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International Journal of Engineering, Science and Technology
Vol. 16, No. 4, 2024, pp. 99-115

INTERNATIONAL JOURNAL OF ENGINEERING, SCIENCE AND TECHNOLOGY
www.ijest1-ng.com
www.ajol.info/index.php/ijest

The influence of feed molar flow rate on key streams properties and duties in ethanol-water azeotropic distillation process

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Abstract

Investigation on the influence of near azeotropic feed molar flow rate on properties of key streams connecting main process units of an ethanol-water azeotropic distillation pilot processis presented. The heterogeneous azeotropic distillation model with cyclohexane entrainer was configured in Aspen Plus® V10 commercial simulation software. Property analysis and prediction of plant's performancewere achieved using Non-Random Two Liquid Redlich-Kwong thermodynamic model. Both residual curve maps and ternary diagrams were used to determineseparation possibility and presence of ethanol-water azeotrope in the formed ternary mixtureduring distillation synthesis. The process convergence was addressed using flowsheet convergence and balance node. Distillation of ethanol-water azeotropic mixture was simulated at constantrecycle ratio (R = 5), numberof stages (N = 12) and pressure (P = 1 atm). Data obtained were analysed in MS Excel 2013. Results showed that simultaneous increase ofmolar flow rate of the near azeotropic feed and feed ethanolconcentration improves ethanol purity but results in retrograde phenomenon which may humper plant's performance and increase stream flow rates and therefore increase energy duties. The condenser duty of the main column wasaround 90.94% higher than the recycle column'scondenser duty. Also, reboiler duty of the main column were nearly 90.25% higher than the recycle column's reboiler duty.It was concluded that setting 18 to 20 kmol/h feed molar flow rate enhances higher energy efficiency and improves ethanol product purity. Careful distillation synthesis and plant's monitoring are recommended to improve ethanol-water azeotropic distillation plant's performance and address retrograde phenomena.

*Keywords:*Feed Molar Flow Rate, Azeotropic Distillation Process, Key Stream Properties, Duties, Entrainer, Feed Composition

DOI: http://dx.doi.org/10.4314/ijest.v16i4.8

Cite this article as:
Jeremiah J., Monge E., Mohamed M., Msuya N. and Manyele S. 2024. The influence of feed molar flow rate on key streams properties and duties in ethanol-water azeotropic distillation process. *International Journal of Engineering, Science and Technology*, Vol. 16, No. 4, pp. 99-115. doi: 10.4314/ijest.v16i4.8

Received: February 14, 2024 Accepted: April 24, 2024; Final acceptance in revised form: December 29, 2024

1. Introduction

The impacts of overdependence on fossil fuels for energy generation on the earth's climatic condition has become one the compelling forces towards energy transition to renewable energy sources like pure anhydrous alcohol so as to lessen the effects of rapid changing climate. Despite of its vast usage in various applications, ethanol is considered as the best potential biofuel which is a promising fossil fuel alternative (Kumar *et al*., 2010; Battisti *et al*., 2019). Further, absolute ethanol is used as a raw material in ester synthesis, pharmaceutical formulations as an organic solvent, chemical reagents and detergent's additive, medicines, aerosols, paints and perfumes as well as in electronic industries (Marnoto *et al*., 2018; Silva *et al*., 2021).

Ethanol is mostly obtained through fermentation of sugar which decomposes under the influence of ferments and enzymes (Baek *et al*., 2008 and Maicas, 2020). However, fermentation process produces dilute ethanol-water mixture, from which an absolute ethanol can be obtained by repeated distillation followed by dehydration processes (Luyben, 2012). Dehydration processes is further employed sinceconventional distillation process cannot produce absolute ethanol because when ethanol concentration reaches89.5% at 1 atm pressure and 78.156°C ethanol-water mixture form an azeotropic mixture which cannot be separated further by normal or conventional distillation method (Li *et al*., 2022).

According to ChemAnalyst (2023), the requirements for pure anhydrous ethanol greater than 95% has increased over the years. The expected ethanol demand in the world is projected to the compound annual growth rate (CAGR) of 4.75% from 100 million tons in 2022 to 162 million tons in 2035. This indicates the increase in ethanol profile demand. This has led to the continued advancement in ethanol dehydration process technologies.

The current ethanol dehydration technologies include the advanced distillation (i.e., vacuum, reactive, extractive, pressure swing and azeotropic distillation), membrane separation (i.e., membrane, pervaporation and diffusion) and process intensification (Mahdi *et al*., 2015). However, more study efforts are concentrated on the advanced ethanol dehydration and fuel-grade production techniques (Marnoto *et al*., 2018). Various advanced ethanol dehydration methods such as vacuum distillation, reactive distillation (Forner *et al*., 2008; An *et al*., 2014; Su *et al*., 2020), pressure swing distillation (Knapp and Doherty, 1992; Yu *et al*., 2012; Yang *et al*., 2020), extractive distillation (Meirelles *et al*., 1992; Donis *et al*., 2003; Gil *et al*., 2012; Dongmin and Yanhong, 2018), liquid-liquid extraction including salting-out extraction, adsorption on molecular sieves (Weitkamp *et al*., 1991), pervaporation (Le *et al*., 2012), homogeneous and heterogeneous azeotropic distillation (Gomis *et al*., 2015; Rojas *et al*., 2016; Miranda *et al*., 2020; Guido *et al*., 2021) may be used to produce pure ethanol. However, selection of the suitable ethanol dehydration processes depends on factors such as azeotrope properties of the components to be separated, desired dehydrated ethanol purity, throughput, cost, safety and environmental threats.

Azeotropic distillation is an advanced separation process which is widely used for strongly non-ideal and ethanol-water azeotropic mixtures in order to produce absolute alcohol (Chen *et al*., 2004; Gomis *et al*., 2015). The separation principle in azeotropic distillation lies in the addition of an extraneous substance in the mixture called an entrainer so as to increase relative volatility between the azeotropic components (Widagdo and Seider, 1996; Mahdi *et al*., 2015; Guo and Wang, 2019; Guido *et al*., 2021). However, the performance of an Azeotropic ethanol dehydration plant depends largely on the plant process parameters which includes columns operating conditions (i.e., pressure, number of stages, energy duties, and reflux ratio), feed flow, composition, thermal conditions and the location of feed and recycle plates among others. Studies reveals that plant performance may be positively or negatively influenced due to variations in feed molar flow rate. Feed flow rate is a critical parameter for ethanol-water separation performance during distillation process (An *et al*., 2014). In the study by Kovach and Seider (1987),the feed rateand other operating variables were varied for an ethanol dehydration processusing di-sec-butyl ether (DSBE) entrainer and observed that the process gives an erratic behavior that approaches a steady state due to parametric sensitivity though the study did not yield conclusiveresults.

Heterogeneous azeotropic distillation process is characterized by complexities, excessive nonlinearity, multiple points of steady states, long transients, and numerous distillation boundaries which limits process operating ranges under different feed disturbances (Zhao *et al*., 2017; Zhang *et al*., 2021). Depending on the product flow rates, increase in feed flow rate results either into increase or decrease in residence contact time between the liquid and vapor phases of the key components (ethanol-water-cyclohexane) in the column. Due to high degree of non-ideality and nonlinearity of azeotropic distillation process minor variation in the feed flow rate atthe same feed mole fraction may leads into erratic behavior and unacceptable results (such as when the purity of dehydrated ethanol is less than the purity of near azeotropic feed). Further, studies shows that feed molar flow rate disturbances cause extreme variation of ethanol mole fractions along the column's stages (Taqvi *et al*., 2017). The liquid and vapor phases along the stages of the distillation column increases with an increased molar flow rate of the feed resulting into increase in both top and bottom product flow rates. Studies generally show that the quantity of liquid and vapor phases along the stages of the distillation column increases as the molar flow rates of the feed is increased thereby affecting the column dynamics and separation efficiency. Therefore, to account for changes in the column dynamics and separation efficiency, a careful distillation synthesis based on composition profiles should be conducted to determine control mechanisms of the emerged disturbances in the feed flow.

Variation in feed molar flow rates not only pose some influence on column dynamics and separation efficiency during ethanol-water azeotropic distillation but also it poses some influence onprocess stream properties.Process stream properties are characteristics of materials flowing in a process stream including pressure, temperature, composition and flow rate. The process key streams considered in this study are the input and output streams from the main process blocks, i.e., Column 1 (denoted as COL-1), Condenser, Decanter, Column 2 (denoted as COL-2), and Mixer giving streams*S1*, *S2*, *S3*, *S4*, *S5*, *S6*, *S7*and *S8* with their corresponding flow rates*F1*, *F2*, *F3*, *F4*, *F5*, *F6*, *F7* and *F8.* Stream properties are very important in designing, optimizing and controlling chemical industrial processes.Various studies have shown that Near Azeotropic Feed Molar Flow Rate influences the stream properties. Luyben (2006 a) conducted a study on designing and controlling a multiunit heterogeneous ethanol-water azeotropic distillation process and revealed that the when the flow rate of the feed is increased parameters such as reflux, recycle, product ethanol, and aqueous solution phase flow rates are increased. Also, an investigation on the effects of flow rate of the feed on the performance of a hybrid azeotropic distillation process or molecular sieve dehydration process for the production of ethanol fuel was conducted and results showed that increasing the flow rate of the feed reduced ethanol recovery rate due to insufficient contact time between the feed and dehydration agents (Gryta, 2015).Different studies generally shows thatvariations of feed molar flow rate in an azeotropic distillation column are restricted by column operating throughput and reflux ratio. This is mainly due to the fact that higher increase in thefeed molar flow rate causes column operating problems such as flooding, weeping, conning, blowing and entrainment which results into insufficient separation of the key components while increasing the reboiler duty.

Further studies have shown that the energy requirements increase with increase in the molar flow rate of the near ethanol-water azeotropic feed. This is attributed to the increased quantity of liquid and vapour phases along the stages of the column which results into an increase in the reboiler and condenser duties. The study on sensitivity and plant's dynamics analysis for an industrial ethanol-water azeotropic distillation column revealed that reboiler duty varies directly proportional to the molar flow rate of the feed (Guedes et al., 2007). Thus, the optimum feed molar flow rate is influenced by numerous parameters like the plant capacity, energy consumption, dehydration efficiency (purity of the produced ethanol) and the economic considerations which must be considered when determining the optimal feed flow rate for an ethanol dehydration plant.

In this study, a pilot plant for the ethanol-water azeotropic distillation processto produce ethanol with 95% or higher by employing cyclohexane entrainer is presented. The advanced separation process technique using heterogeneous ethanol-water azeotropic distillation process was due to its extensive usefor an azeotropic systems and strong non-ideal mixtures therebygivinga free duty high liquid-liquid split efficiency (Arifin and Chien, 2007; Gomis *et al*., 2015; Zhao *et al*., 2017). Entrainer selection is a critical point to the successfulethanol-water azeotropic distillation process since it helps in reduction of process complexity (Mahdi *et al*. 2015). Different factors are considered in selecting entrainer including selectivity, relative volatility, toxicity, carcinogenic properties, environmental effects, safety, cost, availability, corrosion, entrainer type and system behavior (Guido *et al*., 2021). Various entrainers have been studied in ethanol-water azeotropic distillation including isooctane, n-butyl acetate, cyclohexane, toluene, benzene, isooctane, hexane, methyl ethyl ketone and ethyl acetate. However, cyclohexane has been found to be suitable and widely used in industrial processes (Udeye *et al*., 2009; Vasconcelos and Wolf-Maciel, 2010; Li *et al*., 2022; Zhang *et al*., 2021). Hence, in this work cyclohexane was mostly considered.

Further, the influence of molar flow rates of the near azeotropic feed on stream compositions, flow rates and energy requirements are analyzed for the aim of determining the molar flow rates of the near azeotropic feed that enhances the performance of ethanol-water distillation plant. In this study, ethanol productpurity was used to measure the performance of ethanol-water azeotropic distillationplant. Modelling and simulation method was used to study the ethanol-water azeotropic distillation process in order to investigate the process design, operation and controls,and optimization of various process parameters before actual construction of the ethanol-water azeotropic distillation pilot plant.Results from this study have catered the knowledge gap on the influence of molar flow ratesof the feed and the feed ethanolconcentrationson the key stream properties and duties of the ethanol-water azeotropic distillation plant.This study gives new insightson ethanol dehydration processes makingresults obtainedverycrucial in enhancing ethanol-water azeotropic distillation processes to obtain anhydrous ethanol. Further, this study provides detailed insights on various parameter characteristics of an ethanol-water azeotropic distillation process with clear relationships between important parameters for successful operations of an ethanol-water azeotropic distillation plants. The study uncovers information on how the near azeotropic feed molar flow rates and the feed ethanol concentrations influences characteristics of the key stream of the plants.

2. Modelling and Simulation of Ethanol-Water Azeotropic Distillation Process

2.1 Process description

The ethanol-water azeotropic distillation process begins by feeding the near azeotropic ethanol-water solutions and sufficient amount of cyclohexane entrainer into the main column (i.e., COL-1 as shown in Figure 1) where azeotropic distillation takes place. Addition of entrainer aims at forming the fluid phase inverse change in the ethanol-water relative volatilities after forming azeotropic mixture. This allows separation of water which exits with cyclohexane at column's top thereby leaving ethanol which is more volatile component to concentrate and then flow through the bottoms of COL-1. The concentration of ethanol product stream (bottoms of COL-1) is supposed to be highest, and modeling was therefore conducted to attain near absolute conditions in stream *S3*. However, some ethanol is still present in the top section vapour product, which again forms a ternary heteroazeotrope mixture of ethanol-water-cyclohexane system (an azeotrope where a vapor phase co-exists with two liquid phases). This happens as vaporscondenses into two immiscible liquids and the resulting liquid mixture flows into the DECANTER for further separation (by gravity or density based natural separation mechanism) into organic and aqueouslayers.

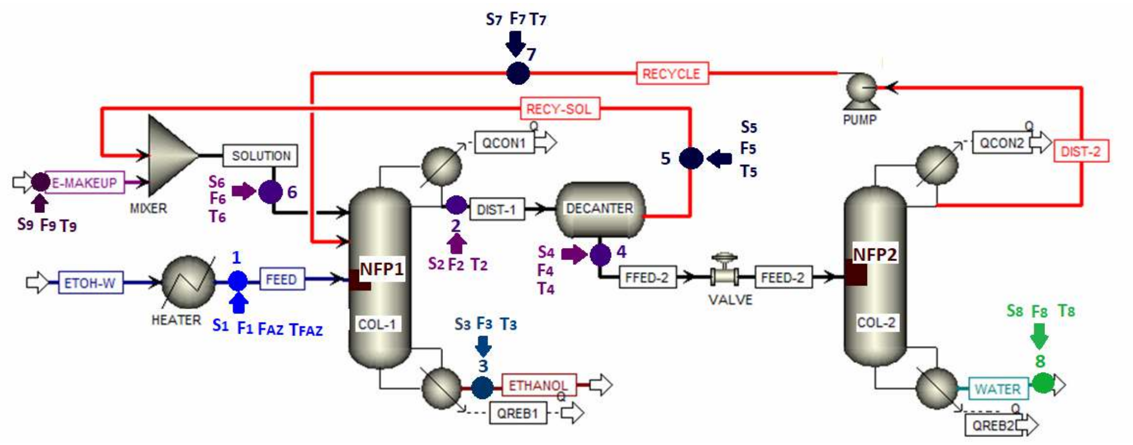


Figure 1. Process flowsheet showing key locations for the performance analysis of the ethanol-water azeotropic distillation plant.

The formed organic layer comprises significantly higher quantity of cyclohexane entrainer. Thus, the organic solution is recycled back through stream S5 (denoted also as RECY-SOL) and mixed up with the entrainer makeup and then fed to COL-1 to enhance ethanol-water separation process. Also, the formed aqueous layer comprises a good quantity of ethanol and cyclohexane which necessitates to be fed in the recycle column, i.e., COL-2 where normal distillation process is conducted. The recovery of water component which is less volatile in the mixture is achieved via the bottoms of COL-2 through stream S8. The distillation product from the top of COL-2 which consists of ethanol-cyclohexane solution mixture is recycled back to COL-1 where azeotropic distillation takes place. This makes two recycle streams (that is S5 and S6) which enters the main column (COL-1).

2.2Process flowsheet development

Development of ethanol-water azeotropic distillation process flowsheet was accomplished in Aspen Plus® V10 commercial simulation software. The work involved defining the azeotropic distillation process connectivity by putting unit operations (blocks) and their respective process streamsfrom the software's model library. Then, the ethanol-water azeotropic distillation process pilot plant was set up withtwo distillation columns and a decanter serving as the primary operational units, as depicted in Figure 1. Column 1 (COL-1) serves as the primary column for azeotropic distillation while column 2 (COL-2) serves as the recycle column. Column 2 is used to recovers the cyclohexane entrainer contained in the aqueous solution exiting from the decanter and recycled back to enhance azeotropic distillation in the main column (Widagdo and Seider, 1996; Mahdi *et al*., 2015;Li *et al*., 2016). As shown in Figure 1, the process flow sheet constituted other units including the mixer, pump, valve and a pre-heater connected using process streams described in Table 1.

Table 1. Process stream description for the ethanol-water azeotropic distillation pilot plant flow sheet

Stream	Stream's name	Stream's flow rate	Process stream's description
S1	ETOH-W	*F1*	Ethanol-water mixture pre-conditioned feed.
	FEED	F_{AZ}	Pre-heated mixture of ethanol-waterfeedto Column 1.
S2	DIST-1	*F2*	Distillate stream from column 1 flowing to decanter for separation to produce high entrainer concentration stream and high ethanol concentration stream
S3	ETHANOL	*F3*	Ethanol product stream from column 1 (COL-1).
S4	FFED-2	*F4*	High ethanol concentration (aqueous liquid phase) stream from the decanter.
S5	RECY-SOL	*F5*	High entrainer concentration stream
S6	SOLVENT	*F6*	Streamof cyclohexane and the organic liquid phase flowing to Column 1 (COL-1) to effect ethanol-water separation.
S7	DIST-2	*F7*	High entrainer concentration distillate stream from Column 2 (COL-2)
	RECYCLE		High entrainer concentration recycle stream from the pump to column 2.
S8	WATER	*F8*	Column 2 (COL-2) bottom product stream.

S9	E-MAKEUP	*MUc*	Makeup stream for an entrainer.
Q	QCON1	Heat	Condenser duty for column 1 (COL-1).
	QREB1		Reboiler dutyfor column 1 (COL-1).
	QCON2		Condenser duty for column 2 (COL-2).
	QREB2		Reboiler dutyfor column 2 (COL-2).

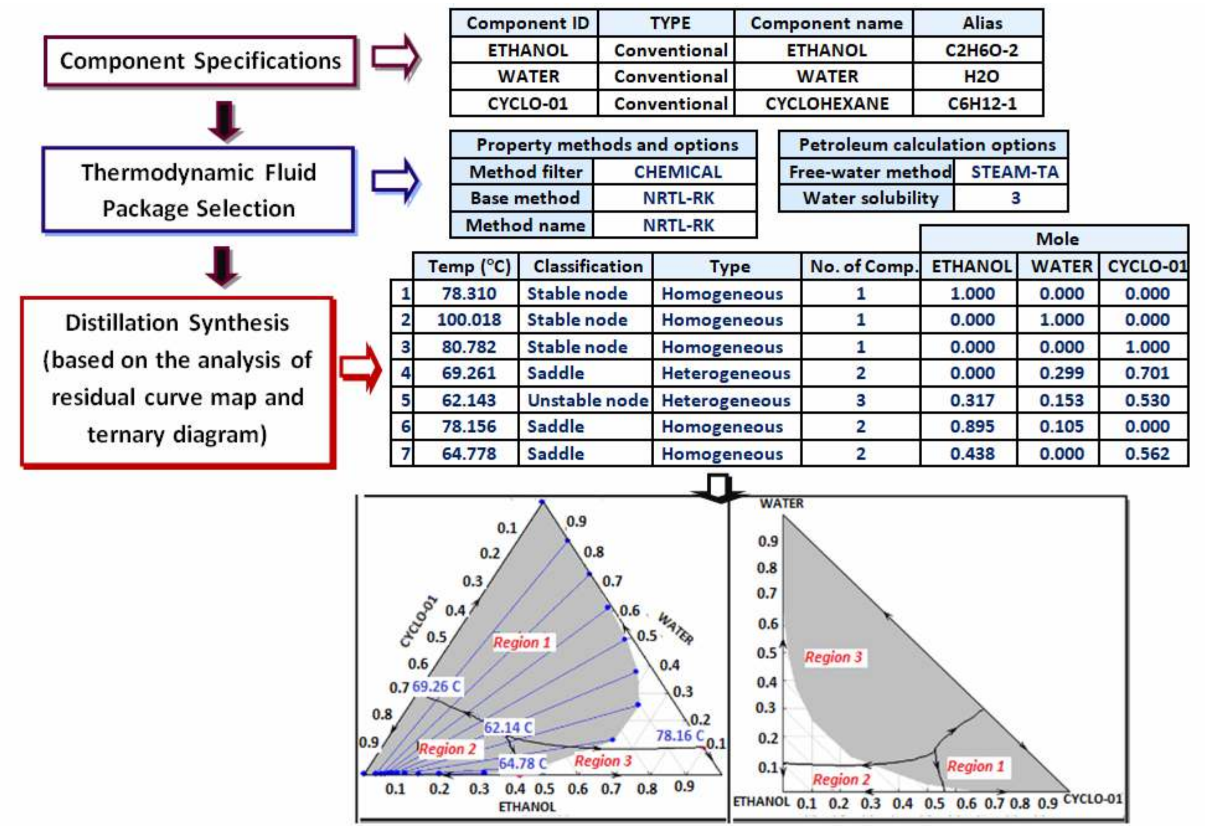
2.3Model build-up and ethanol-water azeotropic distillation process convergence

Creation of simulation model for the ethanol-water azeotropic mixture distillation process was accomplished step by stepin Aspen Plus® V10 simulation software as Figure 2illustrates. Initially, property analysis and specifications were done. The work involved specification of each component, selection of thermodynamic fluid package and the analysis of the distillation synthesis. The process key components in the process were Ethanol (C_2H_6O), Water (H_2O) and Cyclohexane (C_6H_{12}). These components were specified as conventional type since they take part in calculation of the chemical and phase equilibrium. Then, thermodynamic model was selected whereby the chosen model were Non-Random Two Liquid-Redlich Kwong (NRTL-RK). Choice of this model based on its good performance forchemical systems that are non-ideal like ethanol-water systems but also it gives appropriate description of vapour-liquid equilibrium data and liquid-liquid equilibrium data (Haghtalab *et al*., 2011; Taqvi *et al*., 2016). Thereafter, distillation synthesis was followed in order to determine separation feasibility and the presence of ethanol-water azeotropes in the ethanol-water-cyclohexane ternary system. Thestep allows computations of thephase envelopes, distillation boundaries and residue curve maps of the ethanol-water-cyclohexane systems.The next step involved specification ofproperties of the input streamsincluding flow rates, composition, temperature andpressure; selection of the criteria for flowsheet convergence from the convergence block, model configuration for the flowsheet balance to compute the flow rates of cyclohexane makeup stream and that of the recycle streamin order to get solution for the process convergence.

2.4 Setting Up Operating Conditions of theEthanol-Water Azeotropic Distillation Pilot Plant

The operating conditions for the convergence was determined by setting up twin RadFrac distillation columns that took into account for the vapor-liquid phases equilibrium and the strong non-ideal liquidequilibrium. The key components of decanter were specified, these are operating duty, pressure and amount of water. The maximum amount of water was specified to be 0.5 mole fraction so as to ensure liquid phasesseparation in the decanterby natural action of gravity. Modeling of the pre-heater involved utilizing pressure and either vapour fraction or temperature as flash type dependent on the feed thermal conditions of the near azeotropic ethanol-water mixture. The mixer unit's design was based on the operating pressure of the vapour-liquid vaili phase (a term used in the context of thermodynamic calculations and phase equilibrium modeling). The valve function was adjusted with the help of adiabatic flash to compute the outlet pressure (pressure changer) as the calculation type. To maintain the operating pressure of the main column, the pump was designed with a pressure ratio of 1.

The equilibrium was used as the calculation type in setting the twin RadFrac distillation columnsfor vapour-liquid valid phases and strong non-ideal liquid was set as the criteria forprocess convergence. The decanter unit was specified for its operating duty, operating pressure andwater as the key component which allowed identification of the second liquid phase component. A threshold of 0.5 mole fraction for water as the key component was specified so as to ensure gravity separation of liquid phases in the decanter since water mole fraction in the ethanol-water heteroazeotrope mixture is small compared to the threshold value. Depending on feed thermal conditions of the near azeotropic ethanol-water mixture, modelling of the pre-heater used pressure with vapour fraction or pressure with temperature as flash type. Mixer unit specification used pressure for vapour-liquid valid phases. Operation of the valve were set by the application of adiabatic flash as the calculation type for a given pressure of anoutlet (that is pressure changer). Modelling of the pump was done by applying pressure ratio of 1 so as to maintainpressure in column 1.



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

	Temp (°C)	Classification	Type	No. of Comp.	Mole		
					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. Simulation workflow in Aspen Plus® V10 software for the property specification and analysis.

To achieve convergence of the simulation model, flow sheet convergence and balance node techniques were implemented. Also, it was required to specify the non-ideal convergence algorithm (method used to solve systems of equations representing the non-ideal behavior of chemical processes), and the Newton's method for RadFrac column (a unit operation used for the simulation of radially dispersed distillation columns, using numerical techniques to solve complex sets of equations governing the behavior of the distillation process). The model convergence requires a large number of iterations. Thus, the number of iterations were changed from 25 which was the default number to 150 iterations for COL-1 and to 100 iterations for COL-2. This was necessary to avoid iteration errors. Simulation of the process was conducted several times while varying the molar flow rate of the produced water (independent variable). This accounted for imbalance of materials during distillation and ensuring process convergence. Furthermore, to attain process convergence, another solver with ID CV-1 of type WEGSTEIN was introduced in the flow sheet convergence node. This enabled to account for the influence of recycle streams. Stream *S6* which connect the mixer and COL-1 was specified as tear stream. Stream *S6* were characterized by tolerance or allowable error of 0.0001, and pressure and enthalpy as state variables. The lower tolerance error was set to ensure higher degree of accuracy. Furthermore, a fresh equilibrium block, denoted as B-1, was created from the equilibrium node to compute the cumulative flow parameters for DIST-2 and E-MAKEUP. This was accomplished by designating 'I' as the material balance identifier and opting for both PUMP and MIXER as the primary components to delineate the material balance boundary.

To achieve process convergence, given a highly complex process with large number of strongly interacting variables, some variables were specified and fixed as shown in Table 2. The reflux ratio and the ethanol mole fraction in the feed were set using earlier pre-concentration results from the study by Manyele (2021). Estimation of the molar flow rate of the feed was done by considering the design scale of the pilot plant. The influence of molar flow rate of the feed was studied by varying at the rate of 2 kmol/h due to minimum variation of performance of the plant which were observed to be less than 3%. The operating duty of the decanter was kept constant at 0 MW, that is, no energy was required in the decanter. The product stream *S3* was varied during simulation for acceptable performance results. The total number of trays for both COL-1 and COL-2 are shown in Table 2, which includes two stages for the column condenser and reboiler. The actual number of stages of the column in the physical plant, therefore, is obtained by subtracting two stages of the condenser and reboiler.

In this study a feed near ethanol-water azeotropic mixture ranging from 0.81 to 0.86 mol ethanol/mol was chosen. Ethanol-water forms an azeotrope at about 89% ethanol thus addition of an entrainer breaks the azeotrope and enable separation process to produce anhydrous ethanol through Azeotropic distillation process. A near ethanol-water azeotropic mixture (0.81 - 0.86 mole/mole) is obtained through pre-concentration of dilute ethanol-water mixtures ranging from 7 to 60% ethanol.

Table 2. Simulation parameters for ethanol-water azeotropic distillation pilot plant

Parameter’s name	Parameter’s value
Number of stages for COL-1 and COL-2 (N)	12
Reflux ratio for COL-1 and COL-2 (R)	5
Pressure in COL-1 and COL-2 (P)	1 atm
Feed plates for COL-1 and COL-2 (NFP)	4
Recycle Feed platesfor COL-1 and COL-2 ($NRFP$)	2
Duty at the decanter unit (Q)	0 MW
Feed ethanol mole fraction (X_{FAZ})	0.81 – 0.86 mol/mol
Molar flow rate of ethanol-water feed (F_{AZ})	10 – 20 kmol/h
Operating vapour fraction in the pre-heater	0 - 1

2.5 Simulation of Ethanol-Water Azeotropic Distillation Process

Finally, the pilot plant simulation for distillation of ethanol-water azeotropic mixture was accomplished through variation of the process parameters, namely, operating vapor fraction of the pre-heater, locations of the feed plate on the main column, ethanol mole fraction, and the feed molar flow rates of the near azeotropic ethanol-water mixture. Results obtained after convergence of the simulation process were collected and analyzed in MS Excel 2007.

3. Results and Discussion

3.1 Effect of Variation of Molar Flow Rate of theNear Azeotropic Feed (F_{AZ}) on Stream Properties

The molar flow rate of the near azeotropic feed is among the operatingvariablesthat affects the efficiency of an ethanol-water azeotropic distillationprocess. Due to complexity of an azeotropic distillation plant, increase in feed molar flow rate may result into variation ofmole fractions of components in the key streams which connects the main process units of the azeotropic distillation plant (i.e., Column 1 (COL-1), decanter, pre-heater,andcolumn 2 (COL-2). Figure 3 shows the effects of increasing the feed molar flow rate on the ethanol mole fraction in the streamsconnecting main process units (i.e., *S2*, *S3*, *S4*, *S5*, *S6*, *S7*, *S8*). Results show that when the molar flow rate of the ethanol-water feed to COL-1 is increased from 10 to 20 kmol/h decreasedthe ethanol molefraction from 0.34 to 0.24 mol/mol in column-1 distillate stream (*S2*), 0.69 to 0.49 mol/mol in the aqueous phaseflow stream (*S4*), 0.083 to 0.055 mol/mol in the organic phase flow stream (*S5*), 0.080 to 0.050 mol/mol in the solvent flow stream (*S6*) and 0.79 to 0.45 mol/mol in the water flow stream (*S8*). These observations indicatean inverse relationship between the feed molar flow rate and the ethanol mole fraction in the key streams, and also indicated production of high purity of the near absolute ethanol. Further Figure 3 shows that increase in the near azeotropic feed molar flow rate from 10 to 20 kmol/h results into increasing in ethanol mole fraction from 0.96 to 0.999 mol/mol in the product ethanol stream (*S3*) and 0.10 to 0.70 mol/mol in the recycle flow stream (*S7*). Decrease in the ethanol mole fractionin stream *S8*changes the ethanol mole fraction from low to higher concentration in stream *S7* because of the increase in concentration of ethanol in the overhead vapours produced in the COL-2.

Though the rise in feed molar flow rate results into rise in product ethanol purity from stream *S3*, but a retrograde phenomenon is observed which is represented by fluctuation, i.e., subsequent decrease and increase of product ethanol purity. The phenomenon occurs when feed molar flow rate is 14 kmol/h and the ethanol mole fraction is 0.81 to 0.84 mol/mol, 16 kmol/h and the ethanol mole fraction is 0.85 and 0.86 mol/mol, 18 kmol/h and the ethanol mole fraction is 0.81 mol/mol and 20 kmol/h and the ethanol mole fraction of 0.82 mol/mol. This indicates that plant operation under these conditions must be avoided as the azeotropic distillation performance in terms of product ethanol purity decreases and more energy is required to counteract this effect. Furthermore, it can be observed from Figure 3 that feeding ethanol with a high mole fraction results in a rise in the mole fraction of ethanol in the key streams (*S2*, *S3*, *S4*, *S5*, *S6*, and *S8*). This observation is a result of the rise in ethanol mole fraction throughout the column stages, which is attributed to the high ethanol mole fraction in the overhead vapours generated by the main column.

In general, simultaneous increase of the molar flow rate of the near azeotropic feed and the ethanol mole fraction in the feed leads to an improved ethanol-water separationresulting to high ethanol product purity. The observed results indicate the significance of the feed molar flow rate on ethanol-water azeotropic distillation plant performance as explained by An *et al.* (2014). This is attributed to variations in ethanol concentrations in the key processing streams. Simultaneous variations of ethanol mole fraction in the feed and the near azeotropic feed flow rate gives observations similar to what is reported by Mujiburohman *et al.* (2006). In addition, the presence of retrograde phenomena suggests for a careful distillation process monitoring using residual curve maps in combination with ternary diagrams to conduct the analysis and optimization of ethanol-water separation efficiency.

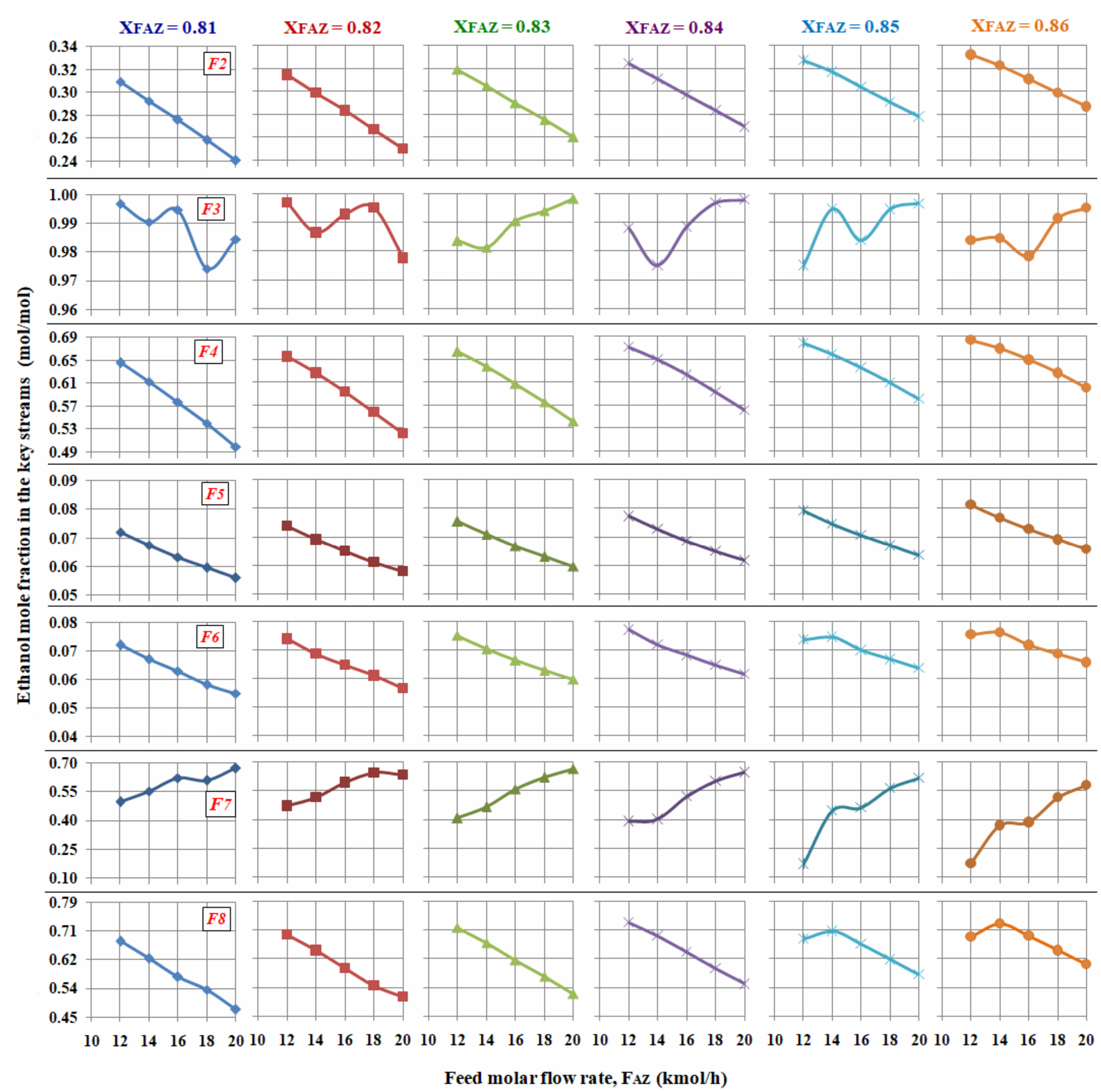


Figure 3. Variation of ethanol mole fraction in the key streams with feed molar flow rate in the azeotropic distillation plant.

The effect of the feed molar flow rate of the near azeotropic mixture on the cyclohexane mole fraction in the key streams (*S2*, *S3*, *S4*, *S5*, *S6*, *S7*, *S8*) is shown in Figure 4. The key streams connect the main processing units of the pilot plant. The mole fraction of the ethanol in the feed is between 0.81 and 0.86 mol/mol. Cyclohexane mole fraction in the key streams vary with near azeotropic feed mole flow rate. The flow rate of cyclohexane in the feed ranges from 10 to 20 kmol/h. The mole fraction of cyclohexane can be found in various streams as follows. The cyclohexane in the stream S2, S3, S4, S5, S7 and S8 has a range of 0.58 to 0.56, 0 to 0.08, 0.11 to 0.01, 0.92 to 0.95, 0.58 to 0.10 and 0.10 to 0.0 mol/mol, respectively. The observed mole fraction of cyclohexane in steam *S6* were the same as in stream *S5*.

Cyclohexane mole fraction in the product ethanol stream (*F3*) decreases with increase in ethanol mole fractionand molar flow rate of the feed as illustrated in Figure 4. This is mainly because of the increase in the performance of the ethanol-water azeotropic distillationplant which leads to the production of near absolute ethanol with higher purity. However, the increase in cyclohexane mole fraction in stream F3 with increase in near azeotropic feed flow rate is observed when the near azeotropic 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. This is attributed to retrograde phenomena which lead to the decrease in ethanol mole fraction in stream *F3*.

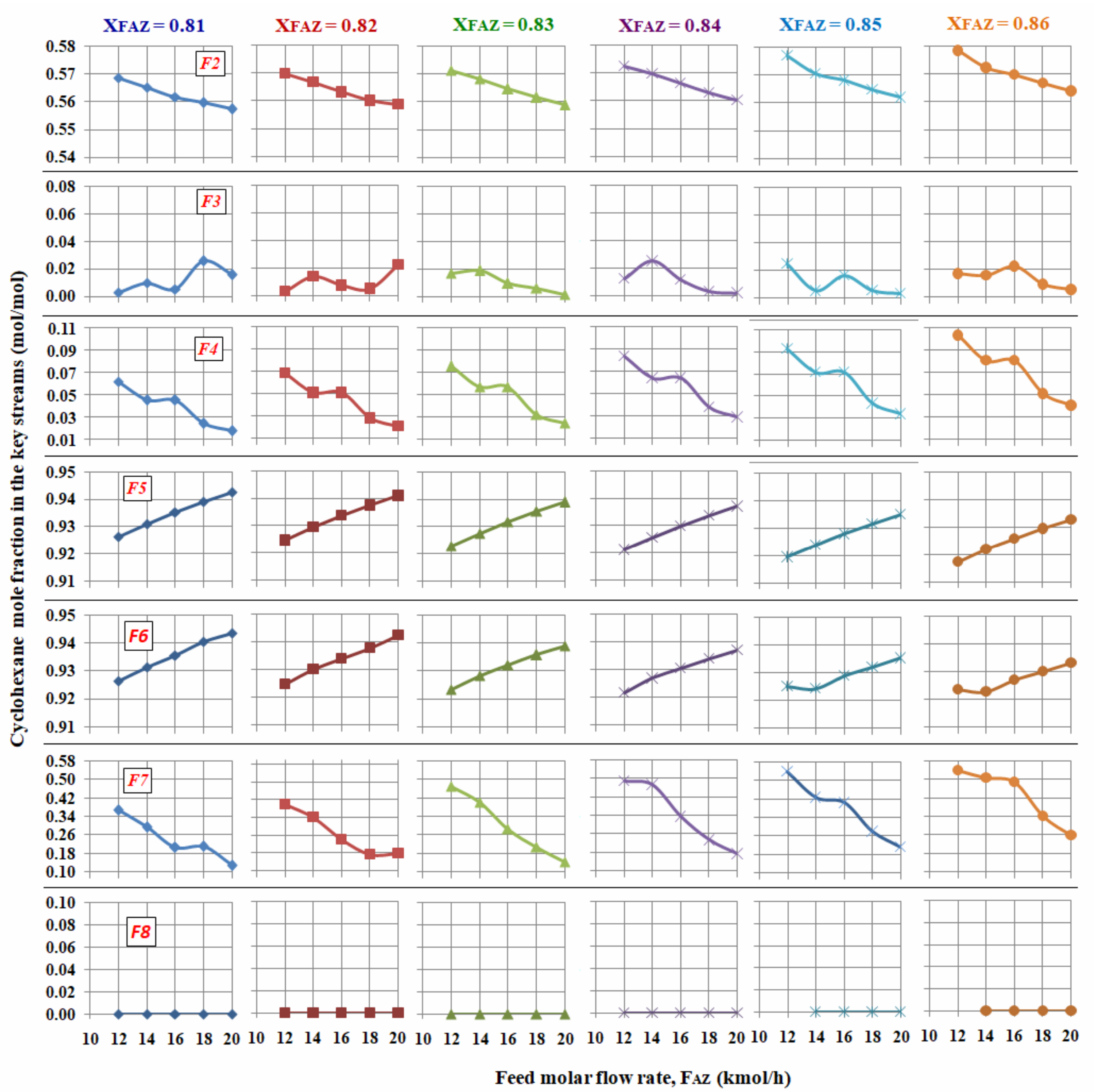


Figure 4. Variation of Cyclohexane mole fraction in the key streams with feed molar flow rate in the azeotropic distillation plant.

Further, from Figure 4 it can be observed that the increase in feed molar flow rate results into an increase in cyclohexane mole fraction in streams *S5* and *S6* which indicates a direct relationship. The decrease in cyclohexane mole fraction in streams *S2*, *S4* and *S7* indicates an inverse relationship. This is due to the increase in the amount of water content in streams *S2*, *S4*, *S5*, *S6* and *S7*. Also, it is observed that the mole fraction of cyclohexane in stream *S6* is approximately 0.15% times greater than the cyclohexane mole fraction in stream *S5* since stream *S6* is obtained after mixing stream *S5* with entrainer (pure cyclohexane) makeup stream. A significantly low cyclohexane mole fraction in stream *S8* indicates better separation performance whereby approximately more than 99% of the entrainer used is recovered during the process operation. Also as illustrated in Figure 4, increase in ethanol mole fractionin the feed results into both decrease in cyclohexane mole fraction in streams *S3*, *S5* and *S6* and increase in cyclohexane mole fraction in streams *S2*, *S4* and *S7*. This is due to increased ethanol and water mole fraction in vapors generated from the column 1 (COL-1). In column 1, the large fraction of water joins the vapor phase (as reported also by Gomis *et al*., 2000), exiting towards the condenser, and then into the decanter. As a result, ethanol, which joins the liquid phase flowing down to the reboiler is in large amount, leading to production of absolute ethanol in the bottoms stream, *S3*. The bottoms stream or product stream, *S3*, contains small traces of cyclohexane. This reflects the reason as to why the increase in ethanol results to the decrease in cyclohexane mole fraction as observed in the obtained results.

The ethanol and water content in the key streams of the azeotropic distillation process were studied in details as part of the plant performance assessment. The main streams are *S2*, *S3*, ..., *S8*, with stream flow rates *F2*, *F3*, ..., *F8* respectively. Figure 5 presents the water mole fraction in the key streams at different feed molar flow rates, F_{AZ}, ranging from 10 to 20 kmol/h. Increasing the feed molar flow rate, F_{AZ}, increased the water content in *S2*, *S4*, *S7* and *S8*, while water content dropped in streams *S5* and *S6*. Since the main purpose is to produce pure ethanol in stream *S3* (with stream flow rate *F3*as shown in Figure 5), the change in water content from 0 to 0.0005 mol/mol as F_{AZ} was changed from 10 to 20 kmol/h, is a good performance feature of the azeotropic distillation plant. Figure 5 shows that the water content in the rest of streams increased directly proportional to the feed molar flow rate as follows: water mole fraction from 0.08 to 0.22 mol/mol for *S2*; 0.20 to 0.50 mol/mol for *S4*; 0.10 to 0.35 mol/mol for *S7*; and 0.18 to 0.54 mol/mol for *S8*.

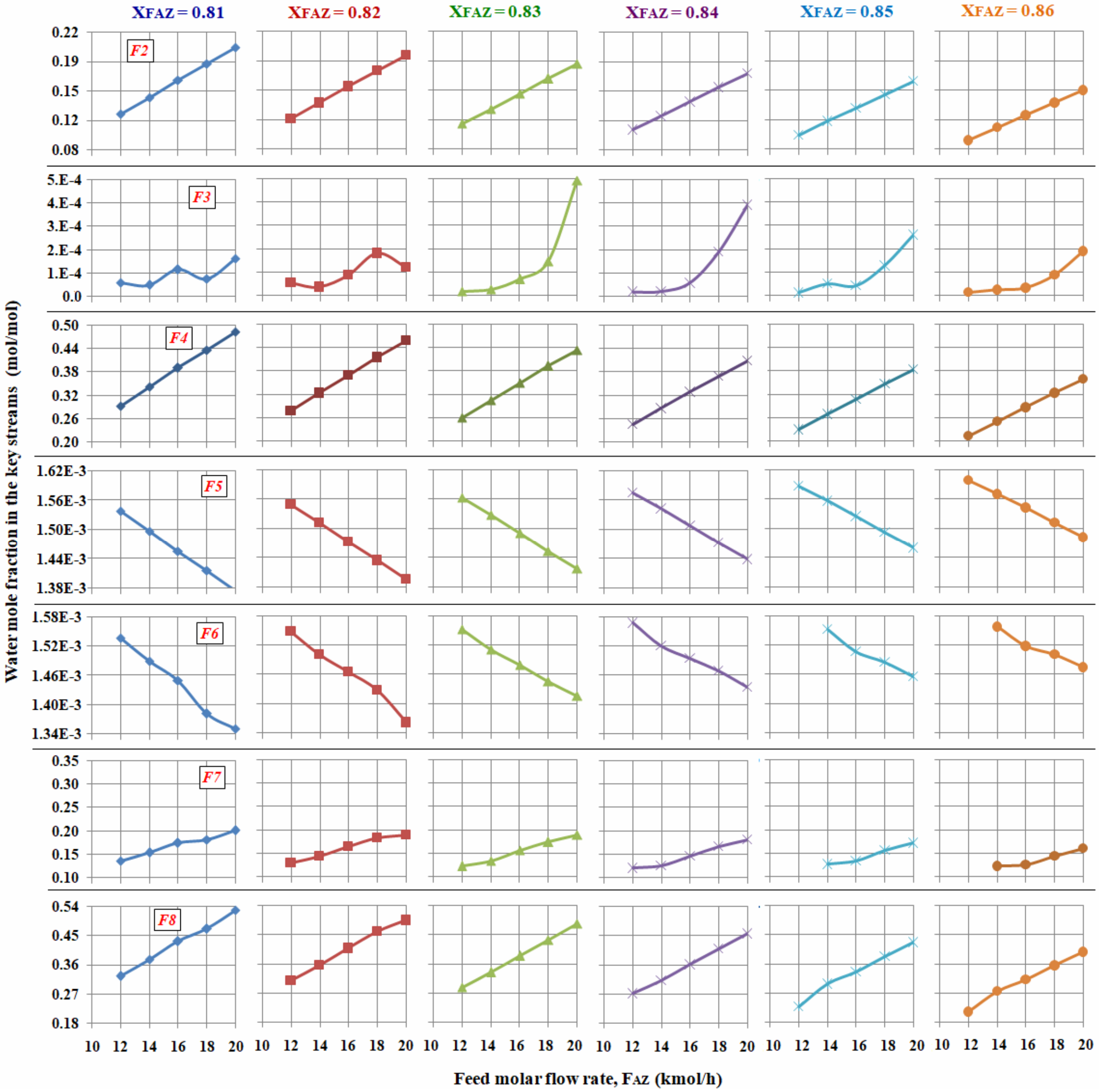


Figure 5. Variation of water mole fraction in key streams with feed molar flow rate in the azeotropic distillation plant.

However, decrease in water mole fraction in streams *S5* and *S6* as the feed molar flow rate was increased can be attributed to the increase in cyclohexane molar composition in the streams. Presence of traces of cyclohexane that accounts to less than 0.08 mol/mol in the product ethanol suggest that further ethanol purification process 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. Also, the presence of ethanol in stream *S8*(with molar flow rates *F8*) that ranges from 0.79 to 0.49 mol/mol indicates the economic potentiality of thestream and suggests that a further downstream processing is required to recover ethanol before discharging the water from the stream. High amount of ethanol mole fraction in stream *S8*is regarded as a process loss, necessitating reusing the stream as new feed to the pre-concentration process. The presence of ethanol fractions instream S8 has also been reported by other researchers to be attributed to difference in number of stages in the recycle column (Cairns and Furzer, 1990; Mortahed and Kosuge, 2003; Font *et al*., 2003; Chen *et al*., 2004; Luyben,2006a; Miranda *et al*., 2020).

From Figures 3, 4 and 5, it can be concluded that ethanol mole fraction varies inversely proportional to both cyclohexane mole fraction for streams *S3*, *S5*, *S6* and *S7* (with molar flow rate *F3*, *F5*, *F6* and *F7* respectively) and water mole fraction for streams *S2*, *S4* and *S8* and varies directly proportional to both cyclohexane mole fraction for streams *S2* and *S4*(with molar flow rate *F2* and *F4* respectively) and water mole fraction for streams *S5*, *S6* and *S7* (with molar flow rates *F5*, *F6* and *F7*). These relationships as observed in literatures indicate that production of 100% pure ethanol, water and cyclohexane cannot be achieved due to the fact that the distribution of components varies depending on the employed process. In general, the purity of near absolute ethanol produced and the overall performance of ethanol dehydration plant is affected by both ethanol mole-fraction in the feed, X_{FAZ}, and the feed molar flow rate, F_{AZ}.

3.2 Effect of Variation of Near Azeotropic Feed Molar Flow Rate (F_{AZ}) on Streams Flow Rates

Performance of an azeotropic distillation pilot plant is affected by both feed molar flow rate and the key stream's molar flow rates. This study revealed that the feed molar flow rates (between 10 and 20 kmol/h) have a positive linear relationship with the product ethanol molar flow rate. Similar observations were also reported by Luyben (2006b). The effects of feed mole flow rate on streams *S2*, *S4*, *S5*, *S6*, *S7*, *S8* and an entrainer makeup stream (*MUc*) for the given ethanol mole fraction are shown in Figure 6. As the ethanol-water molar flow rates were increased from 10 to 20 kmol/h, it affected the flow rates in the key streams. The observed changes in flow rates for stream *S2, S4, S5, S7, S8* and *MUc* are 18.80 to 20.60, 7.8 to 8.8, 11 to 12, 0 to 1.6, 6.9 to 7.9 and 0 to 1 kmol/h respectively. However, decrease in the flow rate from 12.05 to 11.85 kmol/h were observed in stream *S6*.

Also, from Figure 6, it is shown that the streams from the main operating unit affect the overall performance of an ethanol-water distillationprocess based on purity of the ethanol product. Higher molar flow rate of the main column distillate in the range of 18.80 to 20.60 kmol/h as compared to other streams is attributed mainly due to the fact that both recycle stream (*S6*) from the top of the recycle column and solvent mixture of entrainer makeup together with the organic solution phase from decanter are fed into the main column resulting into increase in the amount of condensed vapour at the top of the column for a fixed ethanol molar flow rate from the bottom of the column. Organic and aqueous solution phase molar flow rates are obtained due to liquid-liquid separation of condensed distillate heteroazeotrope on the basis of 0.5 mol/mol threshold value of water as the key component. This results into an average of 58.51% organic-aqueous phase split in the decanter.

Lower molar flow rate of entrainer makeup stream required to maintain ethanol dehydration plant performance that ranges from 0 to 1 kmol/h and recycle stream *S2* from the recycle column (COL-2) that ranges from 0 to 1.6 kmol/h, results from material balance model calculation around the mixer and pump respectively, to ensure plant convergence of the recycled streams. The lower flow rate of recycle stream from the top of recycle column indicates that more than 83.14% of the aqueous solution phase fed into the recycle column is produced as the recycle column bottom product.

The entrainer makeup stream (*MUc*) appears to behave similarly to the water stream F8 when the feed molar flow rate increases from 10 to 20 mol/h.

Conversely, as shown in Figure 6, the behavior of the entrainer makeup stream (*MUc*) is different from that of the main column distillate (*S2*)., recycle stream (*S7*), organic (*S5*) and aqueous phase solution (*S4*). This indicates that the increase in amount entrainer makeup required in achieving the desired ethanol dehydration performance in terms of product ethanol purity results into decrease in all key process streams flow rates. Thus, for effective separation and better ethanol dehydration plant performance a low amount of entrainer makeup is required. However, a higher flow rate of the key streams is preferred during azeotropic distillation plant operation due to the fact that high amount of entrainer can easily be recovered. This has been pointed also by Mortahed and Kosuge (2003).

A nearly perfect inverse relationship between stream *S6* with increasing in feed molar flow rate is a result of decrease in the amount of entrainer makeup stream (*MUc*). Additionally, a subsequent fluctuation occurred in the key streams (*S2*, *S4*, *S5*, *S7*, *S8*, and *MUc)* as the feed mole flowrate was changed from 14 to 20 kmol/h with a concentration between 0.81 and 0.86 mol/mol. Product ethanol purity and temperature in the ethanol enrichment section of the main column decrease as a result of retrograde phenomena, which in turn decreases the amount of overhead vapour.

Further, from Figure 6 it can be observed that for ethanol molefractionof 0.85 and 0.86 mol/mol in the feed a high amount of entrainer make up is required for effective azeotropic separation when feed molar flow rate is 12 kmol/h. Thus, at this operating condition, the performance of ethanol azeotropic distillation plant is low as compared to when ethanol mole fraction in the feed falls within the range of 0.81 to 0.84 mol/mol. This results into production of 97.51% and 98.45% product ethanol purity for the ethanol mole fraction of 0.85 mol/mol and 0.86 mol/molin the feed respectively. Nevertheless, the increase in key streams molar flow rate which in turn results into decrease in the required amount of entrainer makeup indicates a higher ethanol-water azeotropic distillation plant performance. These results concur with the study reported by Mortahed and Kosuge (2003). It was determined that entrainer recovery can be accomplished effectively by raising the flow rates of important streams and ensuring that pure ethanol produced from the main column has improved dehydration performance. Improvement of an ethanol-water azeotropic distillation plant's performance based on product ethanol purity is achieved when the feed molar flow rate and ethanol mole fraction in near-azeotropic feed are increased.

flow rates which result into the need of low amount of entrainer makeup hence saving energy and plant operating costs.

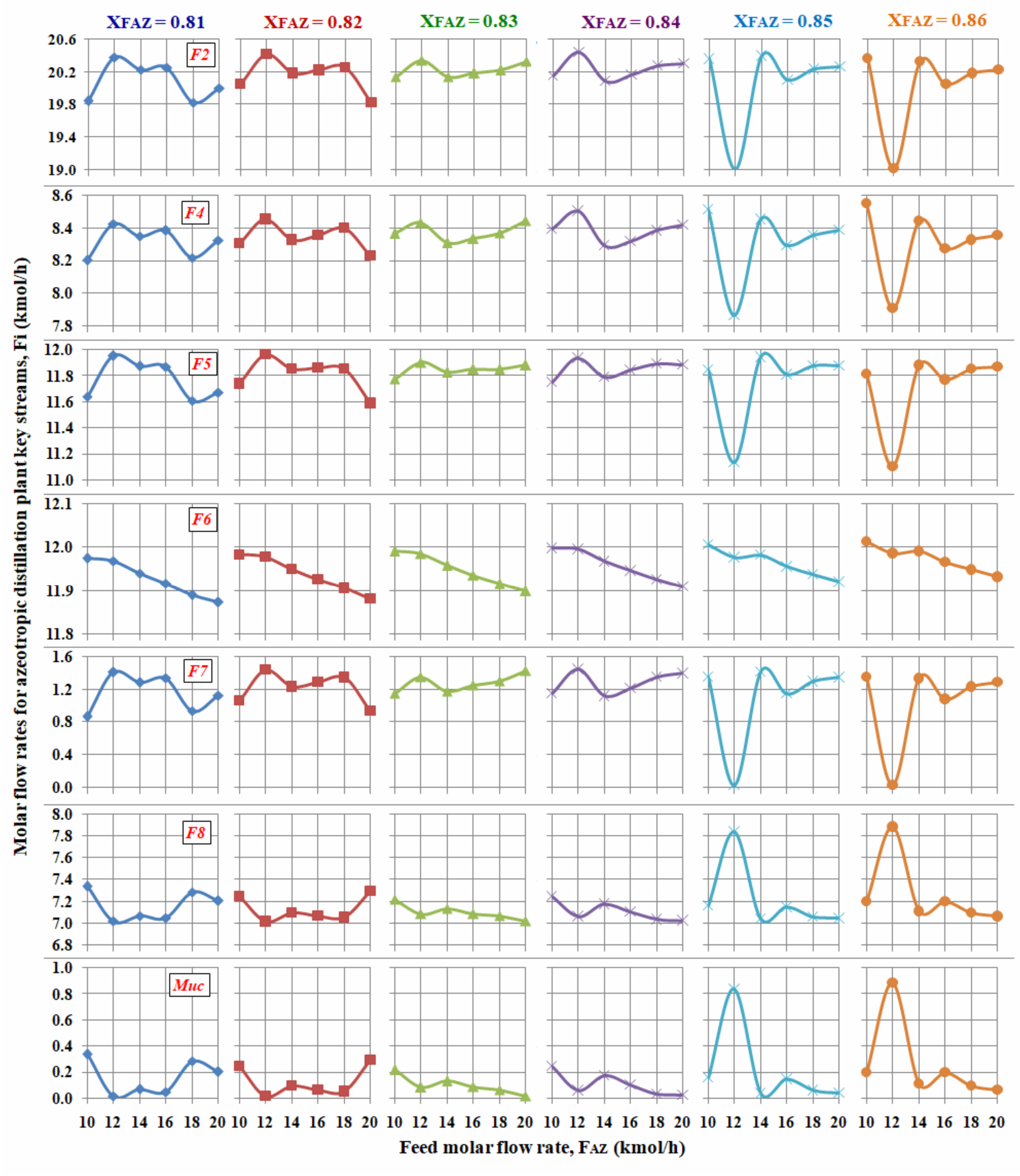


Figure 6. Variation of plant's key streams molar flow rates with feed molar flow rate for the feed ethanol mole fraction ranging from 0.81 to 0.86 mol/mol.

3.3 Effects of Variation of near azeotropic feed molar flow rate (F_{AZ}) on the energy requirements

Ethanol-water azeotropic distillation plant requires enough heatenergy to bring about separation degree required in the production of adehydrated ethanol. This section gives insight on how duties can be affected whenthe feed molar flow rate is increased and the ethanol mole fraction in the near azeotropic feed is varied from 0.81 mol/mol to 0.86 mol/mol. Figure 7 shows how near azeotropic feed molar flow rate varies withheat duties required bythe main column (COL-1) and the recycle column (COL-2)

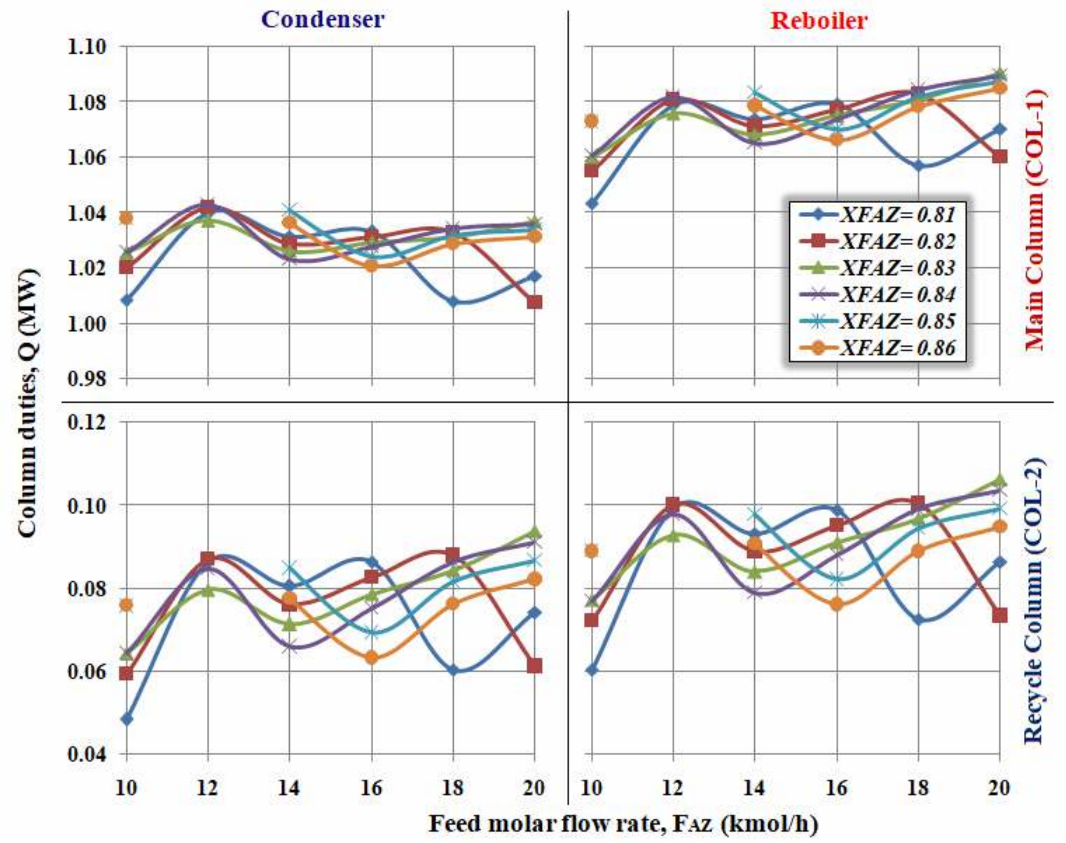


Figure 7. Variation of condenser and reboiler duties with feed molar flow rates in the ethanol-water azeotropic distillation plant.

Results show that column's condenser varies proportionally with their respective reboiler duties. Increase in feed molar flow rate increasesthe condenser and reboiler duties due tothe increased flow rates of recycle streams and improved product ethanol purity. However, decrease in both condenser and reboiler duties occurs when the near azeotropic 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. This is attributed to the effect of retrograde phenomena. Occurrence of retrograde phenomena reduces product ethanol purity and temperature in the ethanol enrichment section of the main column leading to the reduction in the overhead vapour. Decrease in the amount of overhead vapour from the main column, decrease in the condenser duty, which in turn leads to decrease in the reboiler duty.

In comparison, the condenser duty required by column 1 (COL-1) is approximately higher than 90.94% times the condenser duty required by column 2 (COL-2). But also, the reboiler duty required by column 1 (COL-1) is approximately higher than 90.25% times the reboiler duty required by column 2 (COL-2). Higher energy requirement in column 1 when compared to the energy requirement in column 2 is attributed to the fact that fact that column 1 (COL-1) receives high throughputs. This is mainly because the recycle stream (*S7*) flow rate from 0 to 1.6 kmol/h and solvent stream (*S6*) flow rate from 11.85 to 12.05 kmol/h, together with the near azeotropic feed stream, *F1*, flowing from 10 to 20 kmol/h are fed into column 1 whereby an aqueous solution phase stream (*S4*) is fed to the column 2 at the flow rate of 7.8 to 8.8 kmol/h.

The reboiler duty of the main column is approximately more than 3.26% times greater than its respective condenser duty whereas reboiler duty of the recycle column is approximately more than 11.7% times greater than its respective condenser duty. Higher difference between duties requirement in the column 2 is attributed 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. Similar observations were also reported in the work by Manyele (2021). Similarly, for the main column it is observed that the difference between reboiler and condenser duty is significantly low (< 0.06 MW) because the heteroazeotrope distillate vapour produced from the main column contains significant amount of heavy key components (water and cyclohexane). Hence, the condenser will require high amount of energy during cooling and condensation process to produce a liquid distillate.

In general, simultaneous increase of the feed molar flowrate and ethanol concentration in the near azeotropic feed increases the required duties in both columns. The observed results are attributed to the increased flow rates in the key streams of the ethanol-water azeotropic distillation process plant.

Variation of the feed molar flow rates withratios of the condenser to reboiler duties (*Qc*/*Qr*) for the main and recycle columns at 0.81 to 0.86 mol/mol ethanol mole fraction is presented in Figure 8.

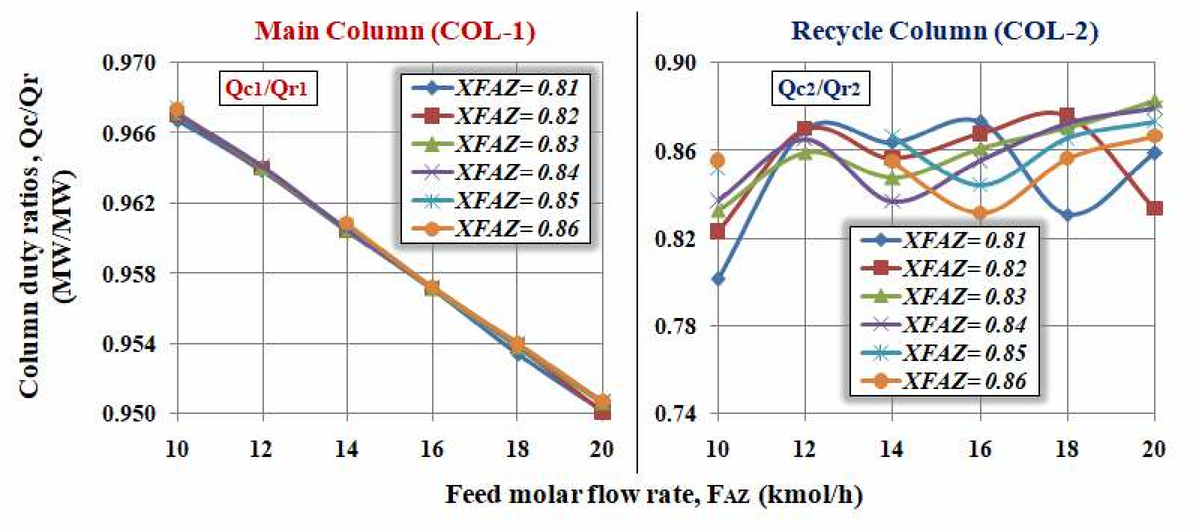


Figure 8. Variation of condenser to reboiler duty ratios (*Qc/Qr*) with feed molar flow rate in the azeotropic distillation plant.

As observed inFigure 8, increasing the feed molar flow rate decreases the ratio of the condenser duties tothe reboiler duties (*Qc/Qr*) from approximately 97% to 95% for the main column indicating an inverse relationship. Also, from Figure 8 it can be observed thatincrease in the feed molar flow rate significantlyeffect on the ratio of condenser duty to the reboiler duty (*Qc/Qr*)for the recycle column where subsequent fluctuation in the ratios is observed. The observed fluctuation in the condenser to reboiler duties(*Qc/Qr*) range isapproximately 90% to 80% for the recycle column.The observed trend of the ratio of recycle column duties when the molar flow rate of the feed is increased is attributed to the fact that the amount of water stream, F8, produced depends on the amount of recycle stream, *F7*, obtained from material balance model envelope around the pump so as to ensure process convergence.

In general, higher ratio of condenser duty to the reboiler duty (*Qc/Qr*) for column 1(COL-1) is observed when the molar flow rate of the feed is varied from 10 kmol/h to 20 kmol/h (i.e., 95% - 97%) as compared to similar ratio for column 2 (COL-2) (i.e., 74% - 90%). Such observation is attributed to large throughput processed in COL-1. This result into an increased column duty caused byan increased amount of vapour and liquid along the stages of the column.

Figure 9 shows variation of the feed molar flow rate of the near azeotropic mixture with duty to product ethanol ratios (*Qc/F3* and *Qr/F3*) at the given ethanol mole fraction ranging from 0.81 to 0.86 mol/mol. It was observed that the ratio of the duty to ethanol product for both column 1 (COL-1) and column (COL-2) (*Qc/F3* and *Qr/F3*) is decreased when the feed molar flow rates is increased. This is expected because increase in feed molar flow rate results into an increase in product ethanol flow rate (Luyben, 2012). As illustrated also in Figure 9, as the feed molar flow rate increases, the condenser duty to product ratio,*Qc1/F3*, and the reboiler duty to product ratio,*Qr1/F3*, forcolumn 1 (> 0.05 MWh/kmol) is greater than the same ratios for column 2(< 0.03 MWh/kmol). This indicates that for production of 1 kmol of ethanol a higher energy will be consumed in the main column mainly because it processes a higher throughput. Higher ratios of the duty to product, i.e., *Qc/F3* and *Qr/F3*, observed in column 1 is attributed to higher rate of throughput in the column as compared to column 2. Additionally, from Figure 9 it was observed that increasing the feed ethanol mole fraction from 0.81 mol/mol to 0.96 mol/mol at constant feed flow rates, results to the slight change ofduty to product ratios in column 1 in comparison to column 2.

In general, the observed decrease in duty to product ethanol ratios (i.e., *Qc/F3* and *Qr/F3*) for both columns when the ethanol-water near azeotropic feed molar flow rate is increased, indicates improved energy efficiency. Thus, in order to effectively utilize the amount of energy required and minimize the operating costs, higher flow rates (16 to 20 kmol/h) are preferred for enhancing energy efficiency and theperformance of ethanol-water azeotropic distillation plant based on ethanol concentration in the product.

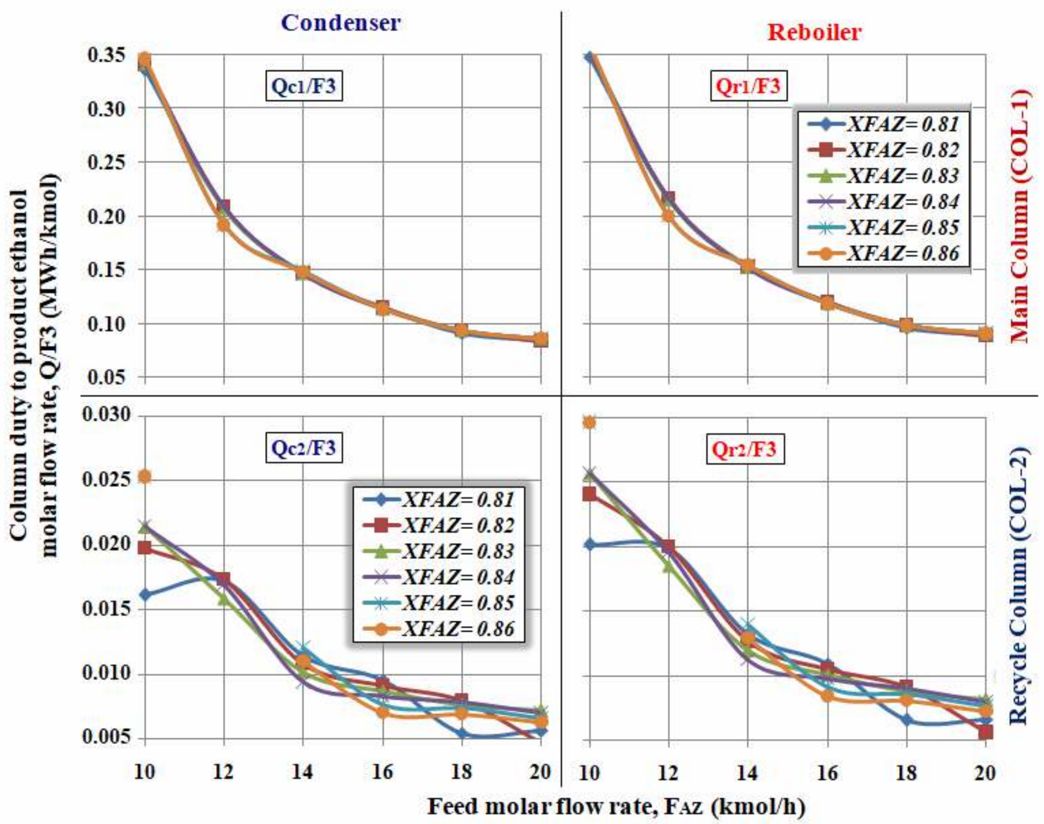


Figure 9. Variation of feed molar flow rate with column's duty to ethanol product ratios at given ethanol mole fractionin the feed.

4. Conclusion and Recommendation

This paper investigated the influence of feed molar flow rate on the key stream properties and energy duties in the ethanol-water azeotropic distillation plant. A pre-concentrated feed with ethanol mole composition near azeotropic point was used, with flow rate ranging between 12 and 20 kmol/h. Results showed that increasing the molar flow rate of the feed significantly affects the performance of ethanol-water azeotropic distillation plant. The desired purity of the product stream approximately greater than 95% was obtained when the ethanolmole fraction in the near azeotropic feed ranged from 0.81 to 0.86 mol/mol. Increasing the feed molar flow rate increase the performance of an ethanol-water distillation process by improving purity of the ethanol product. The condenser duty of the main column was around 90.94% higher than the recycle column's condenser duty and the reboiler duty of the main column were nearly 90.25% higher than the recycle column's reboiler duty. In comparison, higher energy consumption in column 1 than in column 2 was attributed to higher throughput in COL-1 than in the recycle column, COL-2. The ratio of column duty to ethanol product molar flow rates for the main column and recycle column, $Qc/F3$, and $Qr/F3$. The study concludes that to improve energy efficiency and the performance of ethanol-water azeotropic distillation plant for higher ethanol product purity, the plant should be operated at higher flow rate of near azeotropic feed preferably from 18 to 20 kmol/h. Further, a careful synthesis and plant's monitoring were recommended for an improved ethanol-water azeotropic distillation plant's performance and addressing the retrograde phenomena. Also, though the desired purity of greater than 95% product ethanol may be obtained, the presence of some traces of cyclohexane entrainer (< 0.08 mol/mol) suggest that further ethanol purification process is required. Also, significantly higher ethanol content in the bottoms (water stream) from the recycle column indicates its potential for reuse; consequently, the study recommends the stream to be recycled back to the feed in the pre-concentrating column.However, the limitation of this study is that the obtained results are based on simulation experiments. therefore, anempirical study on an actualethanol-water azeotropic distillation plant, using simulation conditions employed in this study,is required in order to validate the obtained results.

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