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Performance Analysis of Batch Reactive Distillation Column using Different Measures

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Batch distillation with chemical reaction when takes place in the same unit is referred to as batch reactive distillation process. The combination reduces the capital and operating costs considerably. Among many different types of batch reactive distillation column configurations, conventional (CBRD) and middle vessel batch reactive distillation (MVBRD) columns are considered here for hydrolysis of methyl lactate and only CBRD is considered for an esterification of acetic acid and ethanol.
Three different measures such as Maximum Profit under Fixed Demand (Measure 1), Maximum Productivity (Measure 2) and Minimum batch time (Measure 3) are used here to evaluate the performances of different columns. Optimal design and or operation policies are obtained under these measures and are compared. A detailed rigorous dynamic model consisting of mass, energy balances, chemical reaction and thermodynamic properties is used for evaluating the column performance.

1. Introduction

Generally, in a CBRD column, the feed is charged into a reboiler (working as reactor too), while in an inverted batch reactive distillation column (IBRD), the feed mixture is charged into the condenser drum. The combination of these configurations is described as MVBRD where the feed mixture is placed into the middle vessel (working as reactor too), and the products are simultaneously obtained from the top and the bottom of the column. In reactive distillation, simultaneous separation of products from reactants while the reaction is in progress, can lead to a much higher level of conversion compared to that can be obtained without separation (Mujtaba and Macchietto, 1997). It allows a significant capital and operational cost savings, especially in the case of equilibrium limited reactions. Various published papers can be found on design studies and steady-state simulation of continuous reactive distillation processes (Taylor and Krishna, 2000). Only few authors have discussed the design, control and optimal operational aspects of batch reactive distillation processes.
Mujtaba and Macchietto (1997) presented computationally efficient framework for dynamic optimization of CBRD for ethanol esterification process using Measure 1 but with unlimited product demand. For a given purity with different prices of the product, the optimization problem was formulated with a profit as an objective function (Measure 1). For the same reaction system using CBRD, Mujtaba and Greaves (2006) replaced rigorous dynamic model by neural network (NN) based dynamic model and developed an NN based optimization framework (Measure 1).
Using Measure 2, Kim et al. (2000) studied the CBRD column performance with hydrolysis reaction of methyl lactate (ML) to produce lactic acid (LA) experimentally. For the same reaction system, Edreder et al. (2011) applied Measure 3 in a CBRD column with different values of product (LA) purity ranging from 0.8 to as high purity as can be achieved and the impact of time dependant reflux ratio policy on the product quality and batch time were analysed. Edreder et al. (2012) considered simulation of MVBRD column using detailed dynamic model for the same reaction system with piecewise constant reflux ratio (multiple time intervals) and single reboil ratio but the performance of the column was not evaluated using any

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particular measure. Comparative study of the performance of CBRD and MVBRD was presented for the same reaction system by Edreder et al. (2013) using Measure 3.
In this paper, comparative review of our earlier work on batch reactive distillation system presented in several PRES conferences with a diverse focus in terms of measuring the performance of the hydrolysis and esterification systems is considered.

2. Different measures for performance evaluation of batch distillation process

A number of measures have been used in the past to evaluate the performance of batch reactive distillation column under fixed or unlimited product demand scenario. They are: (a) Measure 1: Maximum Profit for a given operation horizon; (b) Measure 2: Maximum Productivity; (c) Measure 3: Minimum Operation Time for a given batch production. For example, Edreder et al. (2009) considered Measure 1 and analysed batch reactive distillation process under fixed product demand. Edreder et al. (2010) considered synthesis of ethyl acetate in a batch reactive distillation column using Measure 2. Edreder et al. (2011) optimized production of lactic acid in batch reactive distillation using Measure 3. Edreder et al. (2012) considered Measure 2 in analysing the performance of middle vessel batch distillation column via simulation. Edreder et al. (2013) compare the performance of conventional and middle vessel batch reactive distillation column for the production of lactic acid using Measure 3.

2.1 *Measure 1*: maximum profit

In general the optimization problem can be stated as:

given*:*	the column configuration, the feed mixture, a separation task in terms of product purity (X_P)
determine:	time dependent optimal reflux ratio (R, t)and or reboil ratio (R_b) which governs the operation
so as to*:*	maximize the profit (P)
subject to*:*	equality and inequality constraints (e.g. model equations)

Mathematically it can be stated as:

$$\underset{R/R_b,t}{Max} \quad P$$

Subject to: $X_P = X_P^* \pm \epsilon$ (1)
Process Model (Equality constraint)
Linear bounds on optimisation variables (inequality constraints)

2.2 *Measure 2*: maximum productivity

Here the optimization problem is formulated to maximize the Productivity, (*Prod* = amount of product/batch time). Mathematically the problem can be stated as:

$$\underset{R/R_b,t}{Max} \quad Prod$$

Subject to: $X_P = X_P^* \pm \epsilon$ (2)
Process Model (Equality constraint)
Linear bounds on optimisation variables (inequality constraints)

2.3 *Measure 3*: minimum operation time

Here the optimization problem is formulated to minimize the batch time (t_f). Mathematically the problem can be stated as:

$$\underset{R/R_b,t}{Max} \quad t_f$$

Subject to: $X_P = X_P^* \pm \epsilon$ (3)
Process Model (Equality constraint)
Linear bounds on optimization variables (inequality constraints)

ε is small positive numbering the order of 10^{-3}.

3. Lactic acid production (Case A)

LA is widely used as a raw material for the production of biodegradable polymers, food, chemical and pharmaceutical industries.

3.1 Problem specifications

Hydrolysis reaction of ML and separation of LA are carried out in a 10 stages column (including condenser and reboiler) with a condenser vapour load of 2.5 (kmol/h). The total column holdup is 4 % of the initial feed. Fifty percent of the total holdup is taken as the condenser hold up and the rest is equally divided in the plates. The initial charge to the reboiler is 5 kmol. The feed composition <ML, H_2O, LA, MeOH> is : <0.48, 0.52, 0.0, 0.0>. The reaction with the boiling temperature (K) of the components is:

ML (417.15) + H_2O (373.15) <=> LA (490.15) + MeOH (337.15) (4)

The vapour liquid equilibria of the mixture was taken from Sanz et al. (2003) and the kinetic model was taken from Sanz et al. (2004)

3.2 Optimization problem

The performance of CBRD is evaluated in terms of minimizing the batch time (Measure 3). Three cases are studied. For Case 1, single reflux ratio is used, yielding an optimal constant reflux ratio policy. For Case 2 and Case 3, multiple reflux ratio (two and three intervals respectively) strategy is used. Within each interval the reflux ratio together with the switching time from one to the next interval are optimised. Piecewise constant values of reflux ratio over time intervals concerned are assumed. The amount of bottom product (2.5 kmol) and product purity are specified as constraints in the optimization problem.

3.3 Results and discussions

For all case studies the effect of excess H_2O in the feed on the batch time to achieve high purity of LA is considered and the results for each case are shown below:

Case1: the results in terms of optimal reflux ratio, minimum batch time and conversion of ML to LA are summarized in Table 1. It can be seen from Table 1 that with increasing product purity more time and higher reflux ration are needed. Note, the product purity of 0.95 could not be achieved even with optimal operating time more than 110 h.

Case 2: Two time intervals are considered here. For each purity specification, Table 2 gives the optimisation results in terms of optimal reflux ratio, optimal operating time in each interval, total minimum operating time to achieve the product within the specifications and the conversion of ML to LA. It can be seen from Table 2 that the column operates at lower reflux ratio in the first interval, helping the MeOH to escape as quickly as it is produced from the top of the column as it has the lowest boiling temperature. Note, when the purity of product increases more reactants were consumed to produce more desired product and it takes more operating time and the column needs to operate at higher reflux ratio to meet the product specification. It can be noticed that, the single and two intervals are not sufficient to produce main product at high purity specifications (0.999 mole fraction).

Case 3: Three time intervals are considered here and the results are summarized in Table 3. It can be noticed that the LA with purity of 0.999 mole fraction is possible to achieve with 3 reflux intervals.

The results show that, more effective way to operate the column is by using multi reflux strategy rather than single reflux strategy in terms of saving the operating time which directly affects the operating cost in the column. The operating time saving is about 11.4 % to 25.4 % for two and three time intervals respectively for the product purity range from 0.8 to 0.925.

Table 1: Summary of optimization results using single time interval

x purity (molefraction)	tf (h)	R (reflux ratio)	Conv.%
0.800	11.83	0.912	77.8
0.850	17.05	0.939	82.6
0.900	26.44	0.961	87.3
0.925	34.94	0.970	89.6
0.950*	*	*	*

*Optimal time > 110 h

Table 2: Summary of optimization results using 2 time intervals

x purity (molefraction)	t_1,t_2 (h)	R_1,R_2 (reflux Ratio)	Conv.%
0.800	9.06,2.48	0.901,0.941	77.8
0.900	14.46,7.59	0.941,0.975	87.7
0.925	19.29,8.26	0.953,0.985	90.0
0.975	12.07,22.68	0.941,0.986	95.2
0.990	10.07,38.31	0.933,0.991	96.4

Table 3: Summary of optimization results using 3 time intervals

x purity (molefraction)	t_1,R_1 (h, reflux ratio)	t_2,R_2 (h, reflux ratio)	t_3,R_3 (h, reflux ratio)	tf (h)	Conv.%
0.800	2.96,0.828	5.42,0.934	1.40,0.878	9.78	77.9
0.925	6.42,0.909	2.71,0.954	12.15,0.972	21.28	90.6
0.975	14.0,0.947	18.95,0.985	1.850,0.989	34.80	95.2
0.999	10.77,0.936	20.60,0.985	24.31,0.998	55.70	97.8

It can be concluded that highly purified LA (0.999 mole fraction) can be achieved directly from hydrolysis of ML in the presence of catalyst using batch reactive distillation process.

4. Lactic acid production (Case B)

In this work a comparative study of the performance of MVBRD and CBRD are presented for the same reaction system discussed above. The performance of both columns are evaluated using Measure 3 for a given separation task (defined in terms of the amount of LA and its purity).

4.1 Problem specification

The feed composition <ML, H_2O, LA, MeOH is: <0.5, 0.50, 0.0, 0.0> for both configurations. The reboiler capacity (for CBRD) is 5 kmol while for MVBRD the feed location is plate 5 and the middle vessel capacity is 5 kmol. Other data same as case study A (section 3).

4.2 Results and discussions

Results in terms of optimal reflux (R) for the CBRD column and both optimal reflux ratio (R) and reboil ratio (Rb) for the MVBRD column, which minimizes the batch time are presented in Table 4. The reflux and reboil ratios are defined over single control interval and are assumed to be piecewise constant. Note, the reaction products MeOH (lightest) and LA (heaviest) can be withdrawn simultaneously from the top and bottom of the column using MVBRD.

Table 4: Optimal reflux or and reboil ratios and batch time for both processes

X purity (modelfraction)	R (reflux ratio)	R_b (reboil ratio)	t_f (h)
0.70	0.8530 (0.8638)	0.8362	6.68 (7.37)
0.75	0.8796 (0.9020)	0.8586	8.28 (10.20)
0.80	0.9204 (0.9330)	0.8926	11.98 (14.88)

Note: optimal reflux ratios and batch time for CBRD are shown in the brackets

In all cases, MVBRD performed out CBRD in terms of batch time. It can be seen from Table 4 that, for product purity 0.75 mole fraction, a batch time reduction of 18.8 % is achieved for MVBRD compared to that for CBRD.

5. Ethyl acetate production(Case study C)

CBRD column with 10 stages (N) is used here and the chemical reaction with the components boiling temperature (K) is:

AA (391.1) +EtOH (351.5)<=> EtAc (350.3) + H_2O (373.15) (2)

AA = Acetic acid; EtOH = Ethanol; EtAc = Ethyl acetate. The vapour-liquid equilibria model was taken from Suzuki *et a*l. (1970) and the kinetic model was taken from Bogacki et al. (1989).

5.1 Problem specifications

Here, two cases are considered. In Case 1 the feed is composed of only the reactants (pure feed) and in Case 2 the feed is composed of reactants as well as a small fraction of H_2O (diluted feed). The feeds (kmol) <AA, EtOH, EtAc, H_2O> are: Case 1 - <2.5, 2.5, 0.0, 0.0> and Case 2 -<2.25, 2.25, 0.0, 0.5>.

5.2 Results and discussions

The column performance is evaluated using *Measure 1*. The optimization parameters considered are: vapour load (V), reflux ratio (R) and batch time (t_b). The profit is maximized with fixed product demand ranging from 800 to 1,200 kmol/y. The cost parameters are: (AA = 50 and 40 $/kmol and EtOH = 20 and 18 $/kmol) for Case 1 and Case 2. The price of the product (EtAc = 96 $/kmol) was taken from Greaves et.al (2003).

Case 1: The results in terms of optimal design, operation and the maximum profit ($/y) for each fixed product demand (ranging from 800 to 1,200 kmol/y) are summarized in Table 5. It is clear from the results

that the optimal vapour load (V) and reflux ratio (R) needed to increase (with decreasing batch time t_b) with increasing product demand (by increasing more batches (NB) of product). The maximum profit ($/y) has been achieved for product demand of 1,100 kmol/y with optimum (V = 2.11 kmol/h, R = 0.933, t_b = 18.8 h and NB = 414.5). Note, for the given column configuration (i.e. N = 10), it was not possible to further improve on profitability for other product demands.

Table 5: Summary of the results – Case 1

Demand (kmol/y)	t_b(h)	V (kmol/h)	R (reflux ratio)	N_B (batch/y)	P($/y)
800	26.49 (22.36)	1.29 (1.63)	0.921 (0.937)	296.5 (350.0)	4,556.8 (7,702.6)
900	23.36 (19.66)	1.52 (1.95)	0.924 (0.941)	335.4 (396.8)	5,203.1 (8,527.2)
1000	20.79 (17.48)	1.77 (2.32)	0.928 (0.945)	375.7 (445.0)	5,621.6 (9,002.3)
1100	18.80 (15.66)	2.11 (2.75)	0.933 (0.948)	414.5 (494.9)	5,757.9 (9,051.2)
1200	16.77 (14.13)	2.28 (3.24)	0.934 (0.952)	463.3 (546.7)	5,542.3 (8,595.4)

Note: Summary of the results – Case 2 are shown in the brackets

Case 2: The results are in brackets in Table 5. For each product demand comparison of the results with those for case 1 clearly shows the effect of feed dilution on the design, operation and profitability. Although the maximum profit is achieved for the product demand of 1,wq100 kmol/y (same as Case 1), feed dilution not only reduces the raw material costs but results in much higher profit for each product demand. For example, for product demand 800 kmol/y, the profitability has improved by almost 70 %. Note for Case 2, the column needs to operate at higher reflux ratio but with higher V and thus decreasing the batch time compared to those in Case 1. This results in producing less amount of distillate (on specification) per batch and more number of batches in the production campaign.

6. Ethyl acetate production (Case study D)

6.1 Problem specifications

CBRD column with 10 stages (N) is used here and the column performance is evaluated using *Measure 2*. Five cases with varying amount of reactants in the feed are utilized to improve the productivity of EtAc. The feeds (kmol) <AA, EtOH, EtAc, H_2O> are: Case 1 - <2.0, 2.0, 0.0, 0.0>, Case 2 - <2.0, 2.0, 0.0, 0.2>, Case 3 -<2.0, 2.0, 0.0, 0.4>, Case 4-<2.5, 2.5, 0.0, 0.0> and Case 5 - <2.25, 2.25, 0.0, 0. 5>. Note, the column is not fully charged in the first three cases.

6.2 Results and discussions

Single Reflux Ratio Operation (Scenario 1): Table 6 presents the optimization results for all cases using single reflux ratio. As can be seen that, the operation time is reduced by about 8 %, and productivity is improved by 13 % and the column operated at lower reflux ratio (RR) in Case 1 (no water in the feed) compared to Case 3 (with water in the feed). A comparison of the results between Case 4 and Case 5 (the column operating at maximum capacity of the reboiler i.e. 5 kmol) shows that the productivity improved by 25 % with no water in the feed (Case 4). The column can be also operated at lower reflux ratio and shorter operation time (saving time 6 %) compared to Case 5 (with water in the feed).

Table 6: Summary of the results for both scenarios

	Scenario 1			Scenario 2				
Case	t_f (h)	R (RR)	Prod (kmol/h)	t_f, hr (t, RR)	t_1,R_1 (h, RR)	R_2 (RR)	Prod	IP %
1	9.12	0.932	0.17	6.78	1.99,1.0	0.884	0.21	23.3
2	9.51	0.936	0.16	7.06	1.99,1.0	0.895	0.19	18.8
3	9.90	0.94	0.15	7.28	2.06,1.0	0.899	0.18	20.0
4	9.60	0.92	0.20	7.35	1.92,1.0	0.873	0.24	20.0
5	10.21	0.935	0.16	7.86	2.02,1.0	0.896	0.19	18.8

Multi Reflux Ratio Operation (Scenario 2): The optimisation results for all cases using multi reflux ratio are also shown in Table 6. It can be seen that in the first time interval, an initial total reflux (=1.0) operation was required for all cases. Increasing water in the feed (Cases 2, 3, 5) leads to higher reflux ratio for the second time interval. Table 6 also gives the percent improvement (IP) in productivity for Scenario 2 compared to Scenario 1. It can be seen that the benefit of using multi reflux policy is very clear and results in more effective operation. It can be seen from the results that the increasing of water amount in the feed

leads to reduction the productivity and the column needed to operate at higher reflux ratio and longer operation time compared to the case with no water in the feed. Finally, a comparison of operating scenarios shows that the productivity has been improved by 20 % and batch time saving by 24 % when the column operates with multi-reflux policy.

7. Conclusions

Performance analysis of batch reactive distillation processes (MVBRD and CBRD) for methyl lactate hydrolysis and ethanol esterification reaction systems using different measures have been considered in this work. Different case studies have been considered under fixed or open product demand scenario. Optimal design and or operation policies are obtained for all the reaction schemes. It is observed that multi-reflux ratio operation always led to better performance in terms of productivity (Measure 2) or batch time (Measure 3) for all reaction schemes compared to that obtained using single reflux operation. Feed dilution (in the case of ethanol esterification) led to more profit (Measure 1) even though productivity was found to be lower. This was due to reduction in feed price because of feed dilution. Optimization of design and operation (for ethanol esterification) clearly showed that a single column will not lead to profitable operation for all possible product demand profile. In batch distillation, total reflux operation is usually recommended or observed at the beginning of the operation (as is the case for ethanol esterification). However, in the case of hydrolysis, total reflux operation was observed at the end of the operation. This was due to LA (being the heaviest) was withdrawn as the final bottom product. For Hydrolysis of ML system, it is indicated that MVBRD is more effective than CBRD in terms of saving in batch time (20 % saving is noted for some cases).

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