Pressure Swing Distillation Simulation of Two Azeotropic Systems of TAME- (2-butanol) and MTBE-Ethanol

by

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CERTIFICATE

This is to certify that the work incorporated in this Master's thesis entitled, "**Pressure Swing Distillation of Two Azeotropic Systems of TAME- (2-butanol) and MTBE-Ethanol**", submitted by K. Anandan *to* the Academy of Scientific and Innovative Research (AcSIR), in partial fulfillment of the requirements for the award of the Degree of Master of Technology embodies original research work carried-out by the student. We, further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material(s) obtained from other source(s) and used in this research work has/have been duly acknowledged in the thesis. Image(s), illustration(s), figure(s), table(s) etc., used in the thesis from other source(s), have also been duly cited and acknowledged. It is also certified that this work done by the **K. Anandan**, under my supervision, is plagiarism free.

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ABSTRACT

In this research work Steady state simulation of two Minimum Boiling Azeotropic Systems TAME-2-Butanol and MTBE and Ethanol, which are gasoline additives, is being studied for the Pressure Swing Distillation (PSD). In PSD the change in azeotropic point due to pressure is exploited for the separation of the azeotropes by employing the Low-Pressure Column and High-Pressure Column for the Minimum boiling Azeotropic systems. In this work Pressure of 1 atm and 10 atm is taken for both the systems.

The work has been done till finding the Total Annual Cost (in terms of Millions per year) of the PSD of the Systems, by optimizing the parameters such No of stages, Feed stage, reflux ratio and Distillate rate of the both LPC and HPC of the Azeotropic Systems. Satisfactory results of TAC have obtained for simulation of both systems and the results also indicate the possibility of the Heat integration of the PSD to get minimal TAC and further comparative studies between various distillation methods is possible.

OBJECTIVE OF THE THESIS

In this project the main motives are following:

1) Pressure swing Distillation of the TAME and 2-butanol system; the steady state simulations of the azeotropic system TAME and 2-butanol is done for the pressure swing distillation and optimization of the parameters also studied.

2) PSD of the MTBE and Ethanol; The PSD for the MTBE and Ethanol systems is done in steady state in aspen plus also various parameters are optimized for TAC.

3) Cost analysis: Both the System have Total Annual Cost (TAC) analyzed based on the optimized parameters.

4) Novel Work: PSD work of the systems have not been reported in any sources.

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1. Introduction

Azeotrope is the state in which the liquid and gaseous phase become constant when it the system is in equilibrium. Azeotropic mixtures are also interchangeably called as the constant boiling mixtures. In this there is a difficulty in the separation of the component beyond the azeotropic point as there become two or more distillation boundaries depending upon the systems. An azeotropic mixture can be formed between two or more components simultaneously, like Binary(common), ternary, quaternary and multicomponent azeotropes [1]

1.2. Types of the Azeotrope

1.2.1. In terms of the Boiling Points

1.2.1.1. Minimum Boiling Azeotropic mixture

Minimum-boiling azeotropes can occur weather the constituents of substance are different and opposing forces are high. This is indicated by activity coefficients greater than unity. In the Minimum boiling mixture, the Azeotrope has the Minimum boiling point than pure components of the system. It follows positive deviation from the Raults Law so it is also called as the positive azeotrope. Ethanol and water, acetone and methanol, and isopropanol and water are typical instances. Most of the systems i.e >90% fall under this category of the azeotropic systems [2].

1.2.1.2. Maximum Boiling Azeotropic Mixture

Maximum-Heating azeotropes can occur weather the constituents of substance are attracted to one another and the less than unity activity coefficients. In the Maximum heating Mixture, the azeotrope has Higher boiling Point than the pure components of the system. Due to its negative deviation from the Raults Law it is also known as Negative Azeotrope. Some of the Azeotropic mixture such as Acetone -Chloroform, Water-Formic Acid, Methyl Acetate-Chloroform.

1.2.1.3 Double Azeotrope

Sometime the Azeotropic mixture shows both Minimum and Maximum Boiling type. It (Gmehling et al 1977) has been seen that in the case of the Benzene-hexafluorobenzene 2 distinct azeotropic points had occurred for the temperature range of 30-80 ^{o}C [13]. This behaviour was also reported by Christensen and Olsen 1992 for the system Acetic acid - Isobutyl Acetate for which they reasoned strong real behaviour shown in the gaseous phase.

1.2.2. In terms of the State of the Azeotrope

1.2.2.1 Homogeneous Azeotrope

In this type of Azeotropic mixture the both the liquid phases are perfectly in miscible condition. The Vapour Liquid Equilibrium (VLE) is used for the computing the systems' liquid and vapour phases. Typical example includes Acetic Acid-Water, Toluene-Ethanol and THF-Water.

1.2.2.2. Heterogenous Azeotrope

Decanter must be used as part of the separation configuration in order to prevent heterogeneous (two liquid phases) minimum-boiling azeotropes from forming in the event that the repulsive forces are very high. In this type of systems Vapor- Liquid-Liquid Equilibrium (VLLE) is used for the calculating the concentration of the Vapor and Liquid phase of the systems. Water-toluene and Water-Benzene are typical examples.

2. Different distillation processes for separating an azeotropic mixture

2.1 Zero-Point Distillation Method

Azeotropic distillation is a specialized process utilized to separate the components of an azeotropic mixture. Azeotropic mixtures are made up of two or more liquids that are almost identical in their proportions to each other in the vapours that are produced during boiling, making them impossible to separate by straightforward distillation. To break the azeotrope, an additional component called an “entrainer” is introduced. The entrainer has a low boiling point and low density. In this type of distillation, using one or more pure components, the entrainer creates an azeotrope., resulting in a heterogeneous azeotrope. Following the removal of the heavier component from the first column's bottom, the heterogeneous mixture can be separated in a decanter. However, due to the added costs associated with using a decanter and purity concerns, this method is receiving less attention nowadays.

2.2 Distillation by Extractive Method

Distillation by Extractive Method is a widely used technique that dates to the World War II era [6,7]. In contrast to azeotropic distillation, extractive distillation (ED) involves the addition of a third component known as the solvent. This solvent has a high boiling point and is added to the azeotropic mixture within the extractive distillation column (EDC). The mixture's constituents interact with the solvent, raising their respective volatilities. As a result, the azeotrope is efficiently broken in the distillation columns. Importantly, the mixture's constituents do not cause the solvent to create an azeotrope.

Compared to azeotropic distillation, extractive distillation typically uses a smaller amount of solvent, which reduces energy consumption and, consequently, the total annual costs [7]. Here is how the process works: The extractive distillation column's top is where the lighter component is removed. The solvent is injected onto the Solvent Recovery Distillation Column (SRDC) together with the heavier part of the azeotropic mixture. The solvent is extracted from the bottom of the SRDC, and the other component is extracted from the top. The recovered solvent can be recycled back to the EDC for continuous processing, along with some makeup 2. In summary, extractive distillation relies on the strategic use of a solvent to modify the relative volatilities of components, enabling efficient separation in non-constant boiling point mixtures [3]. It is a valuable technique in the chemical and petroleum industry for separating challenging mixtures.

2.3 Reactive Distillation

This process employs a distinctive approach in chemical engineering known as process integration. Reactive distillation uses a single column to conduct both reaction and separation. Over the past few decades, this process has gained popularity due to advancements in process simulation [8,10]. However, it is important to note that not every reaction is suitable for this method; esterification reactions are more commonly encountered. The process involves three distinct zones: Rectifying zone, Reaction zone, and Stripping zone.

2.4 Pressure Swing Distillation

Recently, distillation without involving a third component has gained popularity, Pressure Swing Distillation despite the process and principles being known for over 50 years. The underlying concept is that altering pressure affects the relative volatility of a liquid mixture. As pressure rises, the azeotropic point moves in the direction of the light essential component's lower content [3]. Here’s how it works: when the feed containing the azeotropic mixture enters the low-pressure column (LPC), The heavy key part breaks away at the base of the column. Meanwhile, the azeotropic mixture at LPC pressure comes from the LPC distillate. To achieve a feasible system, a pump is used to increases the pressure by at least 10-15 degrees to shift the azeotropic point [2,9]. The high-pressure stream then enters the Elevated column pressure (HPC), where the light key component of the azeotropic mixture is separated from the bottom. The azeotropic mixture at HPC pressure exits through the HPC distillate and is recycled back to the LPC. In cases where the azeotrope is insensitive to pressure changes, entrainers are used in small amounts to adjust relative volatility along with pressure [11]. Interestingly, during simulations, an abnormality occurs: the vapor pressure crossover. Beyond a certain pressure

point, the low vapor pressure component becomes the high vapor pressure component, even though the component densities do not cross over. Luyben [12] observed this phenomenon but did not explain why it occurs. It is related to the Bancroft Point, when the compound's heat of vaporisation exceeds its partial molar excess enthalpy, the two components' vapour pressures equalise at this point. The size and polarity of the compound are the main factors that determine the heat of vaporisation. The amount of vaporisation heat has a direct influence on the slope (dT/dP) of the vapor pressure curve at any given point [13]. Advantages include; Cost-Effective Solution: The investment cost is lower due to the reduced number of distillation columns compared to entrainer-based concepts. Energy Efficiency: Continuous pressure swing distillation (PSD) operations result in significant energy savings. No Need for Entrainer: Unlike other methods, PSD does not require additional substances (such as an entrainer) for the separation process. Nevertheless, the Pressure Swing Distillation (PSD) process comes with several drawbacks. These include increased operational complexity, necessitating more complex process management and more advanced automation. Furthermore, because industrial applications are not published frequently, there is a lack of experimental data in the literature. Reliable experimental studies are still rare despite the body of theoretical knowledge that already exists, in part because PSD operations are usually restricted to air circumstances. Gathering data under non-atmospheric conditions such as more than 10 bar is challenging and expensive [14,15].

2.5. Pervaporation

In this method of separation membrane is used to create a bridge between the liquid and gaseous phase of the components. The components' varying partial pressures on either side of the membrane usually provide the driving force. Interestingly, relative volatility does not play a significant role in this process. Furthermore, it is not only applicable to vapor-liquid equilibrium (VLE) but also extends to liquid-liquid extractions. However, one drawback is that the mass transfer process for breaking an azeotrope through a thick membrane can be quite slow.

3. Vapour Liquid Equilibrium

A chemical species' distribution between a vapour phase and a liquid phase is known as vapor-liquid equilibrium, or VLE. It is given by,

$$f_i^v = f_i^l \quad \text{..... (1)}$$

Where f_i^v= Component i fugacity during the vapour phase

f_i^l= fugacity of component i in the liquid state

Further evaluating the equation gives,

$$Y_i P = x_i \gamma P_i^* \text{..... (2)}$$

4. Liquid Activity coefficient models

4.1 Wilson Model

An expression for the liquid activity coefficient can be found using the Wilson Model, which is useful for extremely nonideal systems, especially alcohol-water mixes;

$$\ln \gamma_i = 1 - \ln\left(\sum_j A_{ij} x_j\right) - \sum_j \frac{A_{ji} x_j}{\sum_k A_{jk} x_k}$$

where

$$\ln A_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij} T + \frac{e_{ij}}{T^2}$$

Figure 1:Wilson Equation (from Luyben 2010)

4.2 NRTL Model

The liquid-liquid equilibrium (LLE) and vapor-liquid equilibrium (VLE) scenarios can both be used with the extremely nonideal chemical systems that the NRTL model is appropriate for;

$$\gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T$$

$$\alpha_{ij} = c_{ij} + d_{ij}(T - 273.15\,\mathrm{K})$$

$$\tau_{ii} = 0$$

$$G_{ii} = 1$$

Figure 2: NRTL Model (from Luyben 2010)

4.3 UNIQUAC Model

Applying the UNIQUAC model to liquid-liquid equilibrium (LLE) and vapor-liquid equilibrium (VLE) scenarios is appropriate for extremely nonideal chemical systems;

$$\ln \gamma_i = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} - q_i' \ln t_i' - q_i' \sum_j \frac{\theta_j' \tau_{ij}}{t_j'} + l_i + q_i' - \frac{\Phi_i}{x_i} \sum_j x_j l_j$$

$$\theta_i = \frac{q_i x_i}{q_T}; \quad q_T = \sum_k q_k x_k$$

$$\theta_i' = \frac{q_i' x_i}{q_T'}; \quad q_T' = \sum_k q_k' x_k$$

$$\Phi_i = \frac{r_i x_i}{r_T}; \quad r_T = \sum_k r_k x_k$$

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

$$t_i' = \sum_k \theta_k' \tau_{ki}$$

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij} T + \frac{e_{ij}}{T^2} \right)$$

$$z = 10$$

Figure 3:UNIQUAC Model (from Luyben 2010)

5. About the Chemical Components

5.1 TAME And 2-Butanol System

TAME

Most countries utilise tert-amyl methyl ether, or TAME, as a petrol addition due to its capacity to cut carbon emissions and comply with clean air regulations. The tame is a member of the extended circle of oxygenated gasoline additives. [17].

It has been observed that during warmer seasons, TAME lowers Reid vapour pressure, which restricts the amount of petrol products that can evaporate. TAME is noteworthy because it can reduce the amount of some volatile organic chemicals that are released into the atmosphere.

The conventional method for producing tertiary amyl methyl ether (TAME) involves combining methanol with 2-methyl-l-butene and 2-methyl-2-butene in a tubular reactor. But this reaction is reversible, and chemical equilibrium limits how far it can go. Reactant excesses (e.g., methanol, 2-methyl-l-butene, or 2-methyl-2-butene) are frequently used to increase TAME production, resulting in an excess of that reactant in the reactor effluent.

The effluent is subsequently directed to a downstream separation system, which typically includes one or more distillation columns. By using these columns, TAME is purified in compliance with the criteria needed for petrol additives. Methanol with the C5 components produce an azeotrope, as was previously indicated. However, due to the reversible nature of the chemical reaction involved in production, there are limitations imposed by the azeotrope formation. In a study [16], to separate the methanol-C5 azeotrope and guarantee continuous production, a comparison between extractive distillation and pressure swing distillation was made.

2-Butanol

2-butanol serves multiple purposes, including its use as a solvent, paint remover, flavouring agent, and in the production of Methyl Ethyl Ketone (MEK). Additionally, it finds applications in pharmaceutical drug preparations. Given the urgent need to identify alternative, low-carbon-emission sources for gasoline products, blending 2-butanol with gasoline additives becomes crucial. This blend not only enhances performance but also minimizes environmental pollution. Approximately 95% of sec-butanol is dedicated to MEK production, while the remaining portion supports other processes such as solvents and paint removers.

The typical production of sec-butanol involves indirect hydration of butenes (1-butene and 2-butene) using sulfuric acid. Alternatively, 2-butanol can be derived from biomass through fermentation.

5.2. MTBE and Ethanol System

MTBE

MTBE is the most used chemical for the increasing the octane number of the gasoline products. It is created when methanol and i-butenes react in the reactor. Reversibility exists in the reaction and forms the azeotrope of the methanol and MTBE [19]. MTBE is also less toxic and good alternative to traditional gasoline products. This chemical is part of the Oxygenate group of family and almost 85% of the reformulated gasoline contains MTBE. It also meets the Clean Air Act amendments 1990[20]. The MTBE found its use as solvent also [19].

Ethanol

Mainly ethanol is produced from the bioethanol by fermentation of the corn sugarcane and other cellulosic materials. It is also produced by distillation of the petroleum products. Main uses of the Ethanol are used as the solvents in many industries including paint, pharmaceuticals, household, cosmetics, etc but more importantly it is used as the gasoline additive to increase the octane number [22].

6. LITERATURE SURVEY

6.1 Vapour Liquid Equilibrium Data

The TAME and 2-Butanol VLE data [23] reported the isobaric VLE calculations of the TAME and 2-Butanol for the pressure range 50kPa, 75kPa and 94 kPa. In this research article the author confirmed that there is minimum boiling azeotrope exist between the TAME and 2-Butanol in all the three pressure ranges and the azeotrope is sensitive to the Pressure change. NRTL, Wilson and UNIQUAC models are used as activity coefficient models and it was found that the Wilson Model is the best fit.

For the MTBE and Ethanol system the VLE data [24] shows that Isobaric VLE has been reported for the pressure range of 50kPa, 75kPa and 94kpa. But in this article it has been noted that the at 50 kPa and below there is no azeotropic behaviour shown but for the 75 and 94 kPa there is Minimum boiling azeotrope shown by the chemicals. Similar to the above case the Azeotropic system is sensitive to the pressure. After correlating the Activity coefficient and the boiling points with mole fraction using NRTL, Wilson and UNIQUAC Equations it has been found that Wilson model shows the best fit.

6.2 Material Balance for the Pressure Swing Distillation:

In the Pressure Swing Distillation one of the Most important things is that the material balance. In [12] Luyben has emphasised the importance of material balance. It is given by,

Overall,

$$F = B_1+B_2\ldots\ldots\ldots\ldots()$$

$$zF = B_1x_{B1}+B_2x_{B2}\ldots\ldots\ldots()$$

Bottom Flow rate balances

$$B_2 = F(z-x_{B1})/x_{B2}-x_{B1}\ldots. ()$$

$$B_1 = F-B_2\ldots\ldots\ldots ()$$

For column of low pressure (LPC),

$$F+D_2 = B_1+D_1\ldots\ldots\ldots ()$$

$$zF+D_2x_{D2} = B_1x_{B1}+D_1x_{D1}\ldots\ldots\ldots ()$$

Determine the Distillate Flow Rate by Solving,

$$D_1 = F(z-x_{D2}) + B_1(x_{D2}-x_{B1})/x_{D1}-x_{D2} \ldots\ldots ()$$

$$D_2=B_1+D_1-F_2 \ldots\ldots\ldots\ldots ()$$

Where, F stands for feed flow rate(kmol/hr)

B1 and B2 are the Bottom flow rates of the LPC and HPC respectively(kmol/hr)

The distillate flow rates of the HPC and LPC are D1 and D2. (kmol/hr)

F2 is the recycle feed(kmol/hr)

z is the mole feed composition (mole fraction)

The mole fraction of the bottoms of LPC and HPC are, respectively, represented by the values x_{b1} and x_{b2}.

The mole fraction of the Distillate of LPC and HPC are, respectively, represented by the values x_{d1} and x_{d2}

6.3 Total Annual Cost Calculations

From Pravin et al [25] we can find that the overall yearly expense (TAC) calculations for the pressure swing distillation and of the Extractive distillation. Total yearly operating costs plus total capital costs divided by the payback period equals the TAC. Only the major equipment costing is done like capital cost of the vessel, condenser and reboiler and rest such as reflux drums, pumps and valves are including because the cost is negligible as compared to the former. For safety reasons, it is assumed that the column is 20% taller than it is, and that there are 0.61 metres between each tray. The equations are given below;

Column Diameter (D): Aspen tray sizing

Height (H) of a distillation column,

$H=1.2 \times 0.61 \times (NS - 2)$ (D and H are in meters)

Column cost ($) = 17640 × (D) 1.066 × (H)0.802

Condenser:

Area (m2), $Ac=Qc/(Uc \times \Delta Tlm)$

Heat transfer coefficient (Uc) = 0.852 kW/m2K

Capital cost ($) = 7296 (Ac) 0.65

Reboiler:

Area (m2), $Ar=Qr/(Ur \times \Delta Tlm)$

Heat transfer coefficient (Ur) = 0.568 kW/m2K

Capital cost ($) = 7296 (Ar) 0.65

Energy costs:

LP steam (433 K) = $7.72 per GJ

MP steam (457 K) = $8.22 per GJ

HP steam (537 K) = $9.88 per GJ

TAC= (Capital cost)/ (Payback period) +Energy cost

Payback Period = 3 years

7. PSD Simulation in Aspen Plus

1) The Vapour Liquid Data Verification and Binary parameters:

The VLE data for the TAME- 2-butanol and MTBE-ethanol systems are correlated with the in-built binary diagrams. Specifically, the T-xy and Y-X diagram are compared with NIST data.

For the TAME and 2-Butanol:

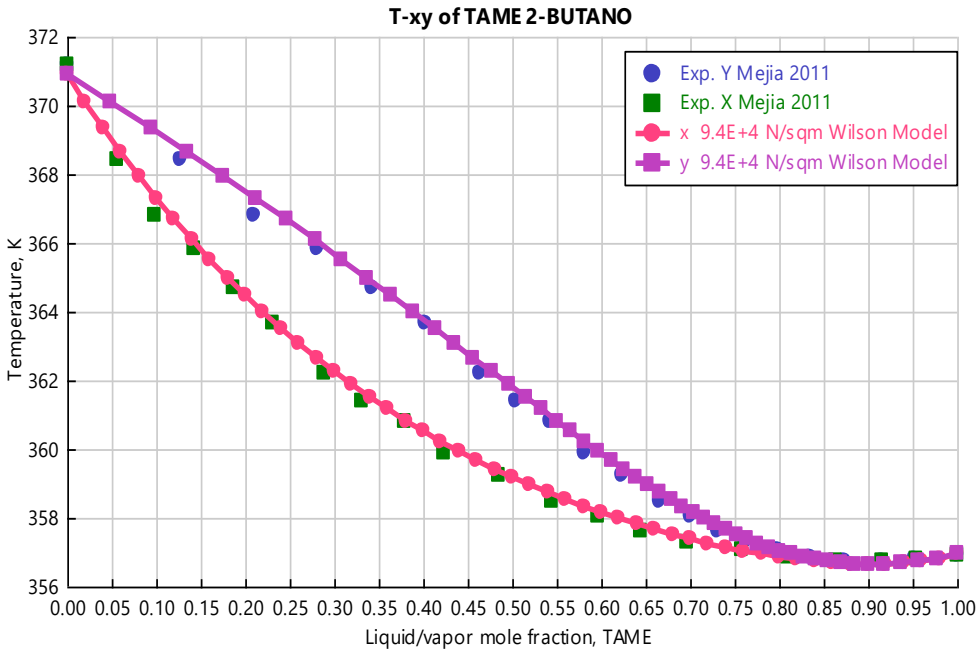


Figure 5: Comparison of the T-xy diagram NIST data and Binary Data with Wilson model for 94kPa

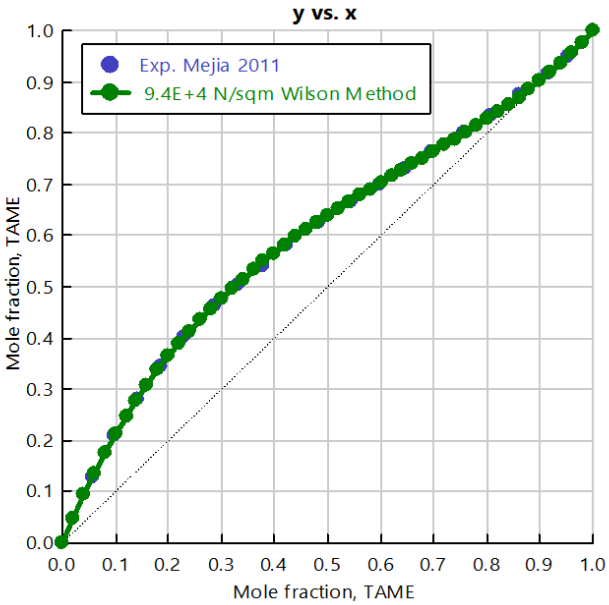
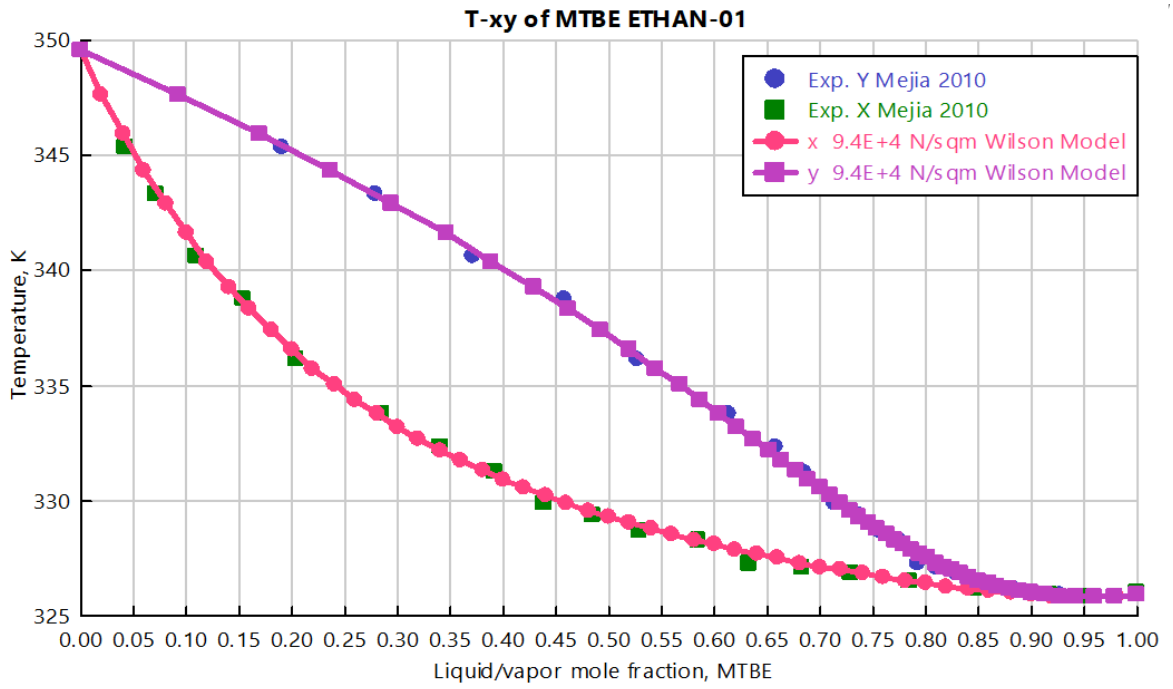


Figure 6: Comparison of the Y-X diagram NIST data and Binary Data with Wilson model for 94kPa

From the graph, we can notice that the Experimental data is closely resembling the Wilson Activity coefficient model for the TAME and 2-butanol which is also reported by the Mejia [23].

For the MTBE and Ethanol system



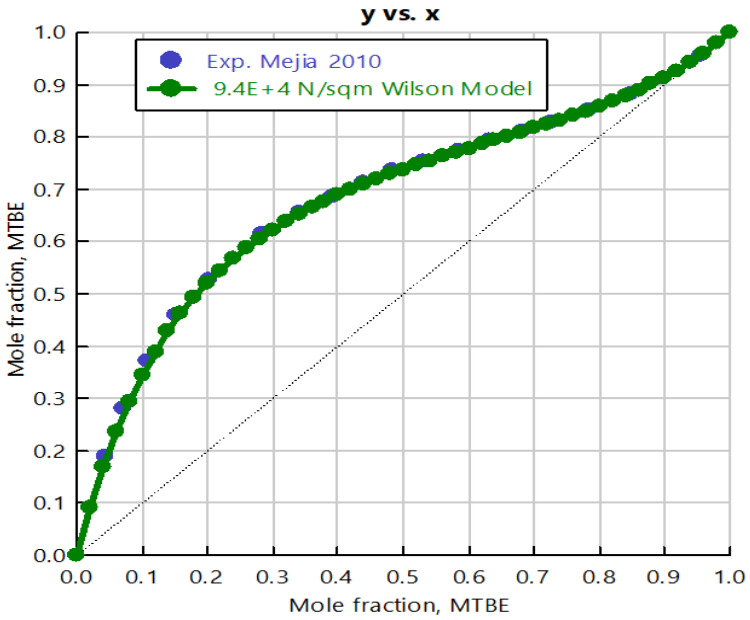


Figure 8: Comparison of the Y-X diagram NIST data and Binary Data with Wilson model for 94kPa MTBE and Ethanol system

Similarly, the Experimental data of the Mejia [24] has matching identity with the Wilson model from the Aspen Plus for the Pressure range of the 94kPa for both the T-Xy and Y-X diagram.

Binary Interactions Parameters for the both Azeotropic systems

Table 1: Binary Interaction Parameters from The Aspen Plus

Component 1	Component 2	Source	A_{ij}	A_{ji}	B_{ij}	B_{ji}	T_{low} °C	T_{high} °C
TAME	2-Butanol	NISTV121 NIST-IG	0.60452	-0.000935	-232.012	-249.744	25	95.29
MTBE	Ethanol	NISTV121 NIST-IG	0.159893	-0.161585	-163.939	-253.313	25	93.1

2) Boiling points and composition of components for 1 to 10 (atm) Pressure:

For the TAME and 2-Butanol System for the Wilson Activity coefficient model and with Vapour Liquid Phase.

Table 2: Binary Interaction Parameters from The Aspen Plus

Pressure (Atm)	Bubble Point of TAME (^{0}C)	Bubble Point of 2-Butanol (^{0}C)	Bubble Point of Azeotrope (^{0}C)	Azeotrope (Mole Fraction of TAME)
1	86.28	99.78	85.91	0.8915
2	111.25	120.11	109.81	0.7801
3	127.9	133.57	125.38	0.7801
4	140.77	143.95	137.24	0.6442
5	151.42	152.53	146.95	0.5934
6	160.59	159.91	155.23	0.5492
7	168.68	166.43	162.49	0.5092
8	175.95	172.30	168.92	0.4725
9	182.56	177.65	174.84	0.4383
10	188.65	182.59	180.22	0.4060

As it is clearly seen from the table that when the pressure is changed and additionally, the component's mole fraction in the azeotrope is altering, and the change is significant for the 10 degrees change of the pressure. It is worth noting from the table that at pressure 6 there is unusual behaviour of the crossover of Boiling point where TAME become high boiling point component than the 2-Butanol.

For the MTBE and Ethanol System for the Wilson Activity coefficient model and with Vapour Liquid Phase.

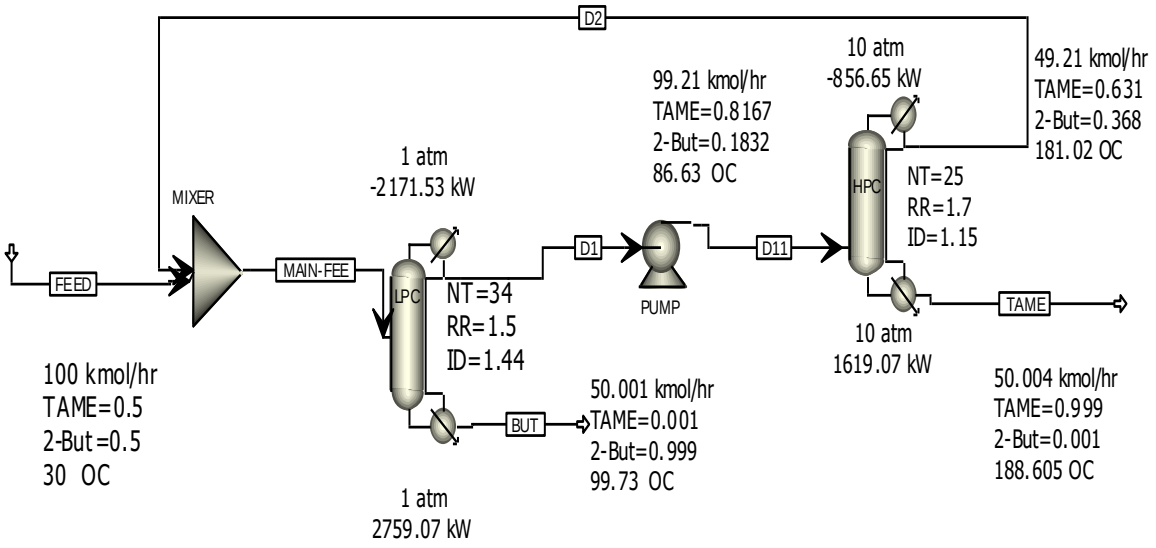
Table 3: Effect of Pressure in the MTBE and Ethanol system

Pressure (Atm)	Bubble Point of MTBE (^{0}C)	Bubble point of Ethanol (^{0}C)	Bubble Point of Azeotrope (^{0}C)	Azeotrope (Mole Fraction of MTBE)
1	55.04	78.31	54.90	0.9457
2	77.79	97.03	76.92	0.8648
3	92.97	109.13	91.20	0.8089
4	104.72	118.30	102.02	0.7650
5	114.46	125.79	110.83	0.7286
6	122.87	132.16	118.32	0.6973
7	130.32	137.74	124.85	0.6696
8	137.03	142.72	130.66	0.6448
9	143.16	147.24	135.92	0.6224
10	148.82	151.38	140.72	0.6018

Similarly for this case also it has been noticed with drastic shift in azeotropic point in the form of mole fraction of the MTBE in azeotropic composition. Because of more than 10-degree shift in azeotropic point it greatly helps in doing the simulation work. In this the increase in the Bubble point of the MTBE is steady with the Bubble point of the Ethanol. But as we can see that at 10 atm the margin between the B.P of MTBE and B.P of the Ethanol is getting less than 3 points. In this table it has not been reported but there is a cross between boiling point at 11 atm.

3) Steady State simulation of the Azeotropic systems in the Aspen Plus

Figure 9: Flowsheet of the TAME and 2-Butanol system



For the TAME and 2-Butanol system

The LPC column is kept at the Atm pressure instead of vacuum which contributes the large utility costs. The HPC column's pressure is maintained at 10 atm to accommodate the larger azeotropic shift which in turn reduces the recycle load in the LPC column. The Initials conditions for the stream and Columns are given in the table

Table 4: Feed Stream Conditions

FEED Stream		
TEMP (^{0}C)	30	
Pressure (Atm)	1	
Total flow rate(kmol/hr)	100	
Mole fraction	0.5(TAME)	0.5(2-Butanol)

The flow rate is taken as 100 kmol/hr due to the fact that it is easier for the mole calculations

and for the industrials perspective also. The temperature is kept at 30 ^{0}C for the easier handling.

Table 5: Low Pressure column initial conditions

LPC Initial Parameters	
Cal type	Equilibrium
No of stages(NT)	30
Condenser	Total
Reboiler	kettle
Valid Phase	Vapour-liquid
Convergence	Azeotropic
Operating specifications	
Distillate rate	74
Reflux Ratio	1.5
Feed Stage	16

Zf(tame)=0.5, Xb1=.005, Xb2=0.999, Also Xd1=0.8715(.2 less than the original azeotrope) Xd2=0.4260(.2 more than original azeotrope) F=100kmol/hr Following results were obtained

D1=74.19 kmol/hr , D2=16.508 kmol/hr ,B1=50.201 kmol/hr, B2=49.798kmol/hr

Table 6: High Pressure column initial conditions

HPC Initial Parameters	
Cal type	Equilibrium
No of stages (NT)	22
Condenser	Total
Reboiler	kettle
Valid Phase	Vapour-liquid
Convergence	Azeotropic
Operating specifications	
Distillate rate	16
Reflux Ratio	1.7

Feed Stage	6

Initially the No of stage (NT) of the LPC is selected to be 30 and distillate is selected to be 74 kmol/hr from the material balance and reflux ration is determined by the sensitivity analysis to get the purity of the 0.999 2-Butanol in the bottom of LPC column and it is 1.5 RR and initially the feed stage is 16 above the stage.

Similarly, for the HPC column also the initials parameters are given and it is decided that no of the stage (NT) to be 22 and D2 16 kmol/hr with RR 1.7 determined from the sensitivity analysis against the mole fraction of the TAME purity of 0.999 mole fraction in the HPC bottom. The feed Stage is given above 6 stages.

Pump is operated at 80% efficiency with discharge pressure of the 10 atm.

The design spec is added in the both columns to get desired purity of the lowermost items within the column. The distillate for the LPC column is varied from the 50-120 kmol/hr (large deviation is due to the fact of minimizing the reflux ration to 1.5) to get the desired purity of .999 Mf of the 2-butanol. Similarly the HPC column the distillate is varied from the 10-80 kmol/hr(for the matching Minium reflux ratio) for 0.999 Mf of the TAME purity.

For the MTBE and Ethanol System:

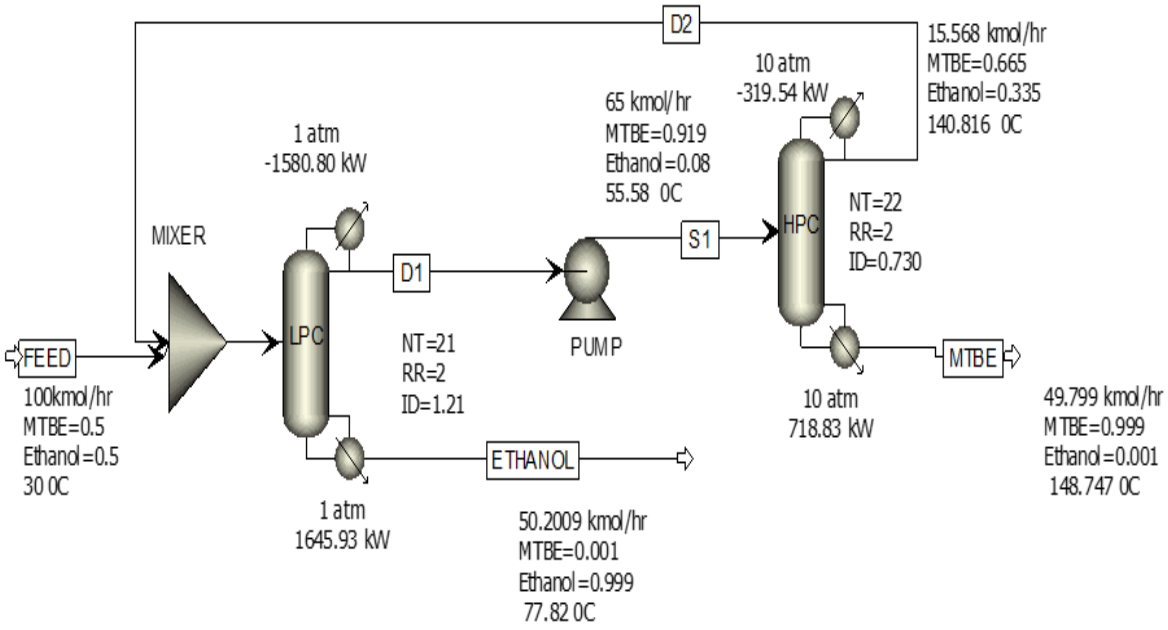


Figure 10: Flowsheet of the MTBE and Ethanol system

Table 7:Flowsheet of the MTBE and Ethanol system

FEED Stream		
TEMP (^{0}C)	30	
Pressure (Atm)	1	
Total flow rate(kmol/hr)	100	
Mole fraction	0.5(MTBE)	0.5(Ethanol)

Similarly, the flow rate is taken as 100 kmol/hr since it is easier for the mole calculations and for the industrials perspective also. The temperature is kept at 30 ^{0}C and the Pressure is kept at 10 atm with mole 0.5 MTBE and 0.5 of ethanol.

Table 8: Low Pressure column initial conditions

LPC Initial Parameters	
Cal type	Equilibrium
No of stages(NT)	25
Condenser	Total
Reboiler	kettle
Valid Phase	Vapour-liquid
Convergence	Azeotropic
Operating specifications	
Distillate rate	65
Reflux Ratio	3
Feed Stage	14

Table 9: High Pressure column initial conditions

HPC Initial Parameters	
Cal type	Equilibrium
No of stages (NT)	20
Condenser	Total
Reboiler	kettle
Valid Phase	Vapour-liquid
Convergence	Azeotropic
Operating specifications	
Distillate rate	16
Reflux Ratio	3
Feed Stage	8

From the Material balance it was found out that the bottom flow rates of LPC and HPC column are to be around 65kmol./hr and 14 kmol/hr. The No of stages (NT) of LPC is taken around 25 and RR to be 3 with Feed stage position above the 14^{th} stage of the LPC column. Similarly, for the HPC column the initial NT is selected to be around 20 and RR to be same as LPC and Feed stage to be above the 8^{Th} stage.

Design Specifications based on the distillate rate is done for the both LPC and HPC against the Purity of 0.999 mole frac of the Ethanol and MTBE. The RR is not taken as the Design Spec because as against the noted literature as there is little impact of the RR in the Purity when it comes to the Pressure swing distillation process. RR is analysed with purity and reduced to 2 for the both cases i.e LPC and HPC.

The Pump is programmed such that the discharge pressure of the pump is 10 atm with efficiency of 80 %.

8. RESULTS AND DISCUSSION

8.1 Optimization of the Parameters with the Total Annual Cost

For the TAME and 2-butanol system

For the LPC, the Total stages (NT1) range from the 30 to 34 while maintaining the same number of HPC stages. Then for after optimizing the NT of LPC for TAC the N_{T2} of the HPC is varied from 21 to 25 stages while keeping the Optimized N_{T1} of the LPC same. Feed stages are also varied for both LPC and HPC. Since in Pravin et al, he mentioned about the using the sensitivity analysis for feed stage of the LPC and HPC against their respective heat duties. But for Greater accuracy in TAC calculations, I go for the Optimization of this parameters also. The RR1 and RR2 was found to be 1.5 and 1.7 respectively after sensitivity analysis.

Table 10: TAME and 2-Butanol PSD outcomes of economic optimization for NT1

Configurations	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	30	31	32	33	34
N_{T2}	22	22	22	22	22
N_{F1}	16	16	16	16	17
RR1(optimal)	1.5	1.5	1.5	1.5	1.5
D1(metre)	1.6309	1.6279	1.6286	1.6295	1.6302
Qc(kW)	2381.363	2313.620	2280.326	2262.835	2253.389
Qr(kW)	3002.936	2924.346	2885.722	2865.396	2854.415
Total Capital Cost ($10^6$$/yr)	5.314	5.236	5.203	5.190	5.187
Overall Cost of Operations	00.348575	00.337371	000.331870	000.328978	00.327416

(MM/year)					
Total Price Per Year (MM/year)	2.120	2.082	2.066	2.059	2.056

Table 11: TAME and 2-Butanol PSD outcomes of economic optimization for NT2

Configurations	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	34	34	34	34	34
N_{T2}	21	22	23	24	25
N_{F2}	6	6	6	6	6
RR2(optimal)	1.7	1.7	1.7	1.7	1.7
D2(metre)	1.22	1.18	1.39	1.14	1.13
Qc(kW)	1038.44	970.117	920.462	888.839	856.662
Qr(kW)	1882.485	1783.518	1711.602	1658.548	1619.192
Total Capital Cost ($10^6$$/yr)	5.383	5.269	5.251	5.128	5.085
Overall Cost of Operations (MM/year)	00.353	00.338	00.327	00.319	00.315
Total Price Per Year (MM/year)	2.147	2.056	2.040	2.028	2.016

Table 12: TAME and 2-Butanol PSD outcomes of economic optimization for Nf1

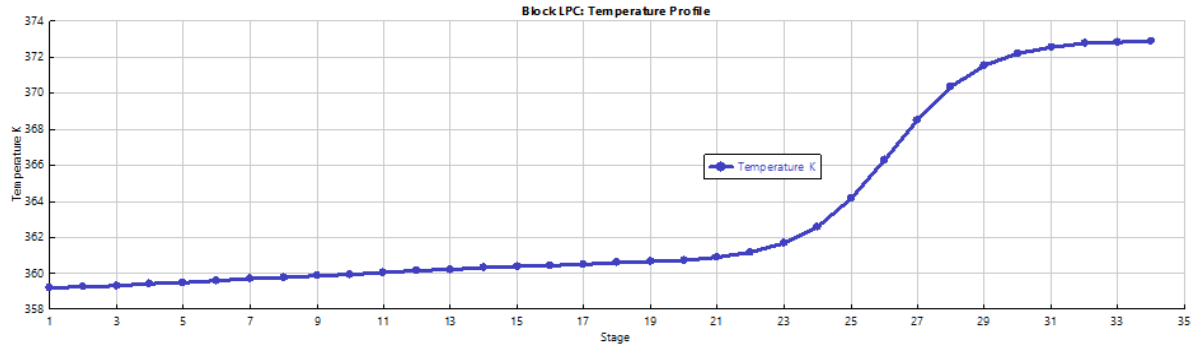
Configurations	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	34	34	34	34	34
N_{T2}	25	25	25	25	25
N_{F1}	16	17	18	19	20
RR1(optimal)	1.5	1.5	1.5	1.5	1.5
D1(metre)	1.59	1.59	1.6	1.6	1.6
Qc(kW)	2184.28	2177.48	2172.96	2171.53	2174.91
Qr(kW)	2773.83	2765.945	2760.718	2759.071	2762.998
Total Capital Cost ($10^6$$/yr)	5.085	5.098	5.093	5.080	5.087
Overall Cost of Operations (MM/year)	00.313	00.314	00.313	00.313	00.313
Total Price Per Year (MM/year)	2.016	2.011	2.010	2.0085	2.017

Table 13: TAME and 2-Butanol PSD outcomes of economic optimization for Nf2

Configuration	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	34	34	34	34	34
N_{T2}	25	25	25	25	25
N_{F2}	6	7	8	9	10

RR2(optimal)	1.7	1.7	1.7	1.7	1.7
D2(metre)	1.1323	1.1323	1.133	1.137	1.170
Qc(kW)	856.653	867.290	891.588	931.661	992.009
Qr(kW)	1619.175	1634.589	1669.783	1727.815	1815.236
Total Capital Cost ($10^6$$/yr)	5.084	5.103	5.144	5.213	5.317
Overall Cost of Operations (MM/year)	00.31343	00.31576	00.32109	00.32987	00.34310
Total Price Per Year (MM/year)	2.0081	2.016	2.0358	2.0677	2.1157

As we can see from the table 10 that Case 5 with NT1=34 gives the minimum TAC while keeping the others parameters same. Change in the diameter for each case is due to fact that there is a change in the Maximum vapour velocity and is determined by the F factor which should be equal to one otherwise the column will flood. Similarly in table 11 keeping the NT1=34 varying the NT2, we can get optimized result 25 NT2. For the Feed stages which are illustrated in the table 12 and table 13 we get optimized results in the Nf1=19 and Nf2=6 . The Final **TAC is 2.008153 ($10^6$$/yr).**



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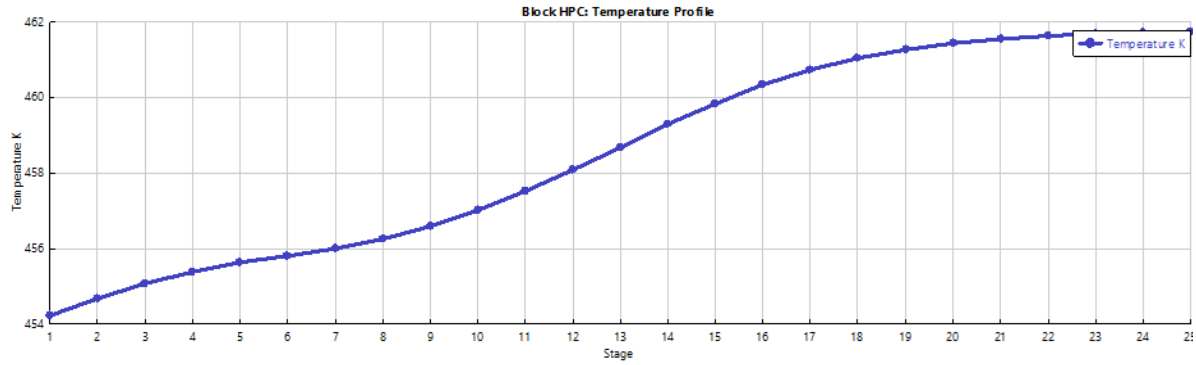
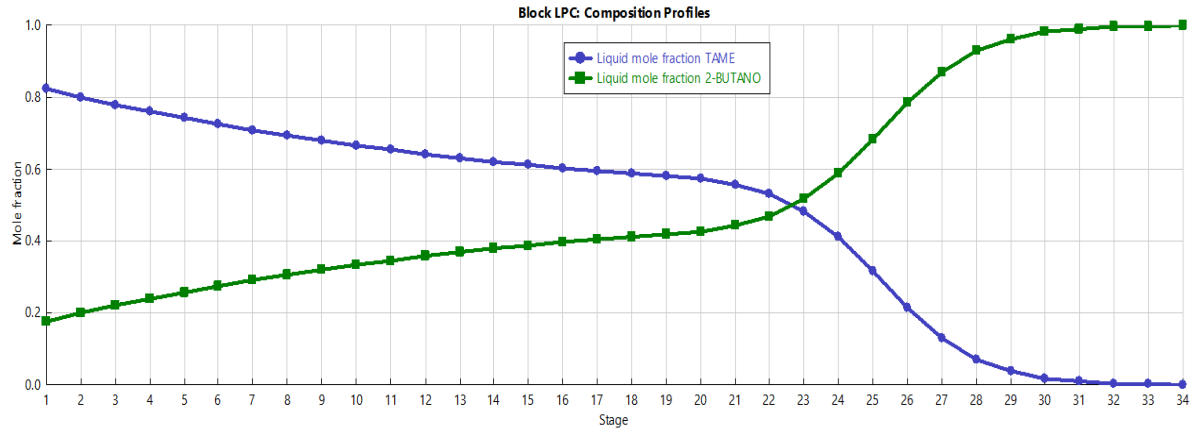
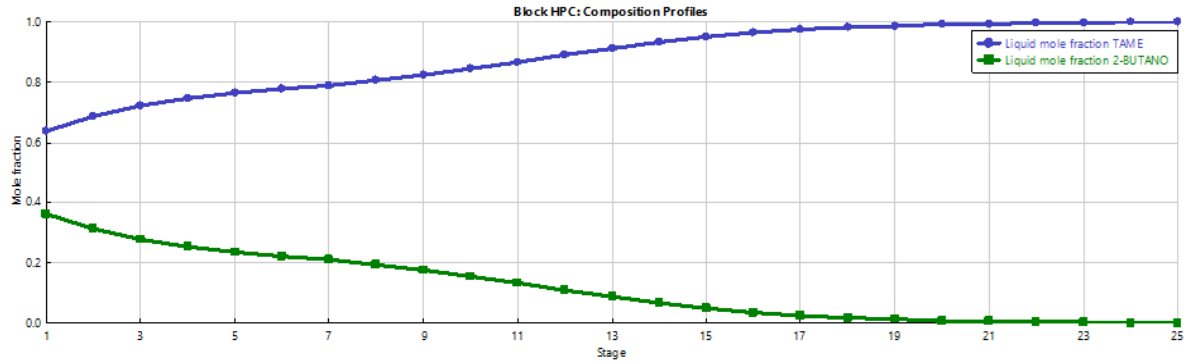


(b)

Figure 11: (a) T Profile of LPC, (b) T Profile of HPC for the TAME and 2-Butanol



(a)



(b)

Figure 12: (a) compositional breakdown of LPC, (b) compositional breakdown of HPC for the TAME and 2-Butanol

For the MTBE and Ethanol system

The Number of stages (N_{T1}) for the Between 20 and 26 LPC is varied while maintaining the NT2 of the HPC is kept same. Then for after optimizing the NT of LPC for TAC the N_{T2} of the HPC is varied from 16 to 20 stages while keeping the Optimized N_{T1} of the LPC same. Feed stages are also varied for both LPC and HPC. The RR1 and RR2 was found to be 2 for the both and decreasing or increasing the RR value can result in simulation errors which due to the limiting factor of minimum RR. Also, the Profiles namely the Temperature and Composition have been plotted for the both LPC and HPC column.

Table 14:MTBE and Ethanol PSD the results of economic efficiency for NT1

Configuration	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	21	22	23	24	25
N_{T2}	20	20	20	20	20
N_{F1}	16	16	16	16	16
RR1(optimal)	2	2	2	2	2
D1(metre)	1.232	1.232	1.232	1.232	1.232
Qc(kW)	1637.125	1637.189	1637.167	1604.42954	1604.316446
Qr(kW)	1690.440	1690.478	1690.459	1663.607	1663.513
Total Capital Cost ($10^6$$/yr)	0.6989	0.7066	0.7143	0.7117	0.7192

Overall Cost of Operations (MM/year)	00.16847	00.16847	00.16847	00.16427	00.16426
Total Price Per Year (MM/year)	00.4014	00.4040	00.4065	00.4015	00.4040

Table 15:MTBE and Ethanol PSD the results of economic efficiency for NT2

Configuration	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	21	21	21	21	21
N_{T2}	18	19	20	21	22
N_{F2}	9	9	9	10	10
RR2(optimal)	2	2	2	2	2
D2(metre)	0.777	0.752	0.756	0.745	0.743
Qc(kW)	398.004	367.266	362.9371	345.031	341.528
Qr(kW)	820.146	779.690	773.998	750.435	745.826
Total Capital Cost ($10^6$$/yr)	0.7039	0.6941	0.6989	0.6959	0.6989
Overall Cost of	00.1743	0.1692	0.1685	00.1655	00.1649

Operations (MM/year)					
Total Price Per Year (MM/year)	00.4089	00.4006	00.4014	00.3974	00.3978

Table 16:MTBE and Ethanol PSD the results of economic efficiency for NF1

Configuration	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	21	21	21	21	21
N_{T2}	21	21	21	21	21
N_{F1}	14	15	16	17	18
RR1(optimal)	2	2	2	2	2
D1(metre)	1.21	1.21	1.21	1.21	1.21
Qc(kW)	1590.640745	1584.488624	1580.838479	1580.808544	1592.552455
Qr(kW)	1653.993	1648.943	1645.950	1645.923	1655.554
Total Capital Cost (10^6\$/yr)	0.6942	0.6917	0.6910	0.6910	0.6933

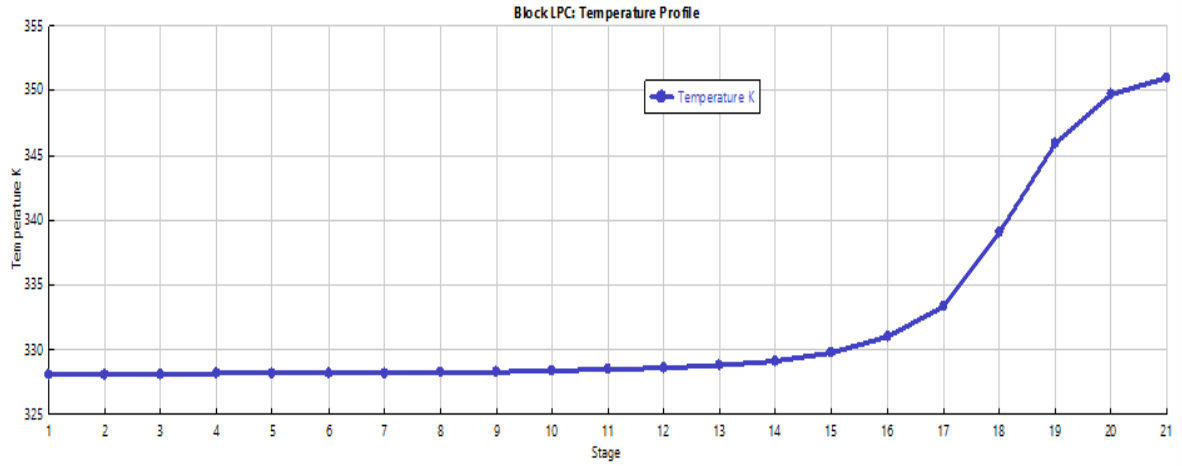
Overall Cost of Operations (MM/year)	00.1625	00.1617	0.1613	00.1613	00.1628
Total Price Per Year (MM/year)	00.3939	00.3923	00.3917	00.3916	00.3939

Table 17:MTBE and Ethanol PSD the results of economic efficiency for NF2

Configuration	Situation 1	Situation 2	Situation 3	Situation 4	Situation 5
N_{T1}	21	21	21	21	21
N_{T2}	21	21	21	21	21
N_{F2}	8	9	10	11	12
RR2(optimal)	2	2	2	2	2
D2(metre)	0.734	0.734	0.734	0.734	0.734
Qc(kW)	319.537	312.081	336.529	368.115	422.064
Qr(kW)	718.826	709.002	741.220	782.787	853.898
Total Capital Cost (10^6\$/yr)	0.6910	0.6891	0.6953	0.7033	0.7166

Overall Cost of Operations (MM/year)	0.1613	0.1600	0.1641	0.1694	0.1784
Total Price Per Year (MM/year)	0.3916	0.3897	0.3959	0.4038	0.4173

As we can see from the table 14 that Case 1 with NT1=21 gives the minimum TAC while keeping the others parameters same. Similarly in table 15 keeping the NT1=21 varying the NT2, we can get optimized result 21 NT for the HPC which is the case 4. For the Feed stages which are illustrated in the table 16 and table 17 we get optimized results in the Nf1=17 and Nf2=9 . The Final **TAC is 0.3897 ($10^6$$/yr).**



(a) And (b)

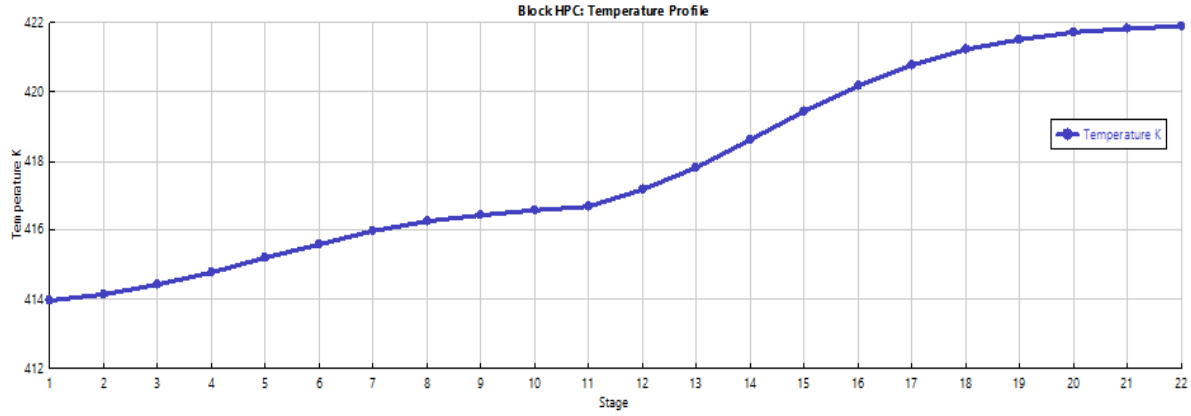
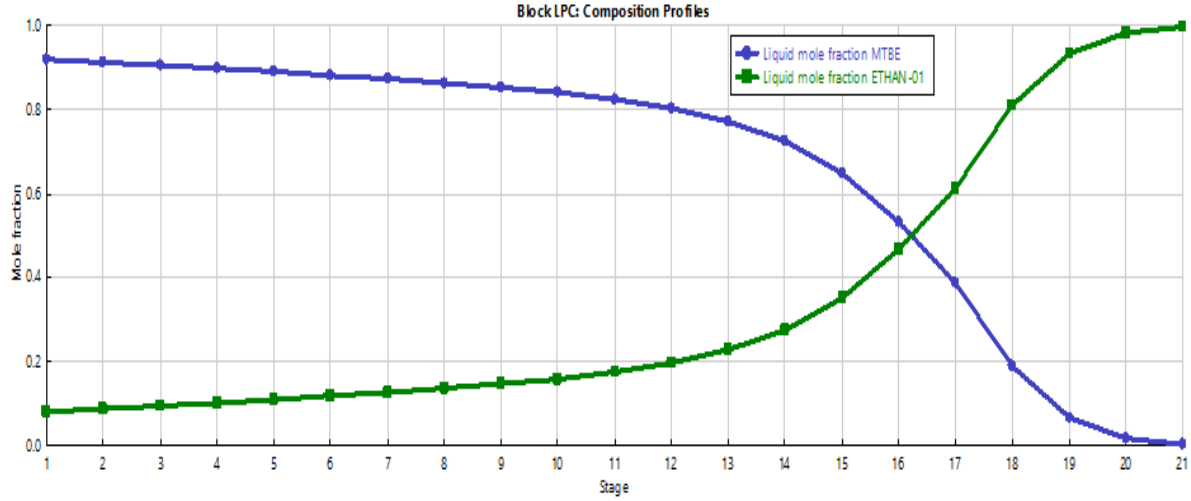
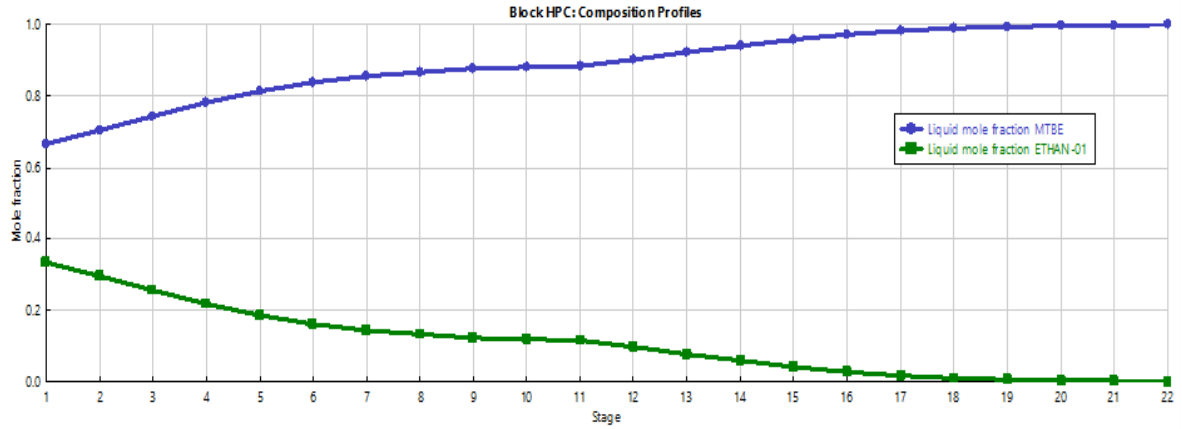


Figure 13:(a)T Profile of LPC, (b) T Profile of HPC for the MTBE and Ethanol system



(a)



(b)

Figure 14: (a) Composition profile of LPC, (b) Composition Profile of HPC of MTBE and Ethanol system

9. CONCLUSION

The study focuses on the Simulation of pressure swing distillation (PSD) in steady-state for separating azeotropic mixtures. Specifically, the systems investigated include TAME and 2-Butanol, as well as MTBE and Ethanol. The goal is needing the products to be extremely pure while minimizing the total annual cost (TAC). For both systems, the pressure conditions are set at 1 atm for the reduced pressure column (LPC) and 10 atm for the Elevated-Pressure Column (HPC). The optimized parameters involve the number of stages in each column (N_{T1} and N_{T2}), as well as the feed stages (N_{F1} and N_{F2}). The observed purity exceeds 0.999 for all desired products.

The final TAC for the TAME and 2-Butanol system is $2.008153 million per year, while for the MTBE and Ethanol system, it is $0.3897 million per year. The study concludes that PSD successfully achieves separation for both systems.

Future Perspectives of this Project:

1) Comparison Studies: Comparing this work with other distillation techniques, such as azeotropic distillation and extractive distillation.

2) Experimental Work: Considering experimental validation, especially since the separation performance remains good even at low pressures.

3) Heat Integration: Exploring the possibility of creating a heat-integrated system by utilizing differences in duties, which could further reduce the TAC.

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