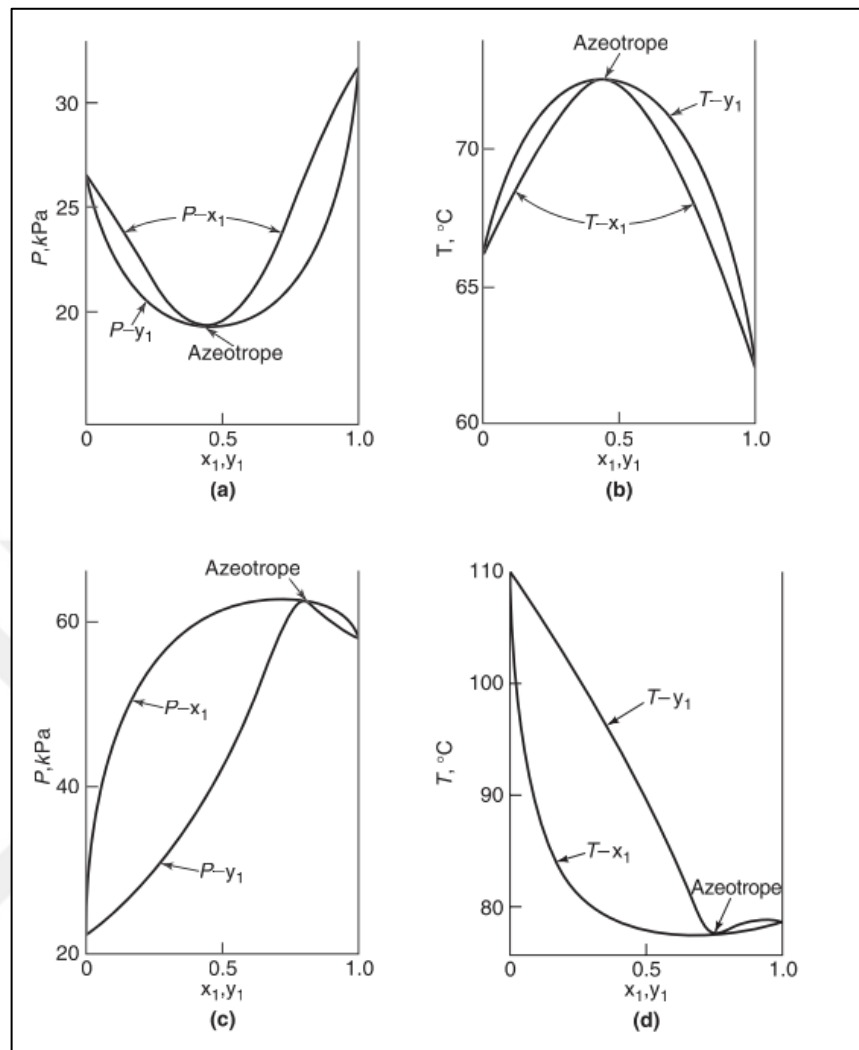


Figure 2.2. Binary mixture phase diagrams (a) P-x-y curve for a maximum boiling azeotrope (b) T-x-y curve for a maximum azeotrope (c) P-x-y curve for a minimum boiling azeotrope (d) T-x-y curve for a minimum boiling azeotrope [20]

2.2. SEPARATION METHODS FOR AZEOTROPIC MIXTURES

Simple distillation method is insufficient for the separation of azeotropic mixtures. Therefore, several special techniques have been developed. The most prominent ones are azeotropic distillation, extractive distillation and pressure swing distillation.

2.2.1. Azeotropic Distillation

Azeotropic distillation (AD) can be classified into two groups; homogeneous and heterogeneous azeotropic distillation.

In homogeneous AD, separation of azeotropic mixtures can be performed without the need for any liquid immiscibility. A third agent termed solvent, entrainer or mass separating agent is added to improve separation and may form a new azeotrope or may not [20,21].

On the other hand, in heterogeneous AD, solvent is introduced to the system to affect the vapor-liquid equilibrium and form a new minimum boiling azeotrope with one or more feed components. Immiscibility is key issue in heterogeneous AD systems. Heterogeneous azeotropic distillation is more common in industry because of the restrictive nature of homogeneous AD [22].

As indicated in Figure 2.3, azeotropic distillation system includes two columns. High purity products are withdrawn at the bottom of the towers. Overhead vapor in first column is first condensed and two liquid phases are formed. The liquid-phase comprising the solvent is fed back to the column and the other phase is sent to the second column. Further purification is performed in second tower and the solvent gained is fed back to the first column. Solvent selection constitutes the core aspect of the azeotropic distillation process; volatility of the solvent should be appropriate to carry out the desired separation.

2.2.2. Extractive Distillation

Extractive distillation (ED) is a prominent technology among the special distillation methods in chemical industry. ED can be adopted for separation of non-ideal mixtures inclusive of minimum and maximum boiling point azeotropes. Similar to azeotropic distillation, an additional component is added to the system to break the azeotrope. In ED, entrainer does not form an additional azeotrope and it only alters the relative volatility of the mixture. The selected solvent plays an important role because it directly affects the efficiency and the economy of the process [23,24].

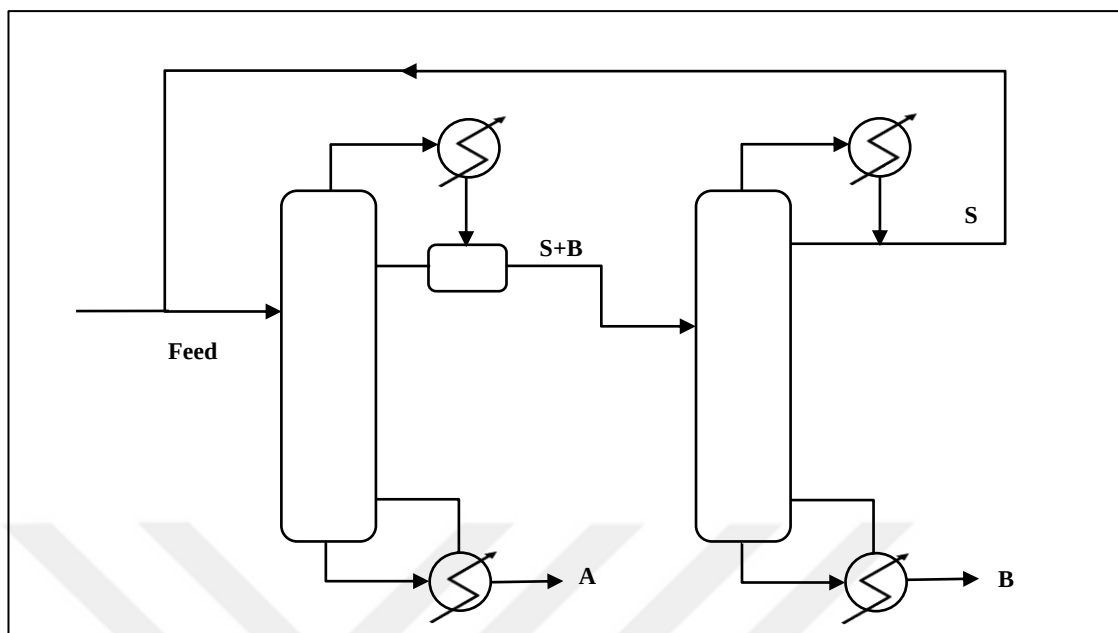


Figure 2.3. Flowsheet of heterogeneous azeotropic distillation

Relative volatility values are evaluated to choose appropriate solvent candidate in ED processes. The relative volatility must be at a sufficiently high level so that the process provides the desired purity. The following features are taken into account in suitable solvent screening; [20]

- not to form new azeotropes with the components in the mixture to be separated,
- easy separation from the other components,
- thermal stability at the process temperatures,
- nonreactivity with the other compounds,
- to be nontoxic, inexpensive and easily available,
- to be noncorrosive to used construction materials,
- to have a low latent heat of vaporization.

2.2.2.1. Column Sequences of Extractive Distillation

Extractive distillation can be classified as continuous, batch and semi-continuous in terms of operation mode. Continuous ED is the most favoured method as a research subject. The

flowsheet of a continuous extractive distillation process with heavy entrainer is shown in Figure 2.4. The system consists of two main columns, extractive column and solvent recovery column. In continuous mode, since the azeotropic mixture and entrainer feed streams are fed to extractive column at different locations, first column is divided into three sections as rectifying, extractive and stripping. The mixture is fed to the first tower in lower stages while solvent is continuously added near the top of the column. Two top products are obtained in the first and second towers. Entrainer stream withdrawn as a bottom product in recovery column is recycled to the first column. Entrainer make-up stream is required to compensate for losing the entrainer during the process [25].

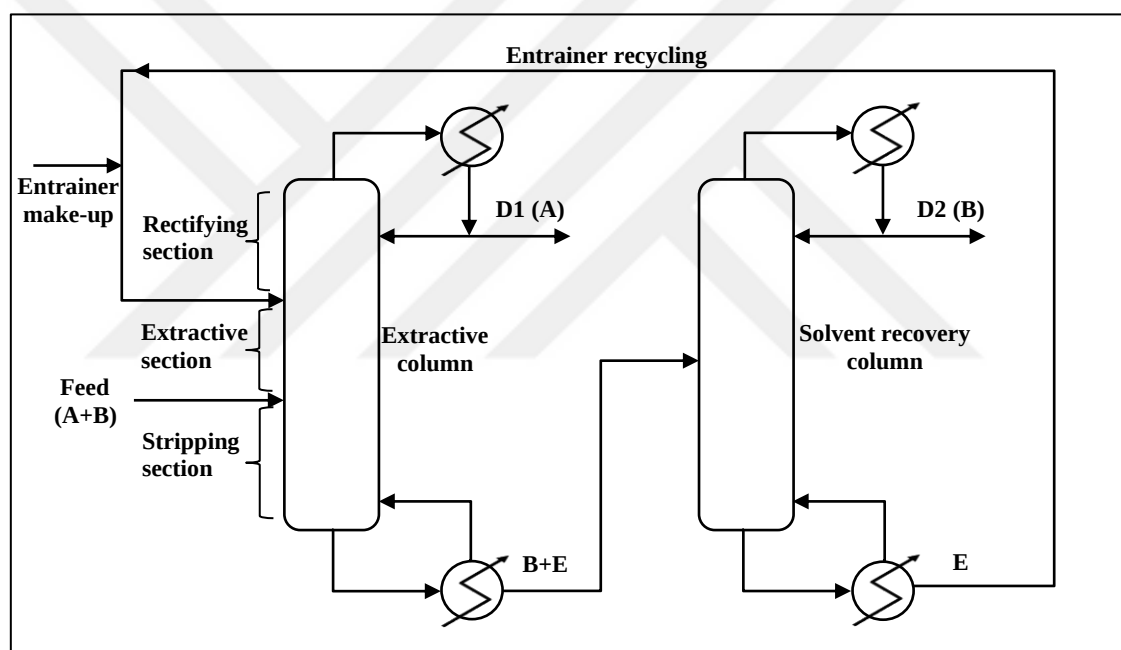


Figure 2.4. Flowsheet of continuous extractive distillation with heavy entrainer.

Batch extractive distillation system with heavy entrainer is illustrated in Figure 2.5. Batch ED is generally preferred in small capacity productions and laboratory studies. It is operated with a single column unit. For batch operation mode, column does not comprise three sections because there is a single feed stream. Depending on the entrainer feed stage, stripping section or rectifying section does not exist. The disadvantages of batch ED are requirement of high capacity reboiler and hard-controllability due to the constantly changing process parameters [26, 27].

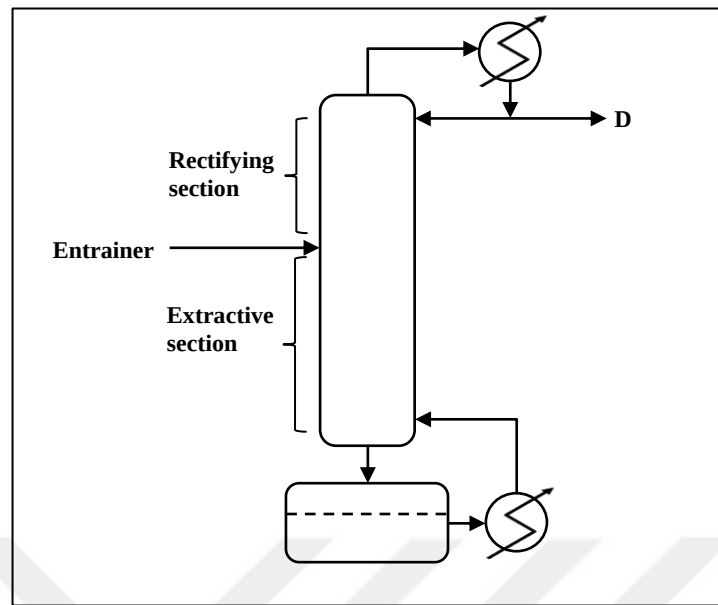


Figure 2.5. Batch extractive distillation process

2.2.3. Pressure Swing Distillation

Pressure swing distillation (PSD) is a widely utilized technique that provides separation of azeotropic mixtures based on the pressure alteration principle without exploiting any additional component. PSD can be used for multicomponent mixtures, both minimum and maximum boiling azeotropes. However, application of PSD method is limited to pressure-sensitive mixtures [20].

The flowsheet of PSD for separation of minimum-boiling azeotrope is illustrated in Figure 2.6. PSD process involves two-column distillation sequence where the distillation columns are operated at different pressures. In the first column operated at P_1 , pure component (A) is removed as a bottom product and the distillate is sent to the second column by varying pressure. The pure bottom product (B) is recovered in the second column operated at P_2 and the distillate is fed back to the first tower [20].

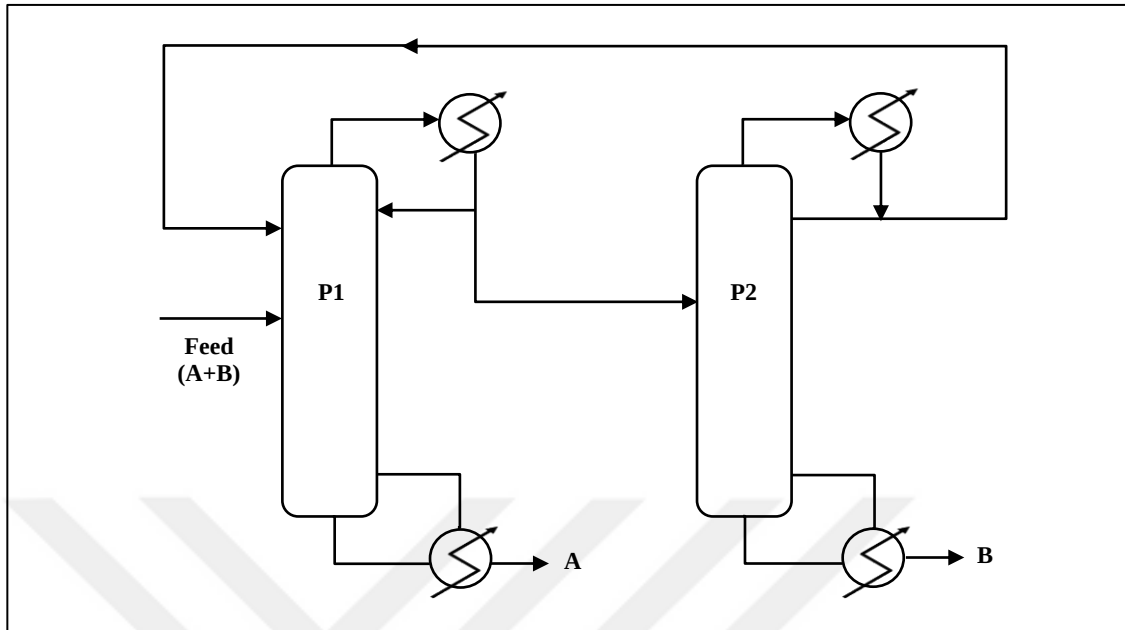


Figure 2.6. Pressure swing distillation sequence for a minimum-boiling azeotrope

2.3. THERMODYNAMIC ANALYSIS

Thermodynamic analysis is a useful design tool to investigate the feasibility of distillation processes. VLE diagrams can be considered as a first step of analysis; they help us understand thermodynamic conditions of the system. In the presence of the azeotropes, VLE analysis gains greater importance and graphical representation becomes much more complex. The VLE graph of a system consisting of n components can be defined in $(n-1)$ -dimensional space. For binary mixtures, one-dimensional diagrams can be plotted and the most common types of them are x - y and T - x - y equilibrium curves under the constant pressure. Representation of VLE graphs of ternary mixtures requires two-dimensional composition space. Each VLE function is a surface in a three-dimensional prism [21, 28].

Residue curve maps provide information similar to phase diagrams but may present it in a more convenient way. Residue curves describe how liquid composition change during the separation process. Collection of these curves is called residue curve map (RCM) [29]. The residue curve maps can be computed by the following differential equation:

$$\frac{dx_i}{d\xi} = x_i - y_i^* \quad i = 1, 2, \dots, n \quad (2.1)$$

where ξ represents dimensionless time, x_i and y_i show liquid and vapor mole fraction respectively for associated component. For non-reactive system, the solution of the set of differential equations gives singular points which are stable node, unstable node and saddle point.

- Stable node: Highest boiling point of the distillation region, it may be pure component or azeotropic point. All residue curves move toward stable node.
- Unstable node: Lowest boiling point of the distillation region, it may be pure component or azeotropic point. Residue curves start to move from the unstable nodes.
- Saddle point: Intermediate boiling points of the distillation region. Residue curves approach to the saddle points.

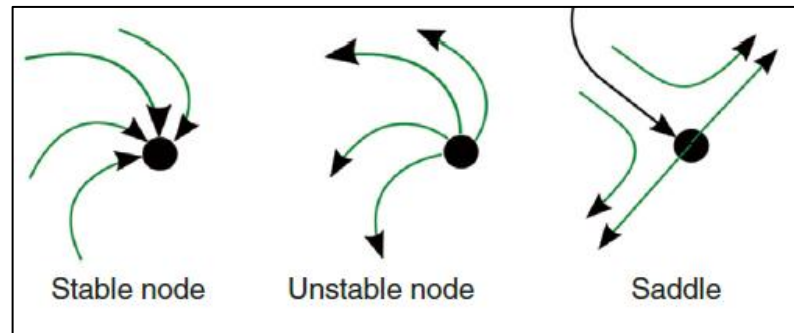


Figure 2.7. Singular points' features [30]

Since the fraction of light component decreases with time in liquid phase, trajectories always proceed in the direction of highest boiling point. Residue curves can form residue curve regions depending on the singular point locations. In Figure 2.8, RCM samples are illustrated for various ternary mixtures. In case of zeotropic mixture, residue curves move from the lowest boiling point component to the highest boiling point component in hyperbolic pathway (see Fig. 2.8 a). Initial point is azeotropic composition in RCM for presence of

minimum boiling point azeotrope as shown in Figures 2.8 b&f. In other cases, it can be seen that the curves divide residue curve map into different regions. A singular point with intermediate boiling temperature is an initial or final point of the residue curves in Figure 2.8 c-e.

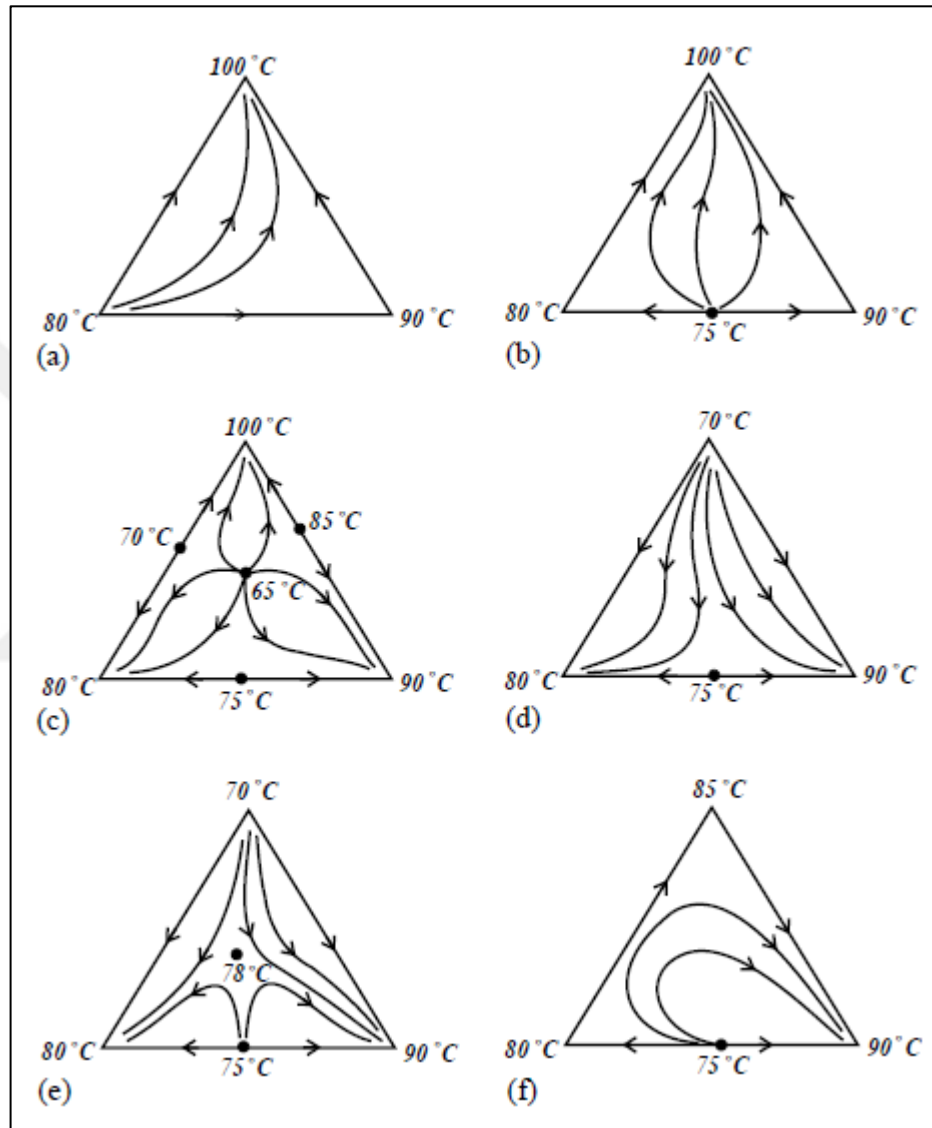


Figure 2.8. Residue curve map samples for different ternary mixtures [28]

General feasibility criteria for ED processes were expressed by Rodriguez-Donis et al., it was stated that “homogeneous extractive distillation is feasible for A-B mixture with an entrainer E if there is a residue curve connecting E to A or B following a decreasing or increasing temperature direction inside the region where A or B is the most volatile component or heaviest component of the mixture”. Univolatility curves ($\alpha_{ij} = 1$) set the

volatility order which is critical information about process design. Location of the univolatility line depicts which component is withdrawn first [31, 32].

2.4. PROCESS INTENSIFICATION

Process intensification (PI) can be defined as technologies that are applied in processes or equipment, making economic and environmental profit, increasing efficiency and product quality. PI was initially noticed in UK in the 1970s through work of Colin Ramshaw et al. They developed technologies such as rotating packed bed gas/liquid contactor, rotating chlorine cell and the polymer film compact heat exchanger. As a consequence of these technological advances, PI was presented to the chemical process industry and it has become a promising way for sustainable process design [33, 34].

The main benefits of the PI technologies in the chemical industry were reported as follows: [35, 36]

- Lower capital cost by reducing the number of equipment
- Reduction of energy demand and lower operational cost
- Inherently safe process design
- Reduction of environmental impact
- Improvement of product quality

Elements of PI technology are classified into two distinct groups; equipment and methods. Process intensifying appliances comprise reactive and non-reactive, while multifunctional reactors, hybrid systems and alternative energy sources constitute the basic methods as shown in Figure 2.9.

PI equipment studies for reaction focus on efficiency, selectivity and high conversion rate. Energy consumption and reaction times can be reduced thanks to the intensive mixing and improved heat and mass transport rates. Spinning disc reactor, static mixer reactor and microreactors are some of the prominent PI reactors. Compact heat exchanger, rotating pack bed and centrifugal adsorbers can be given as an example for PI devices for non-reactive operations [37,38].

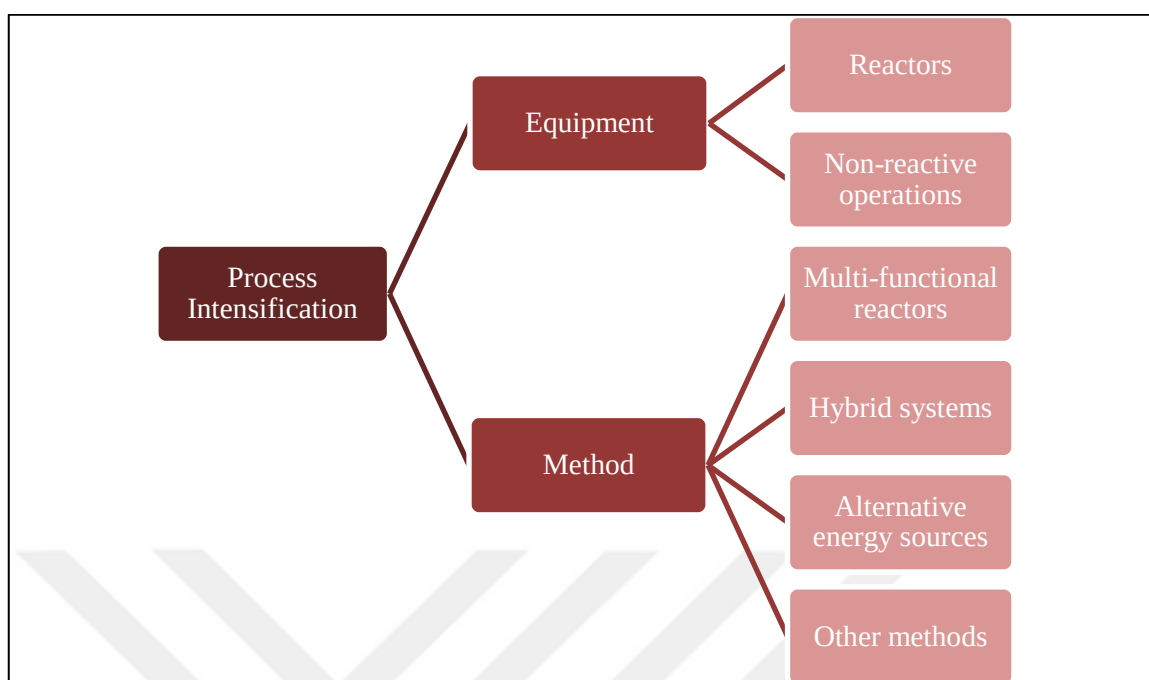


Figure 2.9. Process intensification elements

It is aimed to improve processes and to lower capital and operating costs with process intensifying methods by combining unit operations and functions. The efficiency of the process is enhanced with innovative methods. Some of the significant PI methods are; [35, 39]

- Multi-functional reactors: heat-integrated reactor, reactive distillation, reactive extrusion and fuel cells.
- Hybrid separation systems: dividing-wall column, membrane distillation, membrane adsorption and pervaporation.
- Alternative energy sources: solar energy, microwave, ultrasound, electric fields and plasma technology.
- Other methods: supercritical fluids, periodic operation.

The main principles of process intensification were specified in the study conducted by Stankiewicz and van Gerven. These principles are; [39]

- maximizing the effectiveness of intramolecular and intermolecular events

- providing same process experience to all molecules
- optimizing the driving forces at all scales and maximizing the specific surface area to which these forces apply
- maximizing synergistic effects from partial processes.

2.4.1. Dividing Wall Column

There has been an inevitable trend towards sustainable and greener technologies in the chemical industry. Distillation has a wide range of applications in chemical facilities, but there are some concerns in the installation and operation of traditional columns, such as high energy consumption, capital costs and waste production. DWC is an innovative equipment that is built by placing a partition wall inside a single shell column for separation of multicomponent systems with desired purities. DWC is a beneficial option in terms of lower investment cost, energy demand and space requirement comparing with the conventional ones [40].

In the process of separation of a three-component mixture, two or three column configurations are required by traditional distillation units in series or parallel sequences (see Figure 2.10). In direct sequence case, the lightest compound is obtained in the first column while the heaviest is withdrawn in indirect scheme. In the configuration shown in Fig. 2.10c two further columns are required to obtain pure products. Fully thermally coupled column is another alternative system referred to as Petlyuk column and indicated in Figure 2.11a. Prefractionation arrangement is reported by Petlyuk et al. in 1965. Here, vapor and liquid streams leaving the first column are directly fed to the second column resulting in a substantial savings in capital and operational costs. It is stated that Petyluk column reduces energy consumption rate by approximately 20%-30% compared to conventional sequences for the same separation process. Dividing wall column combining these two columns (prefractionation and main column) is capable of separation of three-component mixture in a single column as illustrated in Figure 2.11b. The lightest component A is obtained as an overhead product, intermediate component B is gained in the middle stages and the heaviest component C is withdrawn as a bottom product. Thanks to the improved vapor-liquid

interaction in DWCs, it can save up 40% in energy compared to traditional distillation systems [40 - 43].

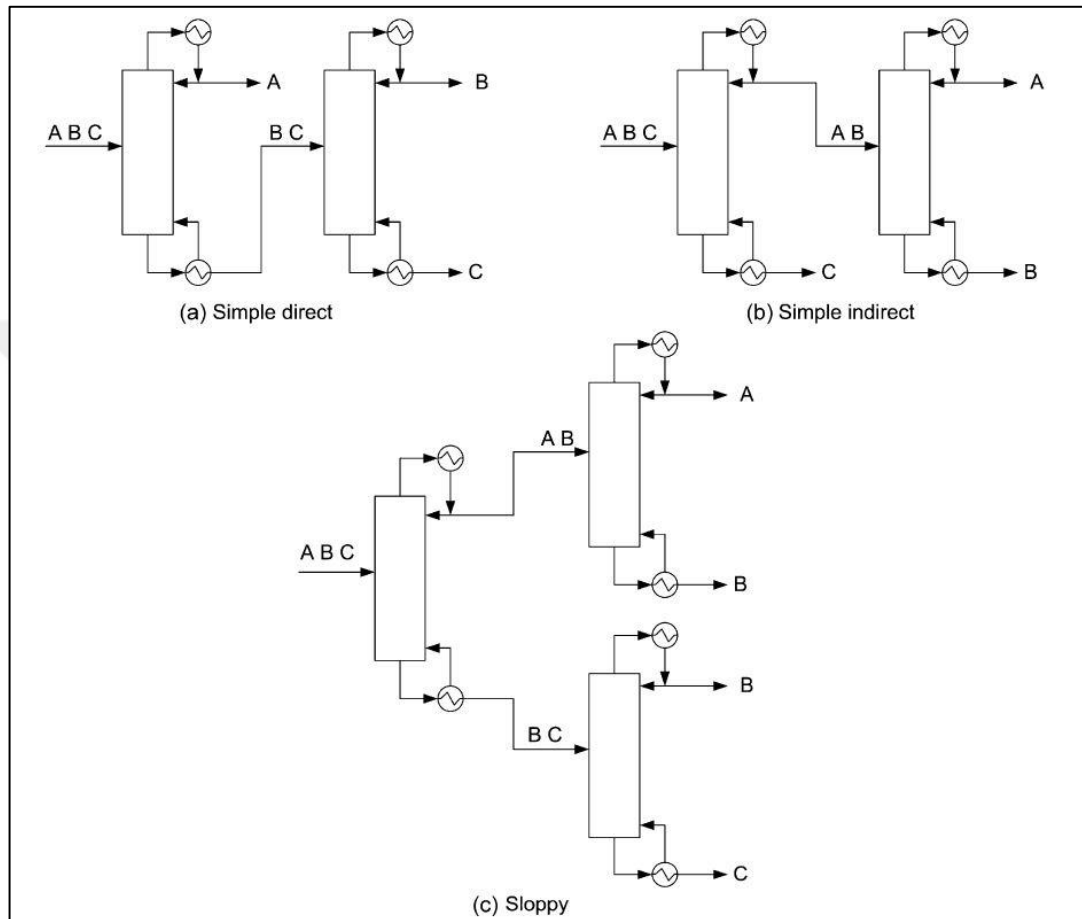


Figure 2.10. Conventional column scheme in series and parallel sequences for separation of a three-component mixture [40]

Initially, there were some difficulties in design procedure, application and control of DWCs because of the plenty number of parameters. In 1985, the first industrial application of DWC was achieved by BASF SE and then, the number of DWCs has grown rapidly and reached more than 100 by 2010. It is predicted by Schultz et al. that DWC technologies might replace conventional ones in the coming years due to increasing economic and environmental concerns [42,44].

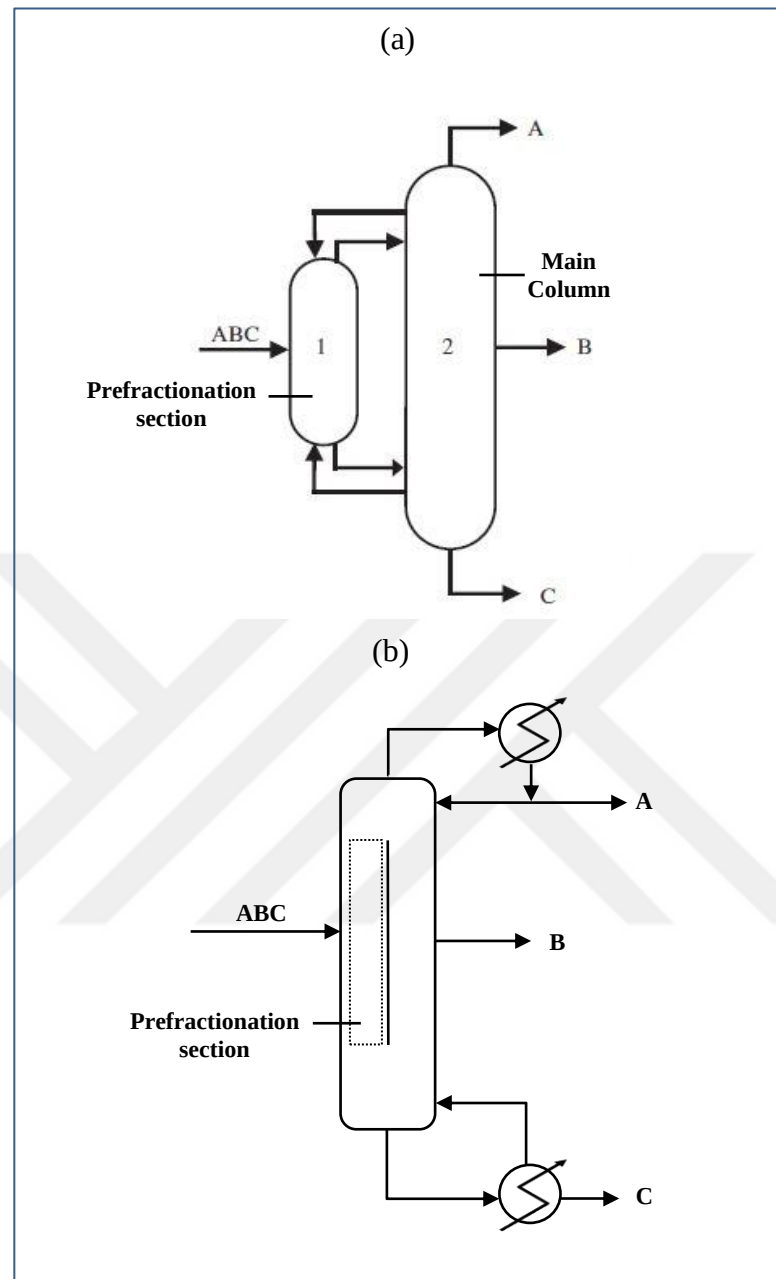


Figure 2.11. (a) Petlyuk column (b) Dividing wall column

2.4.1.1. Configurations of Dividing Wall Column

In DWC columns, the partition wall can be located in different regions. In basic types of DWCs, the wall can be placed in the upper, middle or lower side of the column as shown in Figure 2.12. In case of the wall position shown in Fig. 2.12a, divided-wall column comprises single reboiler and single condenser, on the other hand, two reboilers and two condensers are designed for Fig. 2.12b&c respectively.

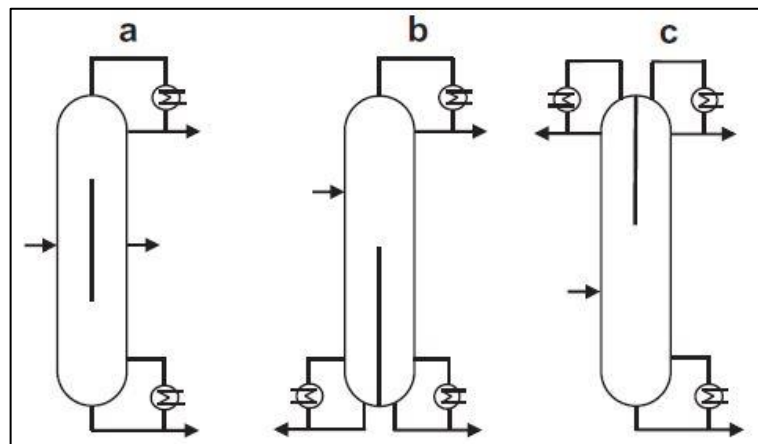


Figure 2.12. Typical wall positions in DWCs [42]

Wall design can be applied in various ways. Location of the wall can be shifted horizontally to the right or left or it may contain diagonal portion as shown in Figure 2.13. DWC internals become more complex when separating mixtures of more than three components. Various column combinations or performing additional dividing wall can be preferred. As the number of components increases, the number of alternative configurations also grows. Determination of appropriate column interior arrangement is critical issue for efficiency, mass and energy transfer rates aspects [42].

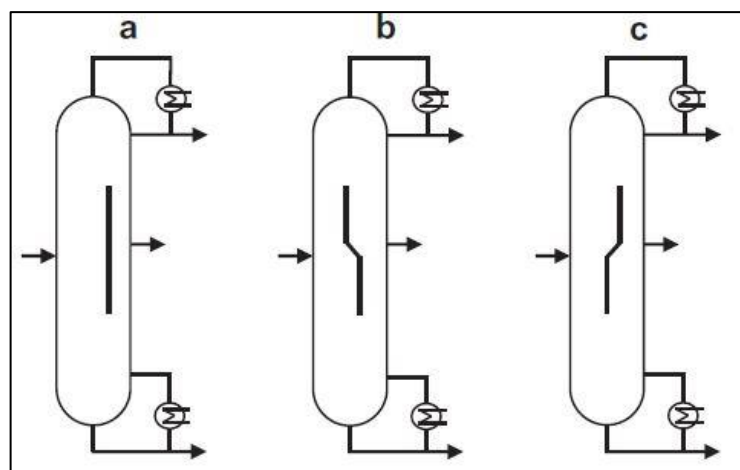


Figure 2.13. Various shapes of wall in different locations in DWC [42]

DWCs can be equipped with trays, packing or both of them. Construction method of DWCs is different in packing and tray columns. Construction of packing columns needs more

complex procedure than tray columns, especially welding of the vertical wall is much more difficult. In building of tray DWCs, welded dividing wall can make the column shell stronger. Recent technological advances have made it possible to implement non-welded walls in DWCs. Unfixed walls developed by Julius Montz GmbH and BASF SE have some advantageous like faster and simpler installation as well as lighter weight and fewer manholes [42].

2.4.1.2. Applications of Dividing Wall Column

At first, DWCs were generally utilized for final purification where the intermediate component as the main product at high purity level. Recently, they are used for broad range of products such as hydrocarbons, alcohols, aldehydes, ketones and amines. Moreover, DWCs can be adopted to azeotropic, extractive and reactive distillation systems [42].

Kolbe and Wenzel [43] reported MORPHYLANETM process for benzene recovery by using DWC for integration of a stripper column and an extractive distillation. Pilot-plant tests were carried out first and then successfully put into practice. It has been stated that 30% to 40% savings were achieved in energy, equipment and land area.

Heida et al. [45] described two-DWCs system for butadiene extraction process similar to conventional columns in series sequences. They reported 10% savings in capital costs, 20% savings in equipment maintenance and 16% reduction in energy demand.

On the other hand, majority of DWC applications in the literature is for the separation of three component mixtures while just a few of them are for more than three components or hybrid systems. This is because there are still some limitations in industrial applications of DWCs [42].

2.4.1.3. Simulation and Optimization of Dividing Wall Column

Simulation and optimization of dividing wall columns is much more complicated than standard columns due to the large number of design parameters to be manipulated. The best way to achieve an optimal DWC design is computer-based simulations. However, current commercial process simulators such as CHEMCAD, ASPEN PLUS or HYSYS do not include DWC unit operation. Therefore, it is necessary to create thermodynamically equivalent column sequences. Some prominent column configurations are pump-around model, two-columns sequence and four-columns sequence [41].

Pump-around model represents a single column consists of various sections as shown in Fig. 2.14. DWC system is reflected with liquid pump-around streams and vapor bypasses. I and IV represent sections above and below of the wall. Section II and III stand for right and left side of the partition wall. Although it seems computationally easier and simpler because of including single column, convergence problems are reported in the literature [41].

There are a few types of two-column sequences, some of which are indicated in Figure 2.15. Fig. 2.15a configuration is one of the most preferred in the literature and 2.15b is another alternative column sequence to set up DWC. The first column represents prefractionation section and the second one is main column. It is a more straightforward choice and easier to build compared to the pump-around model [41].

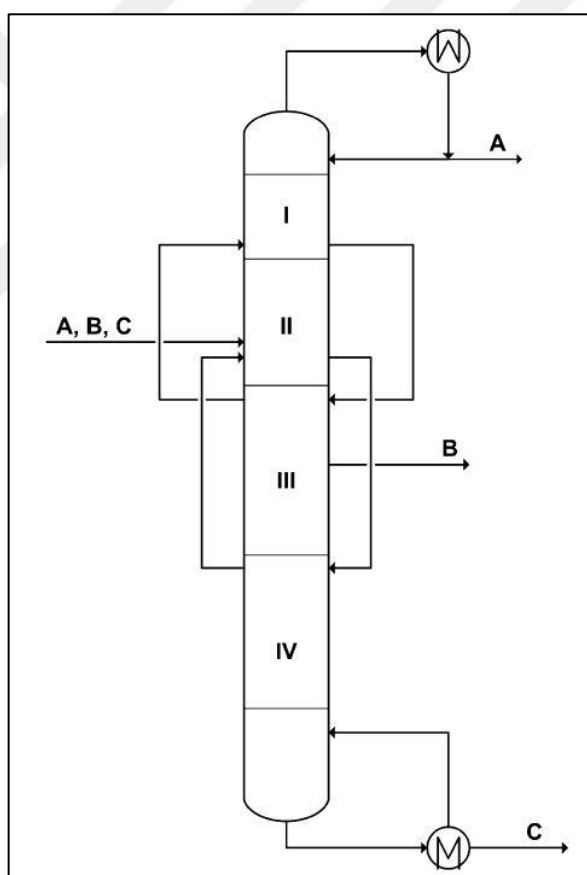


Figure 2.14. Pump-around DWC model [41]

Four-column sequence illustrated in Fig. 2.16 is the best model to simulate DWC. It also, offers much more flexibility than other alternatives due to consisting of many sections and

vapor-liquid split ratios. On the other hand, it provides slowest convergence and it is necessary to have initial estimation for all interconnecting streams [41].

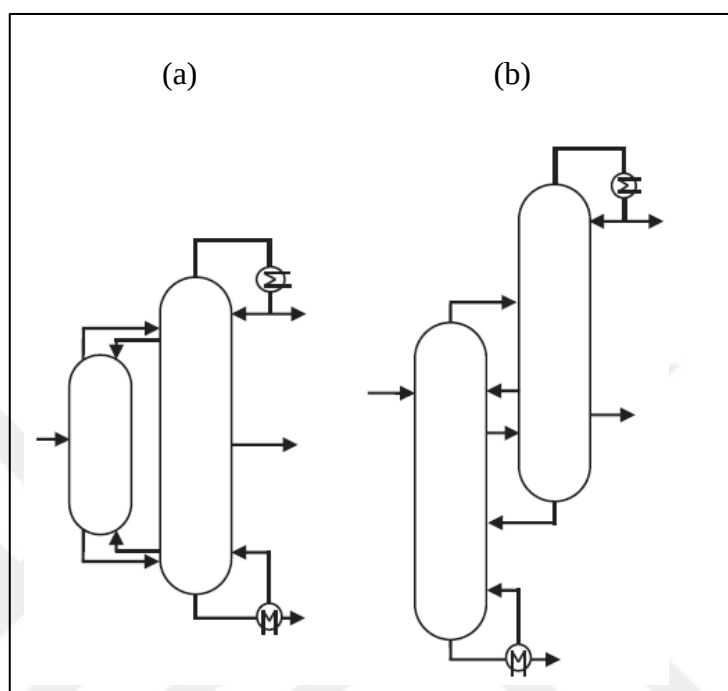


Figure 2.15. Alternative two-column sequences for three-product DWC simulation [42]

As a starting point of optimal DWC design, it is required to get information about initial design values for guidance. For this, shortcut simulation can be performed in software programs. DWC simulation is carried out with appropriate column sequence and global optimal design variables are determined. Rangaiah et al. stated the procedure of simulating and optimizing DWC using Petlyuk column configuration. The steps are as follows; [46]

1. Perform shortcut simulation based on desired product specifications to obtain initial guess of design variables
2. Build simulation with Petlyuk column configuration using the values in step 1
3. Keeping either vapor or liquid split ratio at same value estimated by shortcut simulation, optimize the other to minimize reboiler heat duty
4. Optimize the design variables to determine local optimal parameters based on the minimum reboiler heat duty

5. Locate the global optimum design by varying the number of stages and perform sizing and cost calculations for each combination.

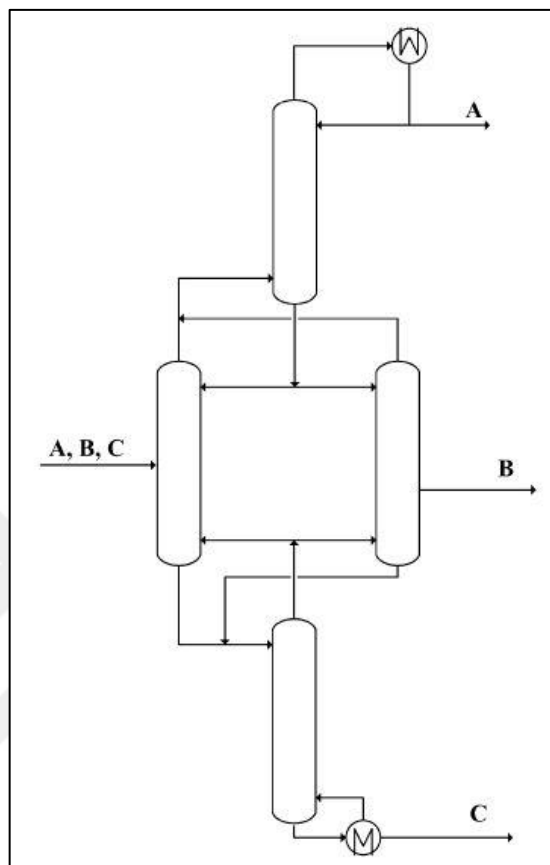


Figure 2.16. Four-column DWC model [41]

2.5. ISOBUTYL ALCOHOL AND ISOBUTYL ACETATE

The environmental effects of solvents, which are frequently utilized in chemical industry for various purposes in many procedures, have become a crucial issue. Increasing concerns about human health and environmental impacts lead researchers to search environmentally-friendly, sustainable, renewable and safe solvents. According to the main principles of Green Chemistry, the following features should be considered in the solvent selection; [59]

- Renewable feed stock
- Recyclability
- Non-flammability

- Easy storage and transportation
- High biodegradability
- Preparation with an economical and energy-saving process.

In the literature, there are several methods for scoring solvents according to Green Chemistry criteria. The environmental, health and safety (EHS) method identifies solvents based on their potential hazards. Both isobutyl acetate and isobutyl alcohol are defined as recommended solvents based on their EHS scores [1].

Isobutyl alcohol can be produced from a various renewable feedstock, including corn, wheat, and sugar cane by using a yeast biocatalyst. Also, it has a wide application area as a solvent/reagent/extractant [4]. Isobutyl acetate is obtained mainly by esterification of isobutyl alcohol and acetic acid. Since the esterification reaction has low conversion rate (70%), a final purification process is required. Due to the formation of minimum boiling point azeotrope in IBA-IBAc mixture, it is necessary to use special separation techniques and intensification methods to obtain IBA and IBAc through economic and energy saving process [2].

Munoz et al. performed separation processes design for IBA+IBAc mixture using conventional ED and PSD methods. They selected butyl propionate as solvent for ED system. IBA is obtained as overhead product in extractive column and IBAc is obtained as distillate in solvent recovery column in extractive distillation system. In PSD, column operating pressures are 19 kPa and 22 kPa respectively. Based on the TAC results, PSD is found more economical method comparing with ED with BUP [10].

Design and control of fully heat-integrated PSD for separating IBA-IBAc was carried out by Luo et al. It was stated that heat integration provided a 21% reduction in RHD values compared to conventional PSD [11].

Wang et al. carried out PSD with heat pump to separate IBA-IBAc mixture. They applied heat exchanger network in heat pump with pre-heater assisted PSD (HPPSD-HEN) system. It was reported that comparing with the conventional PSD, HPPSD-HEN system decreased energy consumption and TAC by 83.99% and 69.8% respectively [12].

Hybrid heat integrated-PSD process are designed by Miao et al. for separation IBA-IBAc azeotropic mixture. Based on their results, compared to the conventional fully heat-integrated PSD process, the hybrid heat integrated-PSD process resulted in lower TAC and higher thermodynamic efficiency [13].

Anokhina et al. are designed partially thermally coupled ED (PCEDS) process for isobutyl alcohol-isobutyl acetate mixture using butyl propionate and dimethyl formamide as solvents. They reported that PCEDS effectiveness depends on the reflux ratio in the solvent recovery column and PCEDS provides reduction in energy consumption by %20.1 (BUP) and %29.8 (DMF) comparing to the conventional methods [14].



3. METHODS

Thermodynamic model is vital for modelling and design of separation processes. Before building simulations, model parameters, phase equilibrium data and residue curve maps are discussed in this chapter. Furthermore, economic and environmental evaluation methods are explained.

3.1. THERMODYNAMIC MODEL

As stated in Chapter 2, thermodynamic analysis of separation processes is an initial step to determine feasible process conditions. In this study, all simulations are built in ChemCAD and the NRTL (non-random two liquid) activity coefficient equation is selected as the thermodynamic model.

The NRTL equation includes three parameters (α_{ji} , τ_{ji} , τ_{ij}). The parameter, α_{ji} is non-randomness parameter and τ_{ji} , τ_{ij} are binary interaction parameters. Parameter equations are defined in Eqs 3.1 & 3.2.

$$\tau_{ji} = A_{ji} + \frac{B_{ji}}{T} + C_{ji} \ln(T) + D_{ji}T \quad (3.1)$$

$$G_{ji} = \exp(-\alpha_{ji} * \tau_{ji}) \quad (3.2)$$

where T and G_{ij} stand for temperature and Gibbs free energy. Using ChemCAD, all required binary interaction parameters between dimethyl sulfoxide, isobutyl alcohol and isobutyl acetate are estimated by fitting the thermodynamic model to experimental data reported in the literature [16, 47]. Estimated model parameters are indicated in Table 3.1 and non-randomness parameter α_{ji} equals to 0.3.

Table 3.1. Binary interaction parameters of NRTL model

Component i Component j	Isobutyl alcohol Isobutyl acetate	Isobutyl alcohol Dimethyl sulfoxide	Isobutyl acetate Dimethyl sulfoxide
Bij	238.15	660	150
Bji	-82.646	-560	360

Figure 3.1 shows the NRTL model results and experimental data. Vapor liquid equilibrium in all the binary systems (IBA-IBAc, IBAC-DMSO and IBA-DMSO) are presented. We observe that there is a good fit between the thermodynamic model and experimental data.

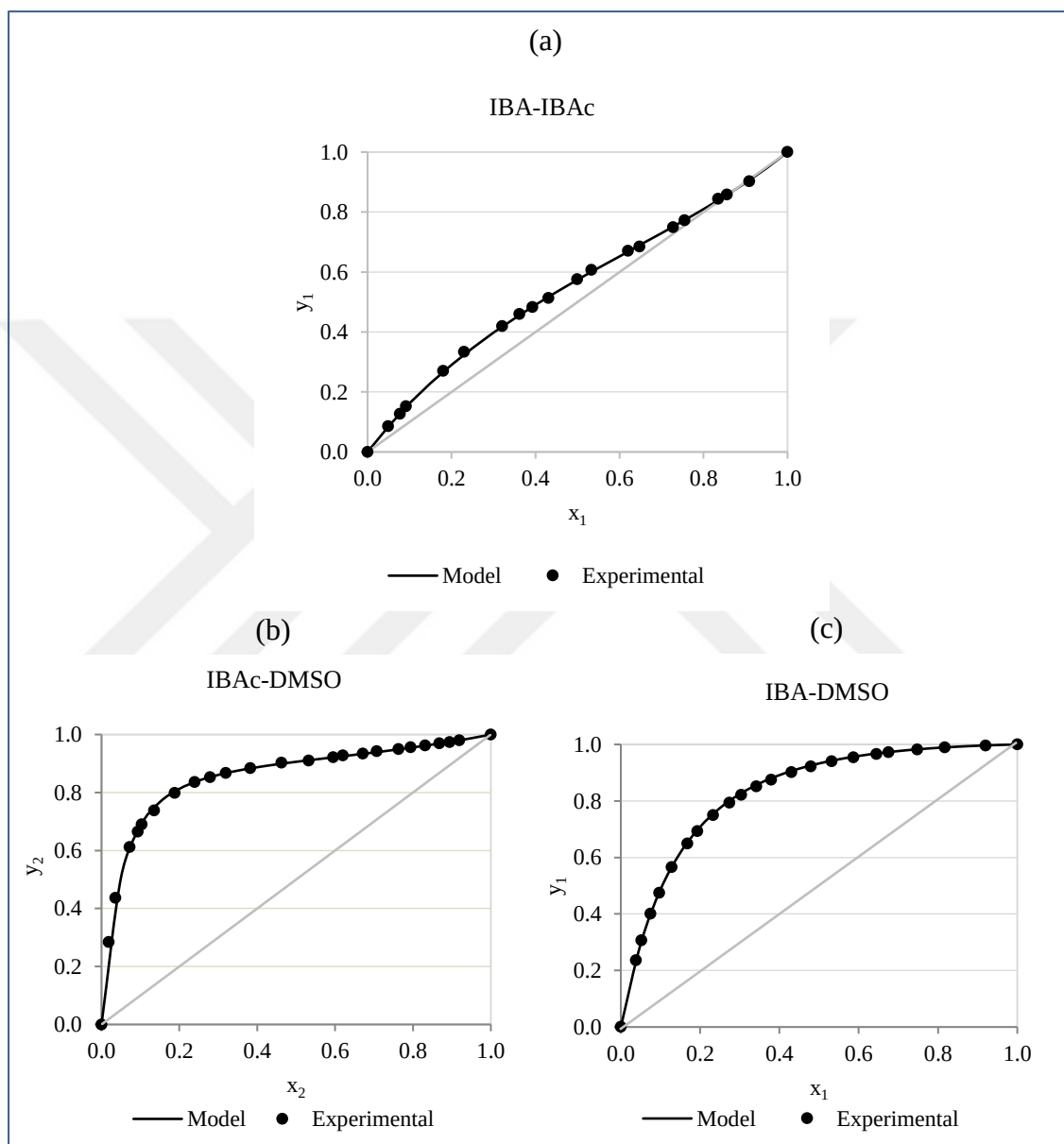


Figure 3.1. Vapor-liquid equilibrium diagrams for (a) isobutyl alcohol (1)-isobutyl acetate (2) system; (b) isobutyl acetate (2)-DMSO (3) system; (c) isobutyl alcohol (1)-DMSO (3) system

It is reported in the literature that DMSO has a decomposition problem above 150 °C [48,49]. Therefore, pressure adjustment is required to keep operating temperatures in the columns

below 150 °C. Fig. 3.2a & 3.2b show how the azeotrope point is affected when the pressure is reduced to 0.3 bar. Azeotropic compositions are found at IBA mole fraction of 0.8721 at 1 bar, and at IBA mole fraction of 0.6369 at 0.3 bar. At 1 bar, the mole fraction of DMSO required to break the azeotrope is 0.36 which matches with the result in study by Liu et al. [16]. These results are obtained using the NRTL model and binary interaction parameters presented in Table 3.1.

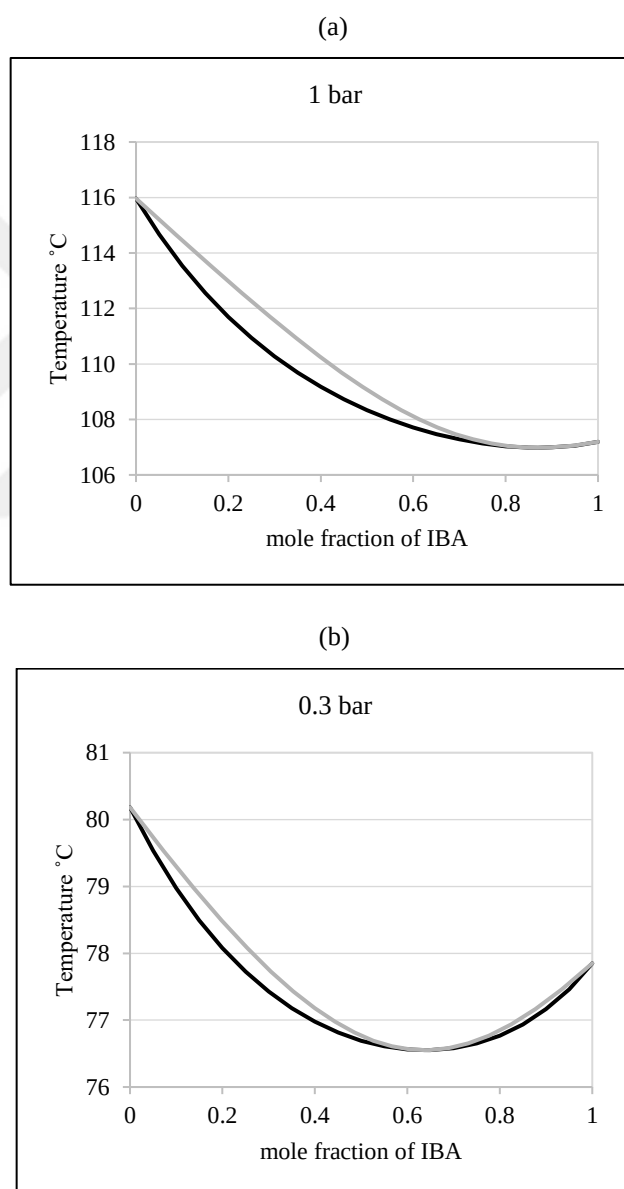
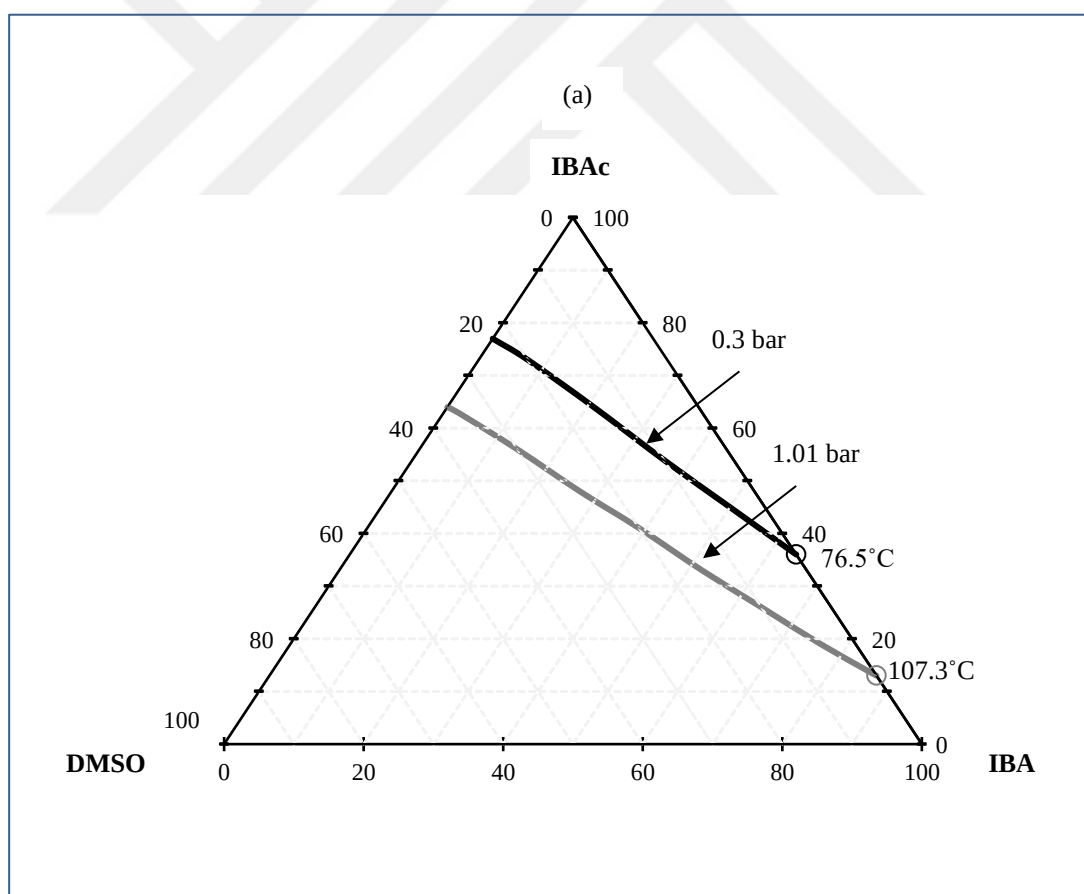


Figure 3.2. IBA-IBAc mixture (a) T-x-y curve at 1 bar (b) T-x-y curve at 0.3 bar

Analysis of univolatility curves and residue curve map is performed to investigate the effect of using vacuum pressure in the separation process. Fig. 3.3a displays univolatility lines at 1 bar and 0.3 bar. The univolatility line approaches the pure isobutyl acetate vertex with the decrease of pressure. This indicates that an easier separation is achieved at a lower operating pressure. This means less amount of solvent and lower energy consumption in the process.

Figure 3.3b illustrates residue curve map at 0.3 bar for IBA-IBAc-DMSO ternary mixture. Since DMSO has the highest boiling point in the mixture, it is a stable node and all curves starting from the minimum boiling azeotrope point (unstable node) intersect at this point. IBA and IBAc, on the other hand, are saddle points, all trajectories are moving toward these points and then, leaving them.



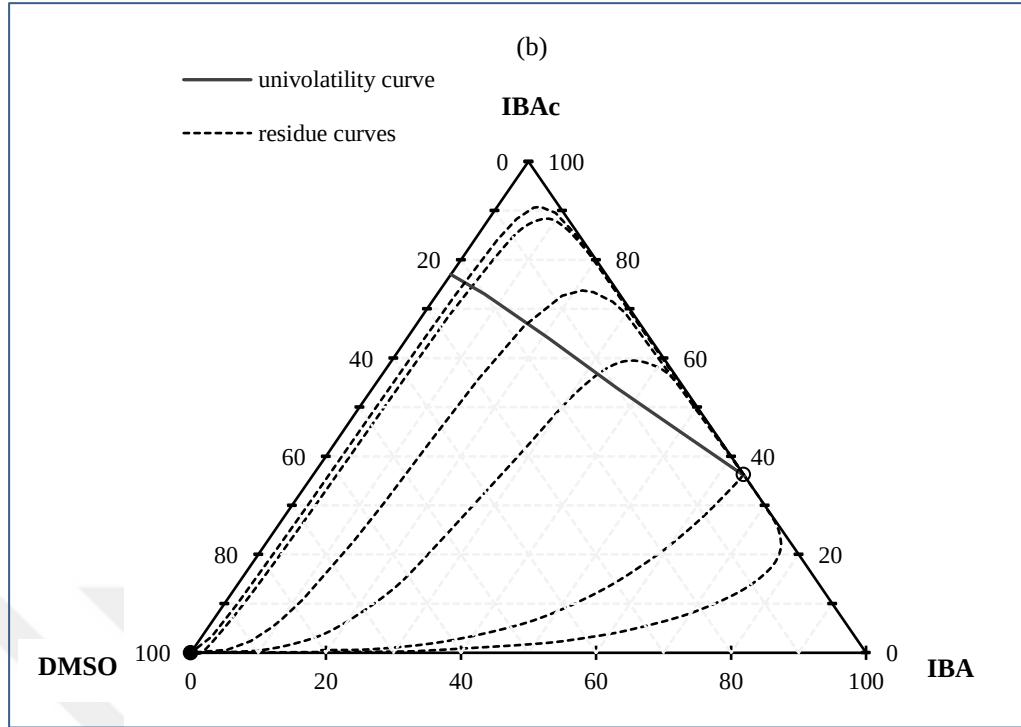


Figure 3.3 (a) Pressure effect on univolatility curves (b) Residue curve map at 0.3 bar for isobutyl alcohol-isobutyl acetate-dimethyl sulfoxide system

In literature, some evaluated solvents such as butyl propionate and 1-hexanol enhance the relative volatility of isobutyl alcohol. For this reason, IBA is the distillate product in first column in ED system [10]. Conversely, in the present study univolatility curves intersect with the DMSO-IBAC side (see Fig. 3.3a) which indicates that dimethyl sulfoxide increases the relative volatility of isobutyl acetate. As a consequence of this, IBAC is obtained as an overhead product of extractive column in the separation process.

The best way to verify effectiveness of a solvent is the calculation of relative volatility, α , which is defined as follows;

$$\alpha = \frac{K_{IBA,S}}{K_{IBAC,S}} = \frac{y_{IBA}/x_{IBA}}{y_{IBAC}/x_{IBAC}} \quad (3.3)$$

Where $K_{IBA,S}$ and $K_{IBAC,S}$ represent K-values for isobutyl alcohol and isobutyl acetate respectively; y_i and x_i denote vapor and liquid phase compositions for related components.

Relative volatility is calculated for different solvent concentrations as $x_{DMSO} = 0.01$, $x_{DMSO} = 0.5$ and $x_{DMSO} = 0.99$, and the simulation results are shown in Table 3.2. We observe that

DMSO enhances the relative volatility of IBAc (average value less than 1.00) with a significant impact.

Table 3.2. Relative volatilities at different DMSO mole fractions (pressure=1 bar)

	$x_{\text{DMSO}} = 0.01$	$x_{\text{DMSO}} = 0.5$	$x_{\text{DMSO}} = 0.99$
$K_{\text{IBA}, S}$	1.10	2.15	7.22
$K_{\text{IBAc}, S}$	1.02	3.02	17.83
α	1.08	0.71	0.40
Average value: 0.73			

3.2. ECONOMIC EVALUATION

Total annual cost (TAC) is used to make an economic comparison between different systems. It is defined as; [50]

$$TAC (\$/year) = OC + FCI * \frac{m * (1 + m)^n}{(1 + m)^n - 1} \quad (3.4)$$

Here, *FCI* stands for fixed capital investment and *OC* is the operational cost. In this study, operational cost comprises medium pressure steam, cooling water, electricity and solvent make-up costs. Capital cost contains distillation columns, heat exchanger and process pump; *m* is the annual interest rate and *n* is the equipment life. Operating time is assumed to be 8000 h/year, interest rate is 15% and equipment life is 10 years. Utility unit prices for operational cost are given in Table 3.3 [51-54].

Table 3.3. Utility unit prices

Process utility	Unit price
Medium pressure steam (\$/1000 kg)	17.4
Cooling water (\$/m ³)	0.762
Electricity (\$/kWh)	0.13
Solvent make-up (\$/kg)	6.0

Bare module costs of process equipment are calculated using the following equations;

$$\log_{10}(Cp^\circ) = K_1 + K_2 * \log_{10}(A) + K_3 * [\log_{10}(A)]^2 \quad (3.5)$$

$$F_{BM} = B_1 + B_2 * F_M * F_P \quad (3.6)$$

$$C_{BM} (\$) = Cp^\circ * F_{BM} \quad (3.7)$$

where Cp° is purchased cost at base conditions. F_{BM} , F_M and F_P represent the bare module cost, material and pressure factors respectively. C_{BM} is the bare module cost. K_i and B_i values are constants unique for equipment [55].

Bare module cost of trays is calculated by the equation defined below;

$$C_{BM} (\$) = Cp^\circ * F_{BM} * N * f_q \quad (3.8)$$

Here, N and f_q stand for tray number and quantity factor for trays [55].

Areas (A) of trays and heat exchanger are calculated with ChemCAD. Carbon steel is the selected material for the distillation columns and the heat exchangers. Stainless steel is chosen for process pump material. Inlet and outlet temperatures of cooling water are 30°C and 40°C. Medium pressure steam temperature is 183°C and pressure is 10 bar. The current prices of all design equipment are calculated according to the Chemical Engineering Plant Cost Index (CEPCI).

Equivalent diameter method is used for the estimation of dividing wall column capital cost. [58]

$$Equivalent D_{DWC} = \sqrt{D_1^2 + D_2^2} \quad (3.9)$$

where D_1 and D_2 show diameters (m) of extractive section and solvent recovery section.

3.3. ENVIRONMENTAL EFFECT EVALUATION

Assessment of the environmental impact of processes is a significant factor and it is related to the amount of energy consumption in the systems. Medium pressure steam used in the reboilers of the distillation towers is obtained by the combustion of fuel and this process causes CO₂ emission. CO₂ emission is calculated according to the simplified equation in the literature [56];

$$[CO_2] = \left(\frac{Q_{fuel}}{NHV} \right) * \left(\frac{C\%}{100} \right) * a \quad (3.10)$$

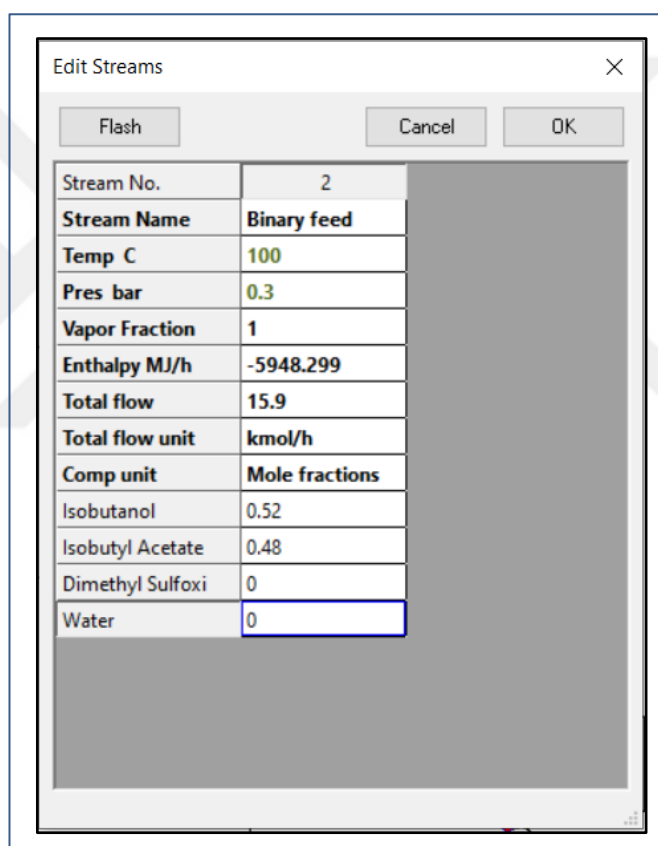
where a is molar ratio of carbon dioxide to carbon (3.67), NHV is net heating value for natural gas (51600 kJ/kg) and $C\%$ is fuel carbon content (75.4 kg/kg). Q_{fuel} is the amount of fuel and it is calculated as follows;

$$Q_{fuel} = \left(\frac{Q_{sys}}{\lambda_{sys}} \right) * (h_s - 419) * \left(\frac{T_F - T_0}{T_F - T_S} \right) \quad (3.10)$$

where Q_{sys} (kW) is required energy of system, λ_{sys} (kJ/kg) and h_s (kJ/kg) are latent heat and enthalpy of hot utility respectively, T_0 is reference temperature (298.15 K), T_F is the flame temperature (2073.15 K) and T_S is stack temperature (433.15 K) [56].

4. RESULTS AND DISCUSSION

Conventional extractive distillation and extractive-dividing wall column systems are built for the separation of IBA+IBAc mixture in ChemCAD. The binary feed stream consists of 52.0 mole % of IBA [10] and physical properties of binary mixture are shown in Figure 4.1. Solvent feed stream is at 50°C and 0.3 bar. The product purities and recovery percentages are set to be 99.9% in all systems.



The screenshot shows the 'Edit Streams' dialog box with the 'Flash' tab selected. The stream is identified as 'Stream No. 2' with the name 'Binary feed'. The properties are as follows:

Stream No.	2
Stream Name	Binary feed
Temp C	100
Pres bar	0.3
Vapor Fraction	1
Enthalpy MJ/h	-5948.299
Total flow	15.9
Total flow unit	kmol/h
Comp unit	Mole fractions
Isobutanol	0.52
Isobutyl Acetate	0.48
Dimethyl Sulfoxi	0
Water	0

Figure 4.1. Binary feed stream properties

4.1. EXTRACTIVE DISTILLATION SIMULATION AND OPTIMIZATION

Extractive distillation simulation basically includes two distillation towers; extractive column and solvent recovery column. While isobutyl acetate is separated in the first column as an overhead product, IBA is drawn as the main product from the top of the second column. DMSO is the single bottom product in the second column and it is recycled to the first column.

In order to find the optimal conditions in extractive distillation process, sequential iterative optimization procedure is applied. The flowchart for the algorithm is indicated in Figure 4.2. In ED system, design parameters are number of stages of extractive column and solvent recovery column (NS_{C1} , NS_{C2}), solvent flowrate (F_S), tray locations of feed streams in column 1 (NT_S , NT_F) and feed tray location in column 2 (NT_{F2}). Design constraints are 99.9% purity of IBA and IBAC and 99.99% purity of DMSO. Distillate flowrates are fixed at 7.63 kmol/h and 8.27 kmol/h in column 1 and column 2 respectively. Simulations are carried out by varying the recovery rate to reach the desired purity values.

In the optimization procedure, converged simulations are established in accordance with the design constraints using initial parameters. Parameter values are determined through the sensitivity analysis and Successive Quadratic Programming (SQP). Sensitivity analyses are used for feed tray locations and SQP is used for continuous design variable solvent flowrate. After each simulation, TAC is calculated and design parameters are updated according to the optimization algorithm until the minimum TAC is obtained. Sensitivity analysis and SQP reports are given in Appendix A. TAC and CO₂ emission calculations of optimal ED processes are given in Appendix B and Appendix C respectively.

The number of stages of extractive column is changed as in the outer loop in the algorithm. For this reason, optimum design variables are calculated for each selected stage number. Four different cases (ED-1, ED-2, ED-3 and ED-4) have been designed for ideal stage numbers of 34 (48 actual trays), 40 (58 actual trays), 50 (72 actual trays) and 60 (86 actual trays).

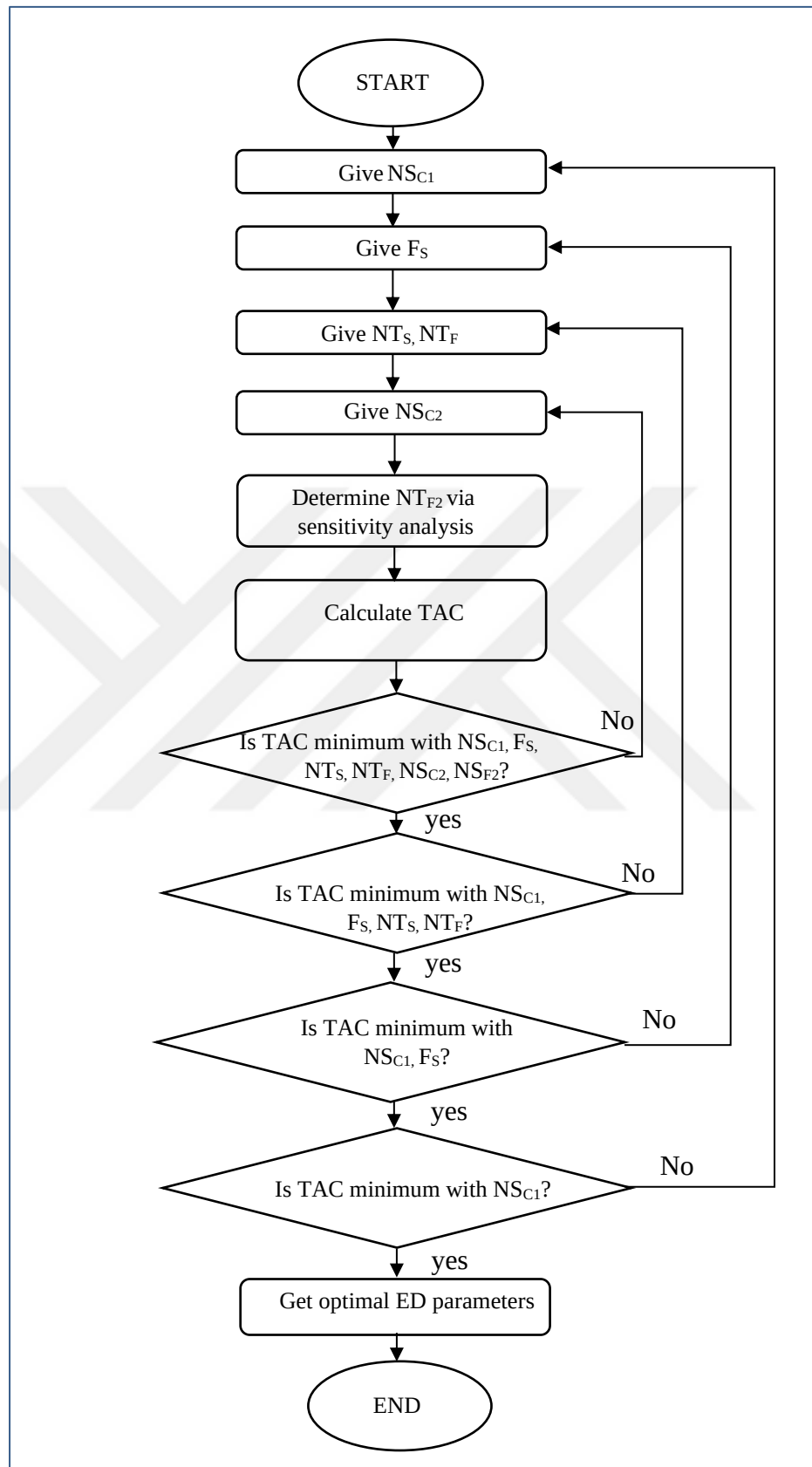
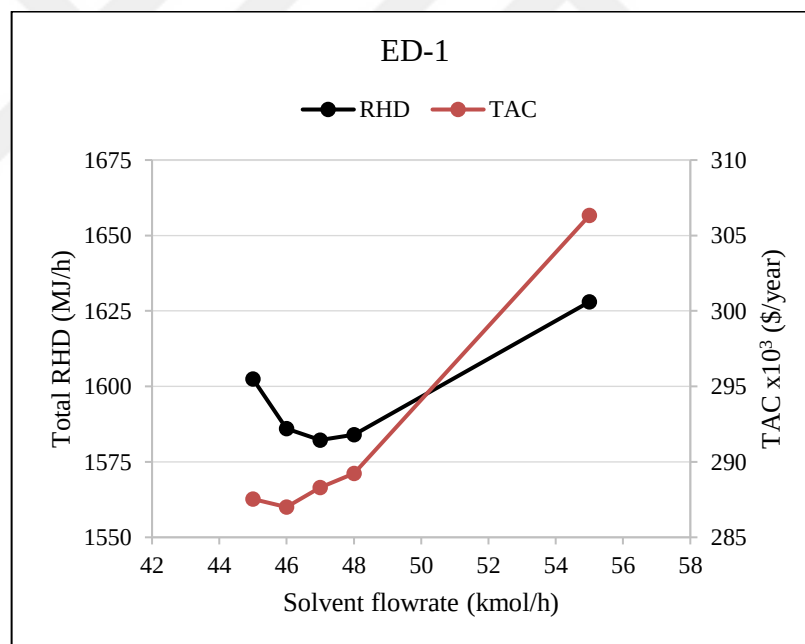
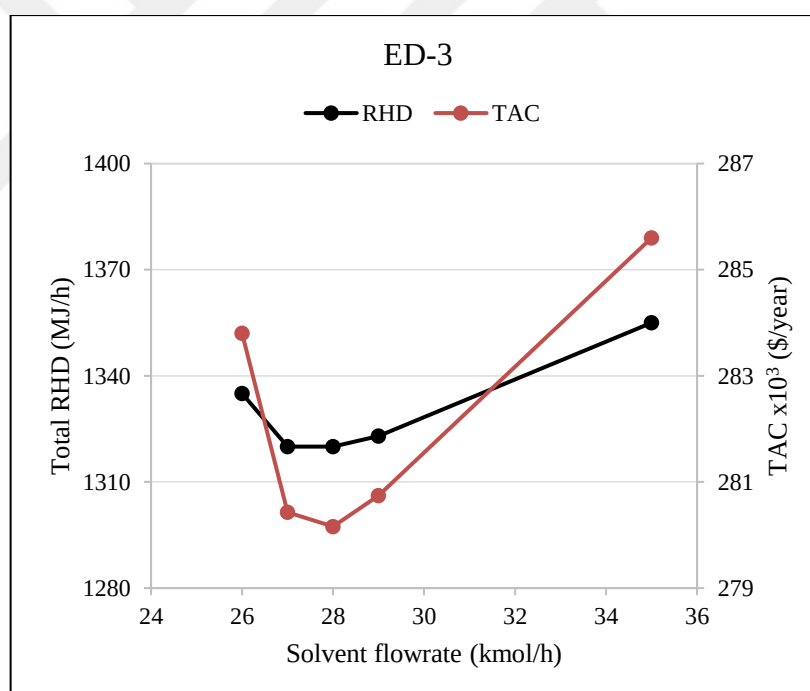
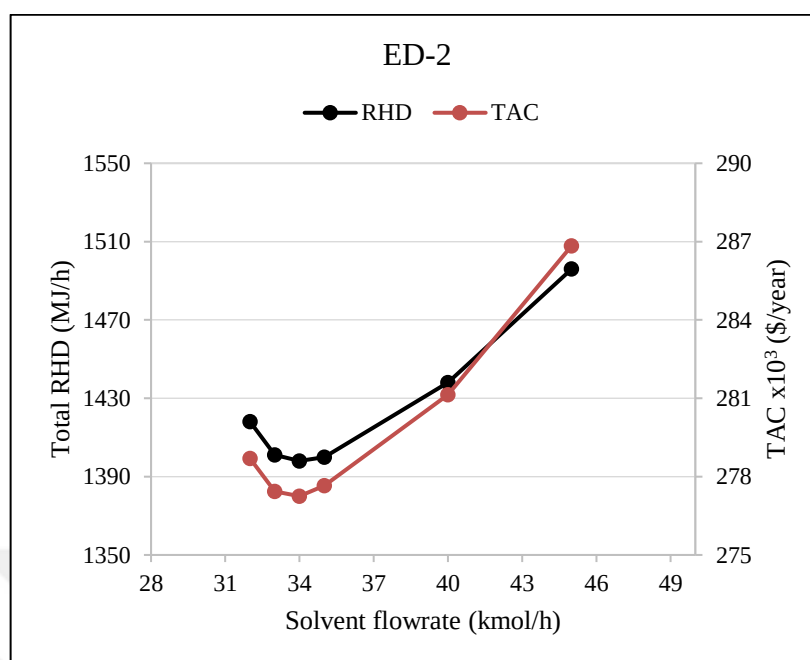


Figure 4.2. Extractive distillation optimization algorithm

4.1.1. Optimal Solvent Flowrate

Since the amount of solvent used in the process has a great impact on the reboiler heat duty (RHD) values, it is crucial to find the optimum amount of solvent for each stage number given for column 1. SQP tools in addition to sensitivity analysis are utilized because the solvent flowrate is a continuous variable. Figure 4.3 illustrates the effect of the solvent flowrate on RHD and total annual cost (TAC) when ideal stage numbers of extractive column are set to 34 (48), 40 (58), 50 (72) and 60 (86). As it is seen from figures, high solvent flowrate results in a considerable increase in RHD and TAC values. The optimum solvent flowrates which meet the design constraints are found as 46 kmol/h, 34 kmol/h 28 kmol/h and 27 kmol/h respectively.





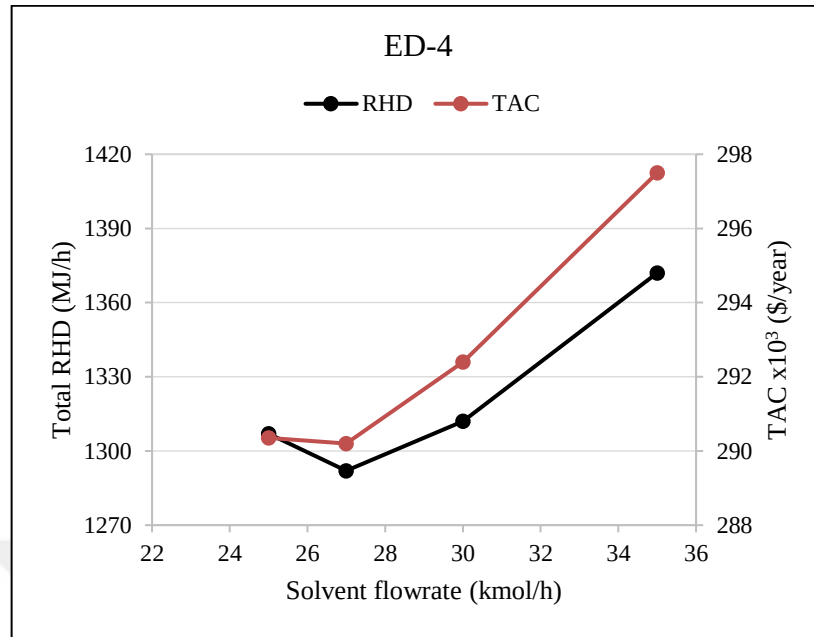
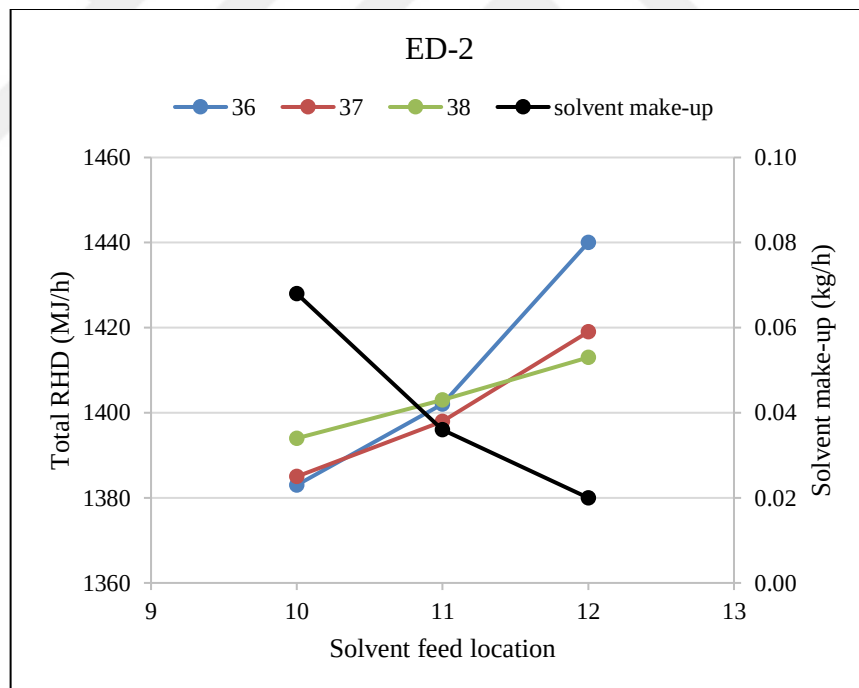
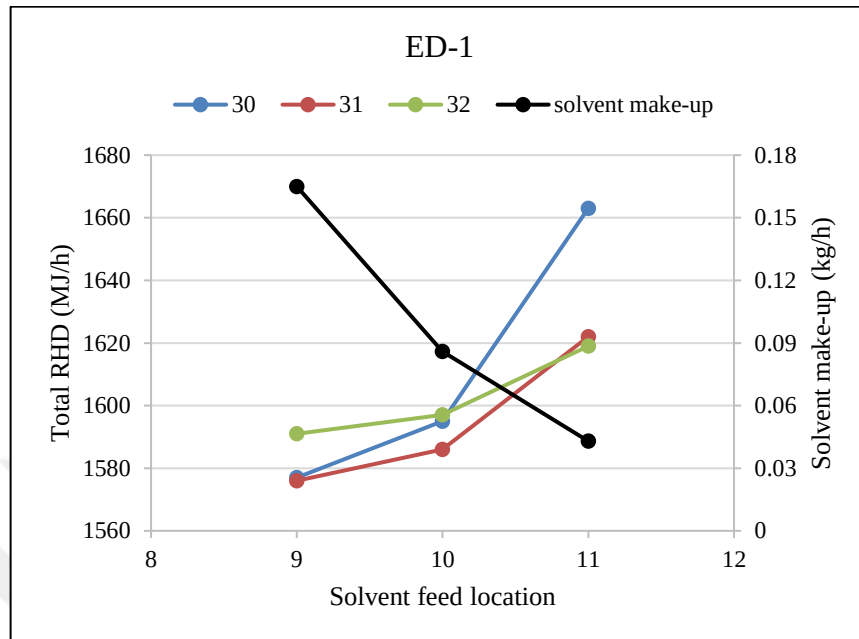


Figure 4.3. Effect of solvent rate on total RHD and TAC for different stage number of extractive column

4.1.2. Optimal Tray Locations

To find the optimum feed entry tray numbers, sensitivity analysis is performed to determine which stages provide the minimum condenser and reboiler heat duty values. TAC is calculated for all tray numbers selected according to the optimization procedure.

Figure 4.4 shows how selected feed tray numbers affect the reboiler heat duty for different tray numbers of column 1. The x- axis displays solvent feed tray numbers and solid lines represent binary mixture feed stages. Varying feed locations cause a change in RHD values and solvent feed entry tray number affects solvent make-up flowrate. We observe that the required solvent make-up flowrate decreases when solvent is fed to the column at lower trays. On the other hand, total RHD increases with the solvent feed tray number. Optimum feed locations are determined based on the TAC calculations. Solvent and fresh feed entry stages are selected as 10-31, 11-37, 12-45 and 14-52 for ED-1, ED-2, ED-3 and ED-4 respectively.



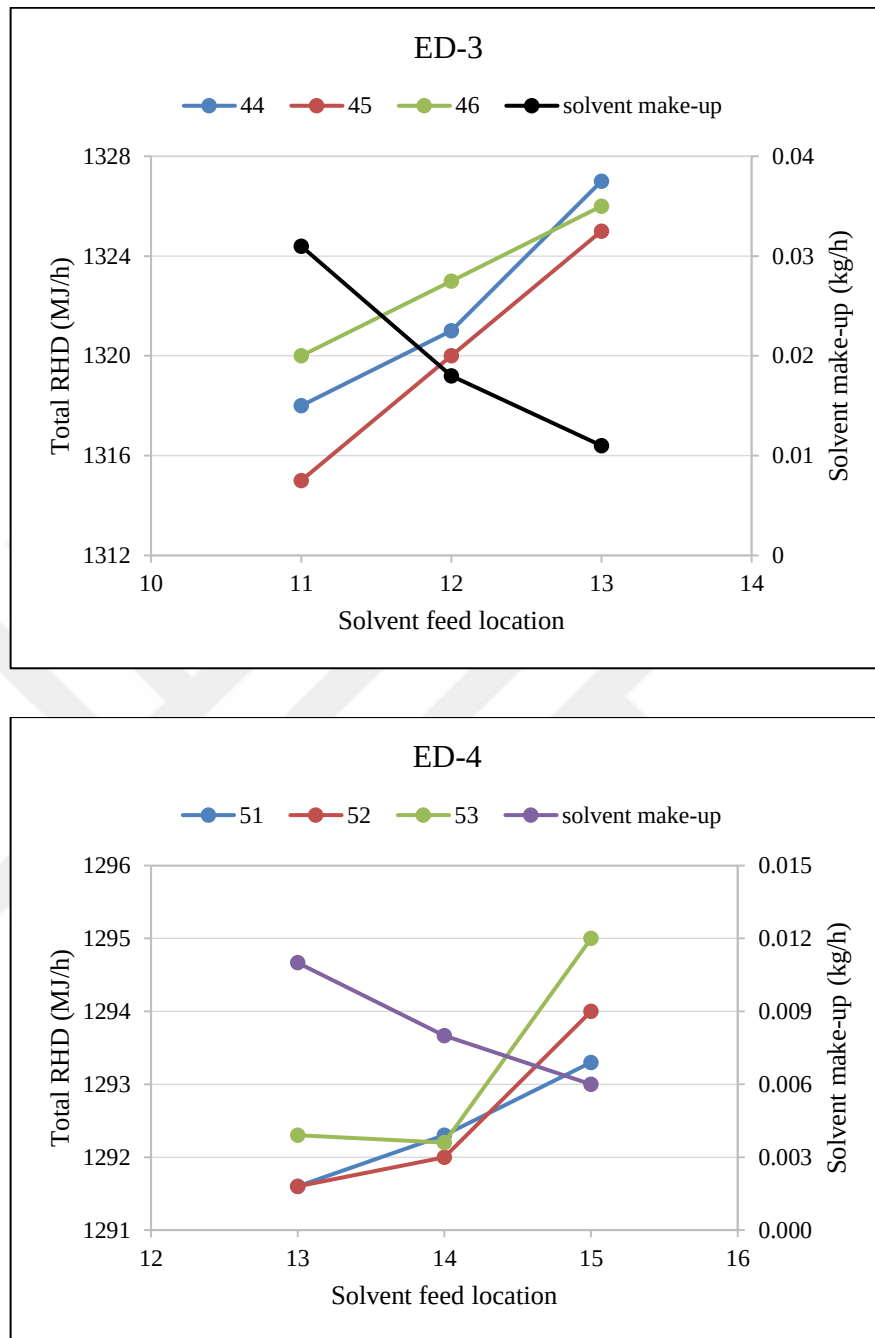
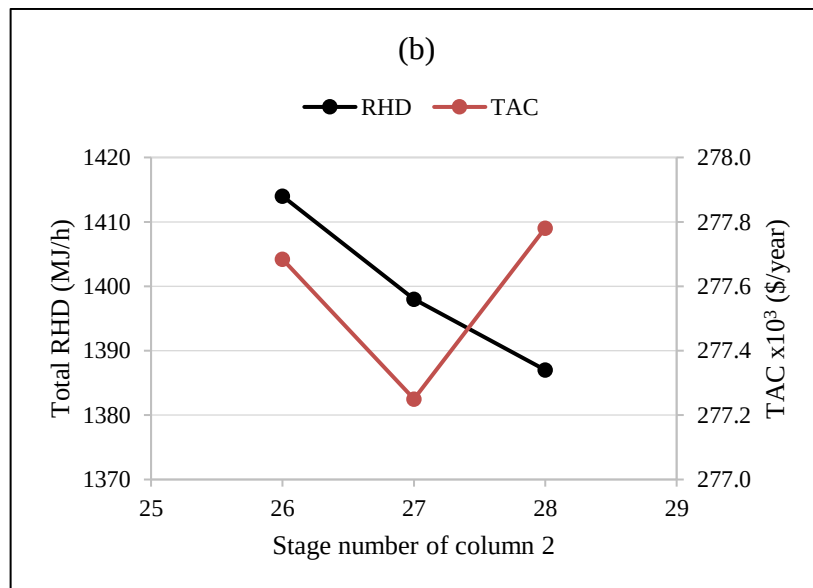
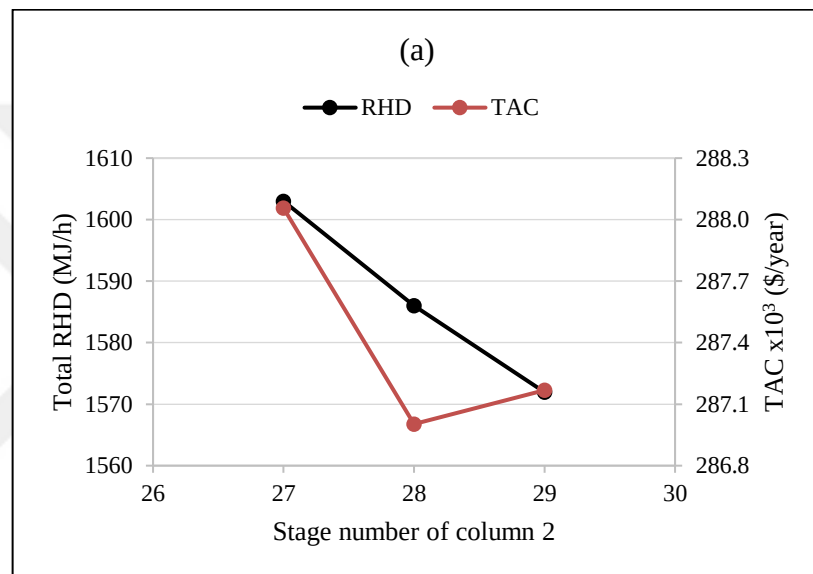


Figure 4.4. Impact of feed entry tray number on RHD and solvent make-up rate (a) stage number of EC:34 solvent rate:46 (b) stage number of EC:40 solvent rate:34 (c) stage number of EC:50 solvent rate:28 (d) stage number of EC:60 solvent rate:27

4.1.3. Optimization of Solvent Recovery Column

In the optimization procedure, solvent recovery column parameters are determined in the inner loop. The stage number of the second column is changed and the sensitivity analysis

is carried out for each stage number to find the optimal feed locations. It is aimed to reach minimum RHD and condenser duty in sensitivity analysis. Figure 4.5 displays the relationship between TAC, RHD and stage number for all alternative cases. Figure 4.6 shows the sensitivity analyses results for the feed location in solvent recovery column. Increasing the total stage number of the solvent recovery column causes an increase in capital cost. On the other hand, RHD decreases with the stage number of column 2.



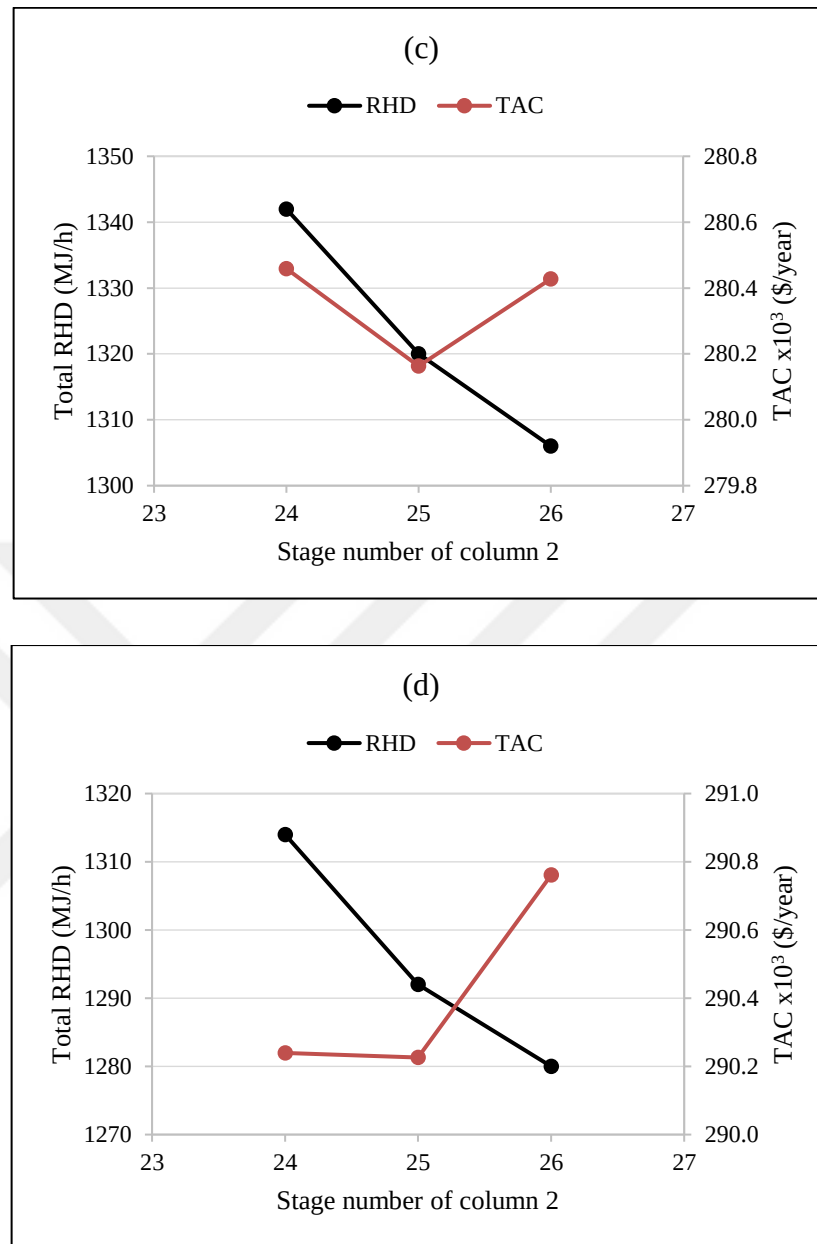
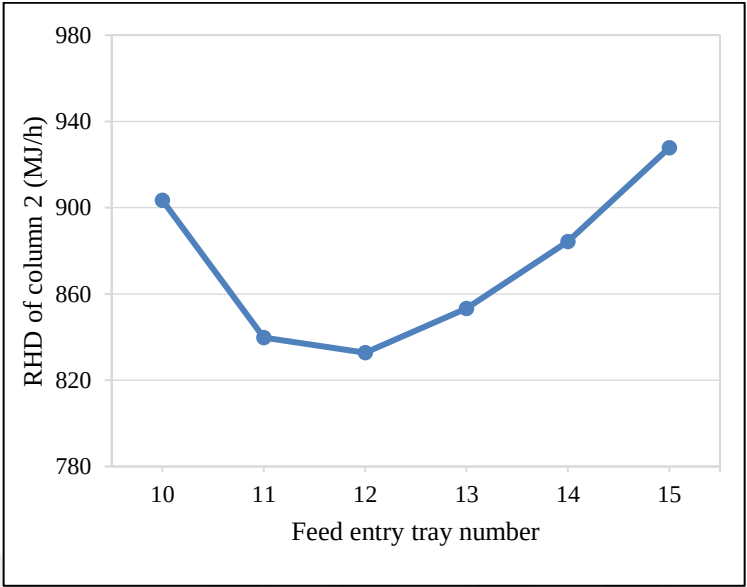
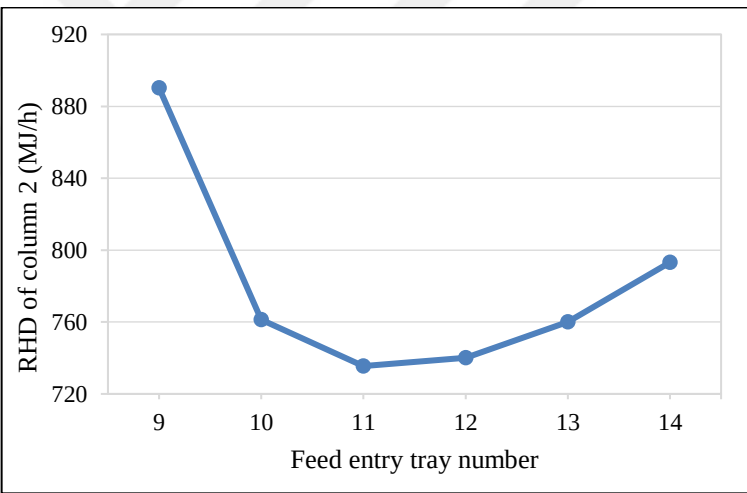


Figure 4.5. RHD, TAC and tray number relationship for solvent recovery column (a) Ideal stage number of first column: 34 (48), Solvent rate: 46 (b) Ideal stage number of first column: 40 (58), Solvent rate: 34 (c) Ideal stage number of first column: 50 (72), Solvent rate: 28 (d) Ideal stage number of first column: 60 (86), Solvent rate: 27.

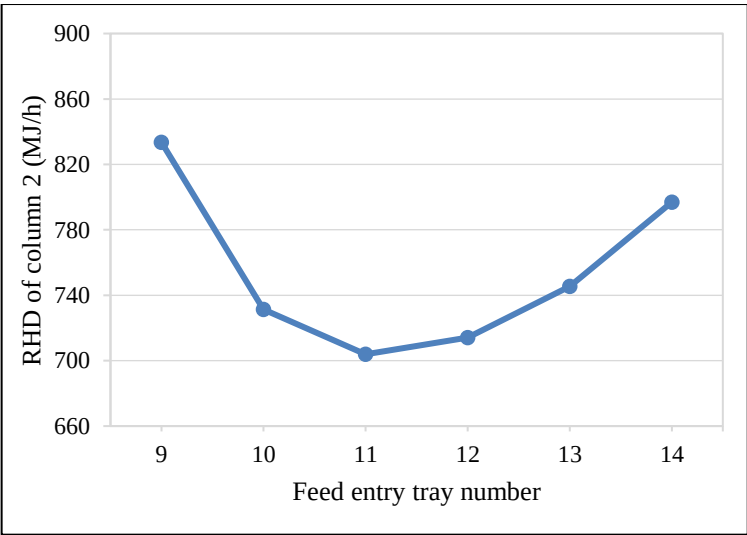
(a)



(b)



(c)



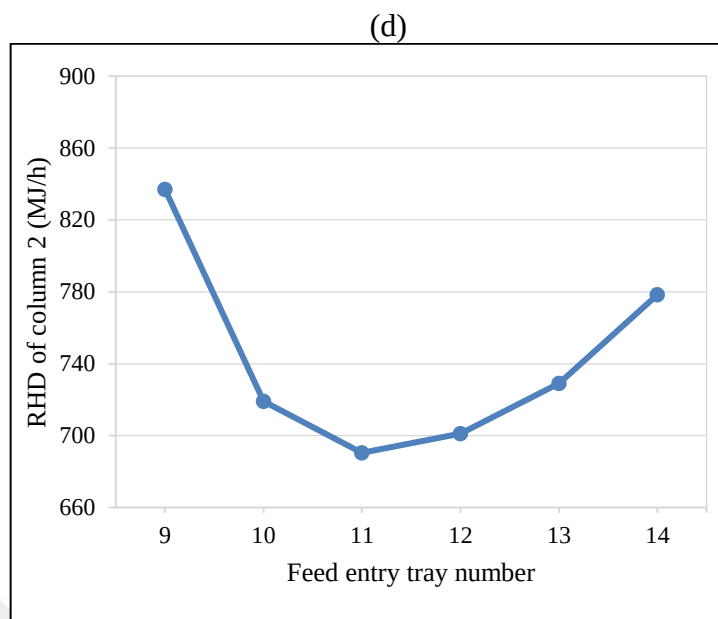


Figure 4.6. Effect of feed location on RHD in solvent recovery column (sensitivity analysis results for (a) Tray number of EC: 48, Solvent rate: 46, Tray number of SRC: 28 (b) Tray number of EC: 58, Solvent rate: 34, Tray number of SRC: 27 (c) Tray number of EC: 72, Solvent rate: 28, Tray number of SRC: 25 (d) Tray number of EC: 86, Solvent rate: 27, Tray number of SRC: 25)

4.1.4. Optimization Results

All optimal design variables are obtained by changing the stage number of extractive column as the outer loop in the iterative optimization procedure. Table 4.1 displays the optimal process parameters in all cases and the optimal conventional extractive distillation process flow diagram is shown in Figure 4.7.

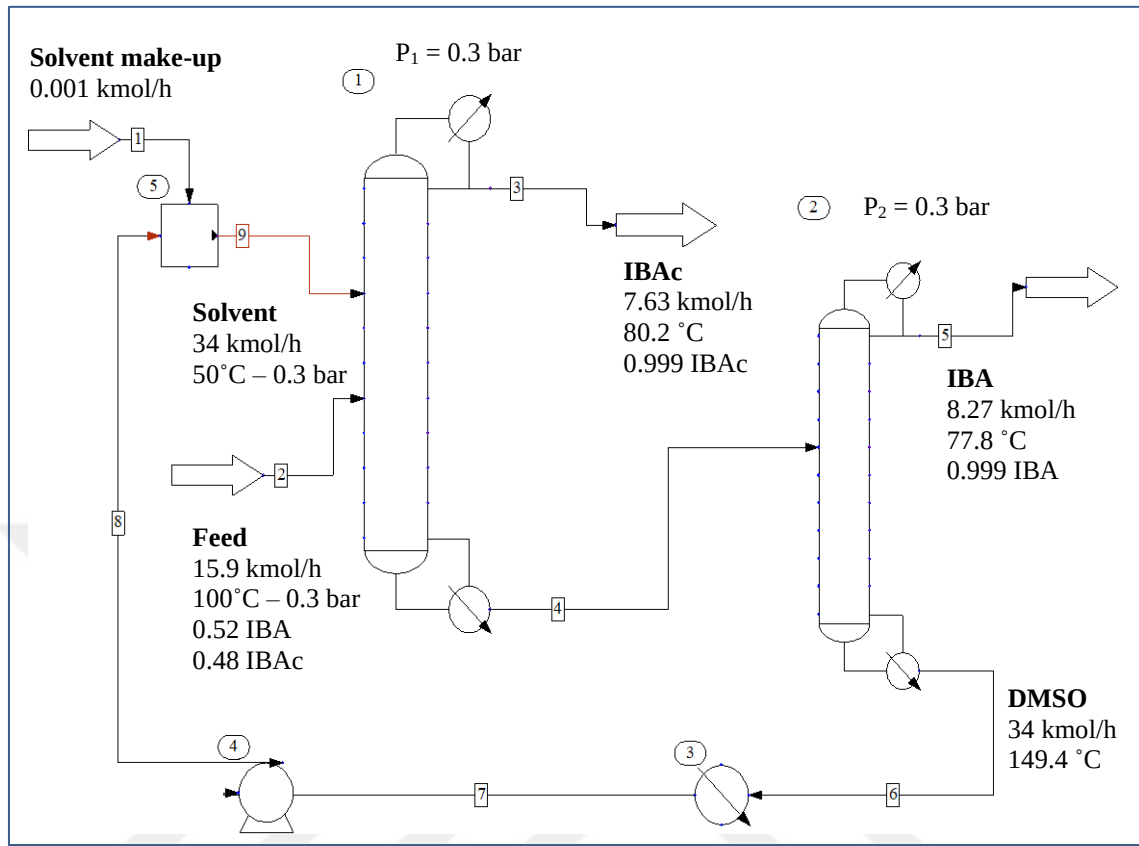


Figure 4.7. Optimal conventional extractive distillation process flow diagram

Tray efficiency is assumed as 0.7. It is clearly seen that increasing the stage number of the extractive column leads to decreases in the solvent flowrate and reboiler heat duty values. The optimum solvent amount is 27 kmol/h in the case of the ideal stage number of 60 in the extractive column (ED-4). When the ideal tray number is reduced to 34 (ED-1) the optimum solvent flowrate becomes 46 kmol/h. Also, there is an approximately 23% increase in total RHD value between case 4 and case 1 process configurations. As the tray numbers of column 1 increase, a gradual rise in the optimum feed entry locations is observed. The optimal feed tray numbers are 11 and 37 for case 2. On the other hand, solvent and binary mixture are introduced to tower at 12th and 45th stages respectively in case of tray number of 72. Heat exchanger condenser duty value is at a minimum in ED-4 configuration due to the decrease in solvent flowrate. In addition, the column diameters remain the same as 0.762 m for the first tower and 0.6096 m for the second tower in all alternative cases.

Table 4.1. Optimal process parameters for all cases

Parameters	ED-1	ED-2	ED-3	ED-4
Extractive column				
Ideal tray number	34	40	50	60
Tray number	48	58	72	86
Feed molar rate (kmol/h)	15.9	15.9	15.9	15.9
Solvent molar rate (kmol/h)	46	34	28	27
Binary mixture feed stage	31	37	45	52
Solvent feed stage	10	11	12	14
Condenser duty (MJ/h)	-553	-637	-677	-676
Reboiler heat duty (MJ/h)	753	663	616	600
Solvent recovery column				
Ideal tray number	20	19	18	18
Tray number	28	27	25	25
Feed stage	12	11	11	11
Condenser duty (MJ/h)	-357	-272	-249	-239
Reboiler heat duty (MJ/h)	833	736	704	692
Heat exchanger				
Heat duty (MJ/h)	-729	-541	-446	-430

Figure 4.8 illustrates the ternary liquid composition profiles in extractive column for ED-1, ED-2 and ED-4 processes. The liquid reaches 99.9 % IBAC purity at the top of the column. As it flows down, mainly solvent mole fraction increases in the rectifying section. After the solvent entry tray, in the extractive section of the column, a sharp increase occurs in the IBA mole fraction since DMSO decreases its relative volatility with respect to IBAC. At the feed entry tray, we observe a jump in composition away from the DMSO vertex. The liquid gradually becomes richer in DMSO and IBA in the stripping section. Since the optimum solvent flowrate in ED-4 is less than the other cases, the composition of the bottom product is closer to the IBA vertex.

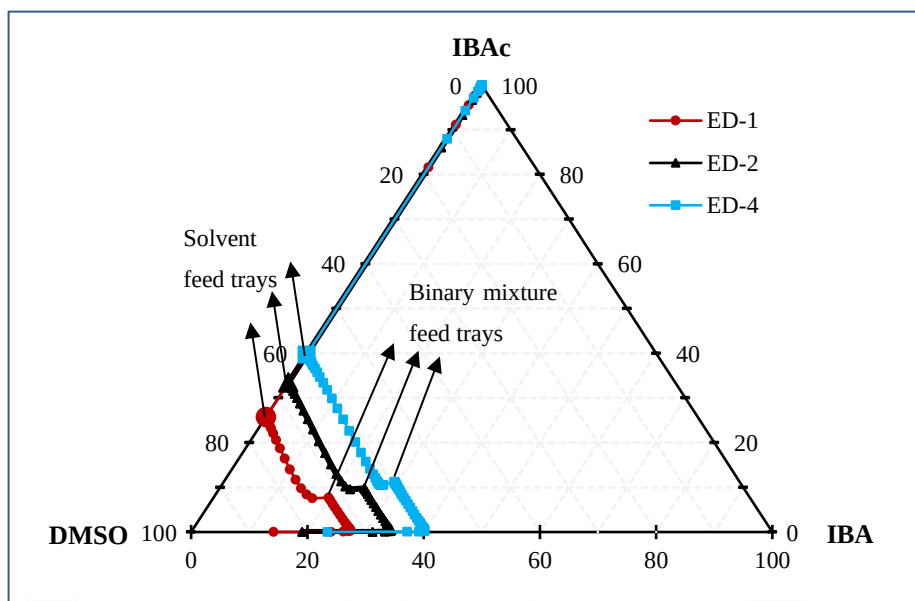


Figure 4.8. Ternary liquid composition profiles of IBA-IBAc-DMSO mixture in extractive column for ED-1, ED-2 and ED-4 processes

Table 4.2 indicates cost results of alternative ED processes. As a result of the optimization procedure, the most economical conditions are obtained when the ideal stage number is fixed to 40. It is seen that the capital cost increases depending on the increase of number of stages in the extractive column and solvent recovery column. On the other hand, operational cost decreases with the increase in number of trays due to the lower energy consumption. By increasing the stage number, the heat exchanger costs fall as a consequence of using less solvent and decrease in heat exchange areas. Minimum cost is calculated as 277250 \$/year for ED-2 system.

Table 4.2. Cost results of alternative ED systems

Equipment (x10 ³ \$/year)	ED-1	ED-2	ED-3	ED-4
Column 1	357.117	400.570	463.849	528.016
Column 2	301.550	300.341	288.583	288.583
Heat exchanger	112.520	106.988	104.259	104.259
Process pump	23.846	24.055	24.073	23.709
Fixed capital investment	795.033	831.954	880.764	944.568
Operational cost	128.591	111.482	104.669	102.163
TAC	287.003	277.250	280.163	290.370

Environmental performance of alternative process configurations is evaluated and the results are shown in Figure 4.9. Since the energy requirement is minimum in the ED-4 process configuration, CO₂ emission value is the lowest among the other alternatives. Here, there is 19% reduction in CO₂ release compared to the ED-1 system. CO₂ emission is calculated as 95.02 kg/h in the most economic extractive distillation system (case 2).

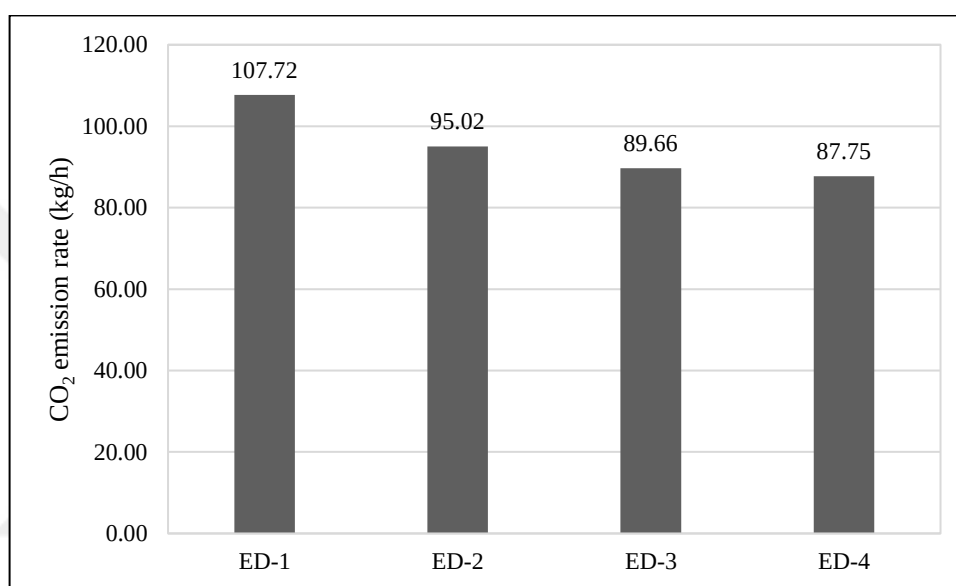


Figure 4.9. CO₂ emission values of alternative ED systems

4.2. DIVIDING WALL COLUMN SIMULATION AND OPTIMIZATION

Extractive dividing wall column for the separation of IBA-IBAc mixture is designed by placing a partition wall on the upper part of column. The reason for selecting this model is that DMSO increases the relative volatility of IBAc which is the intermediate boiling component in the system. Thanks to this model, both IBA and IBAc are obtained as top products of DWC. In ChemCAD, DWC is simulated based on the study of Staak et al. as shown in Figure 4.10 [57]. DWC is represented by three columns, column 1 is the left side of the wall, column 2 is the right side of the wall and column 3 displays the section below the wall. The liquid streams coming from the columns 1 & 2 are collected in the mixer and fed to the first tray of the column 3. The vapor flow from the head of 3rd column is divided and fed to the last trays of the 1st and 2nd columns. The DWC includes two condensers and

one reboiler. While IBA and IBAC are distillate products of DWC, DMSO is drawn as a bottom product. Recycled DMSO is cooled to 50 °C and mixed with the make-up stream.

Physical properties of solvent and fresh feed are set the same as the conventional ED process. Column operating pressure is adjusted to 0.3 bar to keep the temperature under 150°C similar to the ED system. Temperature profile of E-DWC process is shown in Figure 4.11. Maximum temperature of the column is 149°C and temperature difference between left and right side of the wall is approximately 20°C.

In the optimization of the DWC system, design parameters are stage numbers of columns, solvent flowrate (F_S), solvent and fresh feed stream locations, (NT_S, NT_F). The stage number of DWC is changed as the external loop and optimum parameters are determined for each stage number. Six different DWC cases are evaluated with ideal stage number between 40 and 65. Product purity constraints and distillate flowrates are fixed to the same values as the conventional ED system. Optimization procedure includes the following steps;

Step 1: Optimization of F_S via sensitivity analysis and SQP tool to minimize RHD at fixed number of trays and fixed tray locations.

Step 2: Optimization of F_S , NT_S and NT_F via sensitivity analysis to minimize RHD. Here, optimizing of F_S with tray locations at the same time provides more energy saving.

Step 3: Calculation of TAC for each given process parameters until the minimum value is obtained.

Sensitivity analysis and SQP reports are given in Appendix A, TAC and CO₂ emission rate calculations of optimal E-DWC process are shown in Appendix B and Appendix C.

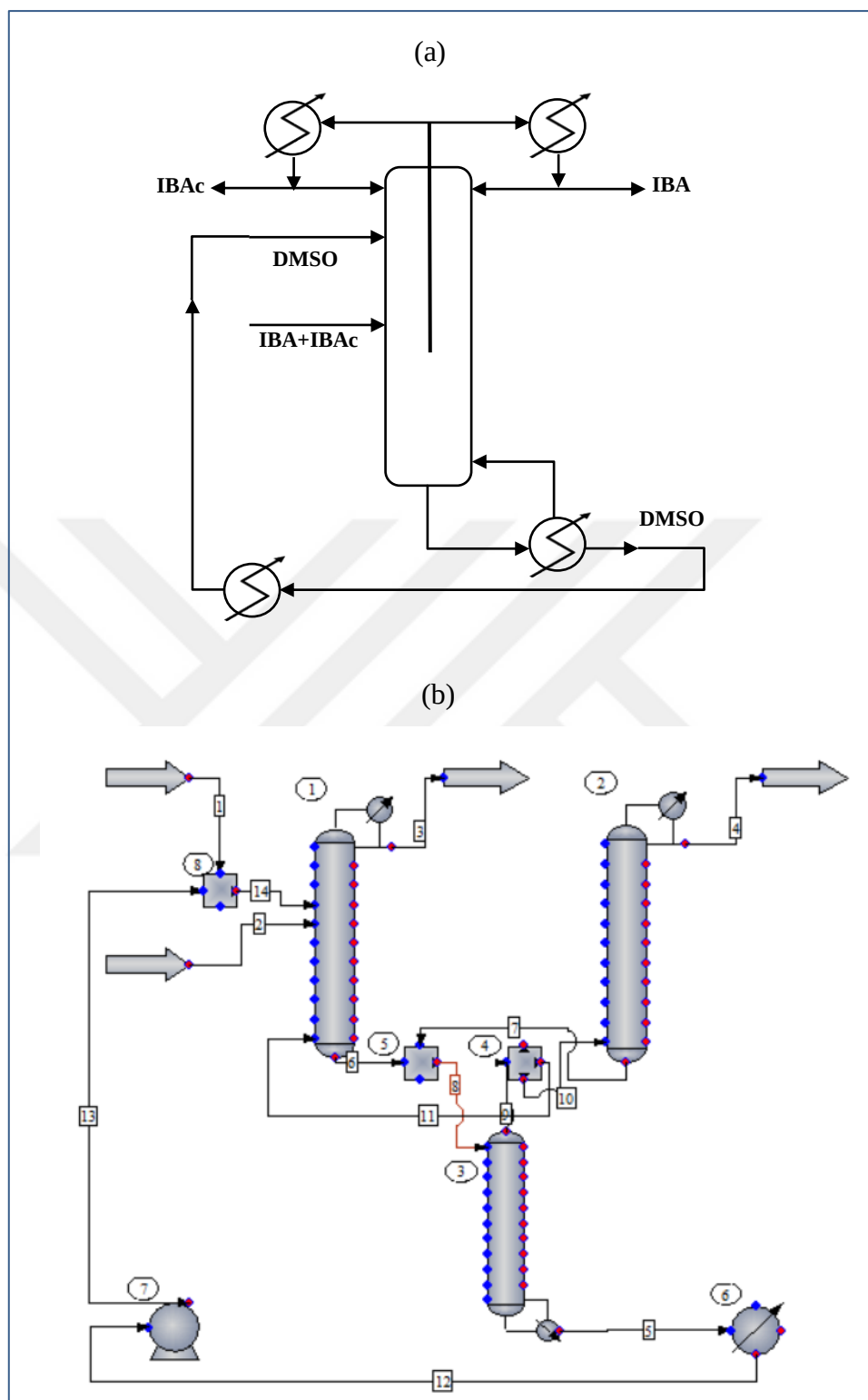


Figure 4.10. (a) DWC system (b) ChemCAD simulation for separation of IBA-IBAc

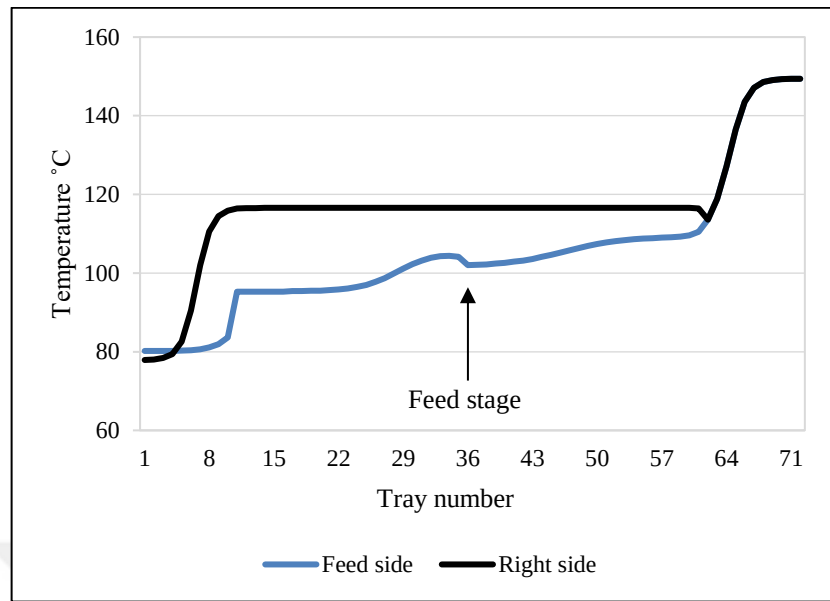
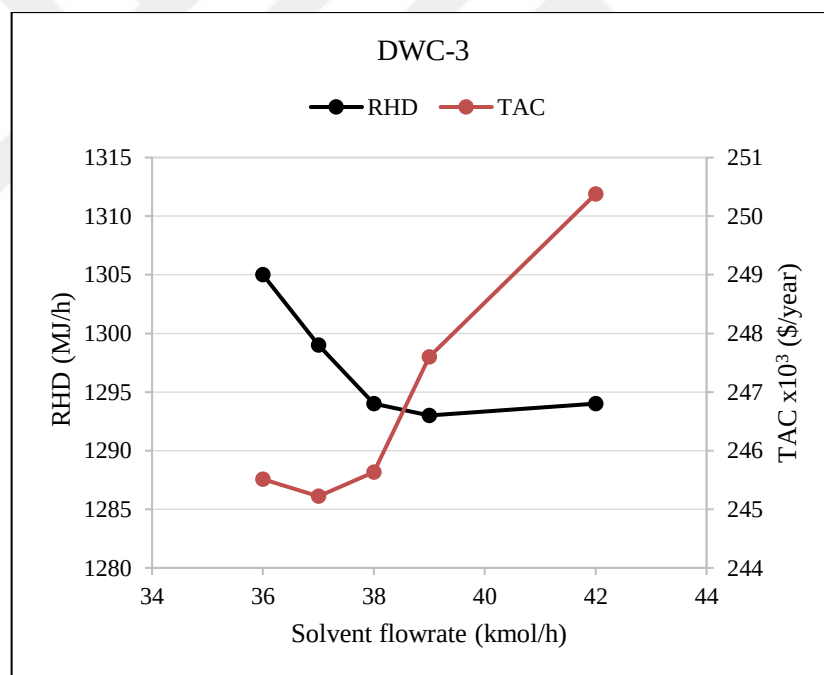
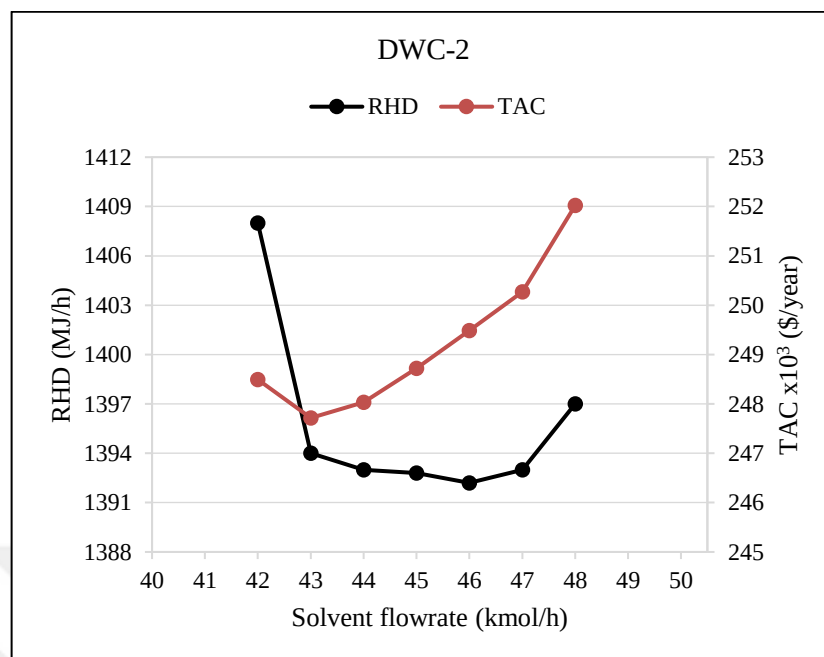


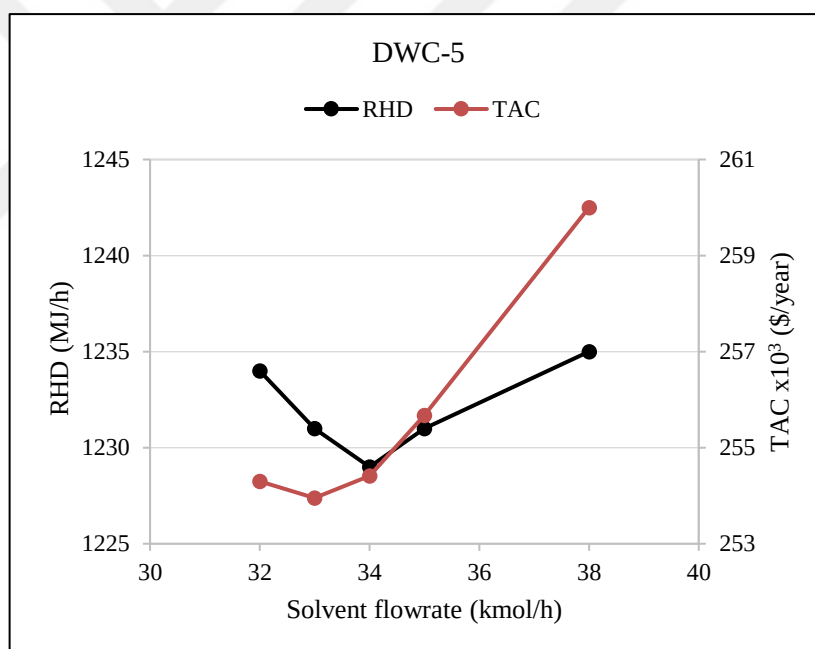
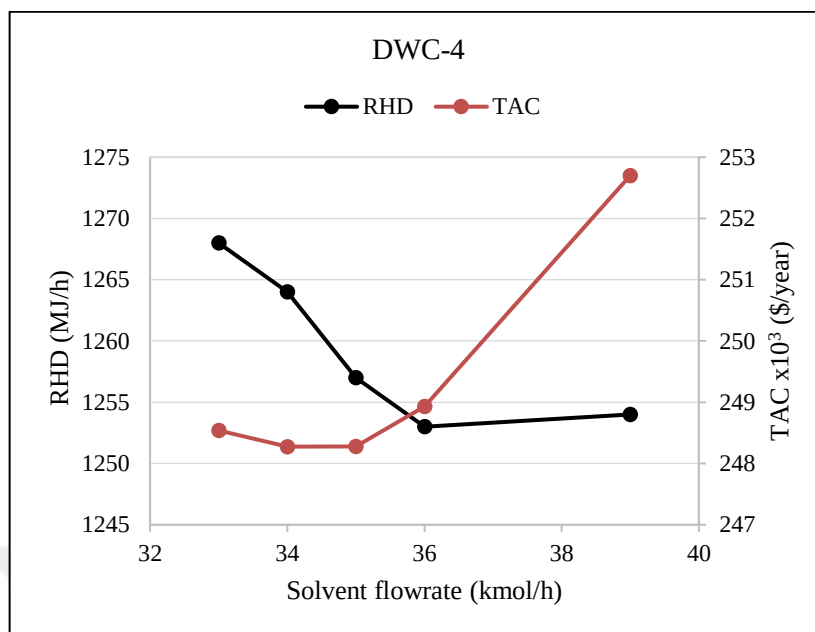
Figure 4.11. Column temperature profile for DWC process (Ideal stage number: 50 Actual tray number: 61)

4.2.1. Optimal Solvent Rate

The effect of solvent flowrate on the RHD and TAC is illustrated in Figure 4.12 in case of ideal stage number set to 45, 50, 55, 60 and 65. When the ideal stage number is fixed at 40, the simulation is not converged under 62 kmol/h solvent flowrate with the selected design constraints. Therefore, TAC calculations are performed between in 62-63 kmol/h and optimum value was obtained for 62 kmol/h solvent rate.

According to results, RHD decreases with increasing solvent rate at first. However, it begins to increase at some point in all alternative processes. TAC values are rising with high solvent rates due to the rising heat exchanger area and solvent make-up rate. Minimum TAC values are obtained at 43 kmol/h (Case 2), 37 kmol/h (Case 3), 34 kmol/h (Case 4), 33 kmol/h (Case 5) and 31 kmol/h (Case 6).





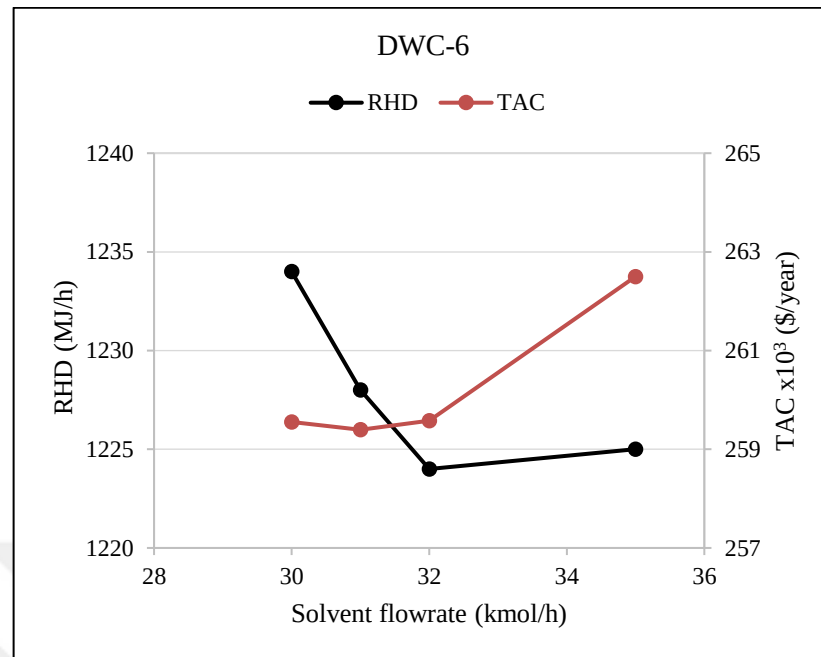
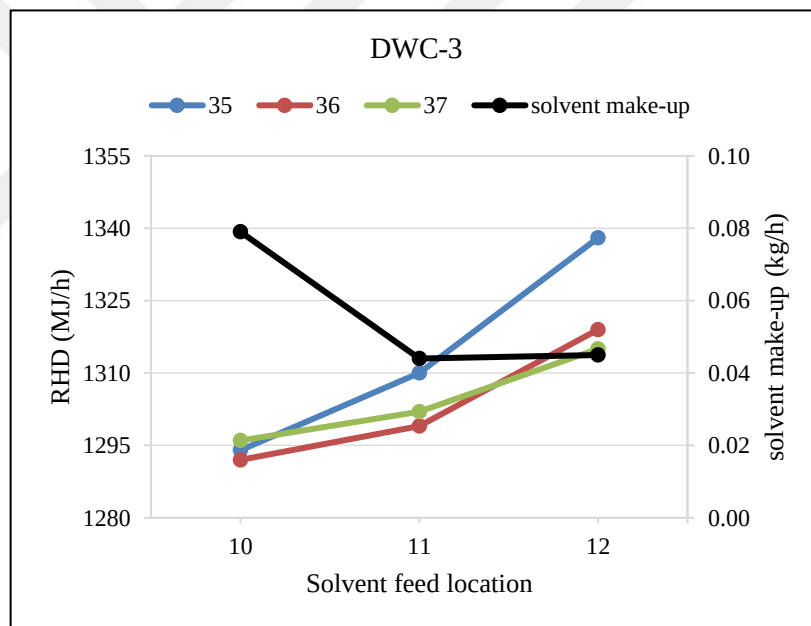
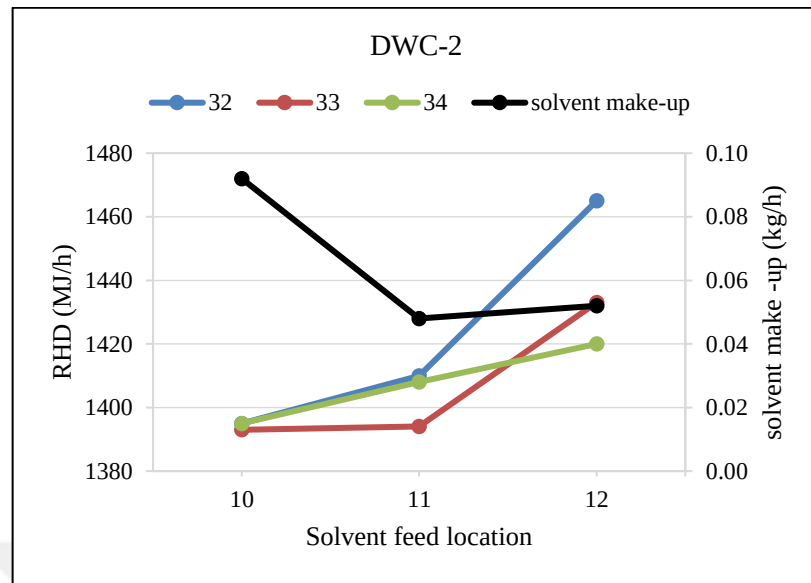
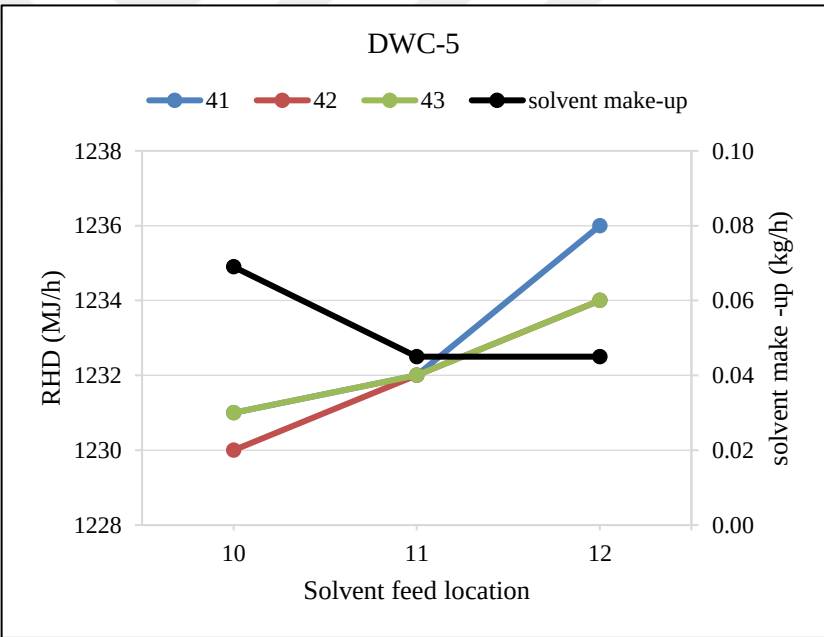
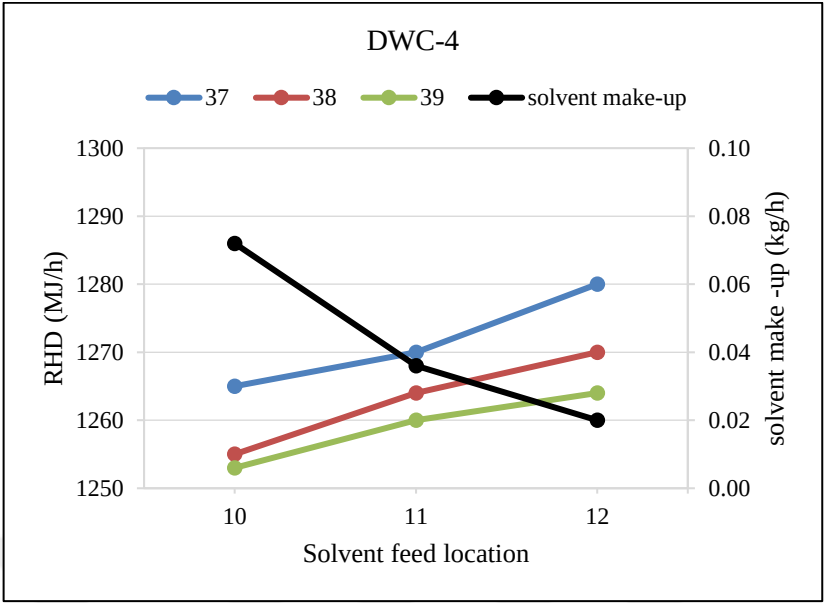


Figure 4.12. Relationship between solvent rate, RHD and TAC in all alternative cases

4.2.2. Optimal Tray Locations

Figure 4.13 shows how RHD and solvent make up flowrate change with feed entry trays for ideal stage number between 45 and 65. In case of ideal stage number of 40 (DWC-1), specific feed entry tray numbers meet design constraints and optimal locations are found to be 11th and 28th stages as a result of the sensitivity analysis. In figures, solid lines represent fresh feed locations and x-axis displays solvent feed stages. As in the ED systems, feeding solvent at higher trays cause a decrease in solvent make-up rates. On the other hand, RHD increases with solvent entry tray number. Based on TAC calculations, optimum feed locations are determined as 11-33 (DWC-2), 11-36 (DWC-3), 11-39 (DWC-4), 11-42 (DWC-5) and 12-46 (DWC-6).





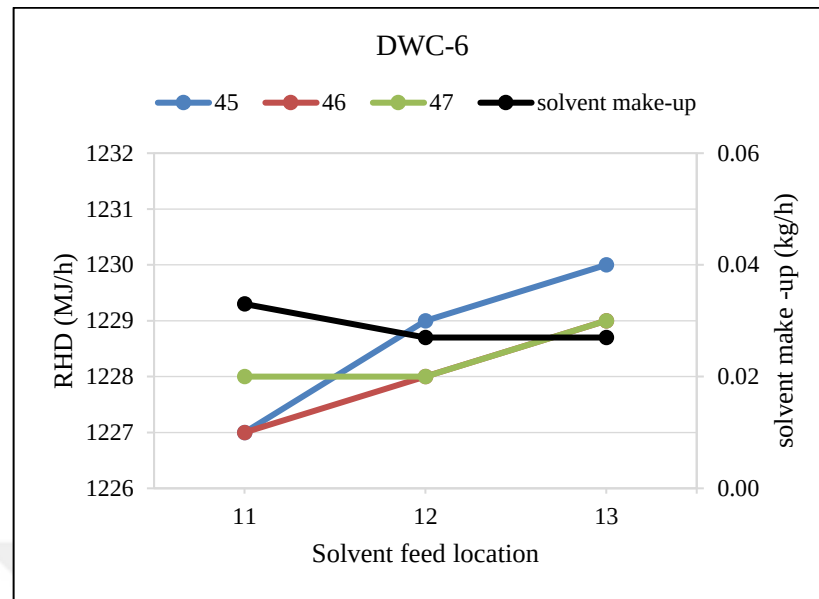


Figure 4.13. Impact of feed location on RHD and solvent make-up flowrate in all DWC configurations

4.2.3. Optimal Stage Number

Figure 4.14 indicates the optimum simulation results for the ideal stage number between 40 and 65. At first, as the ideal number of stage increases, the RHD decreases considerably. However, after stage number of 50, RHD values fall more slowly. Therefore, an increase is observed on the TAC above 50 number of stages due to the rising capital cost.

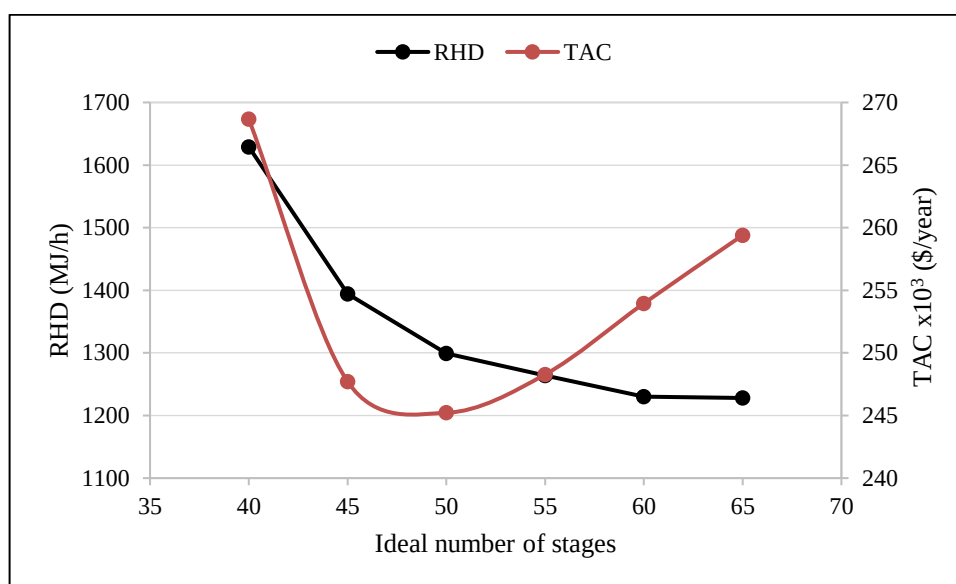


Figure 4.14. Impact of stage number on RHD and TAC

4.2.4. Optimization Results

A summary of optimal key process parameters for all alternative extractive-DWC process configurations is shown in Table 4.3 and the optimum DWC process flowsheet is illustrated in Figure 4.14. Tray efficiency is assumed to be 0.7 for all cases. As it is seen in the table, solvent usage and RHD values decrease as the tray number of DWC increases. Column diameters calculated by the equivalent diameter method are the same at 0.8886-m in all alternative processes. Condenser duty values are lower in DWC systems comparing to the conventional ED systems. On the other hand, heat exchanger duties are higher in DWC processes than the ED simulations due to the higher solvent rates.

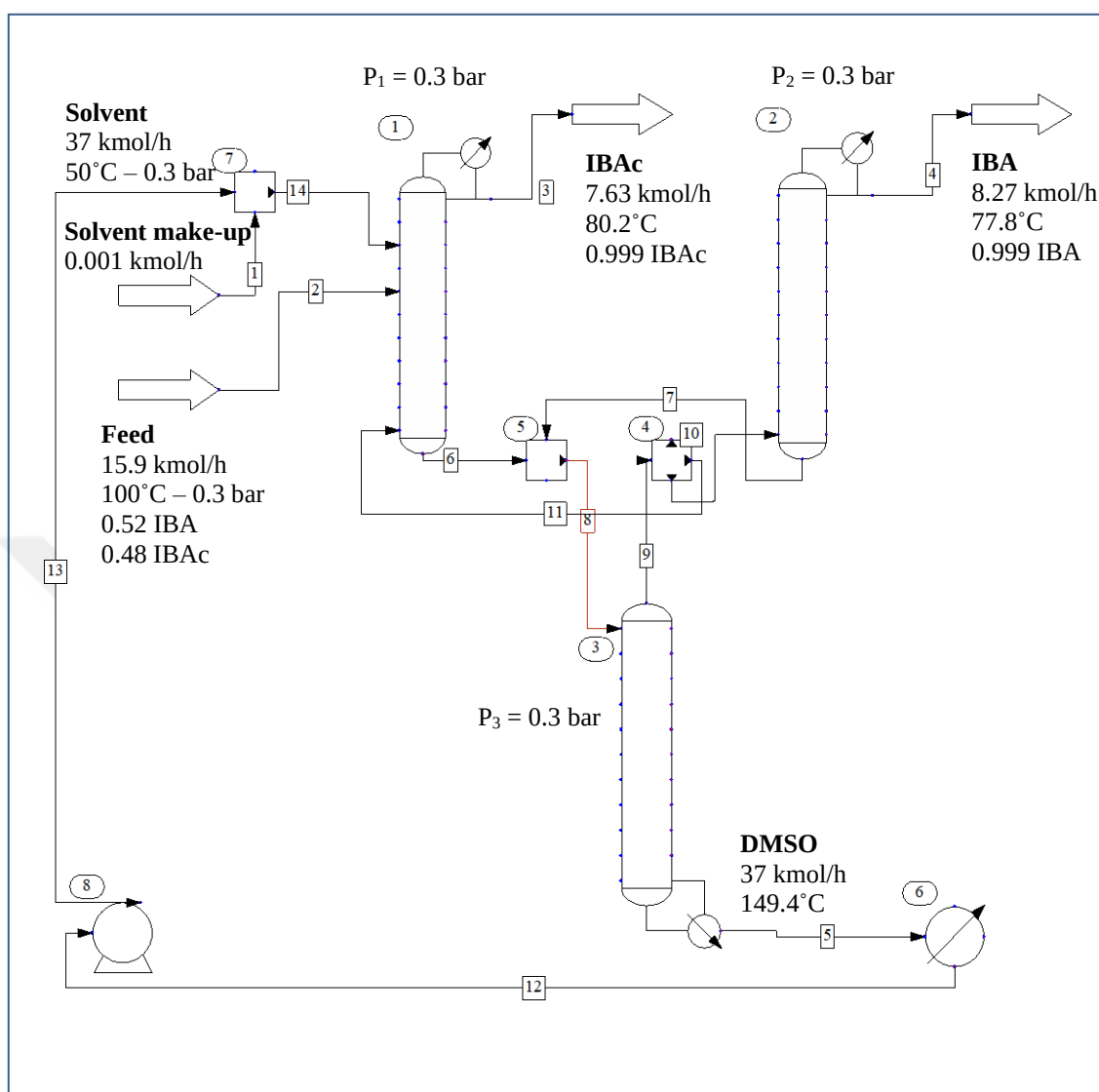


Figure 4.15. Optimum E-DWC process flowsheet

Table 4.3. Optimal process parameters for all cases

Parameters	DWC-1	DWC-2	DWC-3	DWC-4	DWC-5	DWC-6
Ideal tray number	40	45	50	55	60	65
Tray number of wall	45	54	61	67	75	82
Tray number below wall	11	11	11	11	11	11
Feed flowrate (kmol/h)	15.9	15.9	15.9	15.9	15.9	15.9
Solvent flowrate (kmol/h)	62	43	37	34	33	31
Solvent feed stage	11	11	11	11	11	12
Binary mixture feed stage	28	33	36	39	42	46
Condenser1 duty (MJ/h)	-341	-510	-552	-575	-578	-605
Condenser2 duty (MJ/h)	-355	-253	-211	-195	-182	-182
Reboiler heat duty (MJ/h)	1630	1394	1299	1261	1232	1228
Heat exchanger duty (MJ/h)	-987	-684	-589	-542	-525	-493

Cost calculation results for all DWC process configurations are indicated in Table 4.4. It can be observed that the capital investment increase with the number of stages whereas the operational costs decrease. HEX costs are reduced as the solvent flowrate decreases with the increase in the stage number. Minimum TAC is obtained in case of 50 stages of DWC column. We also observe that DWC method has an advantage in reduction of capital costs compared to the conventional ED system.

Table 4.4. Cost results for all DWC systems

Equipment ($\times 10^3$ \$/year)	DWC-1	DWC-2	DWC-3	DWC-4	DWC-5	DWC-6
Divided-wall column	534.239	543.653	575.883	605.980	645.140	680.800
Heat exchanger	118.378	113.096	107.423	107.423	107.423	104.607
Pump	23.457	23.516	23.522	23.522	23.448	23.440
FCI	676.074	680.265	706.828	736.924	776.011	808.847
Operational cost	133.962	112.172	104.384	101.441	99.331	98.231
TAC	268.671	247.716	245.221	248.275	253.952	259.395

Environmental performance of E-DWC systems is summarized in Figure 4.16. The increase in the number of stages provides an advantage in CO₂ emissions. Due to the reduced energy consumption, it is the lowest in the DWC-6 process configuration. CO₂ emission in DWC-1

system is 33% more than DWC-6 system. In the optimal DWC process configuration, emission value is calculated as 88.23 kg/h.

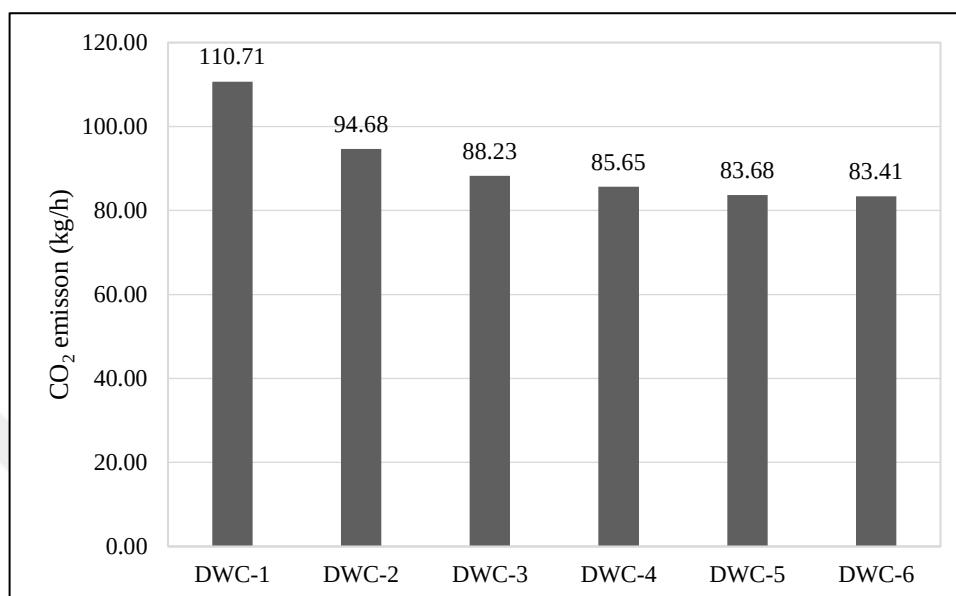


Figure 4.16. CO₂ emission rates of E-DWC processes

4.3. COMPARISON OF ED AND DWC PROCESSES

Based on the total annual costs, the optimum systems obtained for both conventional and the intensified process are ED-2 and DWC-3 systems. On the other hand, the TACs of DWC-3 and DWC-4 are very close to each other, and DWC-4 has lower CO₂ emission rates than DWC-3. Therefore, Table 4.5 indicates the comparison of ED-2, DWC-3 and DWC-4 systems in aspects of economic and environmental assessment. According to the results, DWC-3 provides 11.6% reduction in TAC and DWC-4 has better performance as 9.9% in CO₂ emission values.

Table 4.5. Comparison of ED-2, DWC-3 and DWC-4 processes

% Reduction	DWC-3	DWC-4
FCI	15.0	11.4
OC	6.4	9.0
TAC	11.6	10.5
CO ₂ emission rate (kg/h)	7.1	9.9

4.4. COMPARISON WITH THE LITERATURE RESULTS

Total RHDs are obtained as 1399 MJ/h, 1299 MJ/h in the optimum ED and E-DWC separation processes. Table 4.6 & 4.7 indicate energy consumption values reported in different studies using various solvents and techniques for the IBA+IBAc separation process.

Table 4.6. Energy consumption comparison with studies in literature

Separation method	Feed Properties	Energy Consumption (MJ/h)	IBA Purity (mole%)	IBAc Purity (mole%)	Data reference
Conventional ED (BUP)	100°C 1.1	3350	0.985	0.995	[10]
Conventional PSD	100°C 1.1	4594	0.985	0.995	[10]
PSD with fully heat integrated	100°C 1.1	3630	0.985	0.995	[11]
ED with heat pump (DMF)	100°C 1.1	2210	0.994	0.994	[15]
Hybrid PSD	25°C 1.1	1666	0.985	0.995	[13]

Table 4.7. Energy consumption values in the study conducted by Wang et al.

Separation method	Feed Properties	Energy Consumption (MJ/h)	IBA Purity (mole%)	IBAc Purity (mole%)	Data reference
PSD	25°C 1.1	6458	0.985	0.995	[12]
Heat integrated PSD	25°C 1.1	3532	0.985	0.995	
Heat pump with preheater assisted-PSD	25°C 1.1	1678	0.985	0.995	
Heat pump with preheater assisted-PSD-heat exchanger network	25°C 1.1	1034	0.985	0.995	

In order to make an energy consumption comparison with the literature, the effects of temperature and/or pressure differences in the fresh feed stream are taken into account. The enthalpy difference of IBA+IBAc mixture at 1.1 bar-100°C and 0.3 bar-100°C is calculated as 633 MJ/h. In addition, the required energy for reaching from 25°C-1.1 bar to 100°C-0.3 bar for the feed stream is 908 MJ/h.

For energy comparison, feed specifications and product purities are set to 25°C/1.1 bar and 0.985 and 0.995 mole% for IBA and IBAc respectively, and heat integration is applied in E-

DWC process. IBA (top vapor product of column 2) is compressed to a higher pressure of 0.65 bar. The temperature of the stream also increases during compression. Compressed IBA and hot DMSO streams can be employed as the heat source to heat the feed stream (see Figure 4.17). Total energy requirement of E-DWC system with heat integration is calculated as 1249 MJ/h (reboiler heat duty + compressor duty which is converted to thermal energy multiplying by 3 [60]). CO₂ emission rate and TAC are found as 338302 \$/year and 84.8 kg/h respectively.

Extractive-DWC with DMSO system provides 63%, 66% and 43% reductions in energy consumption compared with conventional ED with BUP, fully heat integrated PSD and ED with heat pump systems respectively. Comparing with the results reported by Wang et al., energy demand of E-DWC with heat integration process is found to be close to that for heat pump with preheater assisted-PSD-heat exchanger network system.

Table 4.8. Cost and CO₂ emission results of E-DWC systems (feed properties are set 25°C-1.1 bar)

Parameter	E-DWC	E-DWC-with heat integration
FCI (x10 ³ \$/year)	745.9	991.9
Operational cost (x10 ³ \$/year)	201.3	140.7
TAC (x10 ³ \$/year)	349.9	338.3
CO ₂ emission rate (kg/h)	141.7	84.8

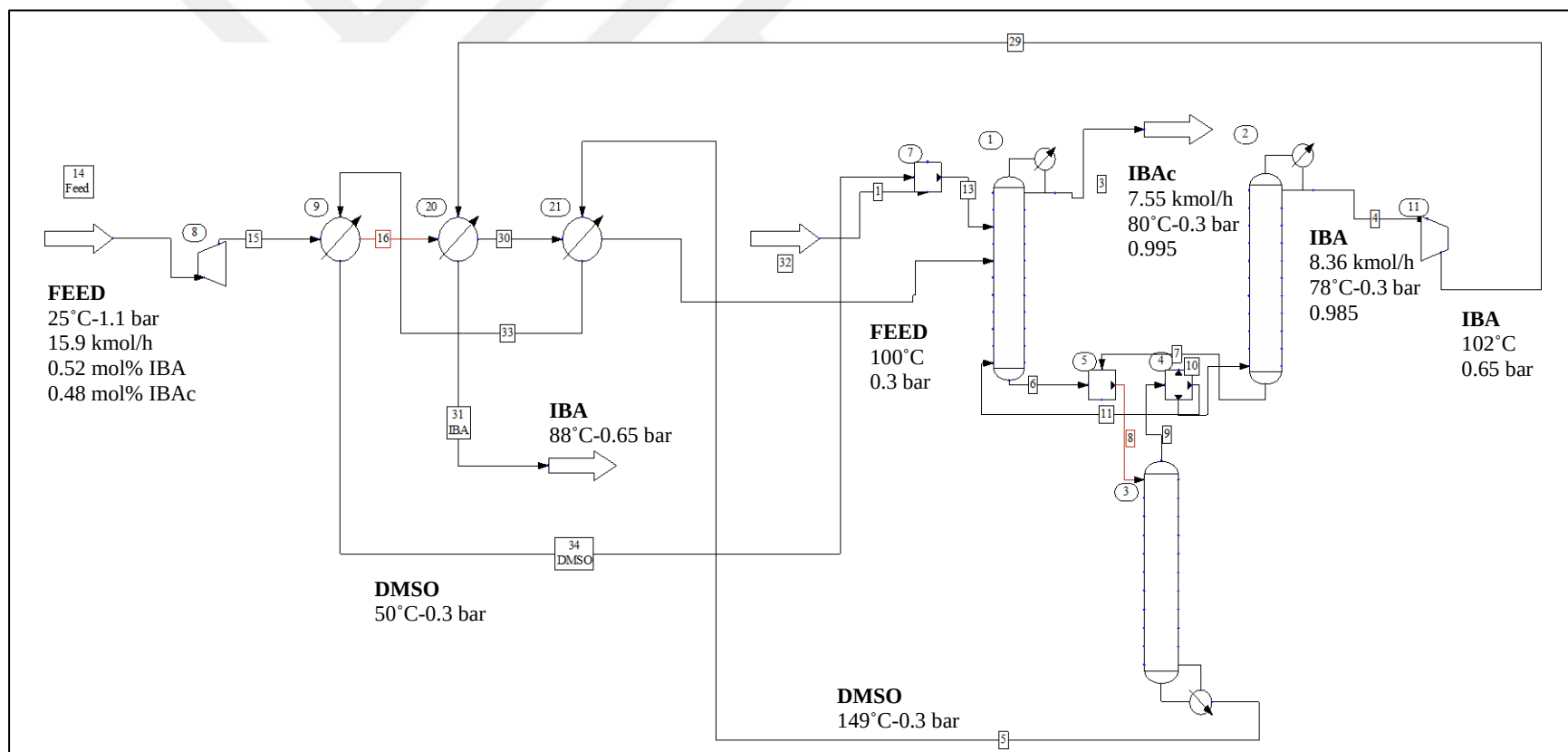


Figure 4.17. Flowsheet of E-DWC process with heat integration

5. CONCLUSION

In this study, conventional extractive distillation and extractive-dividing wall column systems are designed for the separation of IBA+IBAc azeotropic mixture using the software ChemCAD. A novel solvent, DMSO is used for the separation. Optimum solvent to feed ratio, feed locations and stage numbers are determined for total annual cost objective using sensitivity analysis and successive quadratic programming tools in ChemCAD. The processes are also evaluated based on the resulting CO₂ emissions. The following conclusions are drawn:

- DMSO enhances the volatility of IBAc with respect to IBA and reverses the volatility order. The ternary diagram and univolatility curve analyses have indicated that energy and cost savings are achieved in the process by working at vacuum pressures. The low operating temperatures (below 150°C) resulting from low pressures have also eliminated the DMSO decomposition problem reported in the literature
- Process intensification using a dividing-wall column, which has two condensers and one reboiler, provides savings in both capital investment and operational costs. It also reduces the CO₂ emission rates.
- DWC-4 system has resulted in 10.5 % reduction in the total annual cost and 9.9 % reduction in CO₂ emission rates compared to the most economical conventional extractive distillation system, ED-2.
- In comparison with the IBA+IBAc separation processes reported in the literature, E-DWC process with DMSO as the solvent, presents an advantageous alternative with higher product purities.

In this study, the feed composition and the capacity values are taken from the study conducted by Munoz et al [10]. As a future work, the effects of different IBA-IBAc mole fractions and feed flow rates can be investigated in the comparison of conventional ED and E-DWC processes.

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APPENDIX A: SENSITIVITY ANALYSIS AND SQP REPORTS

Table A.1. Feed location sensitivity analysis report for actual tray number of 48 in EC, actual tray number of 28 in SRC

Solvent rate: 46									
Binary feed stage		29.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	731.98	-532.20	836.04	-359.92	0.99901	0.99884	1568.02	-892.11
1	9	813.80	-613.18	833.46	-357.39	0.99917	0.99898	1647.26	-970.57
2	10	1002.85	-800.94	833.76	-358.76	0.99782	0.99992	1836.61	-1159.69
3	11	914.55	-731.36	825.18	-341.84	0.99437	0.98752	1739.73	-1073.20
4	12	944.42	-741.68	832.92	-359.44	0.99534	0.99992	1777.35	-1101.13
5	13	906.77	-703.40	834.09	-360.54	0.99454	0.99988	1740.86	-1063.94
Binary feed stage		30.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	735.85	-569.76	828.02	-343.47	0.99904	0.98646	1563.87	-913.23
1	9	762.17	-561.54	832.78	-356.70	0.99915	0.99897	1594.95	-918.25
2	10	866.49	-665.37	835.41	-359.36	0.99923	0.99905	1701.89	-1024.73
3	11	960.01	-757.96	834.86	-359.86	0.99838	0.99987	1794.87	-1117.82
4	12	961.32	-757.71	832.64	-356.57	0.99333	0.99897	1793.96	-1114.28
5	13	970.86	-767.42	833.08	-359.20	0.99534	0.99989	1803.94	-1126.62
Binary feed stage		31.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	724.23	-524.48	834.11	-357.99	0.99900	0.99883	1558.34	-882.47

1	9	753.16	-552.54	832.75	-356.68	0.99915	0.99897	1585.91	-909.22
2	10	801.39	-600.34	834.85	-358.80	0.99922	0.99904	1636.24	-959.14
3	11	835.90	-632.59	834.37	-358.37	0.99460	0.99910	1670.27	-990.96
4	12	927.63	-724.97	835.14	-360.13	0.99559	0.99975	1762.76	-1085.10
5	13	946.05	-742.20	833.50	-360.03	0.99423	0.99986	1779.55	-1102.23
Binary feed stage		32.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	740.98	-541.15	833.91	-357.79	0.99901	0.99884	1574.89	-898.94
1	9	763.85	-563.24	832.73	-356.66	0.99915	0.99897	1596.58	-919.89
2	10	799.37	-604.92	831.07	-344.33	0.99922	0.98595	1630.45	-949.26
3	11	859.09	-657.83	835.85	-359.80	0.99926	0.99907	1694.94	-1017.63
4	12	710.66	-576.11	822.15	-341.75	0.99425	0.98621	1532.81	-917.86
5	13	1164.21	-961.30	832.64	-356.57	0.99489	0.99897	1996.85	-1317.87
Binary feed stage		33.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	769.17	-569.24	835.13	-359.02	0.99903	0.99886	1604.30	-928.25
1	9	789.46	-588.84	834.71	-358.63	0.99916	0.99898	1624.17	-947.47
2	10	899.54	-762.55	824.94	-342.82	0.99924	0.98708	1724.48	-1105.37
3	11	680.61	-529.46	824.16	-342.08	0.99739	0.98525	1504.76	-871.54
4	12	991.00	-789.66	835.70	-359.67	0.99928	0.99909	1826.71	-1149.32
5	13	777.66	-575.09	834.26	-359.44	0.99603	0.99897	1611.93	-934.53

Table A.2 Feed location sensitivity analysis report for actual tray number of 58 in EC, actual tray number of 27 in SRC

Solvent rate: 34									
Binary feed stage		34.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	635.90	-627.02	724.70	-262.72	0.99884	0.99868	1360.60	-889.74
1	9	662.12	-651.64	726.56	-264.56	0.99904	0.99887	1388.68	-916.20
2	10	727.57	-716.02	725.50	-263.46	0.99915	0.99896	1453.07	-979.48
3	11	605.92	-594.02	721.90	-263.45	0.99693	0.99998	1327.82	-857.47
4	12	607.56	-594.51	726.31	-264.28	0.99462	0.99900	1333.87	-858.79
5	13	826.01	-814.00	724.80	-265.09	0.99859	0.99997	1550.81	-1079.09
6	14	811.58	-798.93	725.93	-263.60	0.99780	0.99750	1537.51	-1062.53
7	15	956.72	-943.53	726.31	-264.28	0.99618	0.99900	1683.02	-1207.82
Binary feed stage		35.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	630.24	-621.39	724.88	-262.90	0.99883	0.99867	1355.12	-884.29
1	9	646.54	-636.12	725.33	-263.33	0.99903	0.99886	1371.87	-899.45
2	10	673.89	-662.66	726.45	-264.43	0.99914	0.99895	1400.34	-927.09
3	11	756.78	-745.18	727.73	-265.71	0.99919	0.99900	1484.51	-1010.89
4	12	1088.73	-1075.30	727.63	-263.31	0.99642	0.99517	1816.36	-1338.61
5	13	1649.35	-1633.53	728.52	-265.51	0.98963	0.99955	2377.87	-1899.04
6	14	813.47	-800.02	726.79	-265.05	0.99594	0.99905	1540.26	-1065.07
7	15	1449.90	-1433.60	723.75	-263.73	0.98868	0.99994	2173.65	-1697.33
Binary feed stage		36.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND

0	8	631.40	-622.54	725.65	-263.67	0.99884	0.99868	1357.05	-886.21
1	9	643.49	-633.07	725.48	-263.48	0.99903	0.99886	1368.97	-896.55
2	10	659.81	-648.61	728.62	-266.60	0.99913	0.99895	1388.43	-915.21
3	11	688.95	-677.36	726.36	-264.34	0.99918	0.99900	1415.31	-941.70
4	12	663.96	-654.55	724.39	-266.06	0.99913	0.99994	1388.35	-920.61
5	13	1102.41	-1089.81	726.31	-264.28	0.99811	0.99900	1828.72	-1354.09
6	14	955.11	-941.28	722.87	-264.01	0.99495	0.99996	1677.98	-1205.28
7	15	780.50	-771.36	726.31	-264.28	0.99840	0.99900	1506.80	-1035.64
Binary feed stage		37.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	637.29	-628.39	722.59	-260.61	0.99884	0.99868	1359.87	-889.00
1	9	647.57	-637.12	727.18	-265.18	0.99903	0.99886	1374.75	-902.30
2	10	659.12	-647.92	728.03	-266.01	0.99913	0.99895	1387.15	-913.94
3	11	676.16	-664.57	726.41	-264.39	0.99918	0.99900	1402.57	-928.96
4	12	709.95	-698.35	725.48	-263.47	0.99921	0.99902	1435.42	-961.82
5	13	602.36	-589.72	726.69	-262.40	0.99335	0.99529	1329.05	-852.13
6	14	86.93	-9067.69	727.25	-265.17	1.00000	0.99875	814.18	-9332.86
7	15	613.18	-600.29	722.84	-264.37	0.99366	0.99996	1336.02	-864.66
Binary feed stage		38.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	647.48	-638.51	725.90	-263.92	0.99885	0.99869	1373.37	-902.42
1	9	657.10	-646.63	727.65	-265.64	0.99904	0.99887	1384.74	-912.27
2	10	666.36	-655.13	726.94	-264.92	0.99913	0.99895	1393.30	-920.06
3	11	677.96	-666.36	726.41	-264.39	0.99918	0.99900	1404.37	-930.75
4	12	697.16	-685.48	726.30	-264.29	0.99921	0.99902	1423.46	-949.77

5	13	739.72	-728.11	728.60	-266.61	0.99922	0.99903	1468.32	-994.71
6	14	915.90	-901.80	725.01	-265.70	0.99465	0.99996	1640.92	-1167.50
7	15	1157.88	-1143.55	722.62	-263.00	0.99454	0.99995	1880.50	-1406.55
Binary feed stage		39.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	661.72	-652.68	726.32	-264.34	0.99886	0.99870	1388.04	-917.02
1	9	671.59	-661.09	726.39	-264.39	0.99904	0.99887	1397.99	-925.48
2	10	679.90	-668.65	726.59	-264.58	0.99914	0.99896	1406.49	-933.23
3	11	688.84	-677.24	726.35	-264.33	0.99918	0.99900	1415.19	-941.57
4	12	701.74	-690.13	727.17	-265.16	0.99921	0.99902	1428.91	-955.29
5	13	724.65	-713.04	727.92	-265.92	0.99922	0.99903	1452.56	-978.96
6	14	787.41	-775.46	726.93	-264.91	0.99923	0.99904	1514.34	-1040.37
7	15	653.37	-639.79	726.31	-264.28	0.99348	0.99900	1379.67	-904.07
Binary feed stage		40.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	8	680.88	-671.73	724.38	-262.40	0.99887	0.99871	1405.26	-934.13
1	9	691.60	-681.03	725.63	-263.63	0.99905	0.99887	1417.23	-944.66
2	10	699.55	-688.01	728.30	-266.26	0.99914	0.99896	1427.85	-954.26
3	11	707.29	-695.69	726.32	-264.30	0.99919	0.99900	1433.61	-959.99
4	12	716.95	-705.36	727.67	-265.67	0.99921	0.99902	1444.63	-971.02
5	13	732.48	-720.86	727.42	-265.42	0.99922	0.99903	1459.90	-986.27
6	14	763.74	-751.81	727.09	-265.07	0.99923	0.99904	1490.83	-1016.88
7	15	781.78	-768.78	724.10	-263.08	0.99747	0.99955	1505.87	-1031.86

Table A.3 Feed location sensitivity analysis report for actual tray number of 72 in EC, actual tray number of 25 in SRC

Solvent rate: 28									
Binary feed stage		40.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	629.88	-694.75	699.83	-245.19	0.99909	0.99892	1329.7	-939.9
1	11	646.47	-707.96	702.95	-247.98	0.99914	0.99895	1349.4	-955.9
2	12	592.93	-653.18	703.39	-249.63	0.99508	0.99901	1296.3	-902.8
3	13	600.83	-660.62	701.29	-248.31	0.99523	0.99999	1302.1	-908.9
4	14	726.30	-789.72	704.01	-246.91	0.99870	0.99402	1430.3	-1036.6
5	15	949.91	-1009.16	701.68	-248.71	0.99515	0.99996	1651.6	-1257.9
Binary feed stage		41.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	618.30	-683.28	700.75	-246.13	0.99909	0.99891	1319.0	-929.4
1	11	626.30	-687.76	704.28	-249.31	0.99913	0.99895	1330.6	-937.1
2	12	648.70	-710.15	703.95	-248.99	0.99916	0.99897	1352.7	-959.1
3	13	655.45	-714.73	702.05	-249.07	0.99537	0.99999	1357.5	-963.8
4	14	617.56	-677.35	701.18	-250.33	0.99609	0.99995	1318.7	-927.7
5	15	-2.66	-	705.72	-248.69	0.00002	0.99480	703.1	-
Binary feed stage		42.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	612.80	-677.84	700.66	-246.04	0.99909	0.99891	1313.5	-923.9
1	11	617.05	-678.55	703.41	-248.44	0.99913	0.99895	1320.5	-927.0
2	12	628.67	-690.12	703.85	-248.89	0.99916	0.99897	1332.5	-939.0
3	13	651.31	-712.77	703.20	-248.25	0.99917	0.99898	1354.5	-961.0

4	14	684.58	-741.98	702.57	-249.61	0.99001	0.99999	1387.1	-991.6
5	15	613.62	-673.77	703.07	-249.56	0.99652	0.99856	1316.7	-923.3
Binary feed stage		43.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	610.65	-675.71	700.38	-245.76	0.99909	0.99891	1311.0	-921.5
1	11	612.93	-674.40	705.45	-250.48	0.99913	0.99895	1318.4	-924.9
2	12	619.83	-681.29	703.90	-248.94	0.99915	0.99897	1323.7	-930.2
3	13	631.57	-693.03	703.92	-248.97	0.99917	0.99898	1335.5	-942.0
4	14	654.79	-716.22	704.31	-249.36	0.99917	0.99899	1359.1	-965.6
5	15	620.52	-680.10	701.40	-248.21	0.99534	0.99902	1321.9	-928.3
Binary feed stage		44.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	610.82	-675.88	701.67	-247.05	0.99909	0.99891	1312.5	-922.9
1	11	613.10	-673.55	704.50	-249.04	0.99913	0.99895	1317.6	-922.6
2	12	616.42	-677.88	703.91	-248.94	0.99915	0.99897	1320.3	-926.8
3	13	623.38	-684.84	703.37	-248.42	0.99917	0.99898	1326.8	-933.3
4	14	635.28	-696.73	704.10	-249.14	0.99917	0.99899	1339.4	-945.9
5	15	659.48	-720.93	703.24	-248.28	0.99917	0.99899	1362.7	-969.2
Binary feed stage		45.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	612.81	-677.84	700.82	-246.20	0.99909	0.99891	1313.6	-924.0
1	11	613.37	-674.83	704.57	-249.59	0.99913	0.99895	1317.9	-924.4
2	12	616.29	-677.75	703.89	-248.93	0.99915	0.99897	1320.2	-926.7
3	13	620.68	-682.13	703.48	-248.53	0.99917	0.99898	1324.2	-930.7

4	14	627.76	-689.22	702.36	-247.41	0.99917	0.99899	1330.1	-936.6
5	15	640.15	-701.60	703.62	-248.67	0.99917	0.99899	1343.8	-950.3
Binary feed stage		46.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	616.35	-681.34	699.50	-244.87	0.99909	0.99891	1315.8	-926.2
1	11	616.59	-678.09	703.54	-248.57	0.99913	0.99895	1320.1	-926.7
2	12	618.65	-680.11	703.90	-248.94	0.99915	0.99897	1322.5	-929.0
3	13	621.53	-683.00	704.45	-249.50	0.99917	0.99898	1326.0	-932.5
4	14	625.93	-687.31	704.03	-249.07	0.99917	0.99899	1330.0	-936.4
5	15	633.30	-694.77	703.44	-248.49	0.99917	0.99899	1336.7	-943.3
Binary feed stage		47.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	10	621.44	-686.39	700.60	-245.97	0.99909	0.99891	1322.0	-932.4
1	11	621.47	-682.94	704.87	-249.90	0.99913	0.99895	1326.3	-932.8
2	12	623.04	-684.50	703.75	-248.79	0.99915	0.99897	1326.8	-933.3
3	13	625.09	-686.54	705.22	-250.27	0.99917	0.99898	1330.3	-936.8
4	14	628.06	-689.51	703.66	-248.71	0.99917	0.99899	1331.7	-938.2
5	15	632.63	-694.09	704.91	-249.95	0.99917	0.99899	1337.5	-944.0

Table A.4 Feed location sensitivity analysis report for actual tray number of 86 in EC, actual tray number of 25 in SRC

Solvent rate: 27									
Binary feed stage		48.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	599.71	-675.83	691.23	-237.80	0.99914	0.99896	1290.93	-913.62
1	13	601.41	-677.51	693.40	-239.98	0.99915	0.99897	1294.81	-917.49
2	14	604.09	-680.19	691.66	-238.24	0.99916	0.99898	1295.75	-918.43
3	15	608.33	-684.44	690.21	-236.79	0.99916	0.99898	1298.54	-921.23
4	16	615.31	-691.42	690.03	-236.61	0.99916	0.99898	1305.35	-928.03
5	17	627.49	-703.59	692.99	-239.57	0.99916	0.99898	1320.49	-943.17
6	18	652.56	-728.66	692.39	-238.98	0.99917	0.99898	1344.95	-967.64
7	19	-336.451	-120.909	-	-	0.99414	0.36260	-	-
8	20	710.93	-785.989	720.80	-237.65	0.99917	0.93591	1431.73	-1023.64
Binary feed stage		49.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	599.00	-675.12	694.09	-240.66	0.99914	0.99896	1293.09	-915.78
1	13	600.11	-676.22	691.32	-237.89	0.99916	0.99897	1291.43	-914.11
2	14	601.81	-677.91	690.47	-237.05	0.99916	0.99898	1292.28	-914.96
3	15	604.47	-680.57	692.28	-238.86	0.99916	0.99898	1296.74	-919.43
4	16	608.69	-684.80	691.01	-237.59	0.99916	0.99898	1299.70	-922.39
5	17	615.70	-691.82	691.07	-237.65	0.99917	0.99898	1306.77	-929.47
6	18	627.97	-704.07	693.35	-239.93	0.99917	0.99898	1321.32	-944.00
7	19	652.96	-729.06	691.52	-238.10	0.99917	0.99898	1344.48	-967.16
8	20	-	-	781.51	-218.07	0.00680	0.99791	-	-

Binary feed stage		50.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	598.75	-674.865	691.65	-238.22	0.99914	0.99896	1290.40	-913.09
1	13	599.51	-675.611	692.39	-238.97	0.99916	0.99897	1291.90	-914.58
2	14	600.59	-676.702	692.70	-239.28	0.99916	0.99898	1293.29	-915.98
3	15	602.30	-678.414	690.92	-237.50	0.99916	0.99898	1293.22	-915.92
4	16	604.96	-681.051	692.22	-238.79	0.99916	0.99898	1297.17	-919.85
5	17	609.19	-685.295	691.20	-237.79	0.99917	0.99898	1300.39	-923.08
6	18	616.22	-692.313	690.29	-236.87	0.99917	0.99898	1306.50	-929.18
7	19	628.58	-704.679	692.99	-239.57	0.99917	0.99898	1321.57	-944.25
8	20	653.65	-729.752	691.96	-238.54	0.99917	0.99898	1345.61	-968.30
Binary feed stage		51.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	598.90	-675.008	691.37	-237.94	0.99914	0.99896	1290.28	-912.95
1	13	599.40	-675.498	693.06	-239.63	0.99915	0.99897	1292.46	-915.13
2	14	600.12	-676.216	691.37	-237.95	0.99916	0.99897	1291.48	-914.16
3	15	601.22	-677.327	692.17	-238.76	0.99916	0.99898	1293.40	-916.08
4	16	602.92	-679.031	691.59	-238.18	0.99917	0.99898	1294.51	-917.21
5	17	605.55	-681.665	690.92	-237.50	0.99917	0.99898	1296.47	-919.16
6	18	609.81	-685.925	691.25	-237.83	0.99917	0.99898	1301.06	-923.76
7	19	616.80	-692.904	692.17	-238.75	0.99917	0.99898	1308.97	-931.66
8	20	629.25	-705.353	692.68	-239.26	0.99917	0.99898	1321.92	-944.61
Binary feed stage		52.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	599.37	-675.478	693.61	-240.17	0.99914	0.99896	1292.98	-915.65

1	13	599.72	-675.813	691.84	-238.42	0.99916	0.99897	1291.56	-914.23
2	14	600.19	-676.297	693.12	-239.69	0.99916	0.99898	1293.31	-915.99
3	15	600.91	-677.007	693.06	-239.64	0.99916	0.99898	1293.97	-916.64
4	16	602.00	-678.117	692.85	-239.43	0.99917	0.99898	1294.86	-917.55
5	17	603.70	-679.811	694.01	-240.59	0.99917	0.99898	1297.71	-920.40
6	18	606.34	-682.444	694.38	-240.97	0.99916	0.99898	1300.72	-923.41
7	19	610.65	-686.754	691.08	-237.66	0.99917	0.99898	1301.73	-924.42
8	20	617.63	-693.73	692.85	-239.44	0.99917	0.99898	1310.48	-933.17
Binary feed stage		53.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	600.15	-676.249	692.87	-239.44	0.99914	0.99896	1293.02	-915.69
1	13	600.40	-676.516	691.94	-238.52	0.99916	0.99897	1292.34	-915.03
2	14	600.72	-676.828	691.53	-238.11	0.99916	0.99898	1292.26	-914.94
3	15	601.20	-677.302	694.05	-240.63	0.99916	0.99898	1295.25	-917.93
4	16	601.91	-678.009	692.99	-239.57	0.99916	0.99898	1294.89	-917.58
5	17	602.98	-679.09	690.72	-237.30	0.99916	0.99898	1293.70	-916.39
6	18	604.73	-680.829	694.17	-240.76	0.99917	0.99898	1298.90	-921.59
7	19	607.37	-683.485	692.65	-239.23	0.99917	0.99898	1300.02	-922.71
8	20	611.66	-687.777	690.21	-236.79	0.99917	0.99898	1301.87	-924.57
Binary feed stage		54.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	601.26	-677.38	693.30	-239.87	0.99914	0.99896	1294.56	-917.25
1	13	601.47	-677.59	692.49	-239.07	0.99916	0.99897	1293.96	-916.65
2	14	601.70	-677.80	693.92	-240.49	0.99916	0.99898	1295.61	-918.29
3	15	602.03	-678.13	692.43	-239.01	0.99916	0.99898	1294.45	-917.13

4	16	602.48	-678.59	691.12	-237.70	0.99916	0.99898	1293.60	-916.29
5	17	603.19	-679.30	692.93	-239.51	0.99917	0.99898	1296.12	-918.81
6	18	604.31	-680.41	691.43	-238.01	0.99917	0.99898	1295.74	-918.42
7	19	606.00	-682.10	692.27	-238.86	0.99917	0.99898	1298.27	-920.96
8	20	608.70	-684.80	693.23	-239.81	0.99917	0.99898	1301.93	-924.62
Binary feed stage		55.00							
Run	Solvent feed stage	RHD	COND	RHD2	COND2	IBAc	IBA	TOTAL RHD	TOTAL COND
0	12	602.77	-678.9	689.92	-236.5	0.99914	0.99896	1292.68	-915.37
1	13	602.95	-679.1	692.39	-239.0	0.99916	0.99897	1295.33	-918.02
2	14	603.12	-679.2	689.10	-235.7	0.99916	0.99898	1292.22	-914.91
3	15	603.31	-679.4	691.60	-238.2	0.99916	0.99898	1294.92	-917.62
4	16	603.64	-679.7	692.79	-239.4	0.99916	0.99898	1296.44	-919.11
5	17	604.13	-680.2	694.19	-240.8	0.99917	0.99898	1298.31	-921.00
6	18	604.83	-680.9	693.57	-240.2	0.99917	0.99898	1298.41	-921.10
7	19	605.95	-682.1	691.45	-238.0	0.99917	0.99898	1297.40	-920.09
8	20	607.68	-683.8	691.23	-237.8	0.99917	0.99898	1298.90	-921.59

Table A.5 SQP report of solvent rate for actual tray number of 48 in EC, actual tray number of 28 in SRC

SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	X[0] =	4.50000E+01	4.60000E+01	
Objective Function		Initial Value	Final Value	
		7.597208E+02	7.520300E+02	
Inequality Constraints		Initial Value	Final Value	
solvent rate-LB	g[0] =	2.272725E-02	4.545458E-02	
UB-solvent rate	g[1] =	2.173918E-02	-1.401290E-16	* Upper bound violation
IBAc-LB	g[2] =	6.587938E-05	5.556192E-05	
UB-IBAc	g[3] =	3.407761E-05	4.439507E-05	
IBA-LB	g[4] =	7.467222E-05	7.467222E-05	
UB-IBA	g[5] =	2.534438E-05	2.534438E-05	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	3			
No. of function calls	9			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	1000			
Default step size	0.003			
Max change factor	0			
Forward differences.				

Table A.6 SQP report of solvent rate for actual tray number of 58 in EC, actual tray number of 27 in SRC

SQP Final Results:			
Independent Variables in User Specified Engineering Units:			
		Estimation	Final Value
solvent rate	X[0] =	3.3400000E+01	3.4000000E+01
Objective Function		Initial Value	Final Value
		6.6951980E+02	6.6249870E+02
Inequality Constraints		Initial Value	Final Value
solvent rate-LB	g[0] =	1.2121240E-02	3.0303000E-02
UB-solvent rate	g[1] =	1.7647000E-02	0.0000000E+00
IBAc-LB	g[2] =	8.0280460E-05	7.9714350E-05
UB-IBAc	g[3] =	1.9676530E-05	2.0242640E-05
IBA-LB	g[4] =	9.4068320E-05	9.3442770E-05
UB-IBA	g[5] =	5.9482700E-06	6.5738280E-06
No. of restarts	1		
Restart Seed	0		
No. of SQP iterations	2		
No. of function calls	7		
No. of cores	4		
Parallel computing	0		
Max. iterations/thread	1000		
Default step size	0.003		
Max change factor	0		
Forward differences.			

Table A.7 SQP report of solvent rate for actual tray number of 72 in EC, actual tray number of 25 in SRC

SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	X[0] =	2.700000E+01	2.800000E+01	
Objective Function		Initial Value	Final Value	
		6.274377E+02	6.161403E+02	
Inequality Constraints		Initial Value	Final Value	
solvent rate-LB	g[0] =	3.846157E-02	7.692313E-02	
UB-solvent rate	g[1] =	3.571431E-02	1.151060E-16	
IBAc-LB	g[2] =	5.556153E-05	5.510769E-05	
UB-IBAc	g[3] =	4.439545E-05	4.484930E-05	
IBA-LB	g[4] =	7.238545E-05	7.081893E-05	
UB-IBA	g[5] =	2.763115E-05	2.919766E-05	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	4			
No. of function calls	11			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	1000			
Default step size	0.003			
Max change factor	0			
Forward differences.				

Table A.8 SQP report of solvent rate for actual tray number of 86 in EC, actual tray number of 25 in SRC

SQP Final Results:			
Independent Variables in User Specified Engineering Units:			
		Estimation	Final Value
solvent rate	X[0] =	2.500000E+01	2.700000E+01
Objective Function		Initial Value	Final Value
		6.172518E+02	6.001476E+02
Inequality Constraints		Initial Value	Final Value
solvent rate-LB	g[0] =	0.000000E+00	7.999999E-02
UB-solvent rate	g[1] =	7.407406E-02	1.671168E-15
IBAc-LB	g[2] =	6.043813E-05	5.987108E-05
UB-IBAc	g[3] =	3.951886E-05	4.008590E-05
IBA-LB	g[4] =	7.812294E-05	7.686905E-05
UB-IBA	g[5] =	2.189366E-05	2.314754E-05
UB-RHD2	g[6] =	3.065859E-02	8.005249E-04
No. of restarts	1		
Restart Seed	0		
No. of SQP iterations	3		
No. of function calls	9		
No. of cores	4		
Parallel computing	0		
Max. iterations/thread	1000		
Default step size	0.003		
Max change factor	0		

Forward differences.				
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Table A.9 Feed location sensitivity analysis report for actual tray number of 56 in DWC

Solvent rate:62						
Binary feed stage		27.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	11	-340.48	-355.09	1629.83	0.99849	0.99836
1	12	-340.60	-355.01	1629.93	0.99807	0.99790
2	13	-340.92	-355.03	1630.26	0.99742	0.99725
3	14	-341.58	-355.28	1631.18	0.99645	0.99634
4	15	-341.89	-355.04	1631.24	0.99504	0.99502
Binary feed stage		28.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	11	-340.41	-355.09	1629.76	0.99865	0.99852
1	12	-340.50	-355.02	1629.84	0.99836	0.99817
2	13	-340.72	-355.02	1630.07	0.99789	0.99769
3	14	-340.97	-354.96	1630.25	0.99721	0.99704
4	15	-341.44	-355.06	1630.84	0.99622	0.99611
Binary feed stage		29.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	11	-340.40	-355.09	1629.77	0.99865	0.99851
1	12	-340.50	-355.04	1629.85	0.99843	0.99824
2	13	-340.61	-355.01	1629.97	0.99810	0.99788

3	14	-340.78	-354.95	1630.08	0.99761	0.99740
4	15	-341.13	-355.00	1630.47	0.99690	0.99674
Binary feed stage		30.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	11	-340.49	-355.09	1629.86	0.99843	0.99831
1	12	-340.55	-355.04	1629.92	0.99828	0.99810
2	13	-340.68	-355.01	1630.01	0.99804	0.99783
3	14	-340.80	-355.00	1630.15	0.99769	0.99748
4	15	-341.60	-355.59	1631.53	0.99720	0.99701
Binary feed stage		31.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	11	-340.72	-355.11	1630.07	0.99791	0.99783
1	12	-340.72	-355.02	1630.05	0.99782	0.99767
2	13	-340.81	-355.02	1630.16	0.99767	0.99748
3	14	-340.91	-355.00	1630.26	0.99743	0.99724
4	15	-341.05	-355.00	1630.40	0.99708	0.99690
Binary feed stage		32.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	11	-341.08	-355.13	1630.45	0.99701	0.99700
1	12	-341.10	-355.06	1630.46	0.99696	0.99687
2	13	-341.12	-355.02	1630.46	0.99687	0.99675
3	14	-341.19	-355.00	1630.51	0.99674	0.99660
4	15	-341.23	-354.96	1630.52	0.99652	0.99639

Binary feed stage		33.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	11	-341.64	-355.16	1631.02	0.99565	0.99575
1	12	-341.66	-355.09	1631.00	0.99563	0.99565
2	13	-341.43	-354.82	1630.53	0.99558	0.99556
3	14	-341.48	-354.81	1630.59	0.99551	0.99546
4	15	-341.59	-354.86	1630.74	0.99540	0.99535

Table A.10 Feed location sensitivity analysis report for actual tray number of 65 in DWC

Solvent rate:43						
Binary feed stage		30.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-510.43	-253.27	1395.21	0.99886	0.99871
1	11	-509.86	-252.81	1394.43	0.99856	0.99843
2	12	-509.88	-252.70	1394.39	0.99810	0.99797
3	13	-509.93	-252.64	1394.49	0.99744	0.99734
4	14	-511.27	-251.74	1392.67	0.99646	0.99642
5	15	-510.28	-252.37	1394.50	0.99523	0.99528
Binary feed stage		31.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-510.64	-253.43	1395.47	0.99906	0.99889
1	11	-509.80	-252.83	1394.41	0.99886	0.99870
2	12	-509.90	-252.68	1394.22	0.99852	0.99836

3	13	-535.17	-228.63	1339.64	0.99689	0.99681
4	14	-509.96	-252.61	1394.45	0.99737	0.99726
5	15	-510.26	-252.35	1394.12	0.99642	0.99639
Binary feed stage		32.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-510.39	-253.29	1395.18	0.99918	0.99901
1	11	-509.79	-252.85	1394.39	0.99904	0.99887
2	12	-509.81	-252.75	1394.31	0.99879	0.99861
3	13	-509.93	-252.63	1394.16	0.99844	0.99827
4	14	-509.90	-252.66	1394.39	0.99795	0.99780
5	15	-509.95	-252.60	1394.47	0.99727	0.99717
Binary feed stage		33.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-510.39	-253.30	1395.18	0.99923	0.99905
1	11	-509.78	-252.86	1394.39	0.99912	0.99894
2	12	-534.23	-229.18	1340.57	0.99820	0.99806
3	13	-509.81	-252.71	1394.31	0.99868	0.99848
4	14	-509.84	-252.69	1394.36	0.99832	0.99814
5	15	-534.40	-229.03	1340.69	0.99658	0.99653
Binary feed stage		34.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-510.39	-253.29	1395.18	0.99917	0.99900
1	11	-509.78	-252.85	1394.39	0.99909	0.99892
2	12	-509.75	-252.79	1394.35	0.99896	0.99876

3	13	-509.79	-252.75	1394.36	0.99877	0.99856
4	14	-510.16	-252.38	1393.61	0.99849	0.99830
5	15	-509.81	-252.71	1394.47	0.99813	0.99796
Binary feed stage		35.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-510.42	-253.27	1395.20	0.99897	0.99881
1	11	-509.81	-252.84	1394.41	0.99891	0.99875
2	12	-509.78	-252.78	1394.37	0.99882	0.99864
3	13	-509.79	-252.75	1394.37	0.99869	0.99850
4	14	-509.80	-252.72	1394.37	0.99850	0.99831
5	15	-509.87	-	1394.18	0.99824	-

Table A.11 Feed location sensitivity analysis report for actual tray number of 72 in DWC

Solvent rate:37						
Binary feed stage		32.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-552.31	-211.66	1300.04	0.99858	0.99845
1	11	-572.48	-192.68	1256.40	0.99653	0.99655
2	12	-551.89	0.00	1230.89	0.99765	-1.00000
3	13	-552.01	-211.46	1300.09	0.99692	0.99691
4	14	-573.02	-192.23	1256.11	0.99315	0.99337
5	15	-574.34	-191.09	1253.84	0.99122	0.99158

Binary feed stage		33.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-552.28	-211.68	1300.01	0.99887	0.99871
1	11	-551.78	-207.38	1299.37	0.99859	0.99490
2	12	-551.82	-211.24	1299.38	0.99819	0.99805
3	13	-572.55	-192.59	1256.44	0.99561	0.99565
4	14	-572.63	-192.53	1256.53	0.99451	0.99463
5	15	-573.01	-192.23	1256.13	0.99310	0.99332
Binary feed stage		34.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-552.24	-211.70	1300.02	0.99907	0.99890
1	11	-551.75	-211.31	1299.35	0.99887	0.99871
2	12	-551.77	-211.26	1299.35	0.99857	0.99840
3	13	-551.81	-211.21	1299.37	0.99815	0.99800
4	14	-572.53	-192.58	1256.45	0.99553	0.99557
5	15	-572.65	-192.51	1256.51	0.99443	0.99455
Binary feed stage		35.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-552.23	-211.70	1299.99	0.99919	0.99901
1	11	-551.72	-211.33	1299.33	0.99905	0.99888
2	12	-551.75	-211.28	1299.33	0.99883	0.99864
3	13	-551.77	-211.24	1299.34	0.99851	0.99833
4	14	-551.83	-211.20	1299.37	0.99808	0.99793
5	15	-551.87	-211.17	1299.43	0.99751	0.99740

Binary feed stage		36.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-552.22	-211.70	1299.98	0.99925	0.99907
1	11	-551.73	-211.33	1299.33	0.99914	0.99896
2	12	-551.73	-211.29	1299.32	0.99898	0.99878
3	13	-551.76	-211.26	1299.33	0.99874	0.99855
4	14	-551.78	-211.23	1299.35	0.99842	0.99824
5	15	-551.82	-211.19	1299.38	0.99799	0.99784
Binary feed stage		37.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-552.22	-211.70	1299.99	0.99923	0.99905
1	11	-551.73	-211.33	1299.33	0.99915	0.99897
2	12	-551.71	-211.29	1299.32	0.99903	0.99883
3	13	-551.74	-211.26	1299.32	0.99885	0.99865
4	14	-551.75	-211.24	1299.33	0.99861	0.99842
5	15	-551.80	-211.21	1299.36	0.99829	0.99812
Binary feed stage		38.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-552.24	-211.69	1300.00	0.99911	0.99893
1	11	-551.74	-211.33	1299.33	0.99904	0.99887
2	12	-551.74	-211.28	1299.33	0.99896	0.99876
3	13	-551.74	-211.26	1299.32	0.99884	0.99863
4	14	-551.75	-211.24	1299.33	0.99866	0.99846
5	15	-551.79	-211.22	1299.34	0.99843	0.99824

Table A.12 Feed location sensitivity analysis report for actual tray number of 78 in DWC

Solvent rate:34						
Binary feed stage		35.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-579.63	-197.61	1265.40	0.99883	0.99867
1	11	-578.93	-197.11	1264.51	0.99854	0.99841
2	12	-578.72	-196.91	1264.21	0.99814	0.99804
3	13	-578.64	-196.79	1264.08	0.99760	0.99755
4	14	-578.66	-196.70	1264.04	0.99691	0.99691
5	15	-578.72	-196.63	1264.08	0.99603	0.99610
Binary feed stage		36.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-579.59	-197.62	1265.39	0.99905	0.99888
1	11	-578.91	-197.12	1264.48	0.99884	0.99869
2	12	-578.66	-196.93	1264.17	0.99853	0.99840
3	13	-578.57	-196.81	1264.03	0.99812	0.99802
4	14	-578.58	-196.73	1263.98	0.99758	0.99752
5	15	-578.61	-196.67	1263.99	0.99689	0.99689
Binary feed stage		37.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-579.39	-197.51	1265.13	0.99920	0.99902
1	11	-578.88	-197.13	1264.46	0.99905	0.99888
2	12	-578.65	-196.94	1264.15	0.99882	0.99867
3	13	-578.55	-196.83	1263.99	0.99850	0.99837

4	14	-578.52	-196.76	1263.93	0.99808	0.99799
5	15	-578.54	-196.70	1263.93	0.99754	0.99749
Binary feed stage		38.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-579.58	-197.64	1265.36	0.99930	0.99911
1	11	-578.86	-197.14	1264.45	0.99919	0.99901
2	12	-578.61	-196.95	1264.13	0.99901	0.99885
3	13	-578.51	-196.84	1263.97	0.99877	0.99862
4	14	-578.45	-196.77	1263.90	0.99845	0.99833
5	15	-578.48	-196.73	1263.89	0.99803	0.99794
Binary feed stage		39.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-579.37	-197.52	1265.12	0.99935	0.99916
1	11	-578.85	-197.14	1264.45	0.99926	0.99908
2	12	-578.61	-196.96	1264.12	0.99913	0.99895
3	13	-578.48	-196.85	1263.95	0.99894	0.99878
4	14	-578.44	-196.79	1263.88	0.99870	0.99856
5	15	-578.43	-196.74	1263.86	0.99837	0.99826
Binary feed stage		40.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-579.37	-197.52	1265.13	0.99933	0.99914
1	11	-578.86	-197.14	1264.45	0.99926	0.99908
2	12	-578.60	-196.95	1264.11	0.99916	0.99898
3	13	-578.48	-196.85	1263.94	0.99902	0.99886

4	14	-578.43	-196.79	1263.86	0.99884	0.99868
5	15	-578.41	-196.75	1263.84	0.99859	0.99846

Table A.13 Feed location sensitivity analysis report for actual tray number of 86 in DWC

Solvent rate:33						
Binary feed stage		40.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-576.06	-182.26	1232.36	0.99915	0.99897
1	11	-575.66	-181.95	1231.82	0.99899	0.99882
2	12	-575.67	-181.91	1231.81	0.99880	0.99861
3	13	-575.68	-181.88	1231.82	0.99854	0.99836
4	14	-575.70	-181.86	1231.84	0.99821	0.99805
5	15	-575.74	-181.83	1231.86	0.99781	0.99767
6	16	-575.80	-181.80	1231.89	0.99731	0.99721
Binary feed stage		41.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-576.03	-182.27	1232.35	0.99923	0.99905
1	11	-575.63	-181.96	1231.81	0.99911	0.99893
2	12	-575.66	-181.92	1231.80	0.99897	0.99876
3	13	-575.65	-181.89	1231.80	0.99876	0.99856
4	14	-575.67	-181.88	1231.82	0.99850	0.99832
5	15	-575.70	-181.85	1231.83	0.99818	0.99801
6	16	-575.73	-181.82	1231.86	0.99777	0.99764

Binary feed stage		42.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-576.02	-182.27	1232.36	0.99927	0.99908
1	11	-575.63	-181.96	1231.80	0.99917	0.99898
2	12	-575.63	-181.93	1231.80	0.99906	0.99885
3	13	-575.64	-181.90	1231.80	0.99891	0.99870
4	14	-575.64	-181.88	1231.81	0.99870	0.99850
5	15	-575.68	-181.86	1231.82	0.99845	0.99826
6	16	-575.71	-181.85	1231.84	0.99813	0.99796
Binary feed stage		43.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-576.03	-182.27	1232.36	0.99924	0.99906
1	11	-575.62	-181.96	1231.81	0.99916	0.99897
2	12	-575.63	-181.93	1231.79	0.99908	0.99887
3	13	-575.65	-181.91	1231.79	0.99897	0.99876
4	14	-575.64	-181.89	1231.80	0.99882	0.99861
5	15	-575.67	-181.87	1231.81	0.99862	0.99842
6	16	-575.68	-181.86	1231.82	0.99837	0.99819
Binary feed stage		44.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-576.04	-182.26	1232.36	0.99913	0.99896
1	11	-575.65	-181.96	1231.81	0.99907	0.99889
2	12	-575.64	-181.92	1231.80	0.99902	0.99882
3	13	-575.63	-181.91	1231.79	0.99895	0.99873

4	14	-575.64	-181.89	1231.80	0.99884	0.99863
5	15	-575.65	-181.88	1231.80	0.99870	0.99849
6	16	-575.67	-181.87	1231.81	0.99851	0.99832
Binary feed stage		45.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-611.19	-153.10	1165.28	0.98356	0.98458
1	11	-575.67	-181.95	1231.83	0.99890	0.99873
2	12	-575.65	-181.91	1231.81	0.99887	0.99867
3	13	-575.65	-181.90	1231.80	0.99882	0.99862
4	14	-575.64	-181.89	1231.79	0.99876	0.99855
5	15	-575.66	-181.88	1231.80	0.99867	0.99847
6	16	-575.66	-181.87	1231.81	0.99854	0.99834
Binary feed stage		46.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-576.09	-182.24	1232.39	0.99869	0.99855
1	11	-575.69	-181.93	1231.85	0.99865	0.99850
2	12	-575.66	-181.91	1231.83	0.99863	0.99846
3	13	-575.67	-181.89	1231.81	0.99861	0.99842
4	14	-575.67	-181.87	1231.81	0.99858	0.99838
5	15	-575.69	-181.87	1231.82	0.99853	0.99833
6	16	-575.68	-181.87	1231.82	0.99845	0.99826

Table A.14 Feed location sensitivity analysis report for actual tray number of 93 in DWC

Solvent rate:31						
Binary feed stage		43.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-604.73	-183.66	1230.66	0.99930	0.99911
1	11	-604.26	-183.31	1230.02	0.99917	0.99900
2	12	-604.18	-183.23	1229.92	0.99902	0.99884
3	13	-604.19	-183.21	1229.93	0.99883	0.99865
4	14	-604.21	-183.19	1229.93	0.99859	0.99843
5	15	-604.24	-183.17	1229.95	0.99830	0.99815
Binary feed stage		44.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-649.72	-139.90	1130.18	0.96936	0.97136
1	11	-636.67	-152.11	1158.70	0.97949	0.98083
2	12	-604.19	-183.24	1229.91	0.99916	0.99897
3	13	-604.18	-183.22	1229.92	0.99901	0.99881
4	14	-604.20	-183.20	1229.92	0.99881	0.99863
5	15	-604.21	-183.18	1229.93	0.99857	0.99840
Binary feed stage		45.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-604.95	-183.80	1230.92	0.99945	0.99924
1	11	-604.24	-183.32	1230.03	0.99935	0.99916
2	12	-604.17	-183.24	1229.91	0.99926	0.99906
3	13	-604.17	-183.22	1229.90	0.99913	0.99893

4	14	-604.18	-183.21	1229.92	0.99898	0.99878
5	15	-604.19	-183.19	1229.92	0.99878	0.99860
Binary feed stage		46.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-636.82	-152.12	1158.68	0.97944	0.98079
1	11	-604.25	-183.32	1230.02	0.99938	0.99918
2	12	-604.18	-183.24	1229.90	0.99930	0.99910
3	13	-604.16	-183.23	1229.91	0.99921	0.99900
4	14	-604.19	-183.22	1229.91	0.99909	0.99888
5	15	-604.20	-183.20	1229.91	0.99894	0.99874
Binary feed stage		47.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-604.70	-183.66	1230.66	0.99942	0.99923
1	11	-604.24	-183.32	1230.01	0.99935	0.99916
2	12	-604.16	-183.24	1229.90	0.99930	0.99909
3	13	-604.17	-183.23	1229.90	0.99923	0.99902
4	14	-604.17	-183.22	1229.90	0.99914	0.99893
5	15	-604.19	-183.21	1229.91	0.99903	0.99882
Binary feed stage		48.00				
Run	Solvent feed stage	COND1	COND2	RHD	IBAc	IBA
0	10	-604.74	-183.66	1230.65	0.99933	0.99915
1	11	-636.64	-152.11	1158.72	0.97946	0.98080
2	12	-604.18	-183.24	1229.90	0.99924	0.99904
3	13	-604.16	-183.23	1229.90	0.99919	0.99899

4	14	-604.18	-183.22	1229.90	0.99913	0.99892
5	15	-604.16	-183.21	1229.90	0.99905	0.99884

Table A.15 SQP report of solvent rate for actual tray number of 56 in DWC

SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	X[0] =	6.300000e+001	6.292191E+01	
Str_8_P	X[1] =	3.000000e-001	3.000000E-01	
Str_8_T	X[2] =	1.184639e+002	1.185368E+02	
Str8C1_Mole	X[3] =	1.831224e+001	1.848107E+01	
Str8C2_Mole	X[4] =	2.561009e-002	2.428936E-02	
Str8C3_Mole	X[5] =	7.365674e+001	7.465253E+01	
Objective Function		Initial Value	Final Value	
		1.622178E+03	1.640802E+03	
Equality Constraints		Initial Value	Final Value	
Str_8_P	g[0] =	0.000000e	-2.857763E-15	
Str_8_T	g[1] =	-5.127644e-004	6.287973E-08	
Str8C1_Mole	g[2] =	-1.769957e-008	6.569643E-08	
Str8C2_Mole	g[3] =	-1.368235e-006	2.193037E-08	
Str8C3_Mole	g[4] =	-9.669338e-003	6.751302E-06	
Inequality Constraints		Initial Value	Final Value	
solvent rate-LB	g[5] =	1.612902e-002	1.4869590E-02	

UB-solvent rate	g[6] =	1.562498e-002	1.6845050E-02	
IBAC-LB	g[7] =	1.198398e-004	2.2404370E-04	
IBA-LB	g[8] =	1.203353e-006	8.1233780E-05	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	11			
No. of function calls	109			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	100			
Default step size	0.003			
Max change factor	0			
Forward differences.				

Table A.16 SQP report of solvent rate for actual tray number of 65 in DWC

SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	X[0] =	4.30000E+01	4.28984E+01	
Objective Function		Initial Value	Final Value	
		1.39420E+03	1.39299E+03	
Inequality Constraints		Initial Value	Final Value	
solvent rate-LB	g[0] =	2.38096E-02	2.13903E-02	

UB-solvent rate	g[1] =	6.52174E-02	6.74263E-02	
IBAC-LB	g[2] =	3.14095E-05	2.05253E-05	
UB-IBAC	g[3] =	6.85475E-05	7.94317E-05	
IBA-LB	g[4] =	5.34442E-05	4.75847E-05	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	4			
No. of function calls	27			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	100			
Default step size	0.003			
Max change factor	0			
Forward differences.				

Table A.17 SQP report of solvent rate for actual tray number of 72 in DWC

SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	X[0] =	3.70000E+01	3.69788E+01	
Objective Function		Initial Value	Final Value	
		1.29696E+03	1.29663E+03	
Inequality Constraints		Initial Value	Final Value	

solvent rate-LB	g[0] =	2.77778E-02	2.71893E-02	
UB-solvent rate	g[1] =	2.63158E-02	2.68733E-02	
IBAC-LB	g[2] =	3.67393E-05	3.22031E-05	
UB-IBAC	g[3] =	6.32177E-05	6.77539E-05	
IBA-LB	g[4] =	5.25025E-05	5.00964E-05	
UB-IBA	g[5] =	4.75141E-05	4.99202E-05	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	4			
No. of function calls	35			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	1000			
Default step size	0.003			
Max change factor	0			
Forward differences.				

Table A.18 SQP report of solvent rate for actual tray number of 78 in DWC

SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	X[0] =	3.300000E+01	3.499998E+01	
Objective Function		Initial Value	Final Value	
		9.975930E+05	1.009496E+06	

Inequality Constraints		Initial Value	Final Value	
solvent rate-LB	$g[0] =$	0.000000E+00	6.060546E-02	
UB-solvent rate	$g[1] =$	5.714286E-02	5.683452E-07	
IBAC-LB	$g[2] =$	-1.069988E-01	-9.694506E-02	* Lower bound violation
UB-IBAC	$g[3] =$	1.070988E-01	9.704501E-02	
IBA-LB	$g[4] =$	-9.869111E-02	-8.942019E-02	* Lower bound violation
UB-IBA	$g[5] =$	9.879113E-02	8.952021E-02	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	8			
No. of function calls	25			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	1000			
Default step size	0.003			
Max change factor	0			
Forward differences.				

Table A.19 SQP report of solvent rate for actual tray number of 86 in DWC

SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	$X[0] =$	3.300000E+01	3.298892E+01	

Objective Function		Initial Value	Final Value	
		1.231057E+03	1.230896E+03	
Inequality Constraints		Initial Value	Final Value	
solvent rate-LB	$g[0] =$	3.125008E-02	3.090383E-02	
UB-solvent rate	$g[1] =$	2.941173E-02	2.973762E-02	
IBAC-LB	$g[2] =$	5.329462E-05	4.354248E-05	
UB-IBAC	$g[3] =$	4.666237E-05	5.641451E-05	
IBA-LB	$g[4] =$	6.390579E-05	5.584974E-05	
UB-IBA	$g[5] =$	3.611080E-05	4.416685E-05	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	4			
No. of function calls	35			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	1000			
Default step size	0.003			
Max change factor	0			
Forward differences.				

Table A.20 SQP report of solvent rate for actual tray number of 93 in DWC

Simultaneous Modular SQP Final Results:				
Independent Variables in User Specified Engineering Units:				
		Estimation	Final Value	
solvent rate	X[0] =	3.080000E+01	3.102652E+01	
Str_8_P	X[1] =	3.000000E-01	3.000000E-01	
Str_8_T	X[2] =	1.065947E+02	1.065630E+02	
Str8C1_Mole	X[3] =	1.811234E+01	1.813165E+01	
Str8C2_Mole	X[4] =	1.759319E-02	1.710399E-02	
Str8C3_Mole	X[5] =	3.597157E+01	3.593565E+01	
Objective Function		Initial Value	Final Value	
		1.227977E+03	1.228378E+03	
Equality Constraints		Initial Value	Final Value	
Str_8_P	g[0] =	0.000000E+00	1.590243E-10	
Str_8_T	g[1] =	3.056488E-04	-5.071061E-06	
Str8C1_Mole	g[2] =	1.731977E-05	2.157118E-06	
Str8C2_Mole	g[3] =	-1.817529E-05	3.967311E-07	
Str8C3_Mole	g[4] =	4.612938E-03	-1.191853E-04	* Equality constraint
Inequality Constraints		Initial Value	Final Value	
solvent rate-LB	g[5] =	2.67E-02	3.42E-02	
UB-solvent rate	g[6] =	6.67E-02	5.98E-02	
IBAC-LB	g[7] =	-8.39E-05	7.93E-05	
UB-IBAC	g[8] =	1.84E-04	2.07E-05	

IBA-LB	$g[9] =$	4.60E-05	9.72E-05	
UB-IBA	$g[10] =$	5.40E-05	2.84E-06	
No. of restarts	1			
Restart Seed	0			
No. of SQP iterations	12			
No. of function calls	120			
No. of cores	4			
Parallel computing	0			
Max. iterations/thread	1000			
Default step size	0.0003			
Max change factor	0			
Forward differences.				

APPENDIX B: COST CALCULATION OF OPTIMAL PROCESSES

OPTIMAL CONVENTIONAL EXTRACTIVE DISTILLATION PROCESS:

COLUMN 1:

Type	Tray column
Material of tower	Carbon steel
Column Diameter (m)	0.762
Column Height (m)	41
Volume (m ³)	18.697
Allowable pressure (bar)	944.582
Tray area (sieve) (m ²)	0.456
Tray material	Stainless steel
Condenser area (m ²)	5.14
Reboiler area (m ²)	2.52
HEX material	Carbon steel
Reflux vessel volume (m ³)	0.5931
CEPCI 2021	776.3
CEPCI 2001	397

For tower:

$$K_1: 3.4974 \quad K_2: 0.4485 \quad K_3: 0.1074 \text{ (tower)}$$

$$C_p^\circ (2001) = 17438$$

$$F_M = 1 \text{ (carbon steel)}$$

$$F_{P,\text{vessel}} = 1.25 \text{ (0.3 bar)}$$

$$B_1 = 2.25 \quad B_2 = 1.82 \text{ (vessel)}$$

$$F_{BM} = 4.525$$

$$C_{BM} (2021) = 154300 \$$$

For trays:

$$K_1: 2.9949 \quad K_2: 0.4465 \quad K_3: 0.3961 \text{ (tray)}$$

$$C_p^\circ (2001) = 774$$

$$N = 58$$

$$f_q = 1 \text{ (N>20)}$$

$$F_{BM} = 1.8 \text{ (Table A.6 - Figure A.19)}$$

$$C_{BM} (2021) = 157992 \$$$

For condenser:

C_p° (2021) = 6050 \$ (ChemCAD-cost estimation)

$F_M = 1$ (carbon steel)

$F_P = 1$

$B_1 = 1.63$ $B_2 = 1.66$ (fixed tube sheet)

C_{BM} (2021) = 19905 \$

For reboiler:

C_p° (2021) = 14586 \$ (ChemCAD-cost estimation)

$F_M = 1$ (carbon steel)

$F_P = 1.02$ (10 bar)

$B_1 = 1.63$ $B_2 = 1.66$ (kettle reboiler)

C_{BM} (2021) = 48562 \$

For reflux vessel (horizontal):

K_1 : 3.5565 K_2 : 0.3776 K_3 : 0.0905 (vessel)

C_p° (2001) = 2989

$F_M = 1$ (carbon steel)

$F_{P,vessel} = 1.25$ (0.3 bar)

$B_1 = 1.49$ $B_2 = 1.52$ (horizontal vessel)

C_{BM} (2021) = 19812 \$

COLUMN 1 COST = 400570 \$

COLUMN 2:

Type	Tray column
Material of tower	Carbon steel
Column Diameter (m)	0.6096
Column Height (m)	19
Volume (m ³)	5.55
Allowable pressure (bar)	944.582
Tray area (sieve) (m ²)	0.164
Tray material	Stainless steel
Condenser area (m ²)	5.14
Reboiler area (m ²)	6.86

HEX material	Carbon steel
Reflux vessel volume (m ³)	0.5931
CEPCI 2021	776.3
CEPCI 2001	397

For tower:

K_1 : 3.4974 K_2 : 0.4485 K_3 : 0.1074 (tower)

C_p° (2001) = 7771

$F_M = 1$ (carbon steel)

$F_{P,vessel} = 1.25$ (0.3 bar)

$B_1 = 2.25$ $B_2 = 1.82$ (vessel)

$F_{BM} = 4.525$

C_{BM} (2021) = 68761 \$

For trays:

K_1 : 2.9949 K_2 : 0.4465 K_3 : 0.3961 (tray)

C_p° (2001) = 774

$N = 27$

$f_q = 1$ ($N > 20$)

$F_{BM} = 1.8$ (Table A.6 - Figure A.19)

C_{BM} (2021) = 128819 \$

For condenser:

C_p° (2021) = 6050 \$ (ChemCAD-cost estimation)

$F_M = 1$ (carbon steel)

$F_P = 1$

$B_1 = 1.63$ $B_2 = 1.66$ (fixed tube sheet)

C_{BM} (2021) = 19905 \$

For reboiler:

C_p° (2021) = 18936 \$ (ChemCAD-cost estimation)

$F_M = 1$ (carbon steel)

$F_P = 1.02$ (10 bar)

$B_1 = 1.63$ $B_2 = 1.66$ (kettle reboiler)

$$C_{BM}(2021) = 63044 \$$$

For reflux vessel (horizontal):

$$K_1: 3.5565 \quad K_2: 0.3776 \quad K_3: 0.0905 \text{ (vessel)}$$

$$C_p^\circ(2001) = 2989$$

$$F_M = 1 \text{ (carbon steel)}$$

$$F_{P,vessel} = 1.25 \text{ (0.3 bar)}$$

$$B_1 = 1.49 \quad B_2 = 1.52 \text{ (horizontal vessel)}$$

$$C_{BM}(2021) = 19812 \$$$

$$\text{COLUMN 2 COST} = 300341 \$$$

HEAT EXCHANGER:

Type	Fixed tube sheet
Material	Carbon steel
Area	25.17

$$K_1: 4.3247 \quad K_2: 0.3030 \quad K_3: 0.1634 \text{ (fixed tube sheet)}$$

$$C_p^\circ(2001) = 16630$$

$$F_M = 1 \text{ (carbon steel)}$$

$$F_P = 1$$

$$B_1 = 1.63 \quad B_2 = 1.66 \text{ (fixed tube sheet)}$$

$$C_{BM}(2021) = 106988 \$$$

PROCESS PUMP:

Type	Centrifugal
Material	Stainless steel
Head (m)	33
Power (MJ/h)	1.24
Efficiency	0.7

$$K_1: 3.3892 \quad K_2: 0.0536 \quad K_3: 0.1538 \text{ (centrifugal)}$$

$$C_p^\circ(2001) = 2497$$

$$F_M = 2.25 \text{ (stainless steel)}$$

$$F_P = 1$$

$$B_1 = 1.89 \quad B_2 = 1.35 \text{ (fixed tube sheet)}$$

$$C_{BM}(2021) = 24055 \text{ \$}$$

$$FCI = 400570 + 300341 + 106988 + 24055 = 831954 \text{ \$}$$

UTILITY COST:

Electricity:

$$0.344 \text{ kW.h} * 8000 * 0.13 = 358.222 \text{ \$/year}$$

Medium Pressure Steam:

$$38.6 \text{ kmol/h} * 18.02 * 8000 = 5564576 \text{ kg/year}$$

$$5564576 \text{ kg/year} * 17.4 / 1000 = 96823.6 \text{ \$/year}$$

Cooling water:

$$1927 \text{ kmol/h} * 18.02 = 34724.54 \text{ kg/h}$$

$$12572 \text{ \$/year}$$

Solvent make-up:

$$0.036 \text{ kg/h} * 8000 * 6 = 1728 \text{ \$/year}$$

$$\text{Operational Cost} = 358.222 + 96823.6 + 12572 + 1728 = 111482 \text{ \$/year}$$

$$\text{TAC} = 277250 \text{ \$/year}$$

OPTIMAL EXTRACTIVE-DIVIDING WALL COLUMN PROCESS:

DWC COLUMN:

Type	Tray column
Material	Carbon steel
Column Equivelent Diameter (m)	0.88864
Column Height (m)	51
Volume (m3)	31.631
Allowable pressure (bar)	944.582
Tray material	Stainless steel
Tray area (sieve) (m2)	0.456
HEX material	Carbon steel

Condenser1 area	5.14
Condenser2 area	2.52
Reboiler area	14.53
Reflux vessel1 volume	0.5931
Reflux vessel2 volume	0.5931
CEPCI 2021	776.3
CEPCI 2001	397

For tower:

K_1 : 3.4974 K_2 : 0.4485 K_3 : 0.1074 (tower)

C_p° (2001) = 25816

F_M = 1 (carbon steel)

$F_{P,vessel}$ = 1.25 (0.3 bar)

B_1 = 2.25 B_2 = 1.82 (vessel)

F_{BM} = 4.525

C_{BM} (2021) = 228425 \$

For trays:

K_1 : 2.9949 K_2 : 0.4465 K_3 : 0.3961 (tray)

C_p° (2001) = 774

N = 72

f_q = 1 ($N > 20$)

F_{BM} = 1.8 (Table A.6 - Figure A.19)

C_{BM} (2021) = 196128 \$

For condenser1:

C_p° (2021) = 6050 \$ (ChemCAD-cost estimation)

F_M = 1 (carbon steel)

F_P = 1

B_1 = 1.63 B_2 = 1.66 (fixed tube sheet)

C_{BM} (2021) = 19905 \$

For condenser2:

C_p° (2021) = 4775 \$ (ChemCAD-cost estimation)

$F_M = 1$ (carbon steel)

$F_P = 1$

$B_1 = 1.63$ $B_2 = 1.66$ (fixed tube sheet)

$C_{BM}(2021) = 15710$ \$

For reboiler:

$C_p^\circ(2021) = 22855$ \$ (ChemCAD-cost estimation)

$F_M = 1$ (carbon steel)

$F_P = 1.02$ (10 bar)

$B_1 = 1.63$ $B_2 = 1.66$ (kettle reboiler)

$C_{BM}(2021) = 76092$ \$

For reflux vessel1 (horizontal):

$K_1: 3.5565$ $K_2: 0.3776$ $K_3: 0.0905$ (vessel)

$C_p^\circ(2001) = 2989$

$F_M = 1$ (carbon steel)

$F_{P,vessel} = 1.25$ (0.3 bar)

$B_1 = 1.49$ $B_2 = 1.52$ (horizontal vessel)

$C_{BM}(2021) = 19812$ \$

For reflux vessel2 (horizontal):

$K_1: 3.5565$ $K_2: 0.3776$ $K_3: 0.0905$ (vessel)

$C_p^\circ(2001) = 2989$

$F_M = 1$ (carbon steel)

$F_{P,vessel} = 1.25$ (0.3 bar)

$B_1 = 1.49$ $B_2 = 1.52$ (horizontal vessel)

$C_{BM}(2021) = 19812$ \$

DWC COST = 575883

HEAT EXCHANGER:

Type	Fixed tube sheet
Material	Carbon steel

Area	25.83
------	-------

K_1 : 4.3247 K_2 : 0.3030 K_3 : 0.1634 (fixed tube sheet)

C_p° (2001) = 16698

F_M = 1 (carbon steel)

F_P = 1

B_1 = 1.63 B_2 = 1.66 (fixed tube sheet)

C_{BM} (2021) = 107423 \$

PROCESS PUMP:

Type	Centrifugal
Material	Stainless steel
Head (m)	43
Power (MJ/h)	1.74
Efficiency	0.7

K_1 : 3.3892 K_2 : 0.0536 K_3 : 0.1538 (centrifugal)

C_p° (2001) = 2441

F_M = 2.25 (stainless steel)

F_P = 1

B_1 = 1.89 B_2 = 1.35 (fixed tube sheet)

C_{BM} (2021) = 23522 \$

FCI = 575883 + 107423 + 23522 = 706828 \$

UTILITY COST:

Electricity:

0.483 kW.h * 8000 * 0.13 = 502.7 \$/year

Medium Pressure Steam:

35.9 kmol/h * 18.02 * 8000 = 5175344 kg/year

5175344 kg/year * 17.4 / 1000 = 90051 \$/year

Cooling water:

1796 kmol/h * 18.02 = 32364 kg/h

11718 \$/year (cooling tower)

Solvent make-up:

$0.044 \text{ kg/h} * 8000 * 6 = 2112 \text{ $/year}$

Operational Cost = $502.7 + 90051 + 11718 + 2112 = 104384 \text{ $/year}$

TAC = 245221 \$/year



APPENDIX C: CO₂ EMISSION RATES CALCULATIONS OF OPTIMAL PROCESSES

OPTIMAL EXTRACTIVE DISTILLATION PROCESS:

RHD1: 663 MJ/h RHD2: 736 MJ/h

$$\lambda_{sys} = 2015.3 \text{ kJ/kg}$$

$$h_s = 2778 \text{ kJ/kg}$$

$$Q_{sys} = (663 + 736) * 1000 / 3600 = 440.6 \text{ kJ/s}$$

$$Q_{fuel} = (440.6 \text{ kJ/s}) / (2015.3 \text{ kJ/kg}) * (2778 - 419 \text{ kJ/kg}) * (2073.15 - 298.15) / (2073.15 - 433.15) = 492.188 \text{ kJ/s}$$

$$[CO_2] = 492.188 / (51600 \text{ kJ/kg}) * (0.754) * (3.67) = 0.026 \text{ kg/s}$$

$$[CO_2] = 0.026 \text{ kg/s} * 3600 = 95.02 \text{ kg/h}$$

OPTIMAL EXTRACTIVE-DIVIDING WALL COLUMN PROCESS:

RHD: 1299 MJ/h

$$\lambda_{sys} = 2015.3 \text{ kJ/kg}$$

$$h_s = 2778 \text{ kJ/kg}$$

$$Q_{sys} = 1299 * 1000 / 3600 = 360.8 \text{ kJ/s}$$

$$Q_{fuel} = (360.8 \text{ kJ/s}) / (2015.3 \text{ kJ/kg}) * (2778 - 419 \text{ kJ/kg}) * (2073.15 - 298.15) / (2073.15 - 433.15) = 457.006 \text{ kJ/s}$$

$$[CO_2] = 457.006 / (51600 \text{ kJ/kg}) * (0.754) * (3.67) = 0.0245 \text{ kg/s}$$

$$[CO_2] = 0.0245 \text{ kg/s} * 3600 = 88.23 \text{ kg/h}$$