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Investigation about Profitability Improvement for Synthesis of Benzyl Acetate in Different Types of Batch Distillation Columns

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In this work, for the first time, the synthesis of benzyl acetate via the esterification of acetic acid and benzyl alcohol is investigated in the reactive distillation system using a middle vessel (MVD), inverted (IBD), and conventional batch reactive distillation columns. The measurement of the performance of these column schemes is determined in terms of profitability through minimization of the batch time for a defined separation task. The control variables (reboil ratio for MVD, IBD columns) and (reflux ratio in case of CBD column) are considered as piecewise constants over batch time. The optimization results obviously indicate that the CBD system is a more attractive process in terms of batch time reduction, and maximum achievable yearly profit as compared to the MVD, and IBD operations.

1. Introduction

Esterification of acetic acid is a well-known operation in the chemical industry, which can be extensively employed in a large number of applications such as solvents for lacquers, nitrocellulose, leather finishes, paints removal, and plastics in polymer industries. Roy and Bhatia (1987) studied the kinetic of esterification of acetic acid with benzyl alcohol catalysed by cation-exchange resin (Amberlyst-15) in the temperature range 328–359 K and at atmospheric pressure using a batch reactor. Kirumakki et al. (2004) considered the esterification of acetic acid with benzyl alcohol over zeolites Hβ, HY and HZSM5 in batch system. They found that the conversion of benzyl alcohol using the zeolite Hβ was higher as compared to others. The resulting catalyst exhibited only 75 % conversion of benzyl alcohol into benzyl acetate under 403 K, 2:1 of molar ratio of acid: alcohol, and catalyst weight of 0.5 g at the reaction time of 1 hr. Ali and Merchant (2009) developed three kinetic models (such as the pseudo-homogeneous model (PH), Eley-Rideal (ER), and Langmuir-Hinshelwood-Hougen-Watson (LHHW) models) to investigate experimentally the kinetic behaviour of the formation of benzyl acetate over Dowex catalyst using a batch reactor at the atmospheric pressure. They concluded that the LHHW model offers better performance for the ethyl benzoate production. However, to author's knowledge, no investigations have been reported to present on the employing of either batch or continuous distillation systems for the synthesis of benzyl acetate. In this work, different types of batch reactive distillation systems, including MVD, IBD, and CBD columns are investigated. A detailed dynamic model with chemical reaction for the system is constructed and is incorporated in the optimisation problem within gPROMS software where the optimization framework is solved using the SQP-based optimization technique algorithm for a different range of benzyl acetate demands at a given composition and amount.

2. Process models

With reference to three column configurations (MVD, IBD, and CBD) presented in Figure 1, the detailed dynamic model contains mass and energy balance equations, rigorous phase equilibria and reaction kinetics. The process model assumes constant vapour holdup, molar holdup on the plates and in the condenser, adiabatic operation, perfect mixing on all trays, fast energy dynamics, no pressure drop and total condensation with no

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sub-cooling. Note, more details about these batch distillation configurations can be found in Mujtaba (2004) and Edreder et al. (2013).

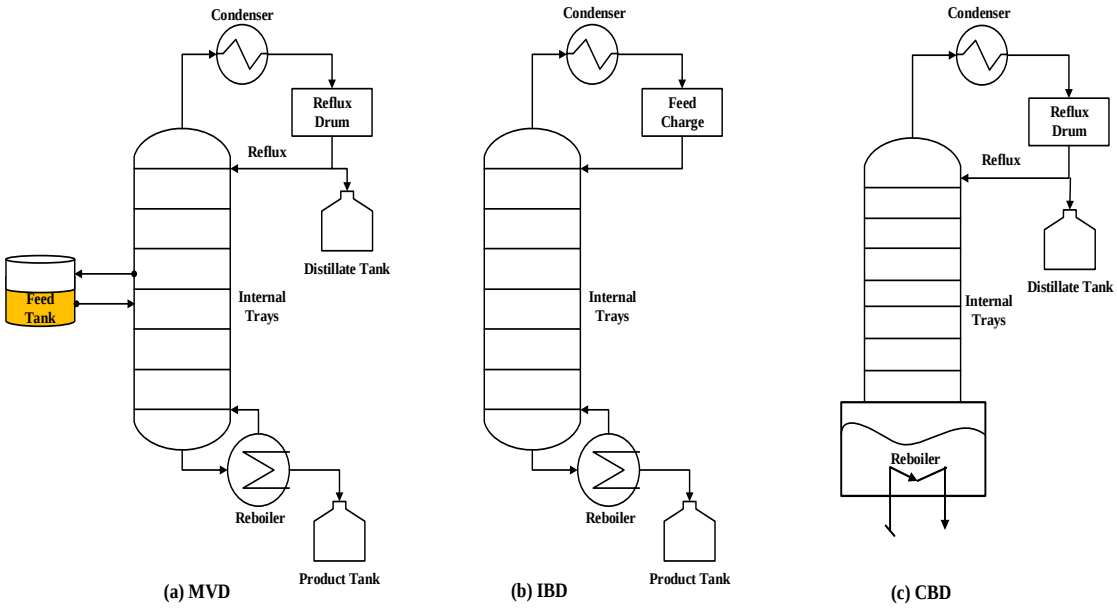

Figure 1: Schematic diagram of three column configurations for producing benzyl acetate: (a) middle-vessel conventional (MVD), (b) inverted (IBD), and (c) conventional (CBD).

3. Dynamic optimization problem

In this work, the optimal processes of MVD, IBD, and CBD modes are determined in terms of maximum annual profit for a defined separation task.

3.1 Maximum revenue problem

The optimization problem can be written as follows:

Given: The column configurations, the feed mixture, the vapour load to the condenser, The desired amount of product and purity

Determine: Reflux ratio (R) and reboil ratio (r_b) (for MVD process)
Or, Reboil ratio (r_b) (for IBD process)
Or, Reflux ratio (R) (for CBD process)

So as to: Maximise the total yearly profit

Subject to: Process constraints, Model equations

In mathematical terms, the optimization problem (OP1) can be stated as follow:

OP1 Max P

R (t), r_b(t) (For MVD Process)

r_b(t) (For IBD Process)

R (t) (For CBD Process)

Subject to :

$B_{BzAC} \geq B^{*}_{BzAC}$ (Inequality Constraints)

$x_{BzAC} \geq x^{*}_{BzAC}$ (Inequality Constraints)

For a defined separation task, the minimization of production batch time will increase the number of batches and thus will increase the total annual profit. Therefore, the maximum yearly revenue problem of those processes can be transformed into minimum operating batch time problem as shown below. Note, the profit function equations for all MVD, IBD and CBD systems and parameters used in this work, are same as those used in our previous work (Aqar et al., 2017).

3.2 Minimum Batch Time Problem

The optimization problem can be written as follows:

Given: The column configurations, the feed mixture, the vapour load to the condenser, The desired amount of product and purity

Determine: Reflux ratio (R) and reboil ratio (r_b) (for MVD process)
Or, Reboil ratio (r_b) (for IBD process)
Or, Reflux ratio (R) (for CBD process)

So as to: Minimise the batch time

Subject to: Process constraints, Model equations

Mathematically, the optimization problem (OP2) can be represented as follow:

OP2 Min t_f

$R(t), r_b(t)$ (For MVD Process)

$r_b(t)$ (For IBD Process)

$R(t)$ (For CBD Process)

Subject to :

$B_{BzAC} \geq B^*_{BzAC}$ (Inequality Constraints)

$x_{BzAC} \geq x^*_{BzAC}$ (Inequality Constraints)

Where, B_{BzAC}, x_{BzAC} are the amount of bottom product (2.5 kmol for all columns), and purity of benzyl acetate at the final batch time t_f (denotes that the B^*_{BzAC}, x^*_{BzAC} are specified).

4. The formation of benzyl acetate system

4.1 Problem specifications

The synthesis of BzAC has taken place in a 10-stages column (including a condenser and a reboiler) with condenser vapour load of 2.5 (kmol/h) for three batch configurations (MVD, IBD, and CBD). The column trays are counted from the top-down. Four percent of the total initial feed is the total column holdup. This strategy of column holdups has been used only for CBD, and IBD columns. For CBD process, fifty percent of this total holdup is taken as the condenser holdup and the rest is taken as the plate holdup (equally divided). While, the reboiler holdup is 50 % of the total column holdup and the rest is equally divided on the plates for IBD process. For MVD column, the total column holdup is 6 % of the initial feed (of which 33.33 % is taken as the condenser hold up, 33.33 % is taken as the reboiler hold up and the rest is equally divided in the plates to make plate holdup). Note, the same policy is utilised for the catalyst weight distribution for three distillation columns. The total initial amount of feed is 5 kmol with the feed concentration <AA, BzOH, BzAC, H_2O> is: <0.5, 0.5, 0.0, 0.0>, respectively. Note, all prices of both reactants (AA and BzOH) were taken from (Alibaba Trade, 2018) and the costs of benzyl acetate at other qualities are evaluated based on the exponential trend method used in (Mujtaba and Greaves, 2006). The prices of chemical reaction (AA and BzOH) and product (BzAC) at various product compositions values are listed in Table 1.

Table 1: The costs of reactant and product reaction

Pure AA Reactant Cost	18.20	BzAC Cost at 83.5 % purity	141.60
Pure BzOH Reactant Cost	25.43	BzAC Cost at 84 % purity	179.60
BzAC Cost at 82.5 % purity	114.90	BzAC Cost at 84.5 % purity	210.00
BzAC Cost at 83 % purity	125.20		

4.2 Reaction kinetics

The reversible reaction schemes together with the boiling points (K) of the components for esterification of acetic acid (AA) and benzyl alcohol (BzOH) to produce benzyl acetate (BzAC) and water (H_2O) over an ion-exchange resin (Dowex 50 Wx8) are:

$$\text{AA (1)} + \text{BzOH (2)} \text{ <==> } \text{BzAC (3)} + H_2O \text{ (4)} \quad (1)$$

B.P (K)	391.05	477.85	486.65	373.15

For the formation of benzyl acetate, a Langmuir-Hinshelwood-Hougen-Watson (LHHW) activity ($a_i = x_i\ \gamma_i$) based kinetic model is employed (taken from Ali and Merchan (2009)) which can be written as:

$$-r_{AA} = M_{cat}\left\{\frac{13.01\times10^5 \exp\left(\frac{-6855.91}{T}\right)\left[a_{AA}\,a_{BzOH} - 906.87\exp\left(\frac{-1279}{T}\right)a_{BzAC}\,a_{H2O}\right]}{[1+2.15\,a_{AA}+1.21\,a_{BzOH}+0.10\,a_{BzAC}+3.25\,a_{H2O}]^2}\right\} \quad (2)$$

4.3 Phase equilibrium (VLE)

The vapour-liquid equilibrium correlation is computed from Eq(3) where (γ_i) is computed using the NRTL equation. The saturation vapour pressure (P_i^{sat}) for each pure component is obtained by using Antoine's equation. The NRTL binary interaction parameters were taken from the data bank of Aspen Plus and the Antoine parameters were taken from Yaws (1997). The enthalpy coefficients for all pure components are taken from Aspen HYSYS V9 package.

$$y_i = \frac{P_i^{sat}\,x_i\,\gamma_i}{P} \quad (3)$$

5. Results and discussions

5.1 MVD column

Table 2 summarizes the optimal operation strategy; including reflux ratios, reboil ratios, the operating batch time, the conversion rate of acetic acid, the number of batches, and annual production rate, as well as the maximum achievable profit for the MVD operation. As can be noted form Table 2 that increasing the quality of BzAC product increases all reflux, reboil ratios, and the processing-batch time. Clearly, increasing the operating time can lead to increase the conversion ratio of AA into BzAC. It can be noticed also from Table 2 that as the product composition and production batch time increase, the number of batches produced over the year and total yearly product progressively decrease. As the bottom product purity constraint increases form (0.825 to 0.835 mole fractions) together with price of BzAC product, the annual profit increases progressively. However, it was not possible to achieve benzyl acetate > 0.840 mole fraction using a middle-vessel batch process. This is due to backward reaction being active and a rapid removal of benzyl alcohol form acetic acid reactant in the feed tank due to the wide difference in boiling points of reactants. Note, higher batch time and lower product purity achieved make MVD uncompetitive system (compared to others) and hence the suggested IBD and CBD modes.

5.2 IBD column

As before, the purity of BzAC product is changed from 0.830 to 0.845 mole fraction in each case, while, the product amount is fixed at 2.5 kmol so that the performance comparison of IBD mode can be made with MVD mode in terms of maximum achievable conversion of acid, and highest yearly profit. The optimization results in terms of reboil ratio, which maximizes the process profitability via the minimization of the operating batch time subject to constraints on the amount and purity of BzAC at the final time are shown in Table 3. It was found that all values of optimal reboil ratio, and the operating batch time with the maximum purity of BzAC, as well as total annual profit, increase progressively with increasing the BzAC concentrations. A comparison of the results between the BzAC purity and the net profit using the IBD column and the MVD operation (Table 2) illustrates that for the same product amount in the bottom tank (2.5 kmol), the IBD system yielded BzAC at a higher purity (0.845 compared to 0.835 mole fraction) and gained more revenue (107936 as opposed to only 387 $/yr).

5.3 CBD mode

Two cases are studied here, one (Case 1) with one-control interval and the second one (Case 2) with two-control intervals policy of operation. The performance of CBD mode is compared to the performance of IBD mode in terms of maximum achievable conversion of acid, batch time, and highest yearly profit.

Optimal operation using single-control interval (Case 1): For the four product purities considered, the summary of optimization results including optimal reflux ratios profile, the operating batch time, the conversion rate of AA, the number of batches, and annual product demand, and the net profit for the CBD column are presented in Table 4. It is clear form Table 4 that the use of CBD mode is found to outperform the IBD operation in many respects. For instance, at 0.845 mole fraction purity the reductions in the batch processing time is almost 15.56 %, and the improvement in conversion rate is about 7.97 %, as compared to IBD column. It is seen form Table 4 that the total annual product demand upgraded is about 15.12 % at product purity of 84.50 % compared to that obtained by the IBD operation. In addition, for the 0.845 of BzAC composition case, comparison of the maximum yearly profit for the CBD column with those obtained using IBD reveals 18.57 % more profit due to low production time demanded to achieve the desired purity requirements. However, note, for 0.845 of product purity, there is a sharp reduce in the product revenue due to massive increase in the operating batch time and reflux ratio (compared to others). This makes even CBD using one control operation uncompetitive operation at higher BzAC concentration and hence the suggested multi-control operation.

Optimal operation using two-control intervals (Case 2): For each quality consideration, Table 5 illustrates the optimal operation results in terms of reflux ratios, switching time, total batch time, conversion ratio of acid, the total number of batches produced over year, and yearly production rate, and the total yearly revenue to fulfil the product within the requirements. It is clear form Table 5 that the use of multi-reflux strategy caused big saving in the operating batch time, and higher improvement in the process revenue as compared to the one-reflux CBD operation (Table 4). For instance, at 0.845 mole fraction purity the reductions in the batch processing time is almost 35.96 %, and the improvement in maximum yearly profit is about 39.55 %, as compared to one-reflux CBD process. It is seen from Table 5 that the total annual product demand upgraded is about 34.76 % at product purity of 84.5 % compared to that obtained by the single-reflux CBD process. It can be realized from Table 5 that for each purity constraint, the CBD process operates at low reflux ratio for the first-time interval to remove water as quickly as it is produced as the top product. Higher reflux ratio is demanded in the second interval to keep both reactants acetic acid and benzyl alcohol in the reaction zone to have further chemical reaction.

Table 2: Summary of optimization results for MVD column

Product Purity Of BzAC	Optimal Reflux Ratio, R	Optimal Reboil Ratio, r_b	Final Batch time, t_F, h	Conversion of AA (%)	Number of Batches, batch/y	Product Demand PD, kmol/y	Total Annual Profit, $/y
0.825	0.951	0.941	17.73	88.33	439	1,097	133
0.830	0.965	0.956	24.44	88.81	321	802	235
0.835	0.975	0.969	35.04	89.31	225	563	387
0.840	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]

[a] Infeasible.

Table 3: Summary of optimization results for IBD column

Product Purity Of BzAC	Optimal Reboil Ratio, r_b	Final Batch time, t_F, h	Conversion of AA (%)	Number of Batches, batch/y	Product Demand PD, kmol/y	Total Annual Profit, $/y
0.830	0.931	12.57	84.05	612	1,530	27,857
0.835	0.937	13.85	84.39	557	1,394	45,552
0.840	0.942	15.38	84.72	504	1,259	86,113
0.845	0.948	17.27	85.06	450	1,125	107,936

Table 4: Summary of optimization results for CBD column for Case 1

Product Purity Of BzAC	Optimal Reflux Ratio, R	Final Batch time, t_F, h	Conversion of AA (%)	Number of Batches, batch/y	Product Demand PD, kmol/y	Total Annual Profit, $/y
0.830	0.390	1.51	88.00	3,986	9,965	347,991
0.835	0.541	2.01	88.70	3,192	7,980	403,510
0.840	0.755	3.76	89.87	1,879	4,697	403,605
0.845	0.937	14.58	92.43	530	1,326	132,552

Table 5: Summary of optimization results for CBD column for Case 2

Product Purity Of BzAC	Optimal Reflux Ratios R_1, R_2	Batch Time Intervals t_1, t_2, h	Final Batch time, t_F, h	Conversion of AA (%)	Number of Batches, batch/y	Product Demand PD, kmol/y	Total Annual Profit, $/y
0.830	0.335, 0.685	1.30, 0.18	1.48	87.98	4,048	10,119	353,851
0.835	0.463, 0.993	1.71, 0.10	1.81	88.62	3,459	8,648	439,854
0.840	0.680, 0.996	2.87, 0.13	3.00	89.60	2,287	5,717	497,804
0.845	0.891, 0.989	8.34, 1.00	9.34	91.69	813	2,032	219,289

6. Conclusions

In this study, for the first time, the performances of different types of batch reactive column configurations are evaluated in terms of maximum profitability via minimisation of production time under single and multi-reflux intervals modes for the synthesis of benzyl acetate through the esterification reaction of acetic acid and benzyl alcohol. Control variables (reflux ratio and/or reboil ratio) are used as a piecewise constant, which are discretised using CVP method. A dynamic optimization problem is developed incorporating the process model within gPROMS modelling software. The product amount and its purity are employed as operating constraints. Observation results using single-reflux strategy (for CBD) and reboil ratio (for IBD and MVD) show that CBD is more suitable than both MVD and IBD columns in terms of minimum operating time, maximum conversion rate, and maximum annual revenue. Furthermore, theoretically, the removal of both reactants in CBD process should improve the conversion ratio of acetic acid and will save operation batch time. Optimal operation of CBD for this system should be considered. In addition, the optimization results clearly demonstrate that the employment of two-control operation is more promising-option and quite interesting compared to the single-control interval in CBD system in terms of minimum batch time and maximum achievable profit improvement.

References

Aqar D.Y., Rahmanian N., Mujtaba I.M., 2017. Significant Profitability Improvement for Methyl Decanoate Production using Different Types of Batch Distillation. Chemical Engineering Transactions, 57, 1075-1080.

Ali S.H., Merchant S.Q., 2009. Kinetic study of Dowex 50 Wx8-catalyzed esterification and hydrolysis of benzyl acetate. Industrial & Engineering Chemistry Research, 48(5), 2519-2532.

Alibaba Trade, 2018. Alibaba Trade <www.alibaba.com/trade> accessed 28.02.2018.

Edreder, E.A., Mujtaba I.M., Emtir M.M., 2013. Comparison of conventional and middle vessel batch reactive distillation column: application to hydrolysis of methyl lactate to lactic acid. Chemical Engineering Transactions, 35, 925-935.

Kirumakki S.R., Nagaraju N., Narayanan S., 2004. A comparative esterification of benzyl alcohol with acetic acid over zeolites Hβ, HY and HZSM5. Applied Catalysis A: General, 273(1-2), 1-9.

Mujtaba I.M., 2004. Batch distillation: design and operation. World Scientific Publishing Company, London, UK.

Mujtaba I.M., Greaves M.A., 2006. Neural network based modelling and optimisation in batch reactive distillation. Institution of Chemical Engineers, Symposium series NO. 152, 868-876.

Roy R., Bhatia S., 1987. Kinetics of esterification of benzyl alcohol with acetic acid catalysed by cation-exchange resin (Amberlyst-15). Journal of Chemical Technology and Biotechnology, 37(1), 1-10.