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Design and Optimization of an Azeotropic Distillation Pilot Plant for the Production of Pure Ethanol

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ABSTRACT

This study aimed to design an azeotropic distillation plant using Aspen Plus® V10 software and determine optimal process conditions for producing pure ethanol greater than 95% from pre-concentrated near-azeotropic ethanol-water solution. The non-random two-liquid Redlich-Kwong thermodynamic model was the base method for property analysis and performance prediction. Modelling and simulation of the converged process were conducted for fixed column variables (R = 5, N = 12 and p = 1 atm). Plant operating parameters were varied in the range of 0 to 1 for the pre-heater vapour fraction, 2 to 10 for the column feed plates (N_{FP}), 2 to 6 for the recycle feed plate (N_{RFP}), 10 to 20 kmol/h feed flow rate (F_{AZ}) and 0.81 to 0.86 mol/mol ethanol concentration (X_{FAZ}). Results show that an increase in F_{AZ} and X_{FAZ} resulted in retrograde phenomena, which hinders plant performance while increasing energy requirements. Further, an increase in N_{FP} and N_{RFP} results in a decrease in dehydration plant performance from 99.84% to 97.5%. It was concluded that high energy efficiency and enhanced plant performance are obtained when the plant is operated with F_{AZ} ranging from 18 to 20 kmol/h. The feed and recycle plates should be located closer to the top of the column, i.e., stage 4 for the feed, stage 2 for aqueous solution and stages 1-3 for the recycle streams. The study recommends a careful distillation synthesis followed by real plant monitoring to address the retrograde phenomena effect and improve the overall ethanol dehydration plant performance.

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INTRODUCTION

Ethanol also known as ethyl alcohol is a product of sugar decomposition under the influence of, also known as ethyl alcohol, is a product of sugar decomposition that is influenced by ferments and enzymatic action. It is the most potential biofuel which can be considered asthat can be considered a fossil fuel alternative (Kumar et al., 2010; Battisti et al., 2019). Ethanol demand is rapidly increasing due to accelerated efforts in energy transition to renewable sources aiming at minimizing overdependence on fossil fuels which have significant effects on, which significantly affects the world's climatic condition. According to ChemAnalyst (2023) the global demand of for ethanol is expected to grow at a compound annual growth rate (CAGR) of 4.75% from 100 million tonnes in 2022 to 162 million tonnes in 2032. Tanzania possesses a variety of raw materials for bioethanol production, but unfortunately, they have not been utilized in large large-scale industrial production; as a result, most of ethanol for industrial use is imported, while a small amount is produced for the production of spirits. Ethanol importation in Tanzania is increasing enormously due to its demand in chemical, pharmaceutical/medical and food industries and also in research and educational sectors attributed by the increase in number of schools, colleges the chemical, pharmaceutical/medical, and food industries and research and educational sectors, which are attributed to the increase in many schools, colleges, and universities. In 2011, ethanol demand and production potential in Tanzania were yearly estimated at a rate of 568 and 4010 million litres, respectively (Mshandete, 2011). Thus, by taking 4.75% as a CAGR, ethanol demand in 2023 is expected to be 991.28 million litres. High ethanol production potential in Tanzania can be utilized in order to cover local consumption demand and exportation. However, with the current limitations in technological capacity, such production rates and qualities cannot be realized to its their fullest potential.

Ethanol produced through the fermentation process is an aqueous mixture consisting of water from which a near absolute ethanol can be obtained by repeated distillation processof water from which a near absolute ethanol can be obtained by repeated distillation (Pachón et al., 2020; Zhao *et al.*, 2021). Ethanol-water system forms a highly non-ideal minimum boiling point azeotrope having. The ethanol-water system forms a highly non-ideal minimum boiling point azeotrope with 89.5% mol of ethanol at 1 atm and 78.156℃ (Gomis *et al.*, 2015). Therefore, this property renders the production of almost pure ethanol with a molar composition greater than 89.5% by a normal distillation column impossible due to the fact that at this pointbecause there is no change in liquid and vapour compositions from tray to tray in distillation columns. The need for pure anhydrous ethanol with a molar composition of approximately greater than 95% has increased over the years because of increased efforts to reduce the transportation cost of dilute ethanol solution in the global market and to increase the value and price of the product. Use The use of ethanol as a renewable energy source will minimize environmental degradation caused by greenhouse gas emissions from fossil fuels. In the chemical industry, absolute or pure ethanol may be used as an organic solvent, a chemical reagent and an additive in detergents, paints, aerosols, medicines and perfumes. Absolute ethanol may also be used as a fossil fuel substitute and as a raw material in synthesising esters and producing synthesis of esters and production of biodiesel, pharmaceutical formulations and electronic industries (Kumar et al., 2010; Marnoto *et al.*, 2018). This has led to research and development on advanced ethanol dehydration process.

Many researchers have worked on advanced ethanol dehydration and fuel-grade ethanol production methods (Marnoto *et al.*, 2018). Various advanced ethanol dehydration methods such as vacuum distillation, reactive distillation, pressure swing distillation (Knapp and Doherty, 1992; Yu *et al.*, 2012), extractive distillation (Meirelles et al., 1992; Restrepo and Arias, 2003), liquid-liquid extraction including salting-out extraction, adsorption on molecular sieves (Garg and Ausikaitis, 1983; Weitkamp *et al.*, 1991), pervaporation (Le *et a*l., 2012; Liu *et al.*, 2021), homogeneous and heterogeneous azeotropic distillation may be used to produce pure ethanol (Gomis *et al.*, 2015; Rojas *et al.*, 2016; Miranda *et al.*, 2020; Guido *et a*l., 2021).

In this research, heterogeneous azeotropic distillation pilot plant for production of technical grade ethanol (with molar composition greater than 95%) by the use ofa heterogeneous azeotropic distillation pilot plant for production of technical grade ethanol (with molar composition greater than 95%) using cyclohexane as an entrainer is sought to address the gap between absolute ethanol demand and production in Tanzania. Selection of heterogeneous azeotropic distillation is attributed by to the fact that it is a widely practiced practised advanced separation process for strongly non-ideal and azeotropic mixtures because it offers a better separation performance as a result of natural liquid-liquid separation with no energy requirement at the decanter (Arifin and Chien, 2007; Gomis et al., 2015; Zhao et al., 2017). The design and simulation of an azeotropic distillation plant together with determination of key operating parameters for enhancement of ethanol dehydration plant performance in this research were accomplished by the use ofand determination of key operating parameters for enhancing ethanol dehydration plant performance in this research were accomplished by using Aspen Plus® V10 commercial simulation software. This research is extremely vital due to the fact that limited research on this subject matter has been conducted in Tanzania, EACbecause limited research on this subject matter has been conducted in Tanzania, EAC, and the SADC region. The research is also important because the production of pure ethanol will contribute to the national economy in terms of domestic use and export. Also, this research provides more insight and details on the behaviour of azeotropic distillation plant, main plant profiles and key parameters that may hinder the performance of ethanol dehydration plant.

METHODS AND MATERIALS

Process description

The overall process (**Figure 1**) consists of a decanter and two distillation columns acting as the main operational blocks. Distillation column 1 is the main column where azeotropic distillation is carried out, and distillation column 2 is the recycle column where the amount of entrainer in the aqueous phase from the decanter is recovered and recycled back to the main column.

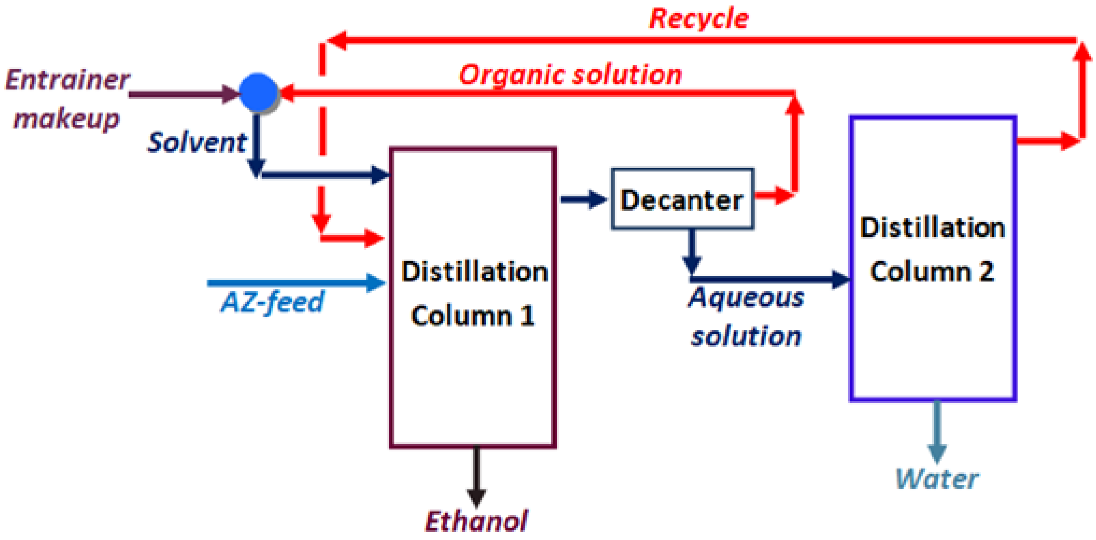


Figure 1: Heterogeneous azeotropic distillation process.

The near-azeotrope feed of ethanol-water solutions together with a sufficient amount of solvent (entrainer or cyclohexane rich solution) to effect changes in the relative volatility of the key azeotropic components are fed first into the main column. In the main column, azeotropic distillation occurs once the added mass separating agent or entrainer (cyclohexane) alters the relative volatilities of ethanol-water near azeotropic system. This results into fluid phase inverse in the column where the least volatile component in the ternary system (water) is separated first and recovered at the top of the main column, whereas, the more volatile component in the ternary system (ethanol) concentrates at the bottom of the main column. Hence, the desired product (a near absolute ethanol) is obtained from the bottom of the main column, whereas the produced vapours at the top of the main column approach a ternary heteroazeotrope of ethanol-water-cyclohexane system.

After a total condenser cools the produced vapours from the top of the main column, immiscible liquid with ethanol-water-cyclohexane molar compositions near the ternary heteroazeotrope is obtained. Therefore, the immiscible liquid is fed first into the decanter to avoid three phase distillation problems, which may lead to erroneous results and an increase in cost and energy requirements. In the decanter, natural liquid-liquid separation is conducted, i.e., gravity separation based on density segregation with no energy requirements. Natural liquid-liquid separation results in the production of organic and aqueous solution phases.

The organic solution phase from the decanter containing a high amount of entrainer (cyclohexane) is recycled back into the main column and mixed with entrainer makeup to generate the necessary amount of solvent required to effect azeotropic separation. The aqueous solution phase from the decanter contains a significant amount of ethanol. Since it falls within different distillation regions in the ternary diagram, conventional distillation can easily be carried out to recover ethanol and entrainer present in the solution. Thus, the aqueous solution phase is fed into the recycle column where conventional distillation takes place with the least volatile component in the ternary system (water) expected to be recovered at the bottom of the recycle column and the distillate with a significant amount of ethanol and cyclohexane at the top of the recycle column. The distillate from the recycle column containing significant entrainer (cyclohexane) and ethanol is then recycled back into the main column. Also, to account for the losses of entrainer (cyclohexane) in the product streams (product ethanol and water), a small amount of entrainer makeup is added so as to maintain the plant's dehydration performance.

Azeotropic distillation model build-up and convergence

The azeotropic distillation pilot plant simulation model was created using Aspen Plus® V10 simulation software. As illustrated in Figure 2, the first step taken in the azeotropic distillation model build-up and convergence was property analysis and specifications, including component specification, thermodynamic fluid package selection and distillation synthesis analysis as described in the following steps.

Step 01: The main components of azeotropic distillation process streams were clearly specified, as shown in Table **1**, so as to determine the appropriate thermodynamic fluid package to be used accurately. The main components specified are pure and of conventional type due to the fact that conventional-type components participate in phase and chemical equilibrium calculations.

Table 1: Main components for the azeotropic distillation plant process streams

Component ID	Type	Component Name	Alias	Formula
ETHANOL	Conventional	ETHANOL	C2H6O-2	C_2H_6O
WATER	Conventional	WATER	H2O	H_2O
CYCLO-01	Conventional	CYCLOHEXANE	C6H12-1	C_6H_{12}

Step 02: Non-Random Two Liquid-Redlich Kwong (NRTL-RK) thermodynamic model was selected as the base method in this study due to the fact that it is highly recommended for non-ideal chemical systems (i.e., ethanol-water systems) and it also describes vapour-liquid and liquid-liquid equilibrium data appropriately (Haghtalab *et al.*, 2011; Taqvi *et al.*, 2016).

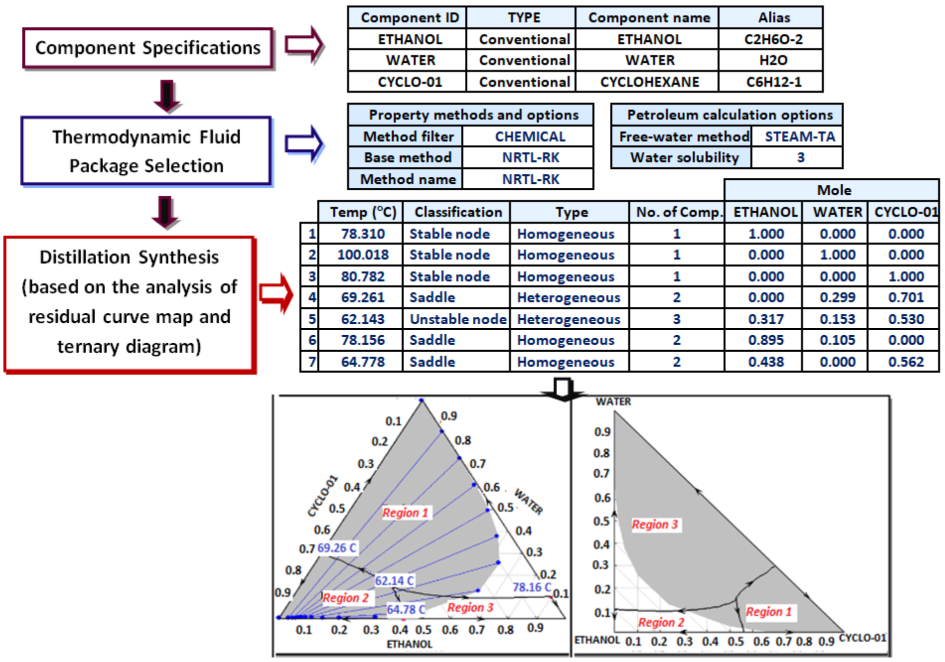
Step 03: Distillation synthesis was conducted to determine split feasibility and azeotropes present in the ethanol-water-cyclohexane multicomponent mixture. This allows computation of their respective distillation boundaries, phase envelopes, and residue curve maps for ethanol-water systems with cyclohexane as an entrainer.

Step 04: Process flowsheet development and simulation, including defining the azeotropic distillation process connectivity by placing the required unit operations (blocks) from the model library and their respective connecting process streams. Moreover, this step also includes: specifying input process stream properties specifications (i.e., pressure, temperature, composition and flow rate), selection the flowsheet convergence criterion from the convergence block and configuring the flowsheet balance model to calculate the molar flow rate of entrainer makeup stream and tear streams (in this case recycle streams) so as to solve process convergence problem.

Step 05: Therefore, after solving the convergence problem, modelling and simulation of the converged azeotropic distillation process were conducted. This was achieved by varying plant operating parameters, including pre-heater operating vapour fraction, column feed plate locations, ethanol molar composition and flow rate of the near-azeotrope feed. The results obtained during heterogeneous azeotropic process modelling and simulation were then collected and analyzed in MS Excel 2007.

Process flowsheet development and simulation

The azeotropic distillation simulation process flow sheet illustrated in Figure 3 was configured block-wise by using unit operations. The latter includes twin RadFrac distillation columns (i.e., main column for heterogeneous azeotropic distillation and recycle column for entrainer recovery), a decanter, mixer, pump, valve and a pre-heater together with their respective connecting process streams as described in Table 2.



Component ID	TYPE	Component name	Alias
ETHANOL	Conventional	ETHANOL	C2H6O-2
WATER	Conventional	WATER	H2O
CYCLO-01	Conventional	CYCLOHEXANE	C6H12-1

Property methods and options	
Method filter	CHEMICAL
Base method	NRTL-RK
Method name	NRTL-RK

Petroleum calculation options	
Free-water method	STEAM-TA
Water solubility	3

					Mole		
	Temp (°C)	Classification	Type	No. of Comp.	ETHANOL	WATER	CYCLO-01
1	78.310	Stable node	Homogeneous	1	1.000	0.000	0.000
2	100.018	Stable node	Homogeneous	1	0.000	1.000	0.000
3	80.782	Stable node	Homogeneous	1	0.000	0.000	1.000
4	69.261	Saddle	Heterogeneous	2	0.000	0.299	0.701
5	62.143	Unstable node	Heterogeneous	3	0.317	0.153	0.530
6	78.156	Saddle	Homogeneous	2	0.895	0.105	0.000
7	64.778	Saddle	Homogeneous	2	0.438	0.000	0.562

Figure 2: Property specification and analysis procedures in Aspen Plus® V10 simulation software.

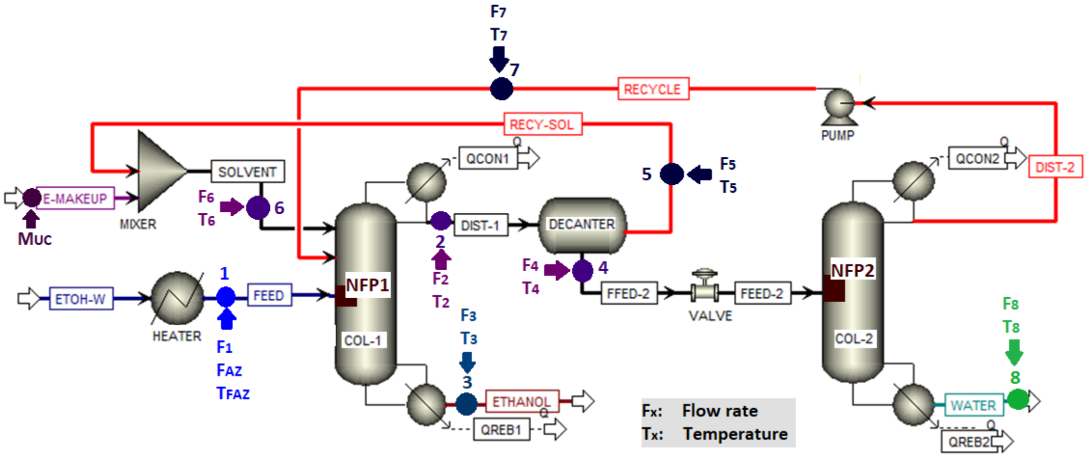


Figure 3: Azeotropic pilot plant process flowsheet indicating key locations for performance analysis.

Table 2: Description of the process streams used in azeotropic distillation process flow sheet

Stream	Name	Type	Description
F1	ETOH-W	Material	Pre-conditioned near-azeotrope feed.
F_{AZ}	FEED	Material	Conditioned near-azeotrope feed from the pre-heater to the main column (COL-1).
F2	DIST-1	Material	Main column distillate enters the decanter to separate ternary azeotropic solution to produce RECY-SOL which contains high entrainer and FFED-2, which contains a significant amount of ethanol.
F3	ETHANOL	Material	Near absolute ethanol is produced from the bottom of the main column.

F4	FFED-2	Material	Aqueous solution from the decanter to the valve.
	FEED-2	Material	Aqueous solution from the valve to the recycle column (COL-2).
F5	RECY-SOL	Material	Organic solution phase from the decanter to the mixer.
F6	SOLVENT	Material	A mixed solvent of the entrainer and organic solution phase is necessary to ensure effective azeotropic separation when fed to the main column.
F7	DIST-2	Material	Distillate of the recycle column containing significant entrainer entering the pump.
	RECYCLE	Material	Distillate of the recycle column from the pump recycled back to the main column.
F8	WATER	Material	The bottom product of the recycle column.
MUc	E-MAKEUP	Material	Entrainer makeup stream.
	QCON1	Heat	Main column condenser duty.
	QREB1	Heat	Main column reboiler duty.
	QCON2	Heat	Recycle column condenser duty.
	QREB2	Heat	Recycle column reboiler duty.

The twin RadFrac distillation columns, namely the main column (COL-1) and recycle column (COL-2), were configured using equilibrium as calculation type for vapour-liquid valid phases and strong non-ideal liquid set as convergence criterion while specifying total condenser and kettle reboiler. Decanter (DECANTER) was specified based on operating duty and pressure, and water was specified as the key component for identifying the second liquid phase, with 0.5 as the threshold molar fraction value for the key component. Selection of 0.5 as the threshold molar fraction value for the key component aimed at ensuring that the liquid-liquid separation in the decanter is attributed to gravity or density segregation only since the molar fraction of the key component (water) in the heteroazeotrope is less than the threshold molar fraction value.

The pre-heater (HEATER) was modelled by using pressure together with either vapour fraction or temperature as flash type depending on feed thermal conditions. On the other hand, the mixer (MIXER) was specified by using pressure for valid vapour-liquid phases, whereas the valve (VALVE) operation was configured by using adiabatic flash for specified outlet pressure (pressure changer) as the calculation type. The pump (PUMP) was modelled by using a pressure ratio of 1 to maintain main column operating pressure.

The simulation model convergence for the azeotropic distillation plant process flowsheet (as illustrated in Figure 3) was achieved using both flowsheet convergence and balance node. Also the convergence algorithm and method for RadFrac column were specified as non ideal and Newton's respectively. The maximum iteration for the main column (COL-1) and recycle column (COL-2) were increased from default value of 25 to 150 and 100, respectively so as to avoid iteration errors during simulation.

To account for material imbalance around the overall azeotropic distillation process and ensure convergence the process simulation was performed repeatedly by changing molar flow rate of WATER produced from the bottom of recycle column (COL-2) based on result calculated from the material balance envelope. Thus, the molar flow rate of water stream becomes an independent variable.

Therefore, in order to account for the effect of recycle streams (i.e., RECYCLE and RECY-SOL) in process convergence, a new solver with ID CV-1 of type WEGSTEIN was created in flow sheet convergence node. SOLVENT stream from the mixer was specified as the tear stream with tolerance error (total allowable error) of 0.0001 and state variables of both pressure and enthalpy. Selection of 0.0001 as tolerance error aimed to ensure approximately 99.99%-degree accuracy is achieved. Also, from the balance node a new balance block B-1 to calculate total flow variables of DIST-2 and E-MAKEUP was created by specifying 1 as material balance number and also by selecting both PUMP and MIXER as the main blocks to define material balance envelope.

Plant Operating Conditions for the Azeotropic Pilot Plant

Due to complexity of the process and large number of variables required to ensure process convergence, some variables (as shown in Table **3**) were specified and fixed during analysis. In this study the fixed value of column reflux ratio and the range of ethanol concentration in the feed were selected based on the former study of Manyele (2023) on the analysis of the effect of reflux ratio on pre-concentrating dilute ethanol solutions to produce near-azeotrope feed.

The molar flow rate of the near-azeotrope feed was estimated based on the expected size of the plant to be designed. Thus, based on the molar flow rate, feed composition and properties volumetric flow rate of the plant streams can be determined and used in plant sizing. Analysis of the feed flow rate on plant ethanol dehydration plant performance was conducted in an increment of 2 kmol/h mainly because at this increment the variation of ethanol dehydration plant performance was minimal (i.e., less than 3%). The decanter operating duty was fixed to 0 MW for the aim of ensuring no energy requirement at the decanter. Similarly, product ethanol molar flow range was analyzed and estimate during simulation in order to obtain acceptable performance results (such as the purity of product ethanol is beyond the ethanol-water azeotropic point and exceeds the purity of near-azeotrope feed).

The total number of column stages for both main and recycle column specified in Table **3** as per system requirement includes the column condenser and reboiler. This indicates that the actual number of column stages that will be designed in a real plant is obtained by using the correlation ($N_a = N - 2$). The feed plate location for both main and recycle column, together with recycle feed plate for the main columns were varied during analysis (as shown in Table **3**) so as to determine their corresponding effect on the plant dehydration performance.

Table 3: Azeotropic pilot simulation model parameters

Parameters	Symbol	Value/Range
Main and recycle column stages	N	12
Main and recycle column reflux ratio	R	5
Main and recycle column pressure	p	1 atm
Main column feed plate	N_{FP1}	4,6,8,20
Recycle column feed plate	N_{FP2}	2,4,6,8,10
Main column recycle feed plates	N_{RFP}	2,3,4,5,6

Ethanol concentration in the near-azeotrope feed	X_{FAZ}	0.81 – 0.86 mol/mol
Feed molar flow rate	F_{AZ}	10 – 20 kmol/h
Pre-heater operating vapour fraction	x_f	$0 - 1$
Feed thermal conditions	FTCs	SCL and FBP ($x_f = 0$)
		PVF ($0 < x_f < 1$)
		VF and PVF ($x_f = 1$)

In real plant changes in the feed and recycle plate location will be effected as illustrated in Figure 4, where an inlet manifold will be designed to accommodate the recommended feed plates. Also operating vapour fraction range for the pre-heater was specified so as to determine the effect of sub-cooled liquid (SCL), feed at boiling point (FBP), partial vapourized feed (PVF), vapourized feed (VF) and superheated feed (SF) feed thermal conditions on ethanol dehydration plant performance.

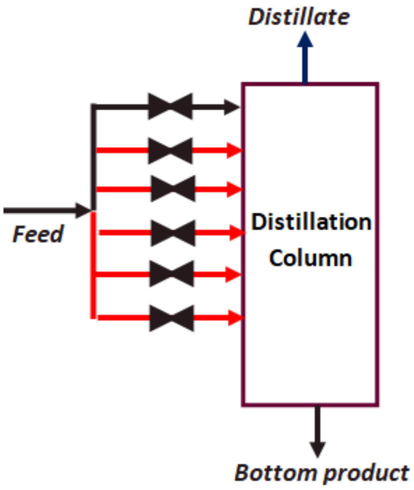


Figure 4: Feed inlet manifold setup.

RESULTS AND DISCUSSION

Product Specification

The quality of main product (dehydrated ethanol) and water stream produced from the designed azeotropic distillation pilot plant is clearly shown in **Figure 5**. The desired purity of product ethanol, i.e., ≥ 95% mol, was obtained from the designed azeotropic distillation process with cyclohexane as a mass separating agent. Although, the desired purity of product ethanol (≥ 95% mol) was obtained but traces of cyclohexane in the product ethanol with molar composition of approximately less than 8% suggest that further ethanol purification process such as membrane separation may be required to produce a cyclohexane free ethanol. Similar results were also reported by Gomis *et al.* (2015) and recommended that production of ethanol-hydrocarbon mixture with negligible water content can be used directly as fuel blend, thus minimizing the costs for further purification. Furthermore, significant amount of ethanol in water stream ranging from 47.27% to 78.83% indicates the economic potential of the stream and hence this stream can be concentrated and reused as a feed before discarding

Axial Plant Profiles for the Main and Recycle Column

Figure 6 shows the azeotropic distillation pilot plant temperature, liquid molar composition, enthalpies and ratio of column to feed molar flow rate axial profiles for main and recycle column. The ratio of axial molar vapour to feed flow rate decreases rapidly to 0 from stage 2 to 1 in both main and recycle column mainly because total condensation occurs at stage 1. High amount of vapour and liquid molar flows across the column stages (2-11) is a result of the molar liquid reflux introduced into the column. From stage 11 to 12 the ratio of axial liquid to feed flow rate decreases rapidly to product ethanol and water molar flow rate from the reboiler of the main and recycle column, respectively.

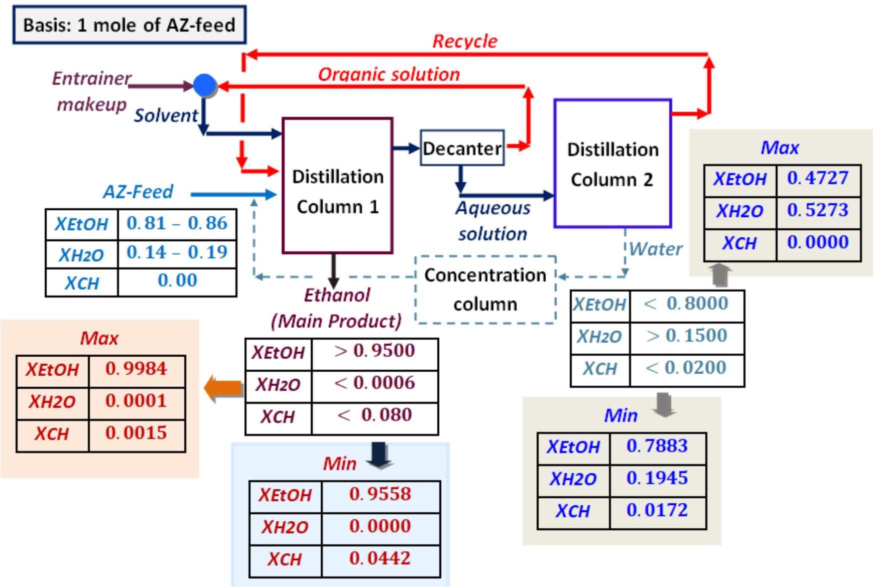


Figure 5: Product specifications and quality.

The behaviour of temperature profile across the main and recycle column stages (as shown in **Figure 6**) is affected by the axial composition profiles. In the main column, from stage 1 to 4 temperature increases slowly from 59.60 to 63.78°C due to deviation from heteroazeotrope composition attributed by decrease in water molar content from 15.85% to 1.77% and increase in ethanol molar concentration from 27.89% to 47.81%. Temperature remains slightly constants for stages (4-8) mainly because at this region water free extractive separation between cyclohexane and ethanol occurs resulting into increase in ethanol molar concentration from 47.81% to 51.52% and cyclohexane molar concentration from 50.41% to 48.45%. Furthermore, from stage 8 to 10 temperature increases rapidly due to increase in ethanol molar concentration from 51.52% to 99.84% and decrease in cyclohexane molar concentration from 48.45% to 0.15%.

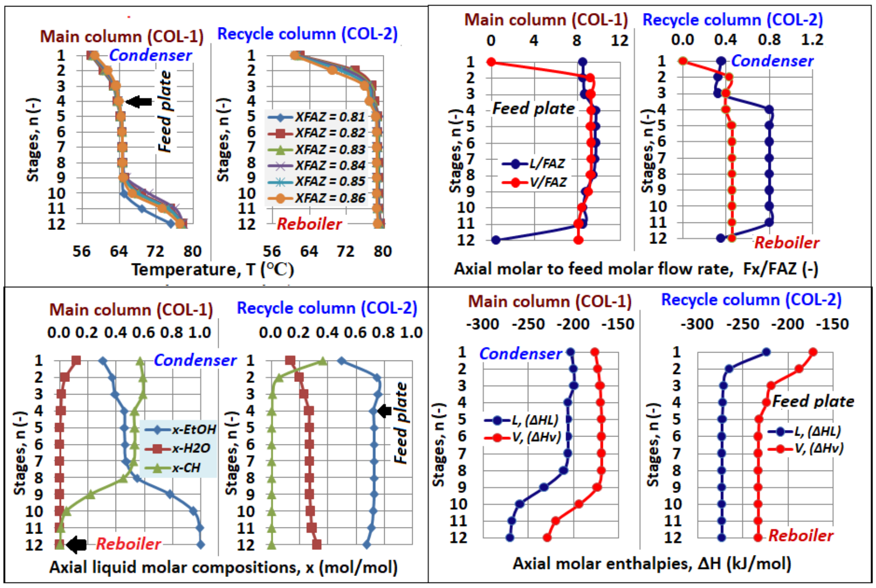


Figure 6: Azeotropic distillation pilot plant axial profiles for the main and recycle column.

Similarly, in the recycle column for stages (1-4) temperature increases rapidly from 56.63 to 77.68°C due to increase in water molar content from 16.77% to 33.66% and rapidly decline in cyclohexane molar concentration from 24.01% to 0.24%. Whereas for stages (4-10) temperature remains slightly constant because at this region cyclohexane free extractive separation between water and ethanol occurs resulting into decrease in ethanol molar concentration from 66.10% to 58.20% and increase in water molar content from 33.66% to 41.80%. Also as illustrated in **Figure 6** axial enthalpy profile across the column is affected by the temperature profile. Vapour and liquid molar enthalpy across the column stages increases with increase in temperature from top to the bottom. The liquid molar enthalpy is approximately 16.17% and 17.72% times greater than the liquid molar enthalpy for the main and recycle column, respectively. This indicates that molar enthalpy of vapourization is the main driving energy potential across the column stages. Furthermore, both vapour and liquid molar enthalpy (shown in **Figure 6**) are relative to the reference of 0 KJ/mol at 1 atm and 25°C

Effect of Ethanol Molar Composition in the Feed, Feed Plate Location, Feed and Product Ethanol Molar Flow Rate on Product Ethanol Purity

Figure 7 shows the effect of ethanol molar composition in the feed, feed thermal conditions, feed plate location, feed and product ethanol molar flow rate on product ethanol purity. The desired purity of near absolute ethanol of approximately greater than 95% is obtained when ethanol molar composition in the feed is greater than 0.83 mol/mol for 10 kmol/h but also ranges from 0.81 to 0.86 mol/mol for 12 to 20 kmol/h (as shown in **Figure 7**). Increase in feed molar flow rate and ethanol molar composition in the feed results into increase ethanol dehydration plant performance and hence the purity of product ethanol, however a retrograde phenomena which may hinder plant performance while increasing energy requirement is observed when feed molar flow rate is 14 kmol/h for 0.81 to 0.84 mol/mol, 16 kmol/h for 0.85 and 0.86 mol/mol, 18 kmol/h for 0.81 mol/mol and 20 kmol/h for 0.82 mol/mol.

The retrograde phenomenon is represented by subsequent decrease and increase in product ethanol purity. Therefore, a careful distillation synthesis based on residual curve maps and ternary diagrams followed by real plant monitoring should be performed in order to address the effect of the observed retrograde phenomena and improve the overall ethanol dehydration plant performance. Also from **Figure 7** it is observed that ethanol molar composition varies inversely proportional with cyclohexane molar composition in the product ethanol. This indicates that cyclohexane molar composition decreases with increasing in ethanol molar composition in the feed and feed molar flow rate. The presence of low water molar content for the product ethanol (< 0.0004 mol/mol) indicates a higher performance of ethanol dehydration plant in the production of a near absolute ethanol.

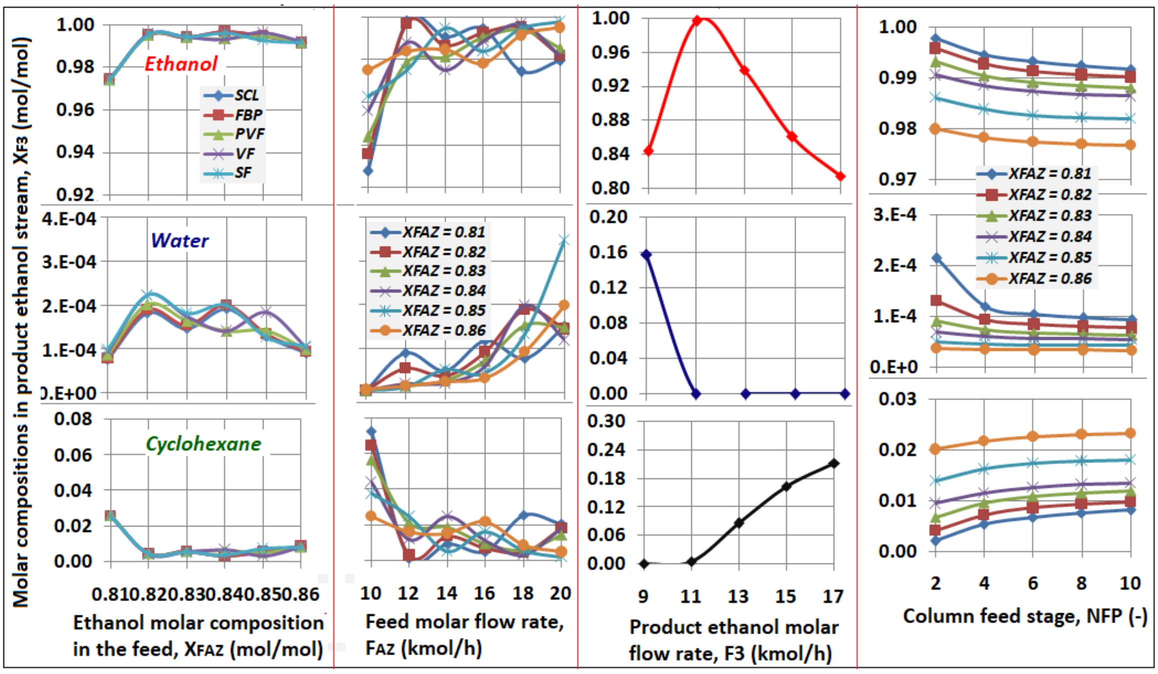


Figure 7: Effect of ethanol molar composition in the feed, feed thermal conditions, feed plate location, feed and product ethanol molar flow rate on product ethanol purity

The purity of product ethanol and hence the dehydration performance is observed to be significantly affected by the changes in the product ethanol molar flow rate. Thus, from **Figure 7** it can be seen that at extremely low molar flow rate of product ethanol (9 kmol/h) the dehydration performance decreases because of formation of two-phase in the column, whereas at extremely high molar flow rate (> 11 kmol/h) beyond the critical flow the dehydration performance decrease because of insufficient contact between ethanol-water-cyclohexane in the column stages. The critical product ethanol molar flow rate at which the desired dehydration performance is achieved (i.e., when the purity of product ethanol is above the ethanol-water azeotropic point and also greater than the purity of near-azeotrope feed) is observed for the product ethanol molar flow rate of 11 kmol/h.

The effect of feed plate location in the distillation column has been investigated by many scholars including, but not limited to Cairns and Furzer (1990), Mortahed and Kosuge (2003) Font *et al.* (2003), Chen *et al.* (2004), Luyben (2006), Albuquerque *et al.* (2019) and Manyele (2021). Feed plate location is one of the column parameters that must be optimized carefully so as to achieve the desired separation. The increase in feed plate location down the column stage 2 to stage 10 (as illustrated in **Figure 7**) results into decrease in the purity of product ethanol caused by increase in the cyclohexane and water molar concentration down the main column. The increase in cyclohexane and water content is attributed by insufficient mass transfer among the key components in the column resulting into inefficient separation.

Effect of Ethanol Molar Composition in the Feed, Feed Plate Location, Feed and Product Ethanol Molar Flow Rate on Energy Requirements

Figure 8 shows the effect of ethanol molar composition in the feed, feed thermal conditions, feed plate location, feed and product ethanol molar flow rate on the main and recycle column energy duties. Increase in feed molar flow rate from 10 to 20 kmol/h results into increase in both condenser and reboiler duties due to increase in the recycle streams flow rates and improved ethanol dehydration plant performance in terms of product ethanol purity. Main column condenser and reboiler duty are approximately more than 90.94% and 90.25% times greater than condenser and condenser and reboiler duty of the recycle column, respectively. The higher energy in the main column as compared to the recycle column is attributed mainly due to the fact that main column receives high throughput than recycle column. Main column reboiler duty is approximately more than 3.26% times greater than its respective condenser duty whereas the recycle column reboiler duty of is approximately more than 11.7% times greater than its respective condenser duty.

The higher difference between condenser and reboiler duties for the recycle column as shown in **Figure 8**, is due to the fact that approximately more than 83.14% of the aqueous solution phase fed into the recycle column is produced as the bottom product hence reboiler tends to process a higher throughput. Furthermore, difference between main column reboiler and condenser duty is significantly low (less than 0.06 MW) because the heteroazeotrope distillate vapour produced from the main column contains significant amount of heavy key components. Hence, the condenser will require high amount of energy during cooling and condensation process to produce a liquid distillate. Therefore, increase in ethanol molar composition in the near-azeotrope feed flow rate from the feed accompanied with corresponding increase in feed molar flow rate results into increase in main and recycle column duties attributed by increase in key streams flow rate for the azeotropic plant.

Feed thermal conditions (as illustrated in **Figure 8**) have significant impact on the reboiler duty of the main column than recycle column due to the fact that the near-azeotrope feed is fed directly into the main column. Based on the result obtained it can be seen that a higher reboiler energy will be needed to generate the amount of vapours required to effect azeotropic separation when the near-azeotrope feed used is sub-cooled liquid and a lower reboiler energy will be needed to generate the amount of vapours required to effect the azeotropic separation when the near-azeotrope feed used is superheated. Therefore, this indicates that reboiler duty for the main column decreases with increase in vapour fraction of the near-azeotrope feed at constant operating pressure. Similar scenario was observed also by Manyele (2021) in his analysis of the effect of feed composition and thermal condition on distillation plant performance using a computer model. Also, from his analysis reboiler duty for SCL was observed to be the highest as compared to other feed conditions mainly because the use of SCL leads to most of the liquid flowing downwards to the reboiler, increasing heat requirements to create vapours.

Increase in product ethanol molar flow rate from 9 to 11 kmol/h results into decrease in the main column condenser and reboiler duty. This is attributed by the decrease in the amount of liquid and vapour in the column. A higher reboiler duty as compared to condenser duty for the main column is due to increase in the concentration of low volatile components (i.e., cyclohexane and water) in the product ethanol. On the other hand, the condenser and reboiler duty of the recycle column increases with increase in product ethanol molar flow rate, mainly because of increase in the concentration of water vapour at the top of the column. A higher condenser and reboiler duty for the recycle column is obtained at critical product ethanol molar flow rate (11 kmol/h) because of sharp increase in the water molar content of the aqueous solution phase.

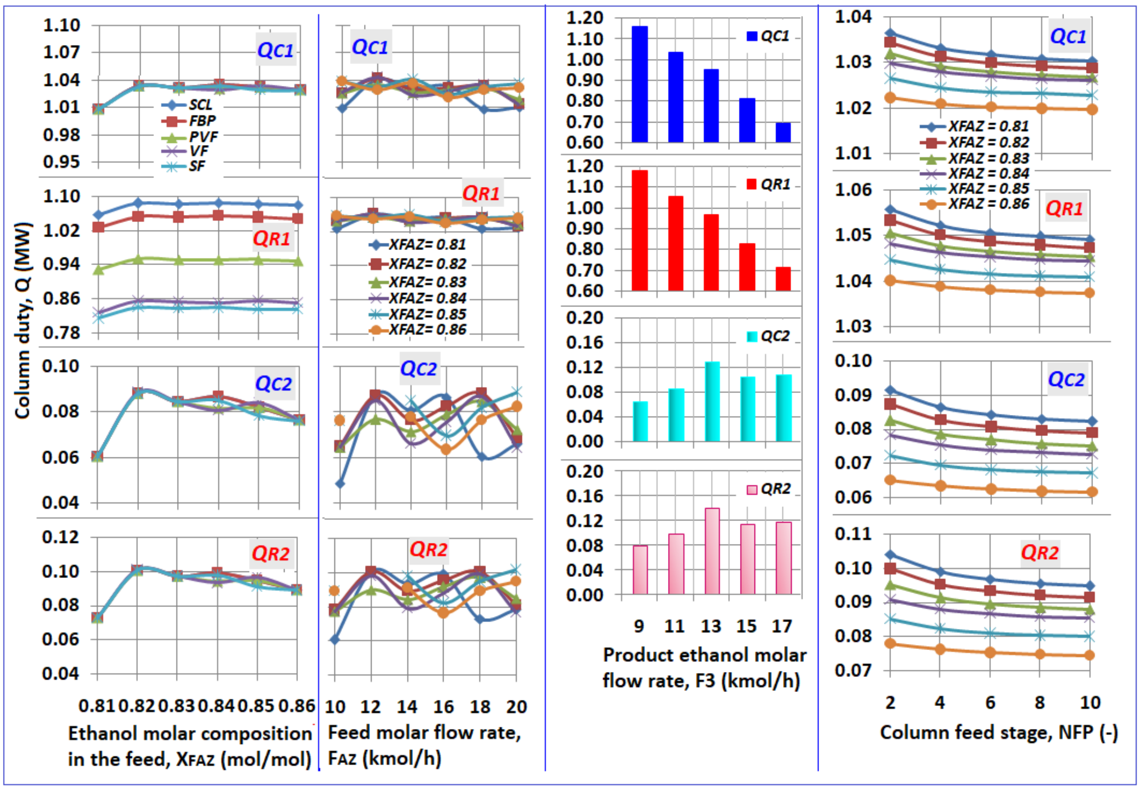


Figure 8: Effect of ethanol molar composition in the feed, feed thermal conditions, feed plate location, feed and product ethanol molar flow rate on the main and recycle column duties.

Moreover, from **Figure 8** it can be observed that reboiler duty is approximately more than 1% and 9% greater than the condenser duty for the main and recycle column, respectively. Also, the main column condenser and reboiler duty are approximately more than 86% times greater than recycle column condenser and reboiler duty. Therefore, in determination of product ethanol molar flow rate, the amount of energy required to produce 1kmol/h of product ethanol must also be taken into account. This is mainly because the energy requirements determine the plant operating expenses and as a result it poses a significant impact on the revenues and project viability.

Increase in the main and recycle column feed plate location from stage 2 to 10 results into decrease in reboiler and condenser duties as illustrated in **Figure 8**. This is attributed by the decrease in the amount of vapours enrichment at the top of the column and also by the fact that when the feed is introduced at the bottom of the column less reboiler energy will be required to generate the necessary vapours. Also from **Figure 8** it can be observed that the reboiler duty is greater than the condenser duty for both main and recycle column. This is due to the increase in the concentration of less volatile components (cyclohexane and water) at the bottom of the column with increase in the feed plate location from stage 2 to 10. Moreover, from **Figure 8** it can be observed that condenser and reboiler duties for both main and recycle column decreases with the increase in the ethanol molar composition in the near-azeotrope feed. This is due to the increase in the amount of more volatile component (ethanol) in the column. Although, feeding at the bottom of the column may be economically attractive due to the decrease in energy requirement, but it is must be avoided due to decrease in the ethanol dehydration plant performance which results into production of product with low purity and hence, low price of dehydrated ethanol.

Generally, since one of the main goals in chemical industry is to effectively utilize the amount of energy required in a process so as to minimize the operating costs. Hence, based on this analysis operating the plant at higher flow rate (18 to 20 kmol/h) will result into higher energy efficiency and enhanced ethanol dehydration plant performance in terms of product ethanol purity

CONCLUSION AND RECOMMENDATIONS

Azeotropic distillation pilot plant model for producing pure ethanol from near-azeotrope pre-concentrated ethanol-water solutions was developed in this study. The designed plant consists of a pre-heater, decanter, main and recycle column acting as the main operational blocks and uses non-random two liquid Redlich-Kwong thermodynamic model as base method for property analysis and performance prediction. The designed process operates under fixed column parameters, i.e., N_a = 10, p = 1 atm and R = 5 mol/mol. The designed plant handles a near-azeotrope feed with F_{AZ} ranging from 10 to 20 kmol/h and produces ethanol at a rate that ranges from 3 to 13 kmol and with purity greater than 95%; the maximum purity of 99.84% was obtained.

Based on the modeling and simulation of the converged azeotropic distillation plant, the key operating parameters affecting ethanol dehydration plant performance in terms of product ethanol purity include feed flow rate (F_{AZ}), feed thermal conditions (FTCs), ethanol concentration in the feed (X_{FAZ}), main column feed plate location (N_{FP1}), recycle column feed plate location (N_{FP1}), solutions and recycle streams feed plate location (N_{RFP}). Changes in the values of key operating parameters causes a completely different plant dynamics, this is due to the complexity of the azeotropic distillation process characterized by high degree of non-linearity, multiple steady states, distillation boundaries and long transients.

Increasing F_{AZ} from 10 to 20 kmol/h accompanied with corresponding increase in X_{FAZ} from 81% to 86% increases the plant operating throughput, key stream flow rates and hence, the main and recycle column energy duties in the range of 0.98 to 1.10 MW and 0.04 to 0.12 MW, respectively. The main column condenser and reboiler duty were approximately more than 90.94% and 90.25% times greater than the condenser and reboiler duty of the recycle column, respectively. Additionally, the increase in F_{AZ} accompanied with the increase in X_{FAZ} enhances the dehydration plant performance in terms of product ethanol purity. However, a retrograde phenomenon which may hinder plant performance while increasing energy requirement was observed.

FTCs significantly affect the reboiler duty of the main column as compared to recycle column, as the near-azeotrope feed was fed into the main column and the aqueous solution with a constant thermal condition that depends on the decanter operating conditions was fed into the recycle column. Effect of FTCs for the main column condenser is significantly low because the overhead vapours approach a ternary azeotrope of an ethanol-water-cyclohexane regardless of the type feed used. Ethanol dehydration plant performance in terms of product ethanol purity and energy duties decreases from 99.84% to 97.5% with increasing N_{FP1}, N_{FP2} and N_{RFP} down the column. Although, feeding at the bottom may be economically attractive due to the decrease in energy requirement, but it must be avoided because it leads to the decrease in dehydration plant performance in terms of product purity.

In general, a higher energy efficiency and dehydration performance of the designed azeotropic distillation plant in terms of product ethanol purity is obtained when the plant is operated with X_{FAZ} ranging from

0.81 to 0.86 mol/mol and at higher flows, i.e., F_{AZ} ranging from 18 to 20 kmol/h. The feed and recycle plates should be located closer to the top of the column (i.e., stage 4 for the near-azeotrope feed, stage 2 for aqueous solution phase and stage 1-3 for the recycle streams). Additionally, the study recommends a careful distillation synthesis followed by real plant monitoring in order to address effects of retrograde phenomena and improve the overall ethanol dehydration plant performance in terms of product ethanol purity while minimizing the plant operating costs. Also, in order to determine best plant operation configuration, minimize plant operating costs and energy, an inlet manifold for stages 1 to 4 should be incorporated in the design and a detailed analysis on the effect of X_{FAZ} should be conducted in real plant experiments based on simulated results obtained. The presence of significant amount of ethanol in the water stream, suggest that the stream may be reused as feed in the pre-concentrating column before discarding it.

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