Simulation of Butanol Production through Hydrogenation of Butanal: Effects of Different Reactor Schemes and Operating Conditions

Mohammed Faraj Saeid[1*], Sim Yee Chin[2]

[1]faraj.saeid@yahoo.com, [2]chin@ump.edu.my

[1]Chemical Engineering Department, Faculty of Engineering, Tobruk University, Tobruk, Libya

[2]Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, Gambang, 26300 Kuantan, Pahang Darul Makmur, Malaysia,

*Corresponding author email: faraj.saeid@yahoo.com

ABSTRACT

The simulation was performed to evaluate the impact of by-passing the second liquid phase reactor in the series due to the catalyst blockage problem leading to the shutdown in a butanol production plant. Butanal hydrogenation for the production of butanol was simulated using the Aspen Plus software package. The process thermodynamics was described by NRTL property model while the kinetic of the main and side reactions was represented by Pseudo-homogeneous model. The attested packed bed reactor model was subsequently used to simulate butanal hydrogenation at different reactor configuration, reactor operating conditions and reactor size. The targeted final total conversion was 99.5% of butanal. The butanal conversion increased with the increase of reaction temperature and residence time. On the other hand, the reactor pressure only affected the performance of the vapour phase reactor but not the liquid phase reactor. Conclusively, the idea of bypassing liquid phase reactor for hydrogenation of butanal in the series could be adopted to achieve the total targeted conversion, provided the plant is allowed to operate at a more severe operating condition. In the modified configuration I, the last reactor should operate at 166.5℃ and 16 bar whereas, in the modified configuration II, the reactor should operate at 285℃ and 30 bar, considering the safety factor.

Keywords: Simulation, butanal hydrogenation, butanol, packed bed reactor, reactor configuration, operating condition

1. Introduction

Butanol is a chemical that has excellent fuel characteristics. It contains approximately 22% oxygen, which will result in more complete fuel combustion when it is used as a fuel extender. Moreover, compared to ethanol, butanol has higher energy density and lower vapour pressure, so butanol is also considered a preferred fuel additive or even a potential replacement for gasoline. The use of butanol as fuel will contribute to clean air by reducing smog-creating compounds, harmful emissions (carbon monoxide) and unburned hydrocarbons in the tailpipe exhaust [1]. Besides, roughly 2 x 10⁶ tons of butanol are produced annually [2] for use as a plasticiser, an industrial solvent, and an intermediate in the production of butyl acetate, a key ingredient in lacquers and varnishes [3]. The demand for butanol is expected to increase in the future as a consequence of recent studies showing that butanol is a viable alternative to ethanol as an additive to gasoline [4,5].

While many processes exist for the production of butanol, such as the aldol condensation of ethanal [6], oxidation of butane [7], or the enzymatic fermentation of sugars [4,8], the overwhelming majority of butanol

is produced in a three-step process involving the homogeneously catalyzed hydroformylation of propylene, separation of the resulting butanal, and subsequent hydrogenation of butanal through a series of high pressure and low pressure hydrogenation packed bed reactor. The Oxo synthesis (hydroformylation) process is based on the reaction of propylene with Oxogas to give a crude mixture of *n-* and iso-butanal to be reacted with hydrogen to form butanol via hydrogenation and distillation [9]. The adoption of a low-pressure rhodium-based catalyst system in place of high-pressure cobalt for the hydroformylation of propylene by reaction with carbon monoxide and hydrogen to produce butanal (an 'oxo' reaction) has brought large cost benefits to oxo producers. The benefits are derived from improved feedstock efficiency, lower energy usage and simpler and cheaper plant configurations [10].

A butanol production plant adopts the technology of using three packed bed reactors in series (1 vapour phase reactor and two liquid phase reactors) for the high pressure and low-pressure butanal hydrogenation respectively. This butanol production plant frequently encountered the catalyst blockage problem in the third reactor, the Low-Pressure Hydrogenation (LPH) reactor, which caused a plant shutdown. In view of minimising the production and revenue loss due to the plant shutdown, the plant operators propose to continue producing the demanded product with the two precede hydrogenation reactors in series, by-passing the third reactor. The proposal of excluding the LPH reactor from the reactor train could be evaluated through simulation analysis. Simulation is a process of designing an accurate operational model of a reactor and conducting investigations with this model for the purpose either of understanding the behaviour of the system or of evaluating alternative strategies for the development or operation of the system [11].

The aim of the present work is to simulate and investigate the effect of the reactor scheme and operating conditions to the reaction performance. The industrial plant data was used to validate the model. Three reactor configurations of butanal hydrogenation were considered for the simulation analysis. Original reactor configuration (single vapour phase reactor followed by two liquid phase reactors), modified configuration I (single vapour phase reactor followed by single liquid phase reactor), and modified configuration II (single vapour phase reactor).

2. Modelling Approach

2.1 Packed bed reactor model

A fixed packed bed reactor consists of a compact, immobile stack of catalyst pellets within a generally vertical vessel. On macroscopic scales, the catalyst bed behaves as a porous media. The fixed beds are thus employed as continuous tubular reactors in which the reactive species in the mobile fluid (gas or liquid) phase are reacting over the catalyst surface (interior or exterior) in the stationary packed bed [12].

As with the PFR, the PBR is assumed to have no radial gradients in concentration, temperature, or reaction rate. The generalised mole balance on species A over catalyst weight AW results in the equation [13].

$$In - Out \; + \; Generation \; = \; Accumulation \tag{1}$$

$$F_{AW} - F_{A(W + \Delta W)} + r'_{A}\Delta W \; = \; 0$$

The differential form of the mole balance for a packed-bed reactor:

$$\frac{dF_A}{dW} = r'_A \tag{2}$$

If the pressure drop and catalyst decay are neglected,

$$W = \int_{F_A}^{F_{A0}} \frac{dF_A}{-r_A} \tag{3}$$

where W is the catalyst weight needed to reduce the entering molar flow rate of species A, F_{A0}, to a flow rate F_A.

The simulation of packed bed reactors for the production of butanol via hydrogenation of butanal was carried out using R-Plug in Aspen Plus. RPlug is a rigorous model for plug flow reactors which assumes that perfect mixing occurs in the radial direction and that no mixing occurs in the axial direction. RPlug can model one-, two-, or three-phase reactors. This model is useful when reaction kinetics is known, including reactions involving solids (Aspen Plus guideline 2016).

The process flow diagram of the original reactor configuration (one vapour phase reactor followed by two liquid phase reactors) is shown in Figure 1. The feed stream entered the first reactor with the total flow rate of 1506.26 kmol.hr^{-1}. It comprised of 0.703 mol% of H_2, 0.213 mol% of CH_4, 0.004 mol% of H_2O, 0.0.058 mol% of n-butanal, 0.017 mol% of i-butanal, 0.0.003 mol% of n-butanol, and 0.002 mol% of i-butanol. The reaction temperatures were 213°C, 159°C, and 167°C for the first, second and third reactor respectively. Whereas the reaction pressures for vapour phase and liquid phase reactors were 21 bar and 16 bar respectively.
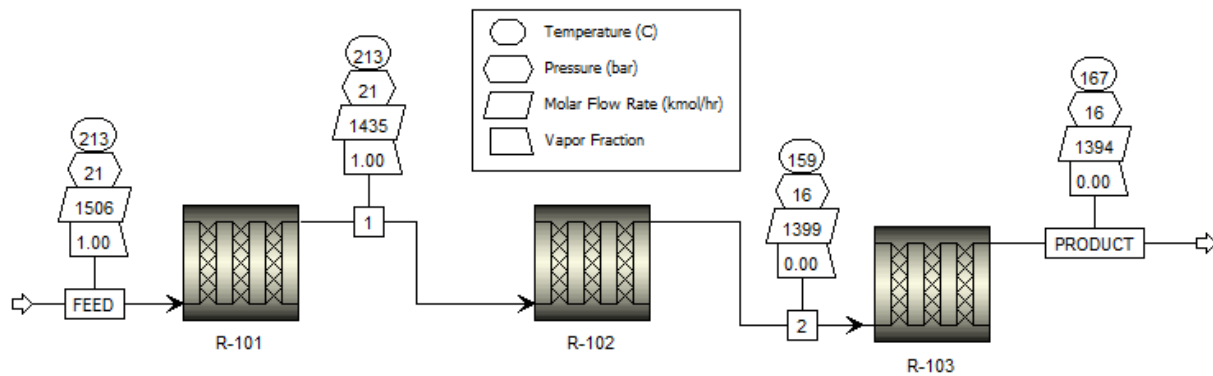

Figure 1: *Original reactor configuration for butanal hydrogenation.*

2.2 Kinetic model

2.2.1 Butanal hydrogenation

Eq.(4) and Eq.(5) show the chemical equation and kinetic model of *n*-butanal and *i*-butanal for the production of butanol through butanal hydrogenation, which is found as endothermic reaction.

$$C_4H_8O + H_2 \rightarrow C_4H_9OH \tag{4}$$

$$r_{bals} = A \exp\left(-\frac{E}{T}\right) P_{bal}^{0.7} P_{H_2}^{0.5} \tag{5}$$

Where r_{bals} = Butanal reaction rate (Moles/liter.hr)

A_g = 33.38 Moles/liter.bar

A_l = 1.59345×10^7 Moles/liter.bar

E_g = 2.9481×10^{10} KJ/kmol

E_l = 60520 KJ/kmol

P_{bal} = Partial pressure of butanal (bar)

P_{H_2} = Partial pressure of hydrogen (bar)

Where "g" and "l" refer to gas and liquid phase reactions.

2.2.2 Side Reaction

Beside butanal hydrogenation, the elevated temperature in this process also promotes side products such as butyl butyrate. Butyl butyrate is produced from the hydrogenation of n-butanol, as shown in eq (6):

$$2C_4H_9OH \rightarrow C_8H_{16}O_2 + H_2 \tag{6}$$

The rate equation for the side reaction is shown in eq (7).

$$r_{byprod} = A \exp\left(-\frac{E}{T}\right) P_{bal}^{1.8} \tag{7}$$

Where r_{byprod} = Byproduct reaction rate (Moles/liter.hr)

A_g = 3744.539 Moles/liter,bar

A_l = 1.92079×10^9 Moles/liter.bar

E_g = 4.9884×10^{10} KJ/kmol

E_l = 100973.53 KJ/kmol

P_{bal} = Partial pressure of butanal (bar)

P_{H_2} = Partial pressure of hydrogen (bar)

2.3 Plant data reconciliation

In order to validate the selected thermodynamics, reactor and kinetic models, the simulated results were compared with the industrial plant data obtained from a packed bed reactor. The present study was limited to the validation of the gas phase reactor due to the unavailability of plant data for the liquid phase reactor. The plant data consists of reaction temperatures and pressure for the vapour phase reaction as well the inlet and outlet mixture composition. The operating conditions are given in Table 1.

Table 1. *Industrial plant data (adopted from [14])*

Parameters	Inlet composition	Outlet composition
Temperature (°C)	125	125
Pressure (bar)	21	21
Flow rate (Kmol.h^{-1})	1506.25	1393.18
H_2 (mol)	0.703	0.679
CH_4 (mol)	0.213	0.230
H_2O (mol)	0.004	0.005
n-butanal (mol)	0.058	0
i-butanal (mol)	0.017	0
n-butanol (mol)	0.003	0.065
i-butanol (mol)	0.002	0.021

2.4 Simulation analysis to investigate the effect of different reactor configurations and operating condition

The effect of different reactor configurations was investigated at a wide range of operating conditions. These reactor configurations included original reactor configuration (single vapour phase reactor followed by two liquid phase reactors), modified configuration I (single vapour phase reactor followed by single liquid phase reactor), and modified configuration II (single vapour phase reactor). Table 2 provides the ranges of reactors operating conditions.

Table 2. *Operating conditions for hydrogenation reactors*

Parameter	Hydrogenation Unit
Reaction temperatures for vapour phase reactor.	135°C - 265°C
Reaction temperature for liquid phase reactors.	128°C - 196°C
Reaction pressure for both vapour and liquid phase reactors.	16 – 21 bar

3. Results and discussion

3.1 Model validation

In order to validate the selected thermodynamic, reactor and kinetic models, the simulated results were compared with the industrial plant data obtained from a packed bed reactor. The present study was limited to the validation of the gas phase reactor due to the unavailability of plant data for the liquid phase reactor. The gas-phase reactor was operated at 125°C and 21 bar. The feed flow rate was 1506.25 kmol/hr with the composition of H_2, H_2O, CH_4, i-butanal, *n*-butanal, i-butanol, and *n*-butanol.

As shown in Table 3 The butanal hydrogenation process is well described by the kinetic parameters since most of the data points of all components except H_2O are within the marginal error lines of 20%. The H_2O outlet composition is not accurately predicted due to its very low absolute value compared to the other components [15]. The *n*-butanal conversion was 99.77% comparing within the literature which is 99.99%. While the conversion of i-butanal was 100% typically the same conversion obtained. The reaction temperature was fixed as 125°C, and the reaction pressure was fixed as 21 bar, based on the literature operating conditions.

In view of the average deviation of less than 10%, the validity of the models was confirmed, and these models were used in the following simulation studies.

Table 3. *Comparison of the simulation results with the industrial plant data*

Industrial plant data [15]	Simulation results	Relative Deviation (%)
Outlet composition		
N (Kmol.h^{-1})	1393.18	1393.48	0.0216
H_2	0.679	0.679	0
CH_4	0.230	0.230	0
H_2O	0.005	0.004	20
n-butanal	0	0.000143	0
i-butanal	0	0	0
n-butanol	0.065	0.065	0
i-butanol	0.021	0.021	0

3.2 Original reactor configuration

The simulation of a reactor configuration with three (3) packed bed reactors in series (one vapour phase reactor followed by two liquid phase reactors) was done. The effects of different operation conditions on the performance of the third reactor were investigated, and the corresponding simulation results are shown in the following sections.

3.2.1 Effect of reaction temperature

Based on the industrial plant data, the conversion of *n*-butanal in vapour phase reactor should achieve 60%, and for the liquid phase reactors, the conversion of the *n*-butanal should be 85% for the first liquid phase reactor and 99.5% for the second liquid phase reactor.

Figure 2. presents the variations of reactants conversions and product yields versus reaction temperature of the last liquid phase reactor in the series. The reaction was carried out at pressure of 21 bar for the vapour phase

reactor and 16 bar for the liquid phase reactors. The reaction temperatures of the vapour phase reactor and first liquid phase reactor were fixed at 213 °C and 158.5 °C respectively. The reactors diameter and length were 2.75 m and 10.92 m, respectively.
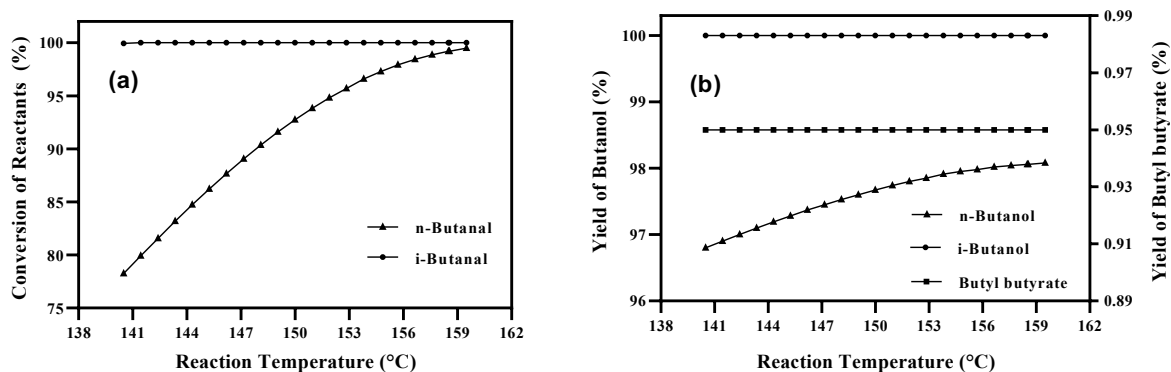

Figure 2: *Effect of reaction temperature of the original configuration on (a) Conversion of reactants (b) Yield of products.*

The conversion of *n*-butanal increased with the increase of temperature. While the conversion of i-butanal was almost constant. With the increase in reaction temperature from 140.5 °C to 159.5 °C, *n*-butanal conversion increased from 78.24% to 99.48%. In addition, the yield of *n*-butanol increased from 96.8% to 98.08%, the yield of i-butanol was unvaried and remained at 100%, and butyl butyrate yield was remained constant with a yield of 0.95%. The highest *n*-butanal conversion is 99.99%. and it was obtained at temperature of 167 °C.

3.2.2 Effect of reaction pressure

The effect of pressure on the conversion of reactants of the third reactor in the series can be seen in Figure 3. The operating temperatures of vapour phase reactor and two liquid phase reactors were fixed as 213 °C, 158.5 °C, and 159.5 °C. The reactors diameter and length were 2.75 m and 10.92 m, respectively.

The effect of pressure was investigated in the range of 16 to 21 bar for the second liquid phase reactor. It can be observed that when the pressure increased, the conversion of reactants was not affected negatively or a positively. Therefore, the conversion of *n*-butanal and i-butanal are remained constant at 99.48% and 100% as the pressure was increased from 16 to 21 bar. The concentration of reactants is insignificantly affected by even relatively large changes in the total pressure. Consequently, the effect of pressure can be totally ignored. Therefore, the pressure of 16 bar was chosen in the subsequent studies.
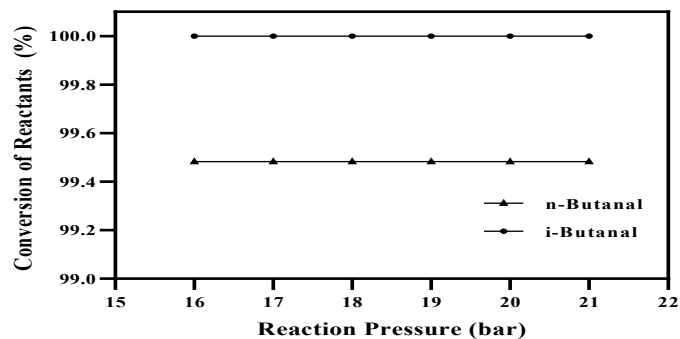
Figure 3: *Effect of reaction pressure of the original configuration on the conversion of reactants*

3.2.3 Effect of reactor size

The effects of the reactor diameter and length were investigated of the third reactor in the series in the hydrogenation of butanal to produce butanol. The reaction was carried out at 213 °C, 158.5 °C, and 159.5 °C of reaction temperature and 21 bar, 16 bar, and 21 bar of reaction pressure for single vapour and two liquid phase reactors. Figure 4 shows the results of the effect of reactor size.

The reactor volume changes with reactor length and reactor diameter. Reactor volume also affects the reaction performance. Therefore, sizing of the reactor is very important when high conversion and yield values desired. Therefore, the conversion of the reactants and the yield of products changes along the reactor. The reaction rate is a function of concentration; hence, it also varies with reactor length. The diffusion of the reactor is effect by the reactor size, which is the spontaneous intermingling or mixing of atoms or molecules by random thermal motion. It gives rise to motion of the species relative to motion of the mixture. In the absence of other gradients (such as temperature, electric potential, or gravitational potential). Molecules of a given species within a single phase will always diffuse from regions of higher concentrations to regions of lower concentrations [14].

An increase in reactor length and diameter of the plug flow reactors caused a significant increase in the butanal conversion and in the yield of the products. The allowable L/D ratio is 4 to 10; therefore, the investigation of varies length and diameter was not exceeding the L/D ratio range through all the discussion. As seen in Figure 4 when the reactor diameter was increased from 1.25 to 2.75 m and reactor length was 10.92 m, *n*-butanal and i-butanal conversions increased from 24.32 to 99.48% and 35.38 to 100%. While the yield of *n*-butanol, i-butanol, and butyl butyrate increased from 49.53 to 98.08%, 64.92 to 100%, and 0.33 to 0.95%. While the reactor length was increased from 10.92 m to 12 m, reactor diameter was 2.75 m, *n*-butanal reaction conversion values increased from 99.48 to 99.98%. While the conversion of *n*-butanal at 12.25 m of reactor length decreased to 99.96% and within increasing of reactor length to 12.5 m, lead to increasing of *n*-butanal conversion with maximum amount of 99.99%. While the conversion of i-butanal was remaining constant at 100%. While the yield of *n*-butanol decreases with reactor length, butyl butyrate yield increases. The highest conversion of *n*-butanal was obtained as 99.99% when the reactor diameter and reactor length was 2.75 m and 12.5 m, respectively.
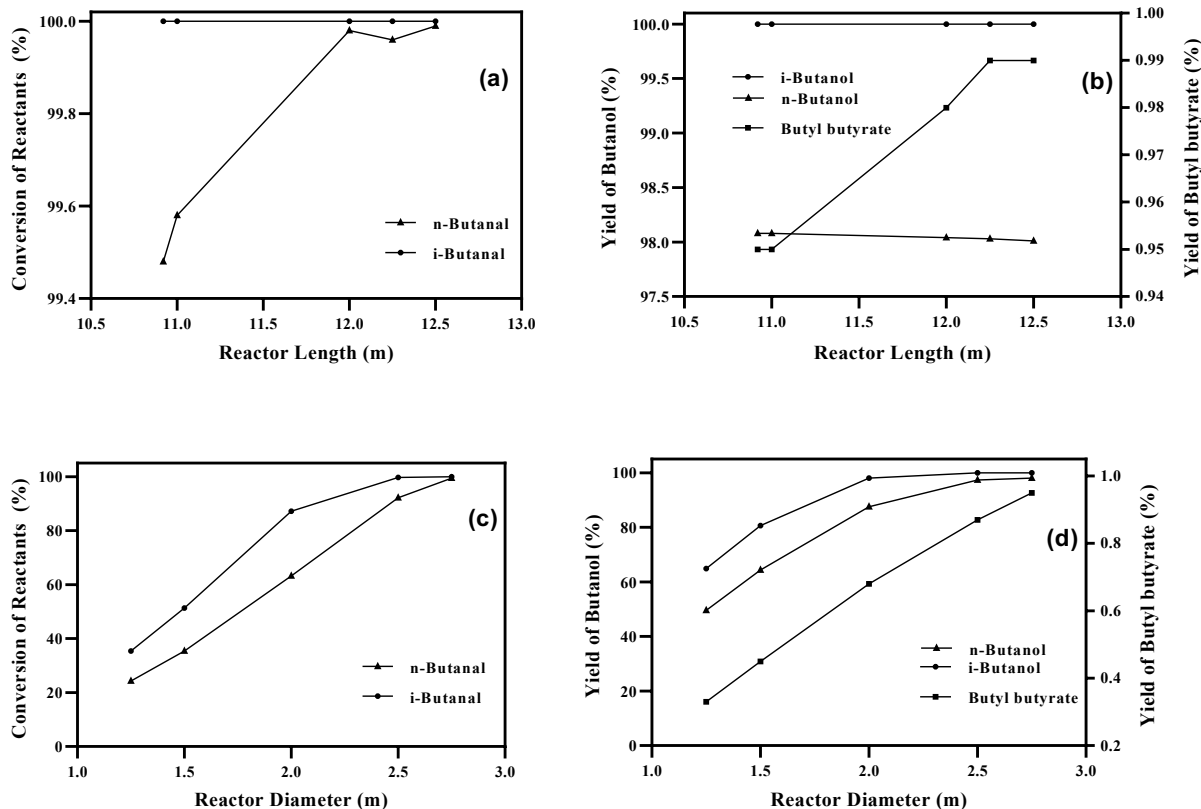
Figure 4: *(a) Effect of reactor length of the original configuration on the conversion of reactants (b) Effect of reactor length on the yield of products (c) Effect of reactor diameter on the conversion of reactants (d) Effect of reactor diameter on the yield of products.*

As shown in Table 4., the residence time of the second liquid phase reactor was calculated at varies reactor lengths and diameters. The reaction was carried out at 213 °C, 158.5 °C, and 159.5 °C in the first, second and third reactors respectively whereas the reaction pressures of these reactors are 21 bar, 16 bar, and 21 bar correspondingly. When the reactor diameter was increased from 1.25 to 2.75 m with the reactor length of 10.92 m, residence time increased from 5.83 to 28.8 minutes. While when the reactors length was increased from 10.92 to 12.5 m and reactor diameter fixed as 2.75m, residence time increased from 28.8 to 33 minutes. It is to conclude that the residence time of liquid phase reactors increases with increases of reactor length and diameter and resulting in increases of conversion values.

Table 4. *The effect of reactor size of the original configuration on the reactor residence time*

Reactor length fixed as 10.92 (m)			
Diameter (m)	Residence time (min)	*n*-butanal conversion (%)	i-butanal conversion (%)
1.25	5.8	24.32	35.38
1.5	8.5	35.36	51.29
2	15.2	63.22	87.15
2.5	23.8	92.17	99.7
2.75	28.8	99.48	100
Reactor diameter fixed as 2.75 (m)			
Length (m)	Residence time (min)	*n*-butanal conversion (%)	i-butanal conversion (%)
10.92	28.8	99.48	100
11	29	99.58	100
12	31.6	99.98	100
12.25	32.3	99.96	100
12.5	33	99.99	100

3.3 Modified reactors configuration

Simulation was also performed using the modified reactor configurations. Modified Configuration I comprised of two reactors in series, a vapour phase reactor followed by a liquid phase reactor, while Modified Configuration II constituted by solely the vapour phase reactor. The effects of variation of temperature, pressure and reactor size are reported as follows.

3.3.1 Modified configuration I- bypassing the second low-pressure liquid phase hydrogenation reactor
3.3.1.1 Effect of reaction temperature

Figure 5 shows the effect of reaction temperature on the conversion of reactants and the yields of products. The reaction was carried out at pressure of 21 bar for the vapour phase reactor and 16 bar for the liquid phase reactor. The reaction temperature of the vapour phase reactor was fixed as 255 °C and the reaction pressure were fixed as 21 bar and 16 bar for the vapour and liquid phase reactors. The reactors diameter and length were 2.75 m and 10.92 m, respectively.

The conversion of *n*-butanal increased with the increase of temperature from 77.32% to 99.45% and the conversion of i-butanal increased from 99.07 to 100 % with a range of temperature from 146.5 °C to 166.5 °. In addition, the yield of *n*-butanol increased from 93.39% to 96.7%, the yield of i-butanol is linear at 100%, and butyl butyrate yield is remained constant with a yield of 1.61%. While the maximum *n*-butanal conversion was obtained at the temperature of 171 °C as 99.99%.
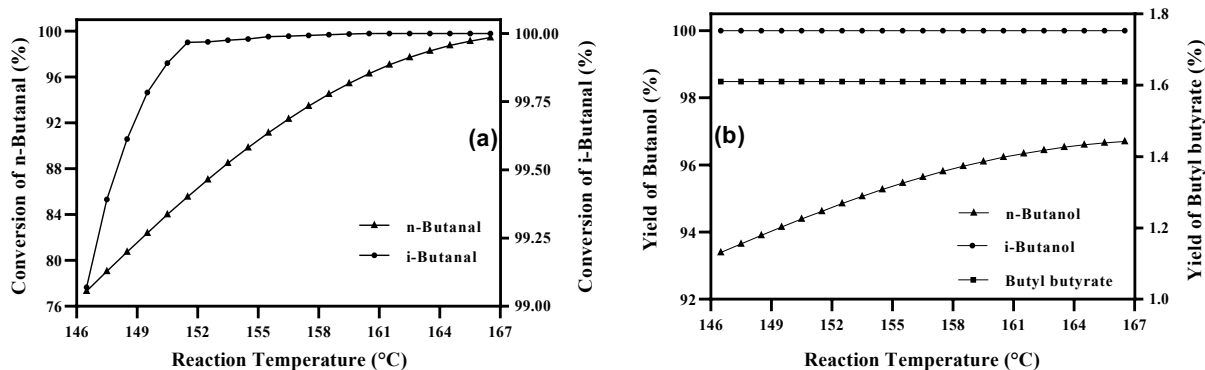
Figure 5: *Effect of reaction temperature of the modified configuration I on (a) Conversion of reactants (b) Yield of products*

3.3.1.2 Effect of reaction pressure

The effect of pressure on the conversion of reactants can be seen in Figure 6. The operation conditions of the vapour phase reactor and liquid phaser reactor were fixed as 255°C, and 166.5°C of the reaction temperature and the vapour phase reactor reaction pressure was fixed as 21 bar. The reactors diameter and length were fixed as 2.75 m and 10.92 m, respectively.

The effect of pressure was investigated in the range of 16 to 21 bar for the liquid phase reactor. It can be observed that when the pressure is increased, the conversion of reactants does not suffer a negative or a positive effect. Higher pressure or even lower pressure do not encourage butanal conversion. The maximum amount of reactants conversion can be achieved at any certain pressure. Therefore, the conversion of *n*-butanal and i-butanal are remained constant at 99.44% and 100% as the pressure was increased from 16 to 21 bar.
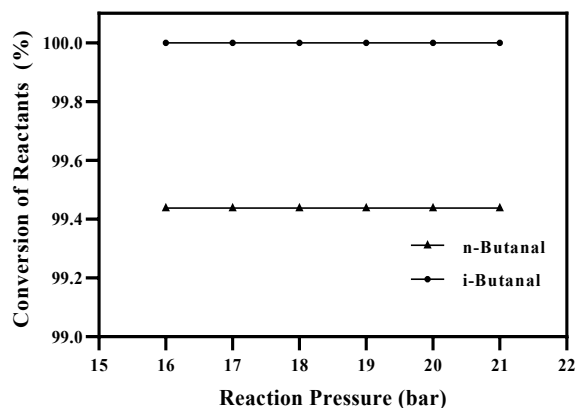

Figure 6: *Effect of reaction pressure of the modified configuration I on the conversion of reactants.*

11

3.3.1.3 Effect of reactor size

The reaction was carried out at 255 °C and 166.5 °C for the reaction temperature and 21 bar and 16 bar of reaction pressure for single vapour and liquid phase reactors. The obtained results are shown in Figure 7.

An increase in reactor length and diameter of the plug flow reactors caused a significant increase in the butanal conversion and the yield of the products. As seen in Figure 4 when the reactor diameter was increased from 1.25 to 2.75 m and reactor length was 10.92 m, *n*-butanal and i-butanal conversions increased from 30.07 to 99.44% and 42.41 to 100%. While the yield of *n*-butanol, i-butanol, and butyl butyrate increased from 49.53 to 98.08%, 64.92 to 100%, and 0.78 to 1.61%. While the reactor length was increased from 10.92 m to 12 m, reactor diameter was 2.75 m, *n*-butanal reaction conversion values increased from 99.44 to 99.99%. While the conversion of *n*-butanal at 12.5 m of reactor length decreased to 99.98%. While the conversion of i-butanal was remaining constant at 100%. The yield of *n*-butanol increases at certain reactor lengths and decreases with others and butyl butyrate yield increases. The highest conversion of *n*-butanal was obtained as 99.98% when the reactor diameter and reactor length was 2.75 m and 12.25 m, respectively.
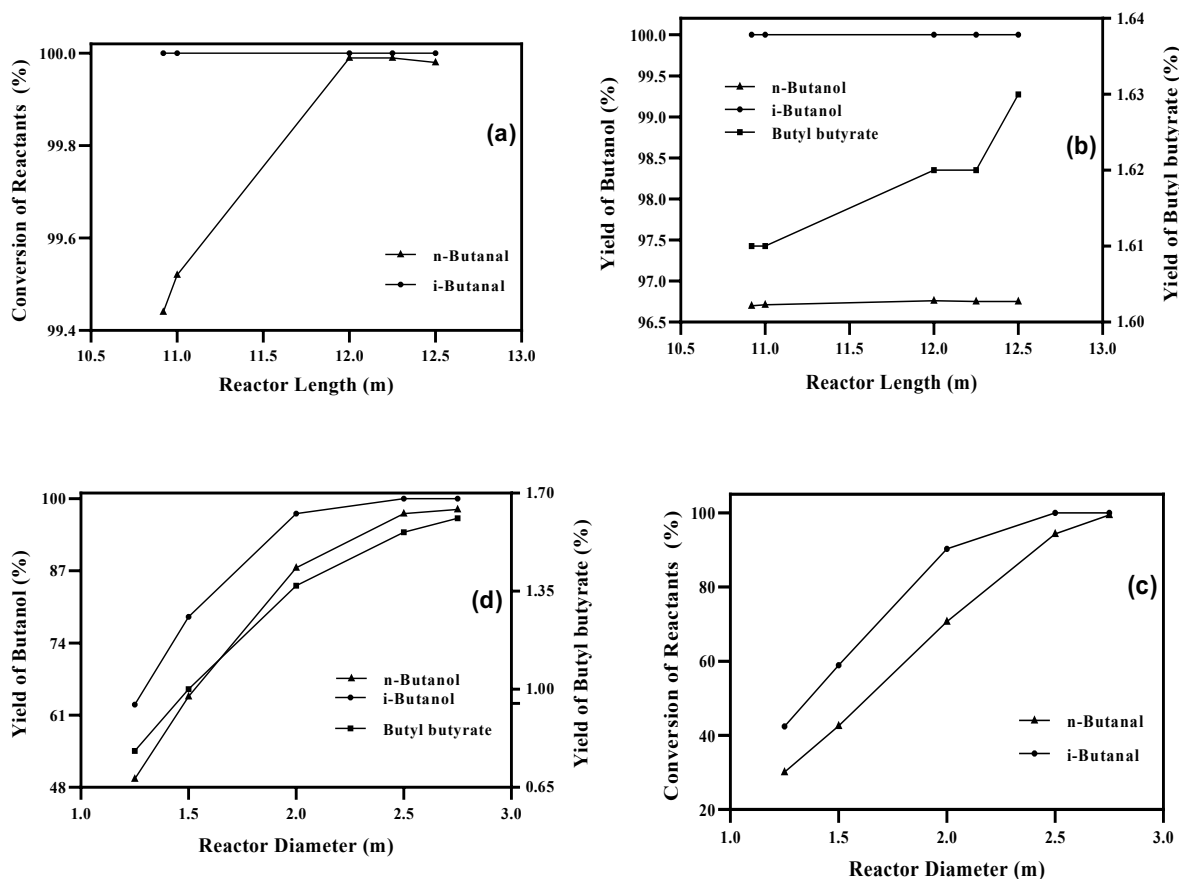

Figure 7: *(a) Effect of reactor length of the modified configuration I on the conversion of reactants (b) Effect of reactor length on the yield of products (c) Effect of reactor diameter on the conversion of reactants (d)Effect of reactor diameter on the yield of products.*

Table 5. Shows the residence time of the liquid phase reactor at varies reactor lengths and diameters. The reaction was carried out at 255 °C, 166.5 °C temperature and 21 bar, 16 bar of reaction pressure for single vapour and liquid phase reactors. When the reactor diameter was increased from 1.25 to 2.75 m, and reactor length was 10.92 m, residence time increases from 5.83 to 28.8 minutes. While when the reactors length was increased from 10.92 to 12.5 m and reactor diameter fixed as 2.75m, residence time increase from 28.8 to 33 minutes. We concluded that the residence time of liquid phase reactors increases with increases of reactor length and diameter and resulting in increasing of conversion values.

Table 5. *The effect of reactor size of the modified configuration I on the reactor residence time*

Reactor length fixed as 10.92 (m)			
Diameter (m)	Residence time (min)	*n*-butanal conversion (%)	i-butanal conversion (%)
1.25	5.8	30.07	42.41
1.5	8.4	42.55	58.95
2	15.2	70.66	90.27
2.5	23.8	94.31	99.98
2.75	28.8	99.44	100
Reactor diameter fixed as 2.75 (m)			
Length (m)	Residence time (min)	*n*-butanal conversion (%)	i-butanal conversion (%)
10.92	28.8	99.44	100
11	29	99.52	100
12	31.6	99.99	100
12.25	32.3	99.99	100
12.5	33	99.98	100

3.3.2 Benchmarking the simulation results of modified configuration I with that in the original reactor configuration

Based on the plant data, the targeted total conversion from the last reactor in the series should be 99.5%. In the Modified Configuration I, the total conversion of 99.44% from the first liquid phase reactor in the series obtained at reaction temperature of 166.5°C and reaction pressure of 16 bar. While the total conversion of the vapour phase reactor was fixed as 85% obtained at reaction temperature of 255°C and reaction pressure of 21 bar. Comparing with those in the original reactor configuration the total conversion of 99.48% from the second liquid phase reactor in the series obtained at reaction temperature of 159.5°C and reaction pressure of 16 bar. While the reactor length and diameter were fixed as 10.92 (m) and 2.75 (m) in the both cases. A more severe reaction temperature was required in the Modified Configuration I for achieving the total targeted conversion.

3.3.3 Modified configuration II- bypassing the first low-pressure liquid phase hydrogenation reactor
3.3.3.1 Effect of reaction temperature

Figure 8. shows the variations of reactants conversions and product yields versus reaction temperature of a single vapour phase reactor. The reaction was carried out at pressure of 21 bar. The reactor diameter and length were 2.75 m and 10.92 m, respectively.

The total conversion of *n*-butanal and i-butanal increased with the increases of temperature. *n*-butanal conversion increased from 54.96% to 89.58% with industrial plant operation conditions limits. Whiles the conversion of i-butanal increased from 69.34 to 97.97 %. In addition, the yield of *n*-butanol increased from

53.31 to 86.06%, the yield of i-butanol increases from 69.34 to 97.97% and butyl butyrate yield is also increased from 0.82 to 1.76.% In the case of want to exceed the industrial plant operation conditions, the maximum *n*-butanal conversion was obtained at the temperature of 285 °C and reaction pressure of 30 bar as 99.99%.
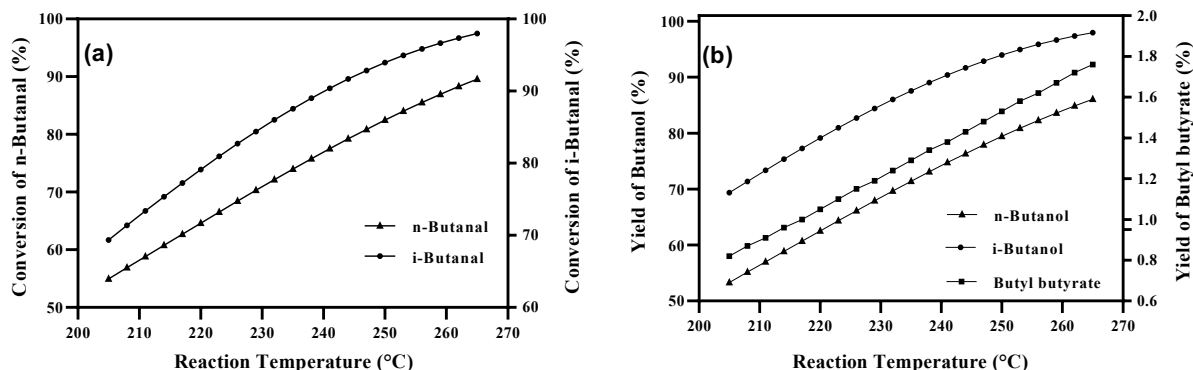

Figure 8: *Effect of reaction temperature of the modified configuration II on (a) Conversion of reactants (b) Yield of products*

3.3.3.2   Effect of reaction pressure

The effect of pressure on the conversion of reactants and the yields of the products can be seen in Figure 9. The operation temperature of vapour phase reactor was fixed as 265°C. The reactors diameter and length were 2.75 m and 10.92 m, respectively.

The effect of pressure was investigated in the range of 16 to 21 bar for the vapour phase reaction. It can be observed that when the pressure is increased, the conversion of reactants has a positive effect. Higher pressure in vapour phase reaction encourages butanal conversion. However. In gas-phase reactions, the concentration of the reacting species is proportional to the total pressure (Scott Fogler 2016). The maximum amount of reactants conversion can be achieved at 21 bar. Therefore, the conversion of *n*-butanal and i-butanal are increased from 76.79 to 89.58% and from 89.8 to 97.97%. While the yields of the products increase from 73.9 to 86.06% of *n*-butanol yield and 89.77 to 97.97% of i-butanol, for the yield of butyl butyrate it increased from 1.45 to 1.76% as the pressure was increased from 16 to 21 bar.
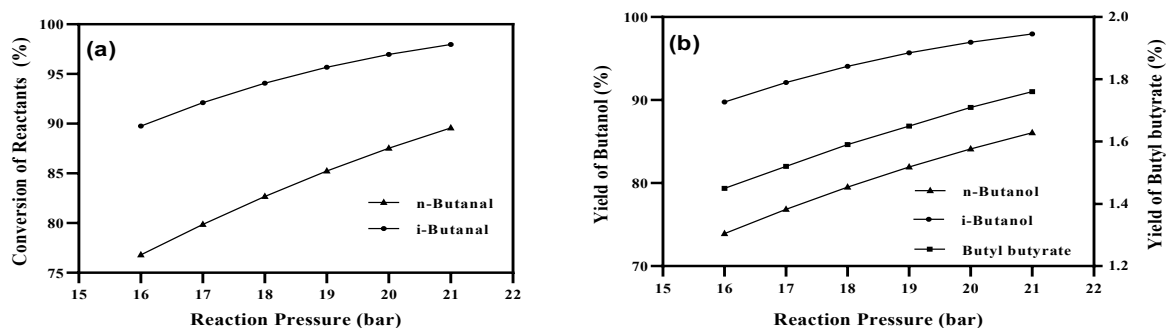

Figure 9: *Effect of reaction pressure of the modified configuration II on (a) Conversion of reactants (b) Yield of products*

3.3.3.3 Effect of reactor size

The reaction was carried out at 265 °C and 21 bar of reaction pressure for vapour phase reaction. The obtained results are shown in Figure 10. The reactor volume changes with reactor length and reactor diameter. Reactor volume also affects the reaction kinetics. Therefore, sizing of the reactor is very important when high conversion and yield values desired. Therefore, the conversion of the reactants and the yield of products changes along the reactor. The reaction rate is a function of concentration; hence it also varies with reactor length. An increase in reactor length and diameter of the plug flow reactors caused a significant increase in the butanal conversion and the yield of the products. As seen in Figure 4 when the reactor diameter was increased from 1.25 to 2.75 m and reactor length was 10.92 m, *n*-butanal and i-butanal conversions increased from 30.46 to 89.58% and 39.57 to 97.97%. While the yield of *n*-butanol, i-butanol, and butyl butyrate increased from 28.62 to 86.06%, 39.57 to 97.97%, and 0.92 to 1.76%. While the reactor length was increased from 10.92 m to 12 m, reactor diameter was 2.75 m, *n*-butanal reaction conversion values increased from 89.58 to 93.66%. While the conversion of i-butanal was increasing from 97.97 to 99.45%. The yield of *n*-butanol and i-butanol increases from 86.06 to 90.12% and 97.97 to 99.45%. The butyl butyrate yield value is small with a variation of reactor length, which is increased from 1.76 to 1.77%. The highest conversion of *n*-butanal was obtained as 93.65% when the reactor diameter and reactor length were 2.75 m and 12.5 m, respectively.
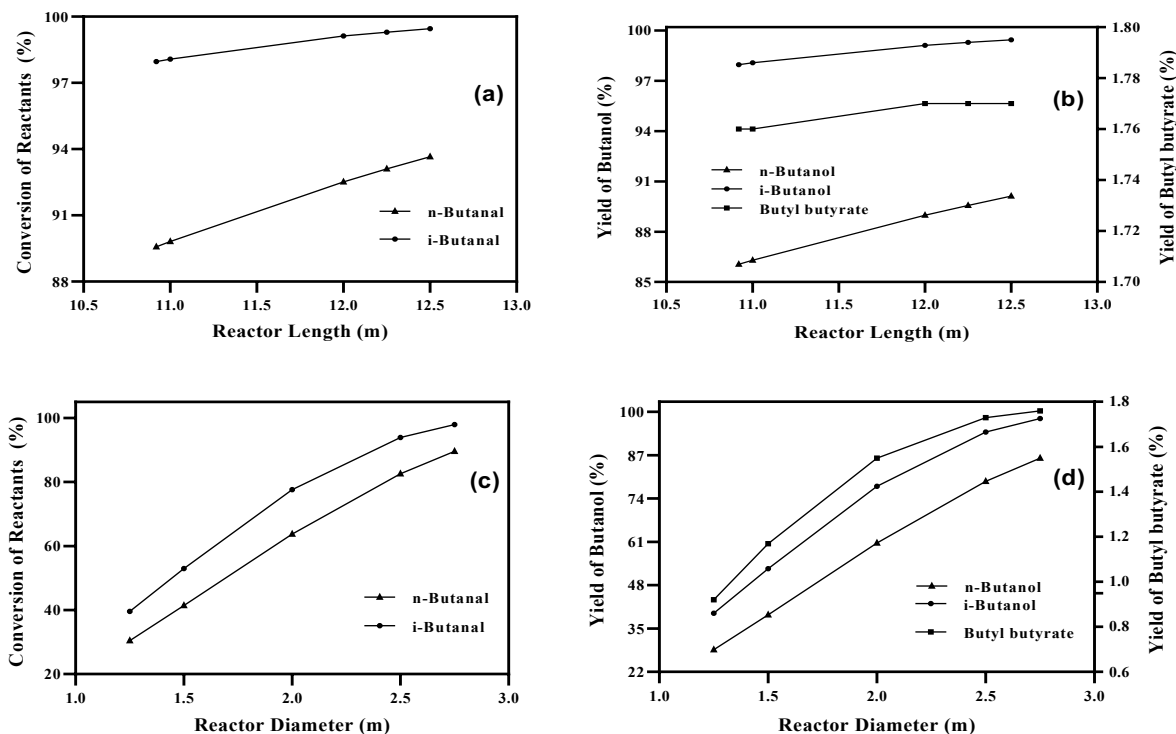

Figure 10: *(a) Effect of reactor length of the modified configuration II on the conversion of reactants (b) Effect of reactor length on the yield of products (c) Effect of reactor diameter on the conversion of reactants (d) Effect of reactor diameter on the yield of products*

Table 6. shows the residence time of the vapour phase reaction at varies reactor lengths and diameters. The reaction was carried out at 265 °C of reaction temperature and 21 bar of reaction pressure. When the reactor diameter was increased from 1.25 to 2.75 m, and reactor length was 10.92 m, residence time increases from 0.257 to 1.3 minutes. While when the length of the reactors was increased from 10.92 to 12.5 m and reactor diameter fixed as 2.75m, residence time increase from 1.3 to 1.5 minutes. We concluded that the residence time of vapour phase reaction increases with increases of reactor length and diameter and resulting in increases of conversion values.

Table 6. *The effect of reactor size of the modified configuration II on the reactor residence time*

Reactor length fixed as 10.92 (m)			
Diameter (m)	Residence time (min)	*n*-butanal conversion (%)	i-butanal conversion (%)
1.25	0.3	30.46	39.57
1.5	0.4	41.45	52.95
2	0.7	63.76	77.63
2.5	1.1	82.59	93.89
2.75	1.3	89.58	97.97
Reactor diameter fixed as 2.75 (m)			
Length (m)	Residence time (min)	*n*-butanal conversion (%)	i-butanal conversion (%)
10.92	1.3	89.58	97.97
11	1.3	89.82	98.08
12	1.4	92.52	99.12
12.25	1.5	93.12	99.29
12.5	1.5	93.66	99.45

3.3.4 Benchmarking the comparison of the simulation results of modified configuration II with that in the original reactor configuration

In the Modified Configuration II, the total conversion from the vapour phase reactor can be obtained when the reaction temperature fixed as 285 °C and reaction pressure of 30 bar. Comparing with that in the original reactor configuration the total conversion value from the second liquid phase reactor in the series obtained at reaction temperature of 159.5°C and reaction pressure of 16 bar. While the reactor length and diameter were fixed as 10.92 (m) and 2.75 (m) in both cases. The total *n*-butanal conversion in the Modified Configuration II was 99.99 % in the case of the reactor operating conditions exceeded the industrial plant operating conditions. While in the original configuration was 99.48%. In relative to the original configuration and Modified Configuration I, the more severe operating temperature and pressure were needed to attain the desired total conversion.

3.4 Comparison of data with that in the literature

Table 7. Compares the *n*-butanal conversion to *n*-butanol obtained from the present study with the findings of other researches about hydrogenation of butanal. In literature, hydrogenation of butanal was mostly carried out experimentally. Among the limited number of simulation studies found in literature, the effect of temperature was usually investigated.

Table 7. *Comparison of conversion values with those in the literature*

Temperature (°C)	Pressure (bar)	Catalyst type	Reactor type	Reaction Phase	Conversion of *n*-butanal (%)	References
139.85	3.1	SX-Rh SILP, and Shvo/SiO$_2$ catalysts	Packed bed reactor	Vapour	90	[16]
125	21	G-66 copper base catalyst	Tubular reactor	Vapour	99.99	[14]
210	5.8	Copper-zinc oxide catalysts	Fixed bed reactor	Vapour	99	[17]
159.5	16	Copper-zinc oxide catalysts	Packed bed reactor	Liquid	99.48	This study
166.5	16	Copper-zinc oxide catalysts	Packed bed reactor	Liquid	99.45	This study
265	21	Copper-zinc oxide catalysts	Packed bed reactor	Vapour	89.58	This study

In this study, the conversion of *n*-butanal was mostly higher than in other studies in the different reaction conditions. Also, in the present studies, the high conversion of *n*-butanal was obtained under the higher temperature according to the literature. The differences between the conversion of values in our study and the values presented in the literature are related to reactor type, reactor size, and reaction phase. Packed bed reactor and NRTL thermodynamic model were chosen in this study. These are important points for the conversion values. The most appropriate reactor type, reactor sizing and thermodynamic model is resulted in high *n*-butanal conversion value. In addition, optimization of operating parameters is also important for the high conversion and yield values.

4. Conclusion

Aspen Plus was successfully applied to simulate and investigate the effect of the reactor scheme and operating conditions to the reaction performance. In order to attain the total conversation of n-butanal as 99.44%, the best-operating conditions for the last reactor in the modified configuration I were 166.5°C and 16 bar. While a total conversion of *n*-butanal of 99.99% was achieved at the best-operating conditions of the modified configuration II at 30 bar and 285 °C in the expense of a condition that exceeded the industrial operating conditions limits. The best parameters obtained from the simulation study for butanal hydrogenation to produce butanol indicates considerable potential and courage for bypassing the last liquid phase reactor in the original reactor configuration.

5. Acknowledgements

References

[1] Ezeji TC, Qureshi N, Karcher P, Blaschek HP. Production of butanol from corn. In: Minteer SD, editor. Alcoholic fuels.

[2]   A. Chauvel, G. Lefebvre, in: Petrochemical Processes, second ed., Editions Technip, Paris, 1989, pp. 81–90.

[3]   P. Durre, Ann. N. Y. Acad. Sci. 1125 (2008) 353.

[4]   S. Lee, M.O. Cho, C.H. Park, Y. Chung, J.H. Kim, B. Sang, Y. Um, Energy Fuels 2 (2008) 3459.

[5]   E. Christensen, J. Yanowitz, M. Ratcliff, R.L. McCormick, Energy Fuels 25 (2011) 4723.

[6]   J.E. Rekoske, M.A. Barteau, Ind. Eng. Chem. Res. 50 (2011) 41.

[7]   S. Marengo, P. Comotti, G. Galli, Catal. Today 81 (2003) 205.

[8]   Y. Lee, J.H. Park, S.H. Jang, L.K. Nielsen, J. Kim, K.S. Jung, Biotechnol. Bioeng. 101 (2008) 209.

[9]   Brito, M., & Martins, F. (2017). Life cycle assessment of butanol production. Fuel, 208, 476– 482. doi:10.1016/j.fuel.2017.07.050.

[10]   Tudor, R., & Ashley, M. (2007). Enhancement of Industrial Hydroformylation Processes by the Adoption of Rhodium-Based Catalyst: Part I. Platinum Metals Review, 51(3), 116–126. doi:10.1595/147106707x216855.

 [11]   Gil Chaves, I. D., López, J. R. G., García Zapata, J. L., Leguizamón Robayo, A., & Rodríguez Niño, G. (2016). Process Analysis and Simulation in Chemical Engineering. doi:10.1007/978-3-319-14812-0.

[12]   Jakobsen, H. A. (2008). Packed Bed Reactors. Chemical Reactor Modeling, 953–984. doi:10.1007/978-3-540-68622-4_11.

[13]   Scott, H. (2016). Elements of Chemical Reaction Engineering, Fifth Edition. Prentice Hall.

[14]   Zhang, H., Zhang, X., & Fang, D. (2005). Mathematical Modeling of the Reactor Synthesizing Butanol from Butyraldehyde by Hydrogenation, Journal of East China University of Science and Technology (Natural Science Edition), 31(1), 5–8.

[15]   Chin, S. Y., Hisyam, A., & Prasetiawan, H. (2016). Modeling and Simulation Study of an Industrial Radial Moving Bed Reactor for Propane Dehydrogenation Process. International Journal of Chemical Reactor Engineering, 14(1). doi:10.1515/ijcre-2014-0148.

[16]   Hanna, D. G., Shylesh, S., Parada, P. A., & Bell, A. T. (2014). Hydrogenation of butanal over silica-supported Shvo's catalyst and its use for the gas-phase conversion of propene to butanol via tandem hydroformylation and hydrogenation. Journal of Catalysis, 311, 52–58. doi:10.1016/j.jcat.2013.11.012.

[17]   John E. Logsdon, Houston; Richard A. Loke, Santa Fe, both of Tex.; Jay S. Merriam, Louisville, Ky.; Richard W. Voight, Houston, Tex. (1989). U.S. Patent No. US4876402A. Washington, DC: U.S. Patent and Trademark Office.