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Parametric Sensitivity Analysis of the Separation Process for N-Butanol Production

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Abstract. n-butanol and iso-butanol are commonly produced by the hydrogenation of n-butyraldehyde and iso-butyraldehyde employing the patented copper catalyst accommodated in the reactors in series. The main cause of the lower n-butanol and iso-butanol yield was due to the catalyst blockage rendering a pressure build-up that could lead to a plant shut down. Bypassing the last reactor from the series could be a potential solution to continue running the plant until the next shutdown plan to replace catalyst. The study adopted simulation approach using Aspen Plus V10 to investigate the effect of bypassing the last reactor in the series to the product purity of the downstream separation processes. The iso-butanol and n-butanol with the desired purity were produced from the distillate and bottom product when the column was operated at the RR of 8.03 and DF of 0.328. The reaction conversion of R-102 was varied from 0.1-0.995 but the variation did not significantly change the composition of the main product. Hence, the present study affirmed that the bypassing of third reactor from the reactor train would not affect the product purity of the main product, n-butanol.

Keywords: n-butanol, iso-butanol, simulation, distillation, separation process

1. Introduction

n-butanol or butyl-alcohol is an alcohol compound with general formula of ROH with R is an n-butyl group. It is a four-carbon straight chained alcohol. The hydroxyl group (-OH), is a functional group of n-butanol which determines its properties like highly polar and capable of forming hydrogen bond with other neutral molecules and anions depending on the position of the hydroxyl (OH) group on the carbon chain [1]. N-butanol forms an important feedstock for the manufacturing of chemicals such as butyl acrylate, glycol ethers, butyl acetate and plasticizers. Among various industrial applications, it serves as an important element in making direct solvent for varnishes, paints, coatings, resins, camphor, dyes, fats, vegetable oils, waxes, shellac, rubbers, and alkaloids. It has also traditionally been the preferred solvent or co-solvent in application [2].

n-butanol was initially produced based on the fermentation of carbohydrates by bacteria but as demand grew, chemical methods were used commercially. One of the techniques in making n-butanol

was catalytic hydroformylation of propylene followed by the hydrogenation of aldehydes formed in a series of two or three reactors depending on the process technology adopted [2]. This reaction yields a mixture of n- and iso-butanol. The mixture then gets separated into their individual components by using distillation process. Normally, two units of distillation are used in series. The first distillation is to refine the n- and iso-butanol by removing moisture and light material, and the second distillation is to separate n-butanol from iso-butanol [3].

The hydrogenation process has been known for a long time as a highly selective, economical route to high-purity butanol. The most preferred catalysts are those containing copper oxide promoted by chromium oxide either in physical mixture or in chemical combination as copper chromate or copper chromite. In the processes for completing catalytic hydrogenation of aliphatic aldehydes, a by-product may be an ester such as n-propyl propionate formed by the hydrogenation of propionaldehyde and n-butyl butyrate can be detected in minor amounts in the reaction mixture resulting from catalytic hydrogenation of n-butyraldehyde [4] [5]. The formation of even a small percentage of esters, represents a serious loss in the potential yield of product alcohol, e.g. n-butanol. Such losses may render the use of a particular hydrogenation catalyst, which otherwise has many advantageous properties, commercially unattractive. Usually the amount of by-product ester formed increases with increasing temperature in the catalytic hydrogenation zone. Hence, in order to minimize formation of by-product ester, it is necessary to operate the catalytic hydrogenation zone at a relatively low temperature, which may in turn result in a somewhat reduced rate of catalytic hydrogenation and hence an increase in catalyst volume and in reactor size. Moreover, since catalyst activity tends to decline with time, it is usually necessary to raise the reaction temperature gradually with passage of time over a period of months of continuous operation in order to compensate for loss of catalytic hydrogenation activity [6] [7]. Such increase in temperature promotes the formation of higher amount of by-product ester and catalyst aging that impairs the structural integrity of the catalyst that eventually requires a change of catalyst [8].

Since n-butanol is highly demanded in the market, shortage of supply can be a major issue for certain countries. One of the greatest challenges in the operation of a large scale catalytic in n-butanol production process is the prevention of catalyst degradation. Catalyst deactivation is inevitable for most processes [9] and it impacts severely on the yield or completeness of the n-butanol production. While waiting for the root cause analysis of the catalyst deactivation or a scheduled plant shut down to change to new catalyst, the process needs to continue running if possible. In the case of catalyst deactivation happens in the 3rd reactor (last reactor) in the reactor train, the production process can be continued by isolating the 3rd reactor. The outlet stream of the 2nd reactor is introduced directly to the next process without disturbing the existing process. The intention of this paper is to underline the findings of the investigation of the effect of by-passing the 3rd reactor and to extent of reaction in the 3rd reactor to the operating condition in the n-butanol refining column [10]. Referring to the literature reviews and reading materials on n-butanol process for the past decade, this study has not been done in the past and it will be covered comprehensively in the present study [9].

2. Methodology
This section discusses on the methodology required for the process simulation of the n-butanol production plant. The process flow diagram and plant data were obtained from the petrochemical industry and literature. Then the suitable thermodynamic property method, reactor, flash tank and distillation column model were selected accordingly for the simulation using Aspen Plus V10 software.

2.2 Development of process flowsheet
Hydrogenation is an exothermic reaction; heat is produced during the process and entropy decreases as the number of molecules decreases. The transformation is thus generally balanced and according to the Le Chatelier principle, hydrogenation reaction is supported by pressure increase and temperature decrease. Heat release is an important parameter which has great influence on the reactor process [11].
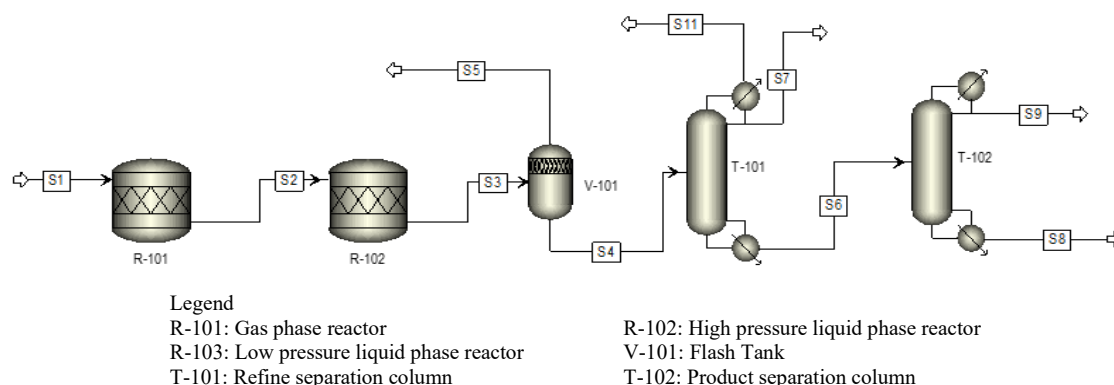
Legend
R-101: Gas phase reactor   R-102: High pressure liquid phase reactor
R-103: Low pressure liquid phase reactor   V-101: Flash Tank
T-101: Refine separation column   T-102: Product separation column

Figure 1. Process flow sheeting for the simulation of n-butanol production using Aspen Plus

Figure 1 shows the process flow diagram of the reaction and separation processes in the n-butanol and iso-butanol production plant. Aspen Plus can provide different reactor models according to different reactor, reaction modes and characteristics. This simulation selected the hydrogenation process using stoichiometric reactor model, R-Stoic which requires the input includes the chemical equation and the conversion of the reaction [11]. The main function of this reactor is to convert the normal butyraldehyde to n-butanol and iso-butyralddehyde to iso-butanol in the presence of catalyst in accordance to the reversible reaction below:

$$C_3H_7CHO + H_2 \leftrightarrow C_4H_9OH \qquad (1)$$

The catalyst can be rhodium mixed with vanadium or a mixture of copper-nickel based catalyst [12]. The present study assumed that the reaction was irreversible because the excess hydrogen used has driven the equilibrium to the forward direction [3]. Table 2 provides the reactor details and its operating range that are adopted in the present study.

Table 1. Details and operating conditions of the reactor

Reactor	Reaction Phase	Type of Reactor	Operating Pressure range	Operating Temperature range
R-101	Gas phase	Fixed bed	40-50 barg	125 - 201°C
R-102	Liquid phase	Fixed bed	5-20 barg	100 - 196°C

The conversion of reactor R-101 is ranged 60-80% while the conversion of second reactor, R-102 is in the range of 92% - 99% [25]. Other side products such as CO_2, butyrate and some other esters are of minute amount [24]. For simplification, this side product was not included in this simulation study.

Exiting from reactor, R-102, this outlet stream goes to the separator due to coexistence of two phases liquid and gas. Therefore, Flash-2 two phase flasher model was selected to simulate the process by flashing off the excess hydrogen gas from the liquid. Once the hydrogen is removed, the outlet from Flash-2 tank enters the refine separation column, T-101. Column T-101 was used to remove water and unreacted aldehydes from distillate. The bottom of column T-101 is fed to column T-102 to separate the mixture to a liquid distillate with 99.5% mol iso-butanol and a liquid bottom product with 99.5% mol n-butanol. The number of theoretical stages, reflux ratio and distillate to feed ratio required for the column was estimated by using simple design model, DSTWU [2]. Since n-butanol with water, and iso-butanol with water can form minimum boiling heterogenous azeotropes [13] and n-butanol and iso-butanol is close boiling mixture to be separated, model RADFRAC was used for the simulation of both separation columns. The production of n-butanol with iso-butanol from column T-

102 was predicted to be at reflux ratio range of 6:1- 17:1 [14]. These two columns were evaluated by identifying the best operating parameters of reflux ratio and distillate to feed ratio for production of n-butanol and iso-butanol with the desired purity. Table 2 shows the distillation column details and operating ranges that were used as a reference for this study.

Table 2. Details and ranges of operating condition of separation column

Separation column	Tray type	Top Temperature range	Operating Pressure range	Bottom Temperature range
T-101	Sieve Tray	40 - 65°C	1000 - 1200 mmbarg	100 - 110°C
T-102	Sieve Tray	120 - 140°C	0.1 - 1.0barg	130 - 150°C

2.3 Selection of Suitable of Thermodynamic Model
The thermodynamic parameter was obtained directly from the simulator database and literature data. This simulator software also requires a correct property selection for the components involved in the process in order to generate a more accurate simulation result.

To ease the selection of the accurate physical property methods, the decision trees were used as a guide to make decision [15]. These approaches can be used when the chemical components and approximate temperature and pressure ranges are known. The four factors that should be considered when choosing property methods are the:

i.   Nature of the properties of interest;
ii.   Composition of the mixture;
iii.   Pressure and temperature range; and
iv.   Availability of parameters.
   Accordingly, Wilson, NRTL, UNIQUAC and UNIFAC were identified as the suitable models, coinciding with the models used by An et al. [16] in the simulation study on the similar reaction. The present study employed Wilson model which was also used in the study carried out [8].

2.4 Design Spec and Sensitivity Analysis
Design Spec and vary function in Aspen Plus V10 were used to identify the best value of reflux ratio and distillate to feed ratio as manipulated variables to attain the products with desired purity [13] . In addition, sensitivity analysis was performed to evaluate the effect of reaction at various conversion to the product purity of the downstream separation processes. These steps are crucial to determine the range of conversion that can produce both the products n-butanol and iso-butanol with desired purity [17] . The overall process and the simulation data were validated by using data from other researches for a similar system.

3. Results and discussion
3.1 Base Case Simulation Study
RADFRAC has been validated as a rigorous method with acceptable accuracy and reliability for the simulation of distillation column. Bessa, Batista and Meirelles [18] compared their simulation results with the industrial plant data of the distillation columns for the alcoholic mixture separation. These mixtures encompassed the compounds such as aldehyde, water, n-butanol and iso-butanol which were also involved in the present study. The validation test of Bessa et. al [18] reported that the experimental and simulated composition of the major compounds were well matched qualitatively and quantitatively. Conversely, the deviations of the composition of the minor compounds from industrial plant data were considerably high but in general the same order of magnitude. These deviations were unavoidable since the minor components had very low range of concentration values. Taking all these

aspects into account, it is to conclude that RADFRAC was able to reproduce satisfactorily the industrial process of butanol purification.

The base case with the reaction conversion of 99.9% in reactor R-102 was simulated based on the conditions stated in table 3. It was discovered that column T-101 operated at reflux ratio (RR) of 5.10 and distillate to feed ratio (DF) of 0.1 was able to separate the water from the butanol, producing the bottom product with the water amount lower than ppm level. However, the loss was 48.89 mol % which was an alarming situation that need to pay attention in further simulation. The iso-butanol and n-butanol with purity of 91.5 mol% and 99.6 mol% were produced from the distillate and bottom product of T-102 respectively when the column was operated at the RR of 12.497 and DF of 0.292.

Table 3. Operating condition and simulation result of the base case study

Equipment Tag Number	R-102		R-103	V-101	T-101		T-102	
Simulation Equipment Model	RStoic		Rstoic	Flash2	RadFac		Radfac	
Pressure, bar	45		20	15	1		1	
Temperature, ^{o}C	150		80	40	50	113.4	107.0	116.2
Total Tray, N_T	NA		NA	NA	6		62	
Feed Tray, N_F	NA		NA	NA	4		34	
Reflux Ratio, RR	NA		NA	NA	5.1		12.497	
Distillate to Feed Ratio, DF	NA		NA	NA	0.1		0.292	
mole fraction for stream	S1	S2	S3	S4	S6	S7	S8	S9
n-butanol	0	0.375	0.543	0.606	0.681	0.242	0.915	0.001
iso-Butanol	0	0.188	0.272	0.303	0.319	0.246	0.085	0.996
n-Butyraldehyde	0.3	0.094	0.001	0.001	0.001	0.005	0.000	0.002
H_2	0.5	0.219	0.092	0.001	0.000	0.000	0.000	0.000
H_2O	0.05	0.078	0.091	0.088	0.000	0.503	0.000	0.000
iso-Butyraldehyde	0.15	0.047	0.001	0.001	0.000	0.003	0.000	0.001

4.2 Determining of the Best Operating Parameter using Design Spec Function

The design specification function was used to determine the best column operating parameters for achieving the desired product purity for both n-butanol and iso-butanol as shown in table 4. The enhancement was done by using the base case design spec at T-102 with the reaction conversion of 99.9% at R-102. The best parameters of Column T-101 was manually identified which by changing the reflux ratio and feed ratio driven from base case study data. Column T-101 operated at reflux ratio (RR) of 5.5 and distillate to feed ratio (DF) of 0.1 was able to separate the water from the butanol, producing the bottom product with the water amount lower than ppm level. Water with purity of 100% cannot be produced due to the formation of ternary azeotrope by n-butanol, iso-butanol and water form [13]. In addition, the losses of n-butanol and iso-butanol were reduced for more than 80% and 60% through distillate albeit there were still minor butanol losses from this column.

The n-butanol and iso-butanol with the desired purity (99.5 mol%) were produced from the distillate and bottom product of T-102 respectively when the column was operated at the RR of 8.03 and DF of 0.33. The RR reduced by 35% and DF increased by 12% from the base case simulation

study. Other parameters were maintained to ensure minimum interruptions to the actual plant operation.

Table 4. Operating condition and simulation result of the design spec study

Equipment Tag Number	T-101		T-102	
Simulation Equipment Model	RadFac		Radfac	
Pressure, bar	1		1	
Temperature, °C	50	113.4	107.0	116.2
Total Tray, N_T	6		62	
Feed Tray, N_F	4		34	
Reflux Ratio, RR	5.5		8.03038	
Distillate to Feed Ratio, DF	0.1		0.327523	
mole fraction for stream	S6	S7	S8	S9
n-butanol	0.6707	0.0400	0.9950	0.0049
iso-Butanol	0.3292	0.0807	0.0050	0.9950
n-Butyraldehyde	0.0000	0.0011	0.0000	0.0001
H_2	0.0000	0.0000	0.0000	0.0000
H_2O	0.0000	0.8775	0.0000	0.0000
iso-Butyraldehyde	0.0000	0.0006	0.0000	0.0000

4.3 Investigation of the Effect of Reaction Conversion on the Product Compositions through Sensitivity Study

The base case and design spec study in the previous section adopted a high total reaction conversion, 99.9 mol% as practised in the industry. The best operating parameters for column T-102 were determined based on the column inlet stream derived from the outlet stream of R-102. Bypassing one of the reactors from the reactor train comprised of one vapour phase and two liquid phase reactors would reduce the degree of reaction completion and hence affecting the product purity of the subsequent unit operations. Therefore, the present study investigated the impact of the conversion towards purity of both product n-butanol and iso-butanol. In addition to the design spec, the conversion was varied from 0.1-0.995 with all the other parameters remained constant as the studies done using design spec. A series of sensitivity analysis was conducted primarily to analyse the changes of the conversion towards the key parameter of T-102 which impacted the purity of end products. As illustrated in figure 2, figure 3, figure 4 and figure 5 the decline in reaction conversion resulted in the presence of significant amount of iso-butyraldehyde at the outlet of reactor R-102, outlet of flash tank V-101 and feed to column T-102. Figure 4 shows that the losses of n-butanol and iso-butanol through distillate of column T-101 were very minimum when the conversion was kept at 0.9 and above.
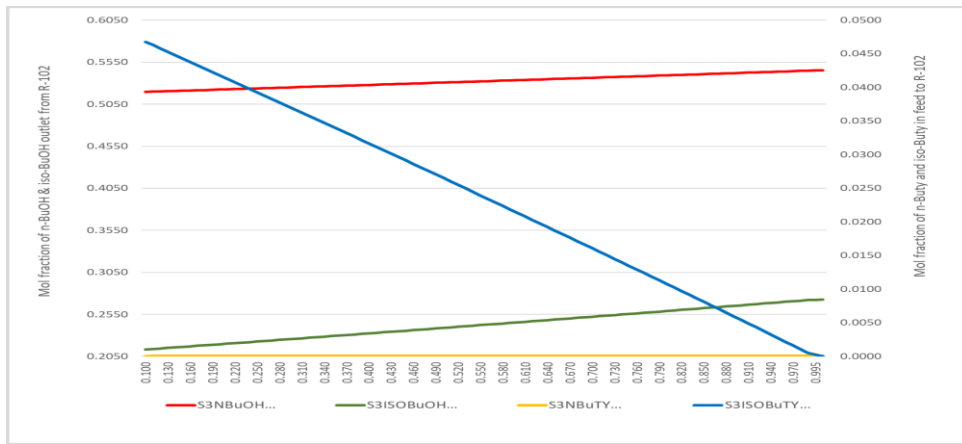
Figure 2. Effect of reaction conversion on theoutlet stream composition of R-102
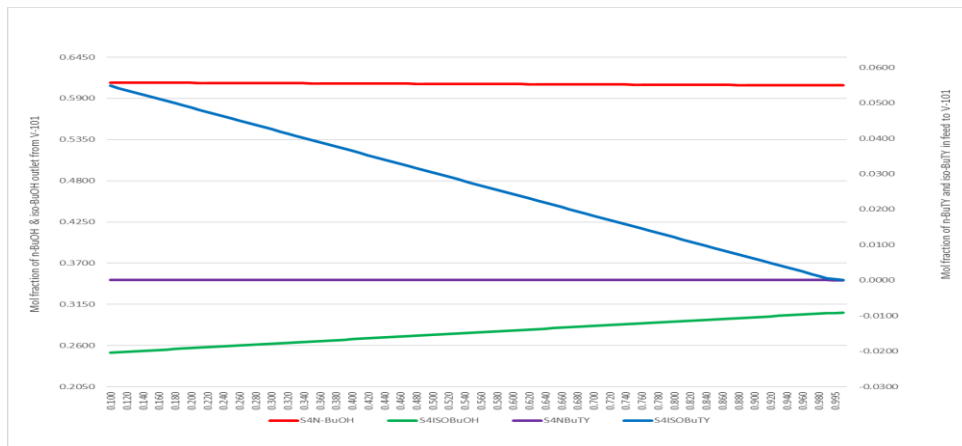

Figure 3. Effect of reaction conversion on the outlet stream composition V101
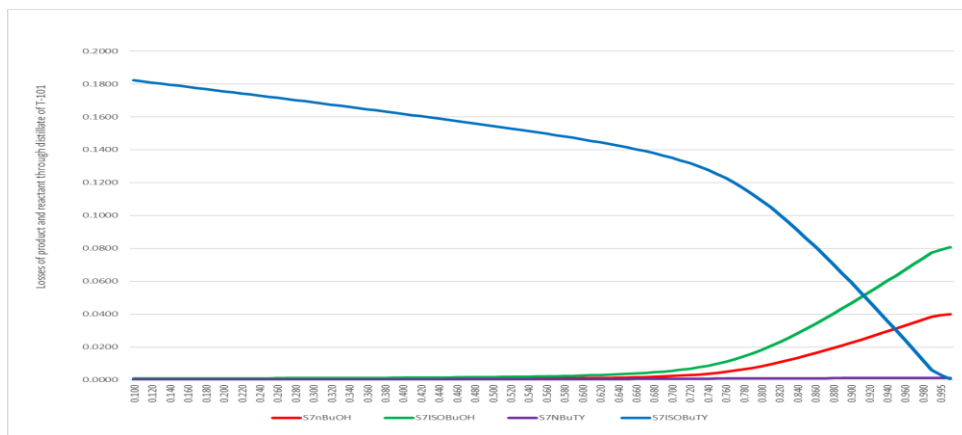

Figure 4. Effect of reaction conversion on the losses through distillate of T-101
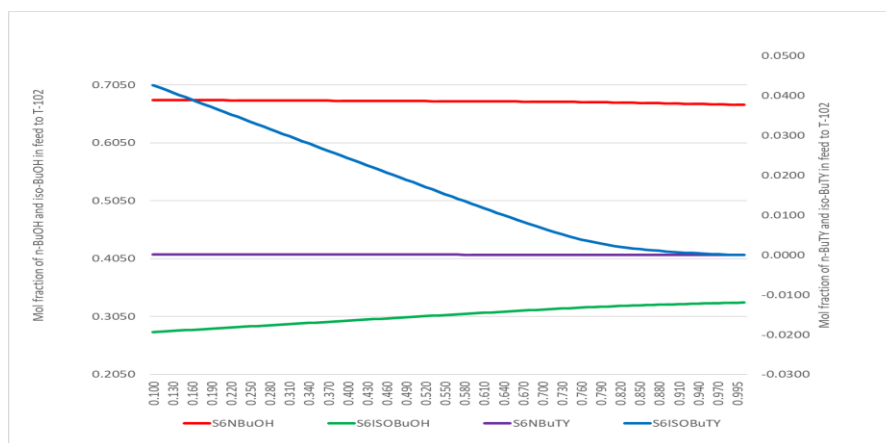
Figure 5. Effect of reaction conversion on the feed composition of T-102

The variation of the conversion did not significantly change the composition of the bottom product of T-102 as shown in figure 6, comprising of approximately 0.005 mol% of iso-butanol and 99.5 mol% of n-butanol and negligible amount of butyraldehyde. On the other hand, the decrease of reaction conversion resulted in the iso-butanol product off specification in the distillate of column T-102 as displayed in figure 7. The product purity of iso-butanol in the distillate reduced from 99.5 mol% to 84.7 mol% when the reaction conversion was declined from 0.995 to 0.1. The deviation from the desired purity of iso-butanol remained even though the reflux ratio of column T-102 was manipulated to get rid of the unreacted iso-butyraldehyde. At T-102, the iso-butyraldehyde was vaporised together with iso-butanol. Table 5 compares the properties of n-butanol, iso-butanol and iso-butyraldehyde. Iso-butyraldehyde possesses the lowest boiling point among these components, making it easily vaporised together with iso-butanol when the top temperature of column T-101 was at or slightly above 107.66 °C

Table 5. Properties of n butanol, iso-butanol and iso-butyraldehyde

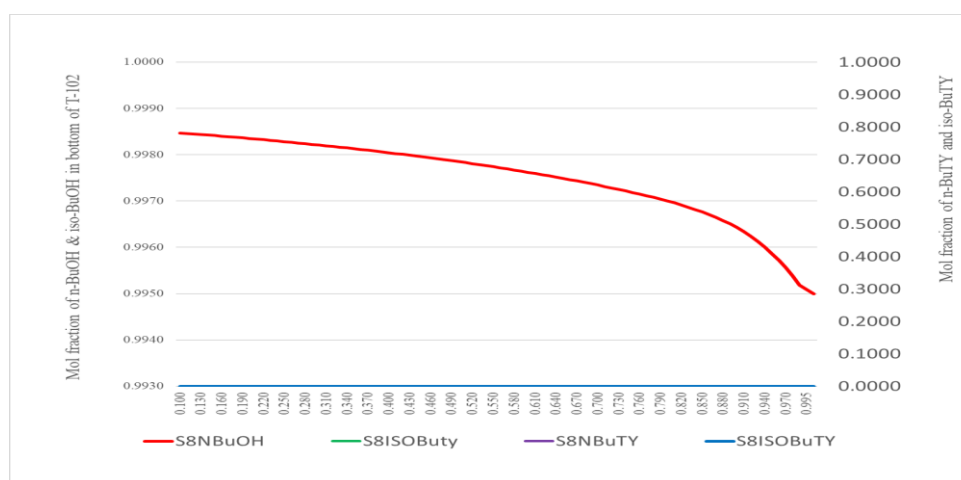| No	Properties Boiling Point at 1 atm (oC)	n-Butanol	iso-Butanol	iso-Butyraldehyde
1		118.75	107.66	74.79

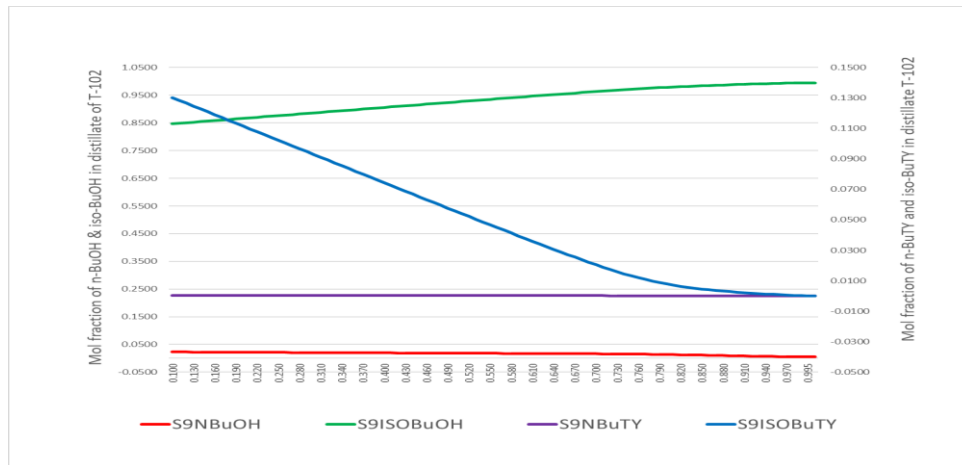**Figure 6**. Effect of reaction conversion on the bottom product purity of T-102

Figure 7. Effect of reaction conversion on the top product purity of T-102

In spite of this, the product purity of the n-butanol in the bottom of column T-102 maintained its desired purity at ≥99.5 mol%. The comparison of purify of n-butanol at bottom and iso-butanol at distillate of column T-102 can be seen clearly in figure 8.
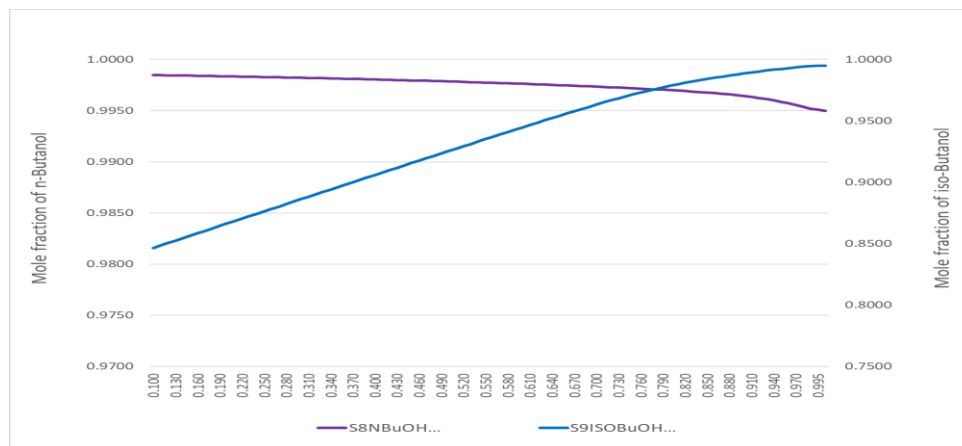

Figure 8. Effect of reaction conversion on product purity of T-102
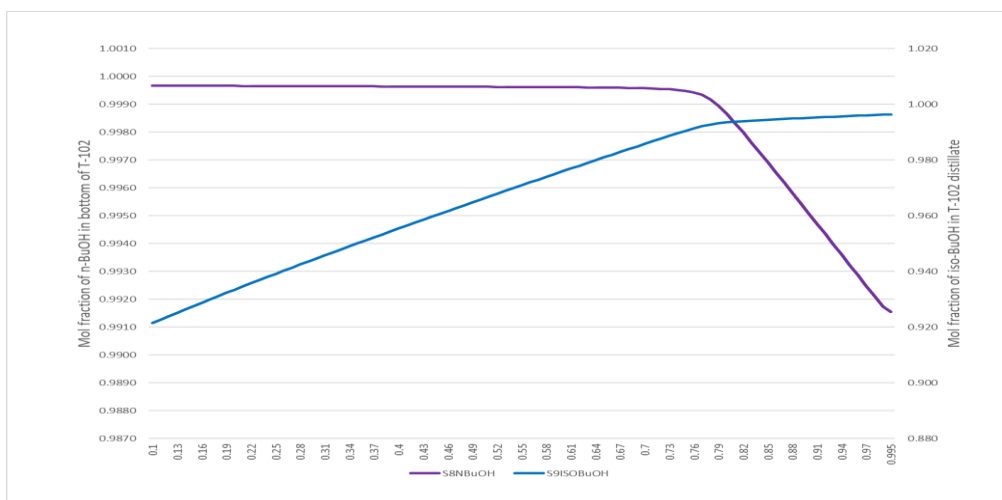

Figure 9. Effect of reaction conversion on product purity at T102 with new setting

To improve the iso-butanol purity, it needs to reduce the reflux ratio of T-101, so that the presence of unreacted n-butyraldehyde and iso-butyraldehyde from low conversion of reactor R-102 can be removed through the distillate of T-101. Further simulation was performed by manipulating manually the reflux ratio and distillate to feed ratio of T-101 and using new design spec of T-102. Manual manipulation was required for T-101 since it would provide simulation error of sensitivity run at T-102 when the reaction conversion changed at R-102. The reflux ratio and distillate to feed ratio were set at 3.567 and 0.156 respectively for T-101 and 11.055 and 0.311 respectively for T-102. The sensitivity study that was run using the new set of operating parameters is shown in figure 9. The purity of iso-butanol improved and able to achieve purity at ≥99.5 mol%. However, the purity of n-butanol started to reduce when reaching conversion of 0.92 and this purity kept reducing until maximum conversion at 0.995. In addition to that, the losses of n-butanol and iso-butanol at T-101 increased to 64%. The reason of the reduction in purity was caused by the presence of iso-butanol at the bottom product. The increment of reflux ratio of T-102 from 8.030 to 11.055 significantly impacted the purity of n-butanol and iso-butanol. Therefore, for further improvement on the purity of both products, it is suggested to manipulate the reflux ratio for T-102 at range of 8.03-11.055 and maintain the other parameters.

From figure 8 and figure 9, it shows that to get purity n-butanol as per desired purity and iso-butanol not less than 99.0%, the best conversion range is 0.92 – 0.995. But to get both purities at desired purity, it needs to be run at conversion range of 0.86 to 0.995 together with improvement that needs to be done for reflux ratio at T-102.

4. Conclusion
The present study affirmed that the bypassing of third reactor from the reactor train would not affect the product purity of the main product, n-butanol. A proposal of bypassing the last reactor from the series could be a potential solution of cost saving project to continue running the plant until the next shutdown plan to replace catalyst, provided the plant is willing to trade off the product purity of iso-butanol around 0.5% at conversion 0.92 or product of n-butanol and iso-butanol in T101 in order to get both purity product at column T-102 at ≥99.5 mol%. The recommended conversion at R-102 is 0.86 to 0.995 if the industries decide to trade off 64% losses of n-butanol and iso-butanol in T-101 distillate. However, for further improvement on the purity of both products, it is suggested to manipulate the reflux ratio of T-102 at range of 8.03-11.055 whilst maintaining the other parameters.

References
[1]   Y. Jiang, J. Liu, W. Jiang, Y. Yang, and S. Yang 2015 *Biotechnol. Adv.* **33**, 1493–1501
[2]   X. Gao, J. Chen, Z. Ma, and L. Yang 2014 *Ind. Eng. Chem. Res.* 53. *37, 14440–14445*
[3]   A. Rom, A. Miltner, W. Wukovits, and A. Friedl 2016 *Chem. Eng. Process. Process Intensif.* **104**, 201–211
[4]   P. Jet 1985 *Geothermics*. **14** 595–599
[5]   N. Y. Meyer Steinberg, Huntington Station 1976 *United States Patent (19)*
[6]   Morrison and Boyd 1998 *Organic Chemistry*. 4th ed
[7]   J. Pang, M. Zheng, L. He, L. Li, X. Pan, A. Wang, X. Wang, and T. Zhang 2016 *J. Catal.* **344** 84–193
[8]   L. M. Li, Y. L. Liu, J. Zhai, L. Y. Sun, and Y. Y. Tian 2015 *China Pet. Process. Petrochemical Technol.* **17** 111–120
[9]   J. N. Armor 2002 *Fundamentals of Industrial Catalytic Processes.* **208** 1–2
[10]   J. Requies, M. B. Güemez, P. Maireles, A. Iriondo, V. L. Barrio, J. F. Cambra, and P. L. Arias 2012 *Appl. Catal. A Gen.* **423–424** 185–191
[11]   G. M. Wells 1991 *Handbook of Petrochemicals and Process.*
[12]   F. Michael W. Bradley, Marton; Norman Harris, Norton; Keith Turner 1993 *Hydrogenation of Aldehydes*
[13]   H. Gai, K. Lin, Y. Feng, M. Xiao, K. Guo, and H. Song 2018 *Chinese J. Chem. Eng.* **26** 2040 –

         2047
[14]   M. Hantouche, S. M. Sarathy, and O. M. Knio 2018 *Combust. Flame.* **196** 452–465
[15]   Aspen 2017 *Guidelines for Choosing a Property Method*
[16]   W. An, Z. Lin, J. Chen, and J. Zhu 2014 *Ind. Eng. Chem. Res. 53.* **14** 6056–6064
[17]   Yang.X 2018 *Chemical Engineering Transactions* **43** 1465
[18]   L. C. B. A. Bessa, F. R. M. Batista, and A. J. A. Meirelles 2012 **45** 603–612