

Effects of ethanol concentration in the feed and feed thermal conditions on the performance of an azeotropic ethanol dehydration plant

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Abstract

The effect of ethanol concentration in the feed (X_{FAZ}) and feed thermal conditions (FTCs) on ethanol dehydration plant performance was investigated. The heterogeneous azeotropic distillation model with cyclohexane as an entrainer was built using Aspen Plus® V10 software. Non-random two liquid Redlich-Kwong (NRTL-RK) thermodynamic model was used for property analysis and performance prediction. The distillate product purity, streams compositions, flows and energy requirements were monitored. The X_{FAZ} was varied from 81% to 86% following pre-concentration while F_{AZ} ranged between 10 and 20 kmol/h. The distillate purity ranging between 95.5% and 99.84% mol ethanol was obtained and the plant consisted of a pre-heater, decanter and twin distillation columns operational blocks. Results show that X_{FAZ} , F_{AZ} and FTCs are the key operating parameters affecting plant performance. The main column operates at higher throughput resulting into higher condenser and reboiler duties compared to the recycle column leading to a higher Q_c/Q_r ratio for the main column. Similarly, the ratios of Q_{c1}/F_3 and Q_{r1}/F_3 were higher for the main column as compared to the ratios of Q_{c2}/F_3 and Q_{r2}/F_3 for the recycle column. Moreover, the ratio of the duty to F_{AZ} was also higher for main column than recycle column. The study concluded that for higher energy efficiency and product purity, the plant should be operated with X_{FAZ} = 0.81 to 0.86 mol/mol and at higher flows, F_{AZ} = 16 to 20 kmol/h, F_5 > 11.8 kmol/h and increased recycle stream flow rate (>1.2 kmol/h).

Keywords: Feed Thermal Conditions; Ethanol Concentration; Ethanol-Water Solution; Azeotropic Distillation; Ethanol Dehydration Plant Performance;

DOI: <http://dx.doi.org/10.4314/ijest.v17i1.5>

Cite this article as:

Monge E.S., Jeremiah J.M. and Manyele S.V., 2025. Effects of ethanol concentration in the feed and feed thermal conditions on the performance of an azeotropic ethanol dehydration plant. International Journal of Engineering, Science and Technology, Vol. 17, No. 1, pp. 76-92. doi: 10.4314/ijest.v17i1.5

Received: February 27, 2024, Accepted: January 14, 2025; Final acceptance in revised form: May 10, 2025

1. Introduction

Ethanol dehydration plant performance is measured in terms of key performance indicators (KPIs). KPIs are quantifiable measurements that indicate the success of the designed process in achieving the desired objective. KPIs are extremely vital for understanding, benchmarking and improving the plant performance (Zhu *et al.*, 2014). In an ethanol dehydration plant KPIs include ethanol purity, energy efficiency, amount of entrainer makeup, operating costs, production throughput, utility usage, maintenance downtime, safety and environmental impacts (Chen *et al.*, 2018). Feed compositions and thermal conditions are among process parameters affecting the distillation column separation efficiency and energy duties. Feed composition disturbances is the most common upset in distillation column and can easily shift the column composition profile causing larger upset in product specifications (Taqvi *et al.*, 2019). Manyele (2021) analyzed the effect of feed composition and thermal conditions on distillation plant performance via a computer model. The author observed that column reboiler duty increases with increase in feed composition and decrease in feed vapor fraction. Disturbances of ethanol concentration in the feed as highlighted by Mujiburohman *et al.* (2006) causes the molar composition changes in the plant process streams. This is due to variation in ethanol dehydration plant performance in terms of the purity of product ethanol as feed composition changes. Increase in ethanol concentration in the feed leads to increase in ethanol in the key process and hence affecting the

composition of both water and cyclohexane in the streams. According to Dongmin and Yanhong (2018) the amount of ethanol across the column stages increases with increase in ethanol concentration in the feed. Furthermore, increase in ethanol concentration in the feed reduces the water molar content in the feed causing all the amount of water to be removed in the vapor phase of the main column leading to production of dehydrated ethanol with small traces of cyclohexane (Gomis *et al.*, 2000). Belincanta *et al.* (2005) investigated the effect feed concentration on the hydrodynamics of the distillation column. The authors found that disturbances in ethanol concentration in the feed results into changes in composition and flows profile inside the column resulting into either increase or decrease in vapor flows. Further, the authors concluded decrease in vapor flows allowed a wider distribution of ethanol across the column stages leading to a better separation. Li *et al.*, (2022) evaluated the effect of feed concentration disturbances on a self-heat recuperative azeotropic distillation for separating an ethanol-water mixture. They reported that the decrease in ethanol composition in the feed causes fluctuations in product purity leading to production of ethanol and water that do not satisfy the requirements. Overall, disturbances of ethanol concentration in the feed and feed thermal conditions have significance impact in column separation efficiency. This is due to fluctuations in vapor and liquid phase distribution and mass transfer across the column stages. Moreover, the use of cyclohexane as an entrainer results into aqueous phase richer in ethanol concentration (Vasconcelos and Wolf-Maciel, 2010).

In addition, disturbances of ethanol concentration in the feed affect the temperature, phase split and mass transfer in the distillation column. This is mainly due to variation in the composition of liquid and vapor phases across the column stages. Variation of these compositions has significant effect on the enthalpy and column operating duty leading to changes in the amount of generated overhead vapors. Changes in the key process streams as a result of disturbances in the feed composition and feed thermal conditions affects the overall dehydration plant performance in terms of dehydrated ethanol purity. Mortahed and Kosuge (2003) analyzed the effect of recycle streams flow rate and discovered that increase in recycle streams flow rates increases the vapor and liquid flow rates across the column stages leading to a better dehydration performance. The authors also suggested that a higher dehydration performance is characterized by low amount of entrainer makeup used. Further, as highlighted by Vasconcelos and Wolf-Maciel (2010) increase in the molar flow rate of aqueous solution phase results into a better dehydration plant performance. Similarly, as pointed out by Manyele (2021) feed thermal conditions have significant effect on vapor and liquid distribution across the column stages. Increase in feed vapor fraction results into increase in the concentration of overhead vapor and consequently leading to decrease in amount of liquid in the stripping section and hence decrease in reboiler duty. Conversely, decrease in the feed vapor fraction results into increase in the amount of amount of liquid in the stripping section and hence more energy in the reboiler will be required to generate necessary vapors for efficiency separation. In summary, fluctuations in vapor and liquid distribution across the column stages due to feed composition and thermal condition disturbances results into variation in intermediate streams flow rates and thus affecting the plant dehydration performance. In an azeotropic plant intermediate streams include organic and aqueous solution phase from the decanter.

Ethanol concentration in the feed is among the process operating parameter that significantly affects the azeotropic process configurations (number of columns and their sequences) and the overall performance of an ethanol dehydration plant in terms of dehydrated ethanol purity (Wang *et al.*, 2014; Li *et al.*, 2022). Number of columns required to obtain absolute ethanol increases with decreasing in ethanol concentration in the feed leading to an increase in the overall plant operating costs and energy requirements. For instance, for very dilute ethanol-water solutions (with ethanol less than 10% mol) four minimum columns will be required, with two columns acting as pre-concentrators. Moreover, for normal ethanol-water solutions (with ethanol ranging from 10% to 60% mol) a minimum of three columns will be required, with one column acting as a pre-concentrator. Energy requirements in azeotropic distillation plant are optimized when the composition of the fresh feed used approaches an ethanol-water azeotrope (Luyben, 2012). According to Belincanta *et al.* (2005) disturbances in feed composition affects the distribution of vapor and liquid phases across the column stages which consequently results into fluctuations in column energy requirements. Miranda *et al.* (2020) investigated the performance of an azeotropic distillation process with cyclohexane as an entrainer and concluded that a better performance of the plant occurs at a higher energy requirement. Conde-Mejía and Jiménez-Gutiérrez (2020) and Silva *et al.* (2021) investigated the effect of ethanol concentration in the feed on the performance of a catalytic distillation process for ethanol dehydration. In these studies, it was found that increasing ethanol concentration in the feed leads to a higher energy consumption due to the increased vaporization heat, but it also resulted in higher production rate and higher ethanol purity. In summary, the molar composition of ethanol in the feed can affect the performance of ethanol dehydration processes, such as the recovery rate, purity, and energy consumption. Ethanol concentration in the feed depends on the specific process and plant design, and it is important to evaluate the effect of various feed compositions to optimize the plant performance.

In general, this study aims at analyzing the effect of ethanol concentration and feed thermal conditions on ethanol dehydration plant in terms of product ethanol purity. The design and simulation of an azeotropic distillation plant in this research was accomplished by the use of Aspen Plus® V10 commercial simulation software. Further, this research provides more insight and details on the effect of ethanol concentration in the feed (X_{FAZ}) and feed thermal conditions ($FTCs$) on energy requirements together with molar flow rates and compositions of the key process streams connecting the main operational blocks (pre-heater, main column, decanter and recycle column) of the azeotropic plant. This study is crucial at it offer optimal solutions in enhancing ethanol-water azeotropic distillation process to produce a near-absolute ethanol by manipulating the feed ethanol concentrations and thermal conditions.

2. Methodology

2.1 Azeotropic distillation model build-up and convergence

The simulation model for an azeotropic distillation pilot plant was developed by using Aspen Plus® V10 simulation software. The procedures taken in model development include: (a) property specification and analysis, (b) azeotropic distillation process flow sheeting and convergence, (c) modeling and simulation of the converged azeotropic distillation process and (d) data collection and analysis. Moreover, the procedures taken in property specification and analysis (as shown in Figure 1) include: (i) component specification, (ii) selection of thermodynamic fluid package and (iii) distillation synthesis. The main components (ethanol, water and cyclohexane) of the plant process streams were specified and selected from Aspen property databanks, so as to accurately determine the appropriate thermodynamic fluid package. The specified components are pure and of conventional type because they participate in phase and chemical equilibrium calculations. The modified non-random two liquid-Redlich Kwong (NRTL-RK) thermodynamic model that uses Equation (1) and Equation (2) was selected as the base method in this study due to the fact that it is highly recommended for non-ideal (ethanol-water) chemical systems and it appropriately describes the vapor-liquid and liquid-liquid equilibrium data (Green and Perry, 2008; Haghtalab *et al.*, 2011; Qasim *et al.*, 2016; Taqvi *et al.*, 2016; Miranda *et al.*, 2020). Distillation synthesis (based on ternary diagram and residue curve map analysis) was thereafter conducted by specifying pressure of 1 atm and vapor-liquid-liquid as the component phases for the aim of determining split feasibility and azeotropes present in the ethanol-water-cyclohexane mixture. This allows the computation of their respective distillation boundaries, phase envelopes and residue curve maps.

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{ki}} \right) \quad (1)$$

where:

$$\begin{aligned} G_{ij} &= \exp(\alpha_{ji} \tau_{ji}) \\ \tau_{ij} &= a_{ij} + \frac{b_{ij}}{T} + e_{ij} \ln T + f_{ij} T \\ a_{ij} &= c_{ij} + d_{ij}(T - 273.15K) \\ \tau_{ii} &= 0 \text{ and } G_{ii} = 1 \end{aligned}$$

The parameter α_{ji} characterizes the tendency of components j and i to be distributed in a non-random manner. Parameters G_{ij} and τ_{ij} represents the non-random coefficient and normalized parameters for symmetric systems, respectively. Binary parameters a_{ij} , b_{ij} , d_{ij} , e_{ij} and f_{ij} are unsymmetrical ($\therefore a_{ij} = a_{ji}$) and can be determined from regression of VLE and LLE data, T is the temperature and the recommended values of c_{ij} are such that 0.30 for non polar substance, 0.20 for saturated hydrocarbons with polar associated liquids and 0.47 for strongly self-associated non polar substance

$$p = \frac{R - T}{V_m - b} - \frac{a}{V_m(V_m - b)} \quad (2)$$

where: p is the gas pressure, R is the universal gas constant, V_m is the gas molar volume, k is the interaction parameter, a and b are correction constants for molecules attractive potential and volume, respectively. For multiple components in the mixture, these constants are determined as follows:

$$\begin{aligned} a &= \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{a,ij}) \\ b &= \sum_i \sum_j x_i x_j \left(\frac{b_i + b_j}{2} \right) (1 - k_{b,ij}) \end{aligned}$$

The development and simulation of an azeotropic distillation plant process flowsheet include defining of the process connectivity by placing the required unit operations (blocks) from the model library and their respective connecting process streams. Moreover, this step also include: specifying input process stream properties (pressure, temperature, composition and flow rate), selection of flowsheet convergence criterion from convergence block and configuring flowsheet balance model to calculate the flow rate of entrainer makeup stream and tear stream (in this case recycle stream) so as to solve the process convergence problem. In addition, during azeotropic distillation plant model development and simulation, column operating parameters ($R = 5$, $p = 1$ atm, $N_{FP1} = N_{FP2} = 4$ and $N_{RFP} = 3$), ethanol concentration in the feed (0.81 mol/mol), feed thermal conditions (SCL at 28°C) and flow rate at 10 kmol/h were fixed in order to minimize the process complexity and address the effect of process convergence and parametric sensitivity. The fixed values of column operating parameters were obtained based on the shortcut and rigorous design of an ethanol-water pre-concentrating column together with the former study of on the analysis of the effect of reflux ratio on pre-concentrating dilute ethanol solutions to produce a near-azeotrope feed. After solving the process convergence problem, modeling and simulation of the converged process was conducted. This was achieved by varying plant operating parameters which includes: pre-heater operating vapor fraction in the range of 0 to 1, column feed plate locations, i.e., from 4 to 10 for main column feed, 2 to 10 for recycle column and for recycle and solution streams, ethanol concentration from 0.81 to 0.86 mol/mol and flow rate of the feed from 10 to 20 kmol/h. The obtained simulation results were then analyzed and exported to MS Excel 2007. The use of MS Excel 2007 was due to the fact that it provides an easy way for organizing and plotting the obtained modeling and simulation results.

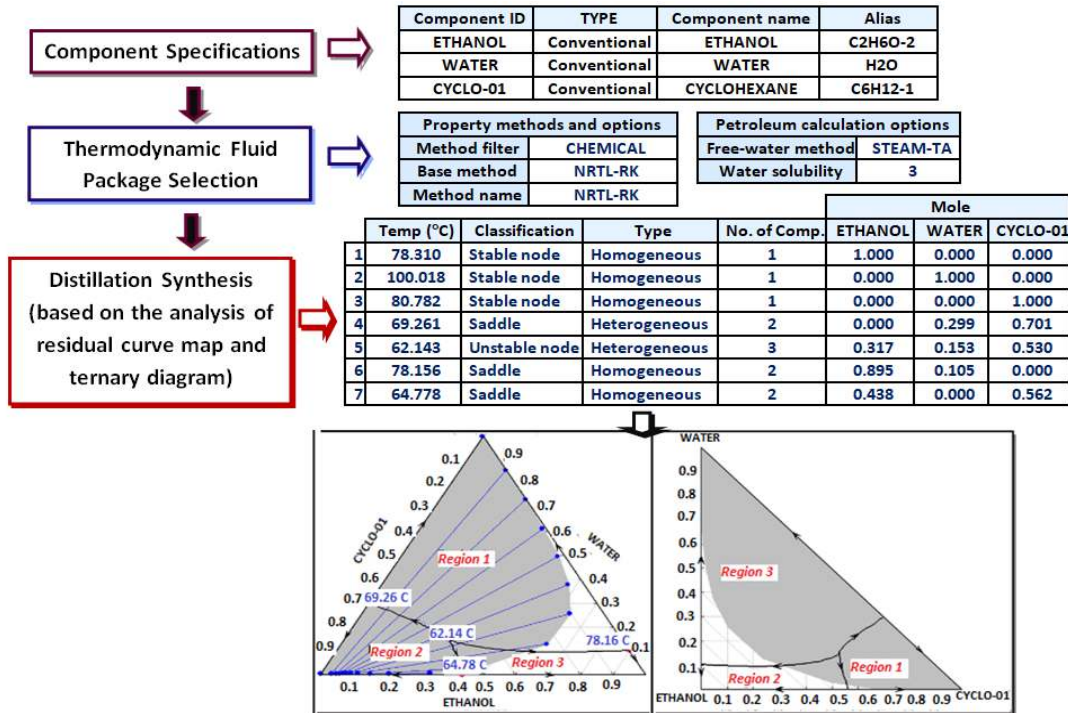


Figure 1. Detailed procedures for the property specification and analysis in Aspen Plus® V10 simulation software.

2.2 Process flowsheet development and simulation

Azeotropic distillation simulation process flow sheet (illustrated in Figure 2) was configured block-wise by using respective unit operations. The latter includes twin RadFrac distillation columns, that is the 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 1. Moreover, as shown in Figure 2 the heat streams for the main column and recycle condenser are denoted as QCON1 and QCON2, respectively. Whereas, the heat streams for the main column and recycle reboiler are denoted as QREB1 and QREB2, respectively. The twin RadFrac distillation columns, that is the main column (COL-1) and the recycle column (COL-2) were configured using equilibrium as calculation type for vapor-liquid valid phases and strong non-ideal liquid set as convergence criterion, while specifying total condenser and kettle reboiler. The decanter, denoted as DECANter in Figure 2 was specified based on not only operating duty and pressure but also by specifying water as the key component for identifying the second liquid phase with 0.5 as threshold molar fraction value for the key component. Selection of 0.5 as threshold molar fraction value for the key component aimed at ensuring that the liquid-liquid separation in the decanter is attributed by 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, denoted as HEATER in Figure 2 was modeled by using pressure together with either vapor fraction or temperature as flash type depending on feed thermal conditions. On the other hand, the mixer denoted as MIXER was specified by using pressure for vapor-liquid valid phases. The operation of valve denoted as VALVE was configured by using adiabatic flash for specified outlet pressure (pressure changer) as calculation type with a value of 1 atm specified and the pump denoted in Figure 2 as PUMP was modeled by using a pressure ratio of 1 for the aim of maintaining main column operating pressure.

The simulation model convergence for the azeotropic distillation plant process flowsheet (as illustrated in Figure 2) was achieved through the use of both flowsheet convergence and balance node. 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 because below these values, iteration errors occur, i.e., non-convergence was observed 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 S_8 produced from the bottom of recycle column (COL-2) by specifying the bottoms rate in COL-2 based on result calculated from the material balance envelope. Thus, the molar flow rate of water stream (S_8) becomes an independent variable. Therefore, in order to account for the effect of recycle streams, i.e., S_5 and S_7 described in Figure 2 as RECY-SOL and RECYCLE, respectively, in process convergence, a new solver with ID CV-1 of type WEGSTEIN was created in the flowsheet convergence node. Stream S_6 (described as SOLUTION in Figure 2) 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 F_7 and F_9 was created by specifying 1 as the material balance number and also by selecting both PUMP and MIXER as the main blocks to define material balance envelope.

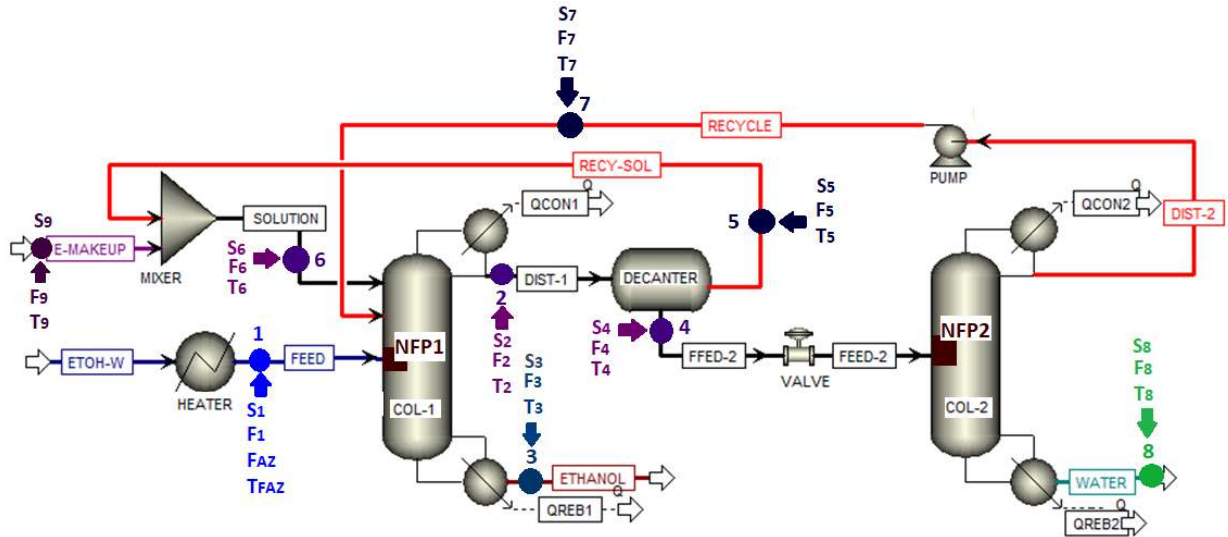


Figure 2. Azeotropic pilot plant process flowsheet indicating key locations for performance analysis (Key: F_x = flow rate; T_x = Temperature for all streams, S_x).

Table 1. Description of the process streams used in azeotropic distillation process flow sheet

Stream	Name	Flow Rate	Temperature	Description
S_1	ETOH-W	F_1	T_1	Pre-conditioned near-azeotrope feed stream with molar flow rate F_1 and temperature T_1 .
	FEED	F_{AZ}	T_{FAZ}	Conditioned near-azeotrope feed stream from the pre-heater to the main column (COL-1) with molar flow rate F_{AZ} and temperature T_{FAZ} .
S_2	DIST-1	F_2	T_2	Main column distillate stream with molar flow rate F_2 and temperature T_2 entering the decanter for separation of ternary azeotropic solution to produce stream S_5 denoted as RECY-SOL that contain high amount of entrainer and stream S_4 denoted as FFED-2 which contain significant amount of ethanol.
S_3	ETHANOL	F_3	T_3	Near absolute ethanol stream from the bottom of the main column with molar flow rate F_3 and temperature T_3 .
S_4	FFED-2	F_4	T_4	Aqueous solution phase stream from the decanter to the valve.
S_5	FEED-2	F_4	T_4	Aqueous solution phase stream from the valve to the recycle column (COL-2).
S_5	RECY-SOL	F_5	T_5	Organic solution phase from the decanter to the mixer
S_6	SOLUTION	F_6	T_6	Mixed solution of entrainer and organic solution phase necessary to ensure effective azeotropic separation fed to the main column.
S_7	DIST-2	F_7	T_7	Recycle column distillate stream which contains significant amount of entrainer entering the pump, with molar flow rate F_7 and temperature T_7 .
S_7	RECYCLE			Recycle column distillate stream from the pump recycled back to the main column.
S_8	WATER	F_8	T_8	Bottom product stream from the recycle column with molar flow rate F_8 and temperature T_8 .
S_9	E-MAKEUP	F_9	T_9	Entrainer makeup stream with molar flow rate F_9 and temperature T_9 .

2.3 Azeotropic distillation pilot plant operating parameters

Due to the complexity of the process and large number of variables required to ensure process convergence, some variables (as shown in Table 2) 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. The molar composition of near-azeotrope feed is reached by operating the main column in a normal distillation mode. Furthermore, the feed molar flow rate was estimated based on the expected size of the plant to be designed. Thus, based on the feed 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 effect of feed flow rate on 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 (< 2%). In addition, the minimum feed molar flow rate of 10 kmol/h was used as initial estimate flow rate mainly due to preliminary model simulation results which indicated that the use of feed molar flow rate below 10 kmol/h resulted into unacceptable result (such as when the purity of dehydrated ethanol is below the ethanol-water azeotrope and feed molar purity). Furthermore, for the aim of ensuring that there is no any energy requirement at the decanter; the decanter operating duty was fixed at 0. The total number of column stages for both main and recycle column specified in Table 2 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 ($N_a = N - 2$). Additionally, in this study the key operating parameters including X_{FAZ} with values of 81%, 82%, 83%, 84%, 85% and 86% were each tested for various FTCs (i.e., SCL, FBP, PVF, VF and SF) with F_{AZ} of 10, 12, 14, 16, 18 and 20 kmol/h for fixed operating conditions as shown in Table 2, i.e., $N = 12$, $R = 5$ mol/mol, $p = 1$ atm, $N_{FP1} = N_{FP2} = 4$ and $N_{RFP} = 3$, while monitoring the product purity, streams compositions, flows and column energy requirements.

Table 2. 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 and recycle column feed plate	N_{FP1}	4
Main and recycle column feed plate	N_{FP2}	4
Main column recycle feed plates	N_{RFP}	3
Ethanol concentration in the near-azeotrope feed	X_{FAZ}	0.81 – 0.86 mol/mol
Near-azeotrope feed molar flow rate	F_{AZ}	10 – 20 kmol/h
Pre-heater operating vapor fraction	x_f	0 – 1 SCL and FBP ($x_f = 0$)
Feed thermal conditions	FTCs	PVF (0 < x_f < 1) VF and PVF ($x_f = 1$)

3. Results and Discussion

3.1 Azeotropic distillation pilot plant

The azeotropic distillation pilot plant model for producing absolute ethanol from near-azeotrope pre-concentrated ethanol-water solutions was developed in this study. The designed plant (as shown in Figure 3) consists of a pre-heater denoted as HEATER for feed thermal conditioning, decanter denoted as DECANter for natural liquid-liquid separation of a ternary heteroazeotrope and two distillation columns (i.e., main column denoted as COL-1 for azeotropic distillation and recycle column denoted as COL-2 for entrainer recovery) acting as the main operational blocks. The model was configured block-wise and uses NRTL-RK model for property analysis and performance prediction of the plant. Further, the designed process operates under fixed column parameters, i.e., $N_a = 10$, $p = 1$ atm and $R = 5$ mol/mol. Figure 3 shows the molar compositions and flow rates of key process streams connecting the main operational blocks of the designed azeotropic distillation plant. The near-azeotrope feed (with X_{FAZ} ranging from 81% to 86% mol, F_{AZ} ranging from 10 to 20 kmol/h) was thermal conditioned via heating process in a pre-heater and sufficient amount of pure entrainer (cyclohexane) makeup ranging from 0.01 to 0.9 kmol/h were fed first into the main column. In the main column, the relative volatilities of ethanol-water solutions were altered due to the presence of cyclohexane across the column stages. This resulted into phase splitting and fluid phase inverse from which water was immediately removed in the vapor phase as highlighted also by Gomis *et al.* (2000). Excess removal of water in the main column enrichment sections causes water-free extractive separation of ethanol-cyclohexane mixture in the stripping section, this consequently led to the production of near-absolute 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. Furthermore, the generated overhead vapors in the main column enrichment section approach a ternary heteroazeotrope of ethanol-water-cyclohexane system. After the produced overhead vapors were cooled by a total condenser, an immiscible liquid with ethanol (24.07%-33.43% mol), water (9.01%-20.20% mol) and cyclohexane (55.73%-57.56% mol) was obtained and then fed first into the decanter in order to avoid three

phase distillation problems which may lead to erroneous results and increase in both cost and energy requirements. In the decanter, a natural liquid-liquid separation based on density segregation with no energy requirements is conducted. Natural liquid-liquid separation resulted into production of organic solution with an average of 13.42%, 0.48% and 97.98% recovery efficiency of ethanol, water and cyclohexane, respectively at 11.1 to 12 kmol/h. An aqueous solution with an average of 86.58%, 99.52% and 2.02% recovery efficiency of ethanol, water and cyclohexane, respectively at 7.82 to 8.6 kmol/h was also produced from the decanter. Organic solution (S_5) containing high amount of cyclohexane (91.71 to 94.26%) was mixed with pure entrainer makeup to generate the necessary amount of solution (ranging from 11.87 to 12 kmol/h) required to effect azeotropic separation and thereafter fed into the main column. Moreover, the aqueous solution (S_4) contains significant amount of ethanol and since it falls within different distillation region in a ternary diagram, it was fed into conventional recycle column. In the recycle column, a recycle stream (S_7) with an average of 17.31%, 6.54% and 100% recovery efficiency of ethanol, water and cyclohexane, respectively at 0.02 to 1.5 kmol/h was produced and recycled back into the main column. Also, from the recycle column, stream S_8 with an average of 82.69%, 93.46% and 0% recovery efficiency of ethanol, water and cyclohexane; respectively at 7.0 to 7.9 kmol/h was produced. The higher the ethanol molar composition in stream S_8 as compared to other literatures is mainly due to the difference in number of stages. Additionally, the low amount of water content ($< 0.02\%$) in product ethanol stream (S_3) and cyclohexane makeup molar flow that ranges from 0.01 to 0.9 kmol/h as highlighted by Mortahed and Kosuge(2003) indicates a better dehydration performance of the plant. Based on the process configuration the cyclohexane makeup used is pure; however, a dilute cyclohexane solution may also be used in the process but must be fed directly into the decanter.

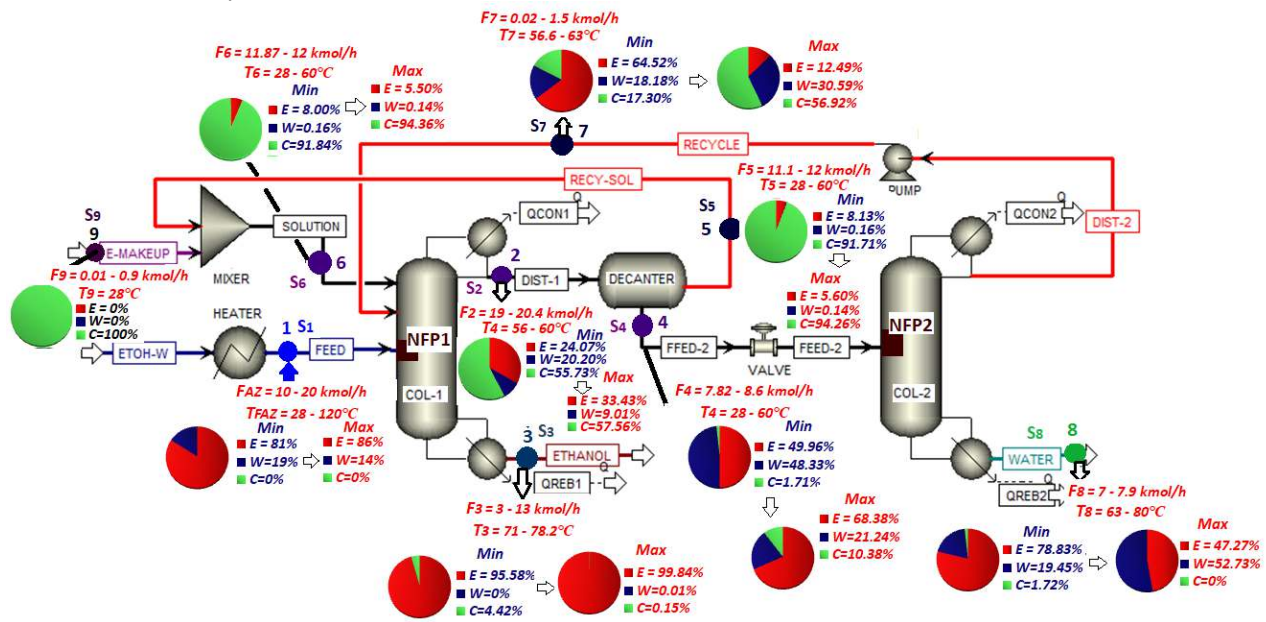


Figure 3. Molar compositions and flow rates of the key streams connecting the main operational blocks of the azeotropic plant (Key: E = ethanol; W = water; C = cyclohexane).

Overall, the production of 99.78% ethanol, 97.98% and 99.52% recovery efficiency of cyclohexane and water in the organic and solution phase, respectively together with 93.46% and 0% recovery efficiency of water and cyclohexane in the water stream S_8 , respectively indicates a better dehydration performance of the azeotropic pilot plant. The stream S_8 contains mainly ethanol (47.27%-78.83% mol) and water (19.45%-52.73% mol), thus this indicates the economic potentially of the stream to be pre-concentrated and reused as a feed in the azeotropic plant before discarding it. A higher dehydration plant performance in terms of product ethanol purity was obtained when feed with X_{FAZ} ranging from 81% to 86% mol/mol was used; this higher concentration can be obtained by initially operating the main column in a normal distillation mode. In addition, based on process configuration the designed azeotropic distillation plant can be operated in different modes. These include azeotropic distillation, pressure swing distillation with the main and recycle column acting as the high- and low-pressure column, respectively and conventional distillation with both main and recycle column acting as pre-concentrators.

3.2 Effect of ethanol concentration in the feed (X_{FAZ}) and feed thermal conditions (FTCs) on stream compositions

Ethanol concentration in the feed (X_{FAZ}) is a process parameter that affects the performance of ethanol dehydration plant in terms of the final product ethanol purity. This section presents the analysis of the effect of X_{FAZ} and FTCs on key process streams of the azeotropic distillation plant, i.e., S_2 , S_3 , S_4 , S_5 , S_6 , S_7 and S_8 . Sub-cooled liquid feed (SCL), feed at boiling point (FBP), partially vaporized feed (PVF), vaporized feed (VF) and superheated feed (SF) are the FTCs analyzed. Figure 4 presents the effect of X_{FAZ} on ethanol molar composition in the key process streams connecting the main operational blocks of the azeotropic distillation plant and for various FTCs. Further, Figure 4 shows the plot of ethanol molar composition in the key process streams (S_2 , S_3 , S_4 , S_5 , S_6 , S_7 and S_8) against X_{FAZ} for feed thermal conditions (SCL, FBP, PVF, VF and SF) together with F_{AZ} ranging from 10 to 20 kmol/h. The increase in the X_{FAZ} from 0.81 to 0.86 mol/mol results into an increase in ethanol

molar composition from 0.24 to 0.32 mol/mol for stream S_2 , 0.50 to 0.68 mol/mol for stream S_4 , 0.055 to 0.083 mol/mol for stream S_5 , 0.053 to 0.083 mol/mol for stream S_6 and 0.48 to 0.79 mol/mol for stream S_8 as shown in Figure 4. Also, increasing X_{FAZ} from 0.81 to 0.86 mol/mol results into variations in the ethanol molar composition in the range of 0.93 to 0.999 mol/mol for the main product stream S_3 and from 0.10 to 0.70 mol/mol for recycle stream S_7 . The ethanol molar composition in the streams (S_2 , S_4 , S_5 , S_6 and S_8) increases with increase in X_{FAZ} . This observation can be attributed by the fact that increase in X_{FAZ} results into increase in ethanol concentration in the key process streams (Mujiburohman *et al.*, 2006) and also increase in ethanol molar content across the main column stages (Dongmin and Yanhong, 2018). This causes an increase in ethanol molar content in the overhead vapors of the main column. On the other hand, the ethanol molar composition in the recycle stream (S_7) decreases with increase in ethanol concentration in the feed due to increase in stream S_8 ethanol molar concentration. This indicates an inverse proportional behavior between the two streams (S_7 and S_8). This relationship is due to the fact that both streams are obtained from the recycle column from which stream S_7 is a distillate product and stream S_8 is a bottom product. The stream S_7 is preferred to contain more ethanol, so as to recycle ethanol back to the main column and minimize loss of ethanol in the water stream S_8 .

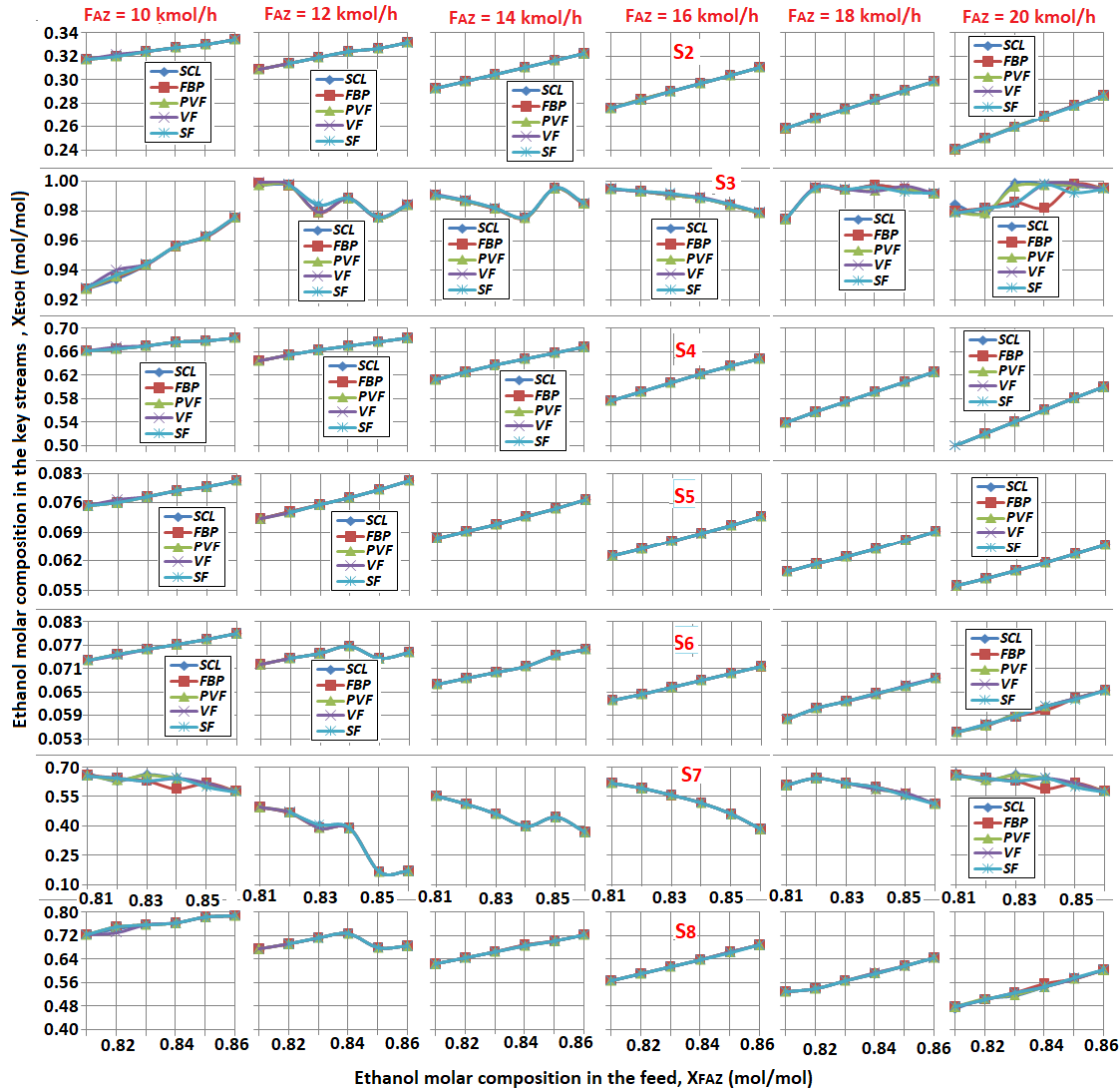


Figure 4. Effect of ethanol concentration in the feed on ethanol concentration in the key streams connecting main operational blocks of the azeotropic distillation plant for various FTCs and increasing feed flow rate, F_{AZ} .

The ethanol molar composition in stream S_3 is largely affected by X_{FAZ} which was varied from 0.81 to 0.86 mol/mol. For higher F_{AZ} ranging from 12 to 20 kmol/h, higher product ethanol purity of approximately greater than 95.50% was obtained. For the feed flow rate of 10 kmol/h lower purity of product ethanol of approximately less than 95.50% was obtained (i.e., when $X_{FAZ} < 0.84$ mol/mol). This indicates that a better dehydration performance in terms of product ethanol purity is obtained when the feed molar flow rate increases. Furthermore, for feed flow rate ($F_{AZ} = 10$ kmol/h) a positive direct relationship between ethanol concentration in the feed and in stream S_3 was observed indicating that increase in X_{FAZ} enhances the dehydration performance of the plant in terms of product ethanol purity. The increase in F_{AZ} results into drastic changes in ethanol molar composition across the column stages leading to different profiles of ethanol concentration in the stream S_3 with increasing X_{FAZ} , as highlighted by Taqvi *et al.* (2019). A subsequent increase and decrease in ethanol molar composition in

stream S_3 was observed when the value of X_{FAZ} was 0.82 and 0.85 mol/mol at 12 kmol/h, 0.83 mol/mol at 18 kmol/h and 0.84 mol/mol at 18 and 20 kmol/h. The subsequent increase and decrease represent a retrograde phenomenon which is characterized by a decrease in dehydration performance of the plant and energy duty. An inverse relationship between X_{FAZ} and in stream S_3 was observed when the flow rate was set at 16 kmol/h and 14 kmol/h (for 0.81-0.84 mol/mol). A similar behavior of profile for the product ethanol stream (S_3) and recycle stream (S_7) can be attributed to a result of fluctuations in ethanol molar content in overhead vapors with increase in X_{FAZ} from 0.81 to 0.86 mol/mol (for $F_{AZ} > 12$ kmol/h).

The performance of ethanol dehydration plant in terms of product ethanol purity is affected differently depending on feed composition and thermal conditions. This is mainly due to variation of the liquid and vapor phase distribution and mass transfer across the column stages (Belincanta *et al.*, 2005). FTCs have significant impact on the retrograde phenomena at higher flow rate ($F_{AZ} = 20$ kmol/h) this is due to changes in distribution of liquid and vapors attributed by the increase in the amount of the liquid and vapors across the column stages and also by the decrease in the residence contact time between the vapor and liquid phases. From Figure 4, it was observed that ethanol concentration in stream S_3 at conditions at which retrograde phenomena occurs (i.e., at 0.84 mol/mol and 20 kmol/h) increases with increase in vapor fraction of the feed. This is mainly due to the fact that the retrograde phenomena results into decrease in energy duty of the column, hence affecting the column separation efficiency due to decrease in amount of vapor. Thus, in order to achieve the desired separation energy duty of the column should be increased. However, this effect can be counteracted by increasing the feed vapor fraction; increasing in feed vapor fractions results into decrease in the amount of liquid in the stripping section leading to a better separation at the same energy duty obtained at retrograde phenomena conditions. Overall, based on the results obtained a higher dehydration performance in terms of product ethanol purity is obtained when the feed molar flow rate ranges from 16 to 20 kmol/h for X_{FAZ} ranging from 0.81 to 0.86 mol/mol. The observed retrograde phenomena effect can be counteracted by increasing the vapor fraction of the near-azeotrope feed due to decrease in the energy duty of the main column.

Cyclohexane molar composition in the key streams (as illustrated in Figure 5) vary with increasing X_{FAZ} in the range of 0.556 to 0.578 mol/mol for stream S_2 , 0.07 to 0.0 mol/mol for stream S_3 , 0.02 to 0.11 mol/mol for stream S_4 , 0.942 to 0.917 mol/mol for stream S_5 , 0.945 to 0.918 mol/mol for stream S_6 , 0.12 to 0.58 mol/mol for stream S_7 and 0.01 to 0.10 mol/mol for stream S_8 . Figure 5 shows cyclohexane molar composition in the key streams connecting the main operational blocks of the azeotropic distillation plant against ethanol concentration in the feed for SCL, FBP, PVF, VF and SF feed thermal conditions. Increasing X_{FAZ} results into an overall increase in ethanol molar content across the main column stages, this result into increase in ethanol content in the overhead vapors leading to a decrease in cyclohexane molar content in the stream S_2 . This behavior was also pointed out by Belincanta *et al.* (2005). Further, lower cyclohexane content in the stream S_2 results into a decrease in the cyclohexane content in the organic phase (S_5) due to an increase in ethanol concentration in the stream. Similar results were also obtained by Vasconcelos and Wolf-Maciel (2010). The decrease in the stream S_5 cyclohexane composition with increasing X_{FAZ} as shown in Figure 5, results into lower cyclohexane composition in stream S_6 . This is because stream S_6 is a mixed solution of entrainer makeup stream (S_9) and stream S_5 . Moreover, increase in cyclohexane molar composition in stream S_4 (as shown in Figure 5) results into increase in cyclohexane molar concentration of vapors in the rectifying section of the recycle column and thus leading to higher cyclohexane molar composition in recycle stream S_7 . Also, from Figure 5, a significant amount of cyclohexane for water stream S_8 was observed when the F_{AZ} was 10 kmol/h and also for 12 kmol/h at 0.85 and 0.86 mol/mol. A higher amount of cyclohexane in this stream indicates appreciable loss of cyclohexane and that a higher amount of entrainer makeup will be required to achieve the desired separation efficiency. The cyclohexane molar concentration was negligible for other operating conditions. As highlighted also by Mortahed and Kosuge (2003) the increase in the amount of cyclohexane makeup represents the decrease in ethanol dehydration plant performance in terms of product ethanol purity.

Further, sharp increase in cyclohexane molar composition at 12 kmol/h for ethanol concentration greater than 0.85 mol/mol in the feed is due to a decrease in ethanol dehydration performance in terms of product ethanol purity from 98.82% to 97.52% for 0.84 and 0.85 mol/mol, respectively. This decrease is a result of the effect of retrograde phenomena, resulting into significant decrease in energy requirements. From Figure 5, it was also observed that cyclohexane composition for streams (S_2 , S_4 and S_7) decreased with increasing in feed flow rate from 10 to 20 kmol/h. This indicates that increasing F_{AZ} results into lower cyclohexane molar composition for the streams (S_2 , S_4 and S_7). On the other hand, the plots of cyclohexane composition for streams (S_5 and S_6) increased with increasing F_{AZ} from 10 to 20 kmol/h. This indicates that an increase in the feed molar flow results into an increase in cyclohexane molar composition for the streams (S_5 and S_6). Overall, the molar composition of ethanol in stream S_3 varies inversely proportional with its corresponding cyclohexane composition with an average proportionality constant of 0.01833. The reason for this relationship has been explained by Gomis *et al.* (2000) is such that the amount of water removed in the vapor phase is relatively high leading to production of dehydrated ethanol with small traces of cyclohexane. Thus, after azeotropic distillation process ethanol-water-cyclohexane system is dominated mainly by ethanol-cyclohexane mixture, indicating that the increase in ethanol leads to a decrease in cyclohexane molar composition.

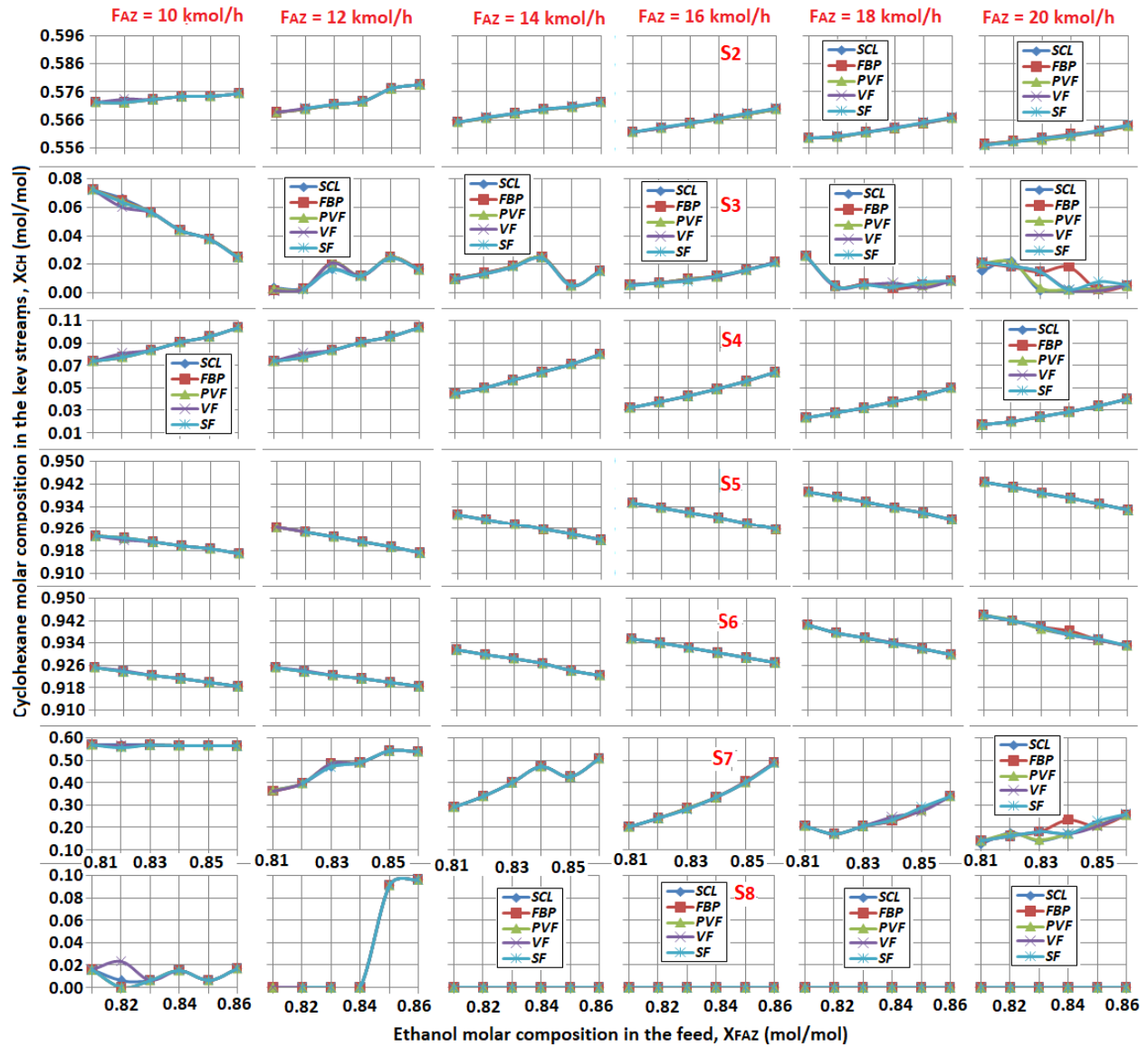


Figure 5. Effect of ethanol concentration in the feed on cyclohexane molar composition in the key streams connecting the main operational of the azeotropic distillation plant for various FTCs and increasing feed flow rate, F_{AZ} .

Furthermore, a pure cyclohexane makeup was used in the process due to the fact that it is mixed with organic solution phase from the decanter. However, dilute cyclohexane makeup may also be used in the process, when it is fed directly into the decanter. In addition, cyclohexane traces in stream S_3 of up to 0.02 mol/mol may require further downstream purification process such as membrane separation or vacuum distillation. From Figure 4 and Figure 5, it was also observed that FTCs have slight impact on changes in stream compositions. In general, X_{FAZ} and F_{AZ} affect ethanol dehydration plant performance in terms of product ethanol purity. Therefore, in order to minimize plant operating costs and energy requirements a detailed analysis on the effect of ethanol concentration in the feed should be conducted in real plant experiments for the aim of determining the best plant operating configuration based on the simulation results.

3.3 Effect of ethanol concentration in the feed (X_{FAZ}) and feed thermal conditions (FTCs) on-stream flow rates

This section presents results and analysis of the effect of ethanol concentration in feed, feed molar flow rate and feed thermal conditions on the key streams molar flow rates. The streams assessed include S_2 , S_4 , S_5 , S_6 , S_7 , S_8 and S_9 . Figure 6 shows the molar flow rates variation of the key streams connecting main plant operational blocks (i.e., pre-heater, main column, decanter and recycle column) against X_{FAZ} . The ethanol concentration, X_{FAZ} , was varied from 0.81 to 0.86 mol/mol while F_{AZ} was varied from 10 to 20 kmol/h. Further, the study was also conducted by varying the FTCs, i.e., SCL, FBP, PVF, VF and SF. Varying X_{FAZ} and F_{AZ} , affects the flow rates of the key streams from the main plant operating blocks leading to changes in the overall ethanol dehydration plant performance in terms of product ethanol purity as shown in Figure 6. Increasing X_{FAZ} from 0.81 to 0.86 mol/mol for fixed FTCs and F_{AZ} results into variations of the key streams molar flows. The molar flow rates changed from 19 to 20.4 kmol/h for stream S_2 , 7.82 to 8.6 kmol/h for stream S_4 , 11.1 to 12 kmol/h for stream S_5 , 11.87 to 12 kmol/h for

stream S_6 , 0.01 to 1.5 kmol/h for stream S_7 , 7 to 7.9 kmol/h for stream S_8 and 0.01 to 0.9 kmol/h for entrainer makeup stream (S_9). Observed changes in the stream flow rate (S_2) with increasing X_{FAZ} at constant F_{AZ} depends mainly on the quantity of overhead vapors generated and the plant dehydration performance in terms of product ethanol purity. As explained in the previous section and also by Miranda et al. (2020) a better dehydration performance occurs at high reboiler duty indicating the presence of higher quantity of overhead vapors in the rectifying section leads to an increase in the flow rate of stream S_2 . This was observed when the feed flow rate ($F_{AZ} = 10$ kmol/h) as shown in Figure 6, indicating that the increase in dehydration performance in terms of product purity attributes to the increase of stream S_2 molar flow rate.

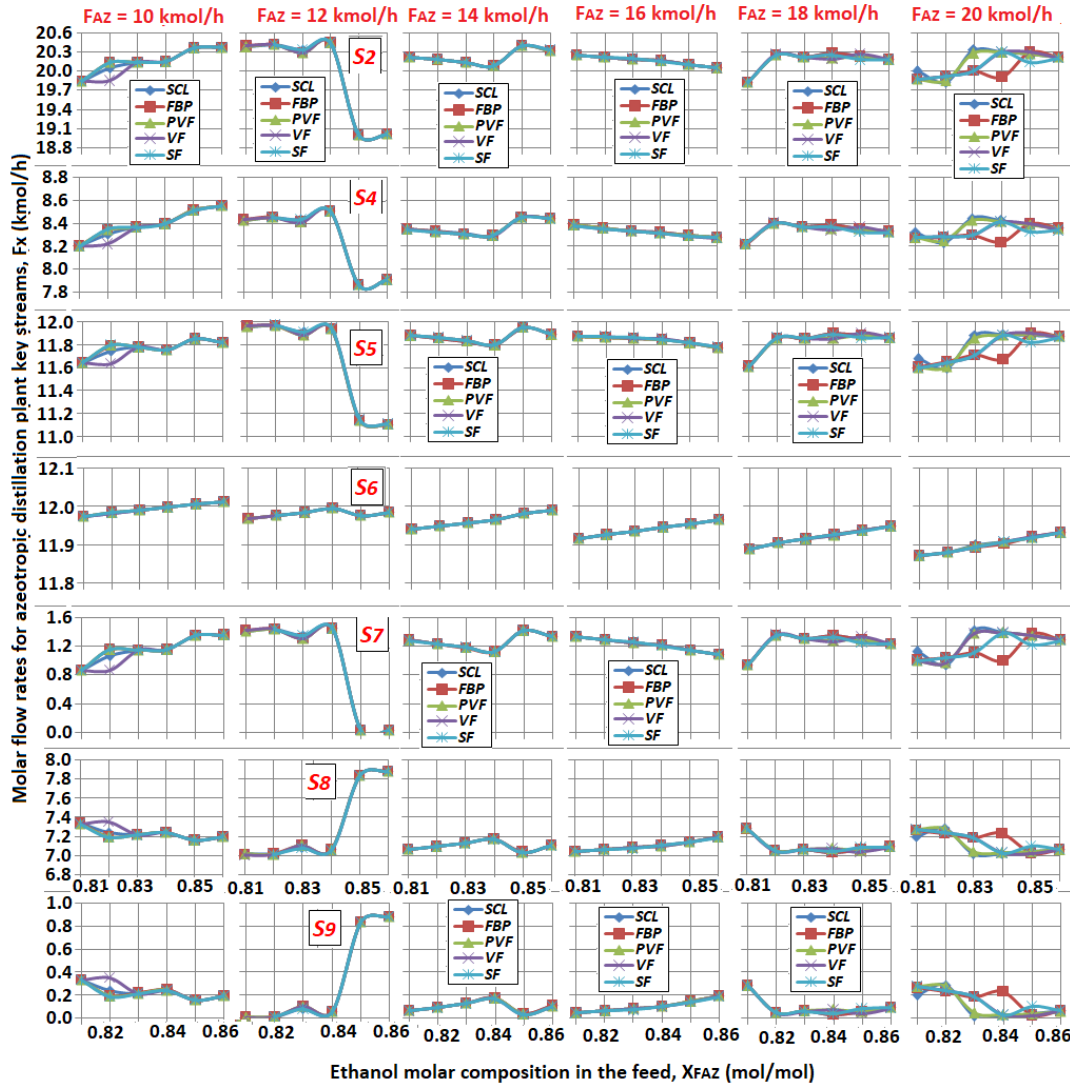


Figure 6. Effect of ethanol concentration in the feed on molar flow rates of the key streams connecting main operational blocks of the azeotropic distillation plant at different feed molar flow rates and for various FTCs.

Moreover, a subsequent increase and decrease in molar flow rate of stream S_2 was observed when X_{FAZ} was 0.82 and 0.85 mol/mol at 12 mol/h, 0.83 mol/mol at 18 kmol/h and 0.84 mol/mol at 18 and 20 kmol/h. The subsequent increase and decrease in stream S_2 molar flows represent a retrograde phenomenon characterized by the decrease in plant dehydration performance in terms of product ethanol purity and energy duty requirements. The decrease in energy duty results into decrease in the amount of overhead vapors in the rectifying section of the column, consequently leading to the decrease in stream S_2 molar flow rate. From Figure 6, similar profiles for streams (S_2 , S_4 , S_5 and S_7) with increasing X_{FAZ} from 0.81 to 0.86 mol/mol were observed. Therefore, increase in stream S_2 molar flow rate, consequently leads to an increase in not only dehydration performance of the plant in terms of product ethanol purity but also increase in molar flow rates for streams (S_4 , S_5 and S_7). Thus, a better dehydration performance is obtained for higher flow rates of intermediate streams (S_4 and S_5) and recycle stream (S_7). Increasing in molar flows of streams S_4 and S_5 with increase in stream S_2 flow rate is because streams (S_4 and S_5) are the products obtained after liquid-liquid separation of stream S_2 in the decanter and varies proportional with stream S_2 flow rate. The increase in aqueous stream (S_4) flow rates, with increase in plant dehydration performance has also been reported by Vasconcelos and Wolf-Maciél (2010). The increase in S_4 flow rate implies that more water is separated from the main column. This leads to an aqueous or heavy stream, containing mainly water.

Changes in stream S_7 molar flow rate of with increasing X_{FAZ} as shown in Figure 6 was observed to vary inversely proportional with the changes of stream S_8 molar flow rate and an average proportionality constant of 5.63. This behavior was attributed by the fact stream S_7 and S_8 are the top and bottom products of the recycle column and as highlighted in literatures the distillate rate increases with decreasing bottoms rate. The increase in plant dehydration performance in terms of product purity accompanied with increasing X_{FAZ} and molar flow rates of streams (S_2 , S_4 , S_5 and S_7) as shown in Figure 6, results into a decrease in the amount of entrainer makeup required in the process. This consequently leads to a similar fluctuation profiles for the streams (S_8 and S_9) with increase in ethanol concentration in the feed. The molar flow rate of stream S_6 , as illustrated in Figure 6, increases with increasing X_{FAZ} . However, the decrease in the stream S_6 molar flow rate for 0.85 to 0.86 mol/mol when F_{AZ} was set at 12 kmol/h is attributed mainly due to the fact that at this condition there is an appreciable drop in ethanol dehydration plant performance leading to decline in product ethanol purity from 98.82% to 97.52% for 0.84 and 0.85 mol/mol ethanol concentrations in the feed, respectively. Additionally, as shown in Figure 6 the molar flow rate of S_6 decreases with increasing F_{AZ} , the main reason for this is due to the fact the increasing in F_{AZ} results into increase in the molar flow rate of product ethanol consequently leading to decrease in the amount of overhead vapors in the main column rectifying section. The effect of X_{FAZ} on streams molar flow rates is directly related to the observed ethanol dehydration plant performance in terms of product ethanol purity. Therefore, based on the obtained results a higher dehydration performance was obtained when the molar flow rate of organic solution (S_5) was high (> 11.8 kmol/h), operating at this flow rate leads to low amount of entrainer makeup (< 0.2 kmol/h) and high amount of recycle streams (> 1.2 kmol/h). Mortahed and Kosuge(2003) analyzed also the effect of recycle stream flow rates on plant dehydration performance and concluded that entrainer recovery is effectively done with increasing in key streams flow rates and a better dehydration performance with a purer ethanol is produced from the main column.

3.4 Effect of ethanol concentration in the feed (X_{FAZ}) and feed thermal conditions (FTCs) on energy requirements

Ethanol concentration in the feed (X_{FAZ}) as seen in previous sections affects the performance of ethanol dehydration plant in terms of product ethanol purity and stream flow rates. The changes in stream flow rates results into variation in the amount of energy required in order to achieve the desired performance and produce pure ethanol. For instance, increasing the molar flow rate of stream S_2 will lead to higher condenser duty. Also, increasing F_{AZ} leads to a higher condenser and reboiler duties. This section gives an insight on how increasing X_{FAZ} from 0.81 to 0.86 mol/mol affects the main and recycle column duties together with their respective ratios. This section also provides an analysis of the effect of X_{FAZ} on the ratio of column duties to product ethanol molar flow rate, i.e., Q/F_3 for various FTCs and F_{AZ} ranging from 10 to 20 kmol/h. The effect of X_{FAZ} on both main and recycle column duties and their respective condenser to reboiler duty ratios, Q_c/Q_r for various FTCs and F_{AZ} are shown in Figure 7. As shown in Figure 7, it was observed that the profile of condenser duty with increasing X_{FAZ} for the main and recycle column varies proportionally with their respective reboiler duties. Thus, increase in reboiler duty results into a proportional increase in condenser duty and vice versa. The increase in reboiler duty leads to an increase in the amounts of generated vapors across the column stages and hence higher condenser energy will be required to generate the necessary liquid reflux to affect the required separation. Moreover, as shown in Figure 7, increase in the main column energy duties results into proportional increase in the recycle column energy. This is due to the fact that increase in the main column duty increases the quantity of overhead vapors generated and condensed, this consequently results into increase in F_2 and hence increase in F_4 . The increase in F_4 results into an increase in recycle column throughput and hence, operating duty.

The main column condenser, Q_{c1} , and reboiler duty, Q_{r1} , are approximately more than 90.94% and 90.25% times greater than the condenser, Q_{c2} , and reboiler duty, Q_{r2} , of the recycle column, respectively. This results into a higher condenser to reboiler duty, Q_c/Q_r ratio in the main column (> 0.9 MW/MW) as compared to the recycle column (< 0.9 MW/MW). The higher energy in the main column as compared to the recycle column is because the main column receives higher throughput than recycle column. A higher throughput increases the amount of vapor and liquid across the column stages and hence increases in column duty. The increase in reboiler duty as a result of increase in throughput has also been reported by Manyele (2021), Conde-Mejía and Jiménez-Gutérrez (2020) and Silva *et al.* (2021). In addition, a higher Q_{c1}/Q_{r1} as compared to Q_{c2}/Q_{r2} is due to the fact that main column has higher D/B that ranges from 1.57 to 6.33 as compared to the recycle column that ranges from 0.0026 to 0.19. Similarly, the changes of energy duties with respect to increase in X_{FAZ} can also be explained in terms of ethanol dehydration performance. As seen in previous section column energy requirements increases with increase in dehydration performance of the plant in terms of product ethanol purity. Thus, the rise and fall features (shown in Figure 7) represent the increase and decrease in ethanol dehydration performance of the plant in terms of product ethanol purity, respectively. The increase in ethanol dehydration performance of the plant in terms of product ethanol purity leads to the sharp increase in temperature in the ethanol enrichment section. This consequently leads to an increase in reboiler duty and hence the overall energy requirements of the plant. Further, subsequent increase and decrease in energy duty representing the effect of retrograde phenomena on energy requirements was observed when X_{FAZ} was 0.82 and 0.85 mol/mol at 12 mol/h, 0.83 mol/mol at 18 kmol/h and 0.84 mol/mol at 18 and 20 kmol/h.

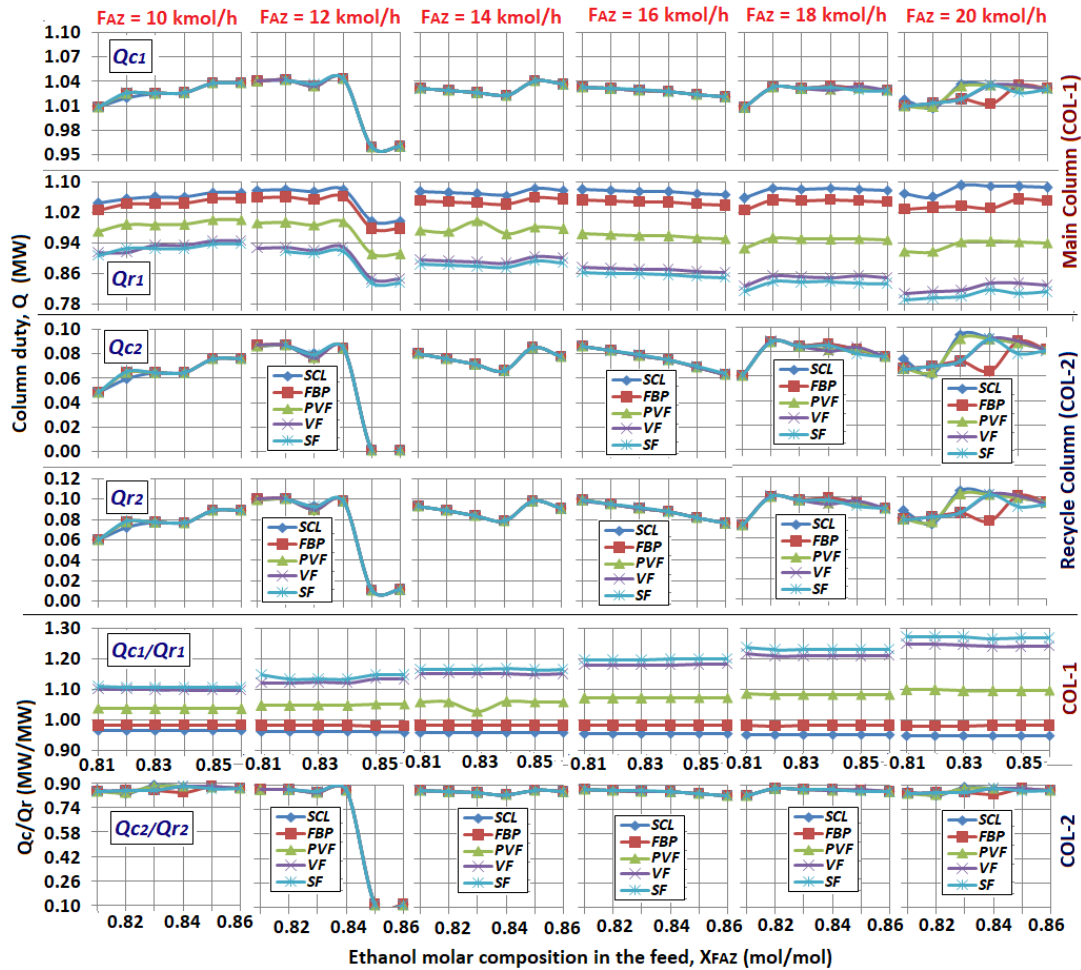


Figure 7. Effect of ethanol concentration in the feed on the main and recycle column duties and on their respective condenser to reboiler duties ratio for various FTCs and feed flow rates.

FTCs have significant impact on the vapor and liquid phase distribution across the column stages. This results into changes in the amount of liquid and vapor in the stripping and rectifying sections leading to changes in reboiler and condenser duties. Changes in FTCs (from SCL and FBP to PVF and then to VF and SF) increases the feed vapor fraction, this causes high vapor enrichment in the column rectifying section and hence reducing the amount of liquid holdup in the stripping section. The decrease in the amount of liquid holdup in the stripping section results into decrease in reboiler duty, this in turn leads to an increase in the condenser to reboiler duty ratio. Thus, the use of SF and SCL feed in the process results into a higher and lower Q_c/Q_r ratio, respectively. Similar scenario of the effect of FTCs was reported also by Manyele (2021) in his analysis of the effect of feed composition and thermal condition on distillation plant performance using a computer model. The author observed a higher reboiler duty for SCL as compared to other feed conditions. This is because the use of SCL leads to most of the liquid flowing downwards to the reboiler, increasing heat requirements to create vapors. FTCs (as shown in Figure 7) have significant impact on Q_{r1} as compared to Q_{r2} mainly because the near-azeotrope feed was introduced into the main column. Also, the effect of FTCs on the condenser duty of the main and recycle column were observed to be very minimal. The former is attributed by the fact that the overhead vapors in the main column approaches a ternary azeotrope regardless of FTCs used. The latter is due to a constant thermal condition of the aqueous solution that depends on the decanter operating conditions. Moreover, due to the fact that FTCs significantly affect only the main column reboiler duty, then the Q_c/Q_r ratio will be highest for SF and lowest for SCL feed. In addition, the increase in F_{AZ} results into an increase in the main and recycle column operating throughput. This consequently leads to an increase in the condenser and reboiler duties. Moreover, a slight impact of FTCs on the main and recycle column energy duties was observed when the feed flow rate was set at 10 and 20 kmol/h for ethanol concentration in the feed ranging from 0.81 to 0.83 mol/mol and 0.82 to 0.86 mol/mol, respectively. Overall, FTCs have significant impact on Q_{r1} as compared to Q_{r2} mainly due to the fact that the near-azeotrope feed is fed directly into the main column. Furthermore, the ratio of condenser to reboiler duty indicates the energy requirements and distribution across the column stages. Increase in the feed vapor fraction results into changes in liquid and vapor distribution as more vapor will concentrate more in the rectifying section of the column and less amount of liquid across the stripping column stages. Consequently, this results into high condenser energy as compared to reboiler energy leading to a Q_c/Q_r ratio greater than 1 MW/MW.

Figure 8 presents the effect of ethanol concentration in the feed on the ratio of main column duty (both reboiler and condenser) to product ethanol molar flow rate, Q/F_3 for various FTCs and feed flow rates. The ratio plots of column duty to product ethanol molar flow rate shift downward with increase in feed molar flow rate from 10 to 20 kmol/h. This indicates that the ratio of column duty to product ethanol molar flow rate decreases with increase in feed molar flow rate representing an inverse relationship. This relationship is due to the fact that product ethanol stream (S_3) varies positively linearly with feed molar flow rate (F_{AZ}). Therefore, as feed flow rate increases the product ethanol flow rate also increases. The ratio of the main column duty to F_3 is higher (> 0.06 MWh/kmol) as compared to the ratio of the recycle column duty to F_3 (< 0.03 MWh/kmol). The higher the ratio of Q/F_3 for the main column is mainly because of the fact that the main column processes higher throughput than the recycle column. FTCs (as shown in Figure 8) have significant impact on the ratio of Q_{r1}/F_3 , because the near-azeotrope feed is fed directly into the main column. Further, FTCs have less impact on the ratio Q_{c1}/F_3 due to the fact that the overhead vapors generated approaches heteroazeotropic conditions of ethanol-water-cyclohexane regardless of the FTCs used in the process.

Additionally, a slight impact of FTCs on the ratios of Q_{c2}/F_3 and Q_{r2}/F_3 was observed when the feed flow rate was set at 10 and 20 kmol/h for ethanol concentration in the feed ranging from 0.81 to 0.83 mol/mol and 0.82 to 0.86 mol/mol, respectively. This can be explained by the changes in the overall dehydration performance of the plant in terms of product ethanol purity. At 10 kmol/h (with $X_{FAZ} < 0.84$ mol/mol), the amount of solution and the residence contact time between the vapor and liquid phases across the column stages increases. This consequently results into decrease in separation efficiency as the increase in vapor-liquid residence contact time may cause formation of two liquid phases in the column. Occurrence of the two liquid phases results into decrease in reboiler duty attributed by the decrease in the temperature across the ethanol enrichment section. Conversely, at a higher feed flow rate ($F_{AZ} = 20$ kmol/h) the amount of solution and the residence contact time between the vapor and liquid phases across the column stages decreases as a result of increase in the molar flow rates of product ethanol (F_3) together with vapor and liquid phases across the column stages. This causes changes in the molar flow rate of aqueous phase, F_4 into the main column resulting into subsequent increase and decrease fluctuations of recycle column to product ethanol molar flow rate.

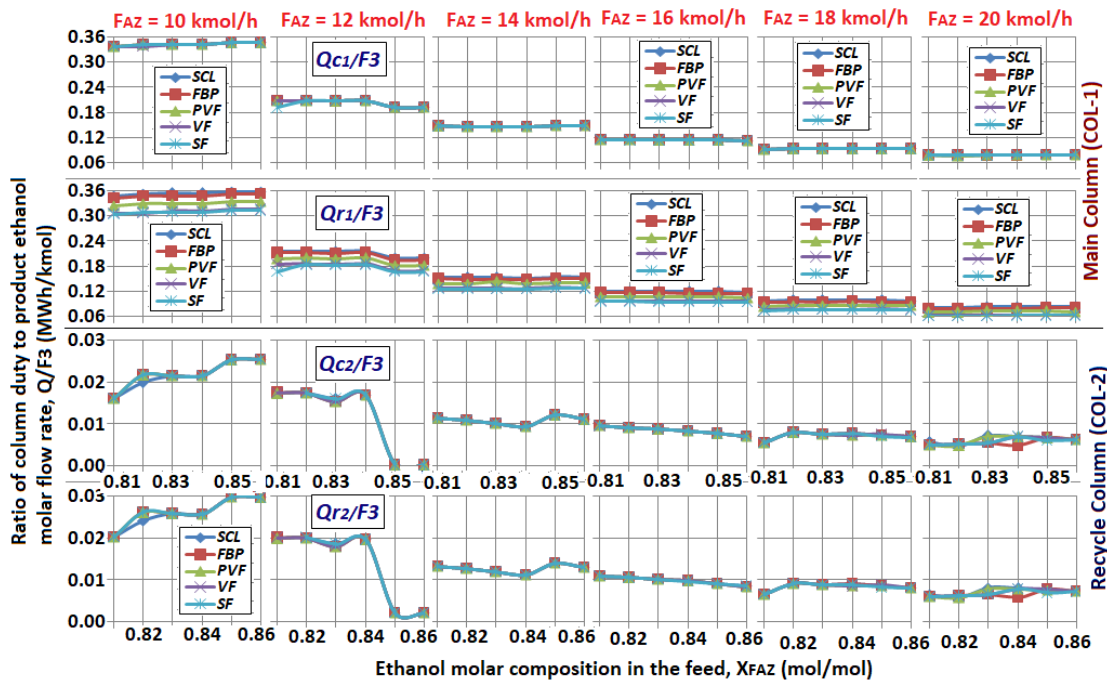


Figure 8. Effect of ethanol concentration in the feed on the ratio of main and recycle column duties (both reboiler and condenser) to the product ethanol stream (S_3) molar flow rate for various FTCs and feed flow rates.

In general, decrease in the Q/F_3 ratio indicates higher production rate of ethanol per unit energy consumption. Therefore, this ratio indicates how efficiently the energy is utilized to produce desired product. Also due to the fact that azeotropic distillation with cyclohexane as an entrainer utilizes high amount of column duty (Miranda *et al.*, 2020). Thus, on basis of this analysis, operating the plant at higher flow rate ranging from 16 to 20 kmol/h, will result into higher energy efficiency and enhanced ethanol dehydration plant performance in terms of product ethanol purity.

Figure 9 shows the effect of ethanol concentration in the feed on the ratio of the main and recycle column duty (both reboiler and condenser) to feed molar flow rate, Q/F_{AZ} for various FTCs and feed flow rates. Due to the fact that, there is a positive linear relationship between product ethanol flow rate, F_3 , and feed molar flow rate, F_{AZ} , hence the ratios of both main and recycle column duties to product ethanol and feed molar flow rate will have similar trends as shown in Figure 8 and Figure 9. Therefore, increasing in the feed molar flow rate results into the decrease in the ratios of both main and recycle column duties to feed molar flow rate, Q/F_{AZ} . The main column processes a higher throughput than the recycle column; this consequently results into a higher ratio of main column duty to F_{AZ} of approximately 90.91% times greater than the ratio of the recycle

column duty to F_{AZ} . Similarly, the FTCs (as shown in Figure 9) have significant impact on the ratio of Q_{r1}/F_{AZ} as compared to the ratio of Q_{c1}/F_{AZ} . The former is attributed by the fact that the near-azeotrope feed is fed directly into the main column whereas the latter is due to the fact that overhead vapors generated in the main column always approaches ethanol-water-cyclohexane heteroazeotropic conditions regardless of the FTCs used in the process. Furthermore, the effect of FTCs on the ratios of Q_{c2}/F_{AZ} and Q_{r2}/F_{AZ} is negligible resulting into similar values. The reason for this is due to the fact that the thermal condition of aqueous solution phase is affected only by the decanter operating conditions. However, a slight impact of FTCs on the ratios of Q_{c2}/F_{AZ} and Q_{r2}/F_{AZ} was observed when the feed flow rate was set at 10 and 20 kmol/h for X_{FAZ} ranging from 0.81 to 0.83 mol/mol and 0.82 to 0.86 mol/mol, respectively. At 10 kmol/h (with $X_{FAZ} < 0.84$ mol/mol), the amount of solution and the residence contact time between the vapor and liquid phases across the column stages is higher resulting into decrease in separation efficiency. The increase in vapor-liquid residence contact time may cause formation of two liquid phases in the column. This consequently results into the decrease in temperature across the ethanol enrichment section and hence decreases in reboiler duty. Moreover, at a higher feed flow rate ($F_{AZ} = 20$ kmol/h) the amount of solution and the residence contact time between the vapor and liquid phases across the column stages decreases as a result of increase in the molar flow rates of product ethanol (F_3) together with vapor and liquid phases across the column stages. This causes changes in the molar flow rate of aqueous phase, F_4 into the main column resulting into subsequent increase and decrease fluctuations of recycle column duty to feed molar flow rate, Q/F_{AZ} .

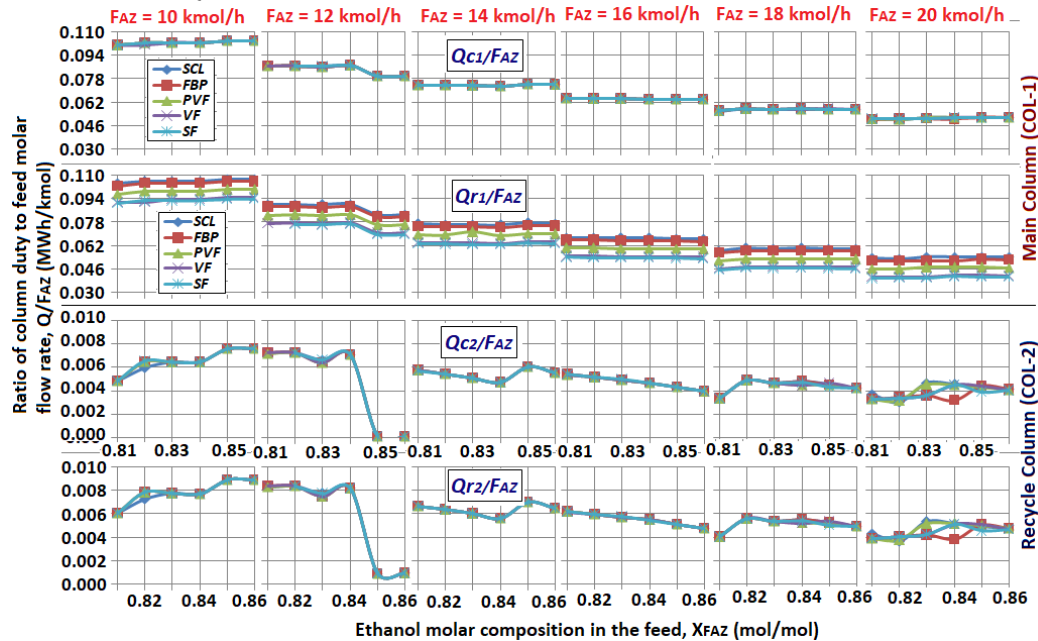


Figure 9. Effect of ethanol concentration in the feed on the ratio of main and recycle column duties (both reboiler and condenser) to the feed molar flow rate for various FTCs and feed flow rates.

In general, feed thermal conditions significantly affect the reboiler duty for the main column and have negligible impact on main column condenser duty and recycle column duties (both condenser and reboiler duty) as shown in Figure 7, Figure 8, and Figure 9. This is mainly due to the fact that the near azeotropic feed is fed into the main column whereas the aqueous solution phase which is fed into the recycle column will have a constant thermal feed condition depending on the decanter operating temperature. Effect of feed thermal conditions for the main condenser is significantly low due to the fact the overhead vapors generated approaches a ternary heteroazeotropic conditions of ethanol-water-cyclohexane system regardless of the type of feed used.

4. Conclusion

In this study, azeotropic distillation pilot plant model for producing pure ethanol from near-azeotrope pre-concentrated ethanol-water solutions was developed. The designed plant consists of a pre-heater, decanter, main and recycle column acting as the main operational blocks. The designed process operates under fixed column parameters, i.e., $N_a = 10$, $p = 1$ atm and $R = 5$ mol/mol 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, feed flow rate (F_{AZ}), feed thermal conditions (FTCs) and ethanol concentration in the feed (X_{FAZ}) are among the key operating parameters affecting ethanol dehydration plant performance in terms of product ethanol purity. Changes in the values of key operating parameters resulted into 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 01.10 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 vapors approach a ternary azeotrope of an ethanol-water-cyclohexane regardless of the type feed used. Furthermore, 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 16 to 20 kmol/h, F_5 greater than 11.8 kmol/h and high amount of recycle streams (>1.2 kmol/h). Operating at this flow rates leads to low amount of entrainer makeup (< 0.2 kmol/h) required to ensure effective azeotropic separation. Additionally, due to the study limitation that it is solely based on the ethanol dehydration plant simulation and modeling the study recommends a detailed distillation synthesis based on residual curve maps and ternary diagrams followed by real plant monitoring should be performed in order to address the observed retrograde phenomena effect and improve the overall ethanol dehydration plant performance. Also, in order to determine best plant operation configuration, minimize plant operating costs and energy, 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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