CHEMICAL ENGINEERING TRANSACTIONS Volume 25, 2011
Editors Jiří Jaromír Klemeš, Petar Sabev Varbanov, Hon Loong Lam
 ISBN 978-88-95608-16-7 ISSN 1974-9791
DOI: 10.3303/CET1125046

Optimization of Batch Distillation Involving Hydrolysis System

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In this work optimization of batch reactive distillation involving hydrolysis reaction of methyl lactate with excess water to produce pure lactic acid and methanol is studied. Lactic acid product amount and purity are used as constraints; reflux ratio profile (piecewise constant) is utilized to the optimization problem. Different values of product purity ranging from 0.8 to 0.999 mole fraction are investigated and the impact of time dependant reflux ratio policy on the product quality and batch time is analyzed.
The optimization results indicate that highly purified lactic acid (0.999 mole fraction) can be achieved directly from hydrolysis of methyl lactate in the presence of catalyst using batch reactive distillation process. Moreover it is noticed that, the column operated with single time interval for reflux ratio could not produce lactic acid at high purity (> 0.925 mole fraction). The multi-reflux interval strategies (2 and 3 time intervals) have been found to be better to produce products with higher purity specifications with shorter batch time. Also it is found to be more effective to operate the column with excess water in the feed to produce high purity of lactic acid.

1. Introduction

Lactic acid (LA) is used in many applications such as in the food, flavor as preservative, in cosmetics, leather processing and pharmaceuticals industries. High purity of LA is required for polymerization and it can be produced by chemical synthesis or by fermentation of renewable carbohydrates. About 90 % of LA was produced by the fermentation routes and carried out in batch mode (Joglekar et al., 2006). Many processes for recovery and purifying LA from fermentation broth has been considered and studied in the past, adsorption process (Lee et al., 2004). An alternative technique beyond these processes have also been suggested where esterification of LA followed by hydrolysis of ester lactate is considered to produce pure LA. Experimentally, purification of LA was considered by several authors (Kim et al., 2000; Kim et al., 2002). The process setup consists of two columns for separation of reactant from products and two reboilers for esterification and hydrolysis reactions. Seo et al., (1999) considered the esterification of LA with methanol followed hydrolysis of methyl lactate in the presence of cation exchange resin (Dowex 50) as catalyst in batch reactive distillation to achieve pure LA (90 %). Sun et al., (2006) used two reactors with a

Please cite this article as: Edreder E.A., Mujtaba I. and Emtir M., 2011, Optimization of batch distillation involving hydrolysis system, Chemical Engineering Transactions, 25, 273-278
DOI: 10.3303/CET1125046

rectifying column to convert LA or ammonium lactate into esters and then hydrolysis of ester into LA as high purity product. Li et al., (2005) investigated the esterification of raw LA from fermentation rout and then hydrolysis of methyl lactate in the presence of homogeneous catalyst for purification of LA. Joglekar et al., (2006) provided a comparative assessment of LA downstream processing options such as reactive extraction, adsorption, electrodialysis, esterification and reactive distillation in terms of the cost. Recently, Edreder et al. (2010) considered the performance of batch reactive distillation in terms of minimum batch time with the hydrolysis reaction of methyl lactate and water (eqimolar feed composition) to produce high purity lactic acid (0.99 mole fraction). Product amount and purity were used as constraints and time dependent reflux ratio was used as control variable which was optimized.

In general, whatever the mode of operation in batch distillation process is chosen, clearly, the amount of energy savings is directly dependent on the reduction in batch time without compromising the product specification which is impacting on environmental pollution reduction (Mujtaba, 2004). In this work, to produce high purity of lactic acid, excess water in the feed of hydrolysis of methyl lactate is investigated. Optimization problem in terms of batch time is chosen as objective function. Product amount and purity are used as constraints. Piecewise constant reflux ratio profile is utilized which are optimized together with the length of the time intervals. A series of minimum time problems were solved at different values of product purity ranging from 0.8 to 0.999 and the impact of time dependant reflux ratio policy on the product quality and batch time are analyzed.

2. Process Model

A detailed dynamic model including mass and energy balance equations, column holdup, rigorous phase equilibria, and chemical reaction taking on the plates, in the reboiler and in the condenser is used.

Internal Plates, i = 2, N-1

Total Mass Balance: $0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j H_j$

Component Mass Balance: $H_j \frac{dx_{ij}}{dt} = L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} - L_j x_{ij} - V_j y_{ij} + r_{ij} H_j$

Energy Balance: $0 = L_{j-1} h^L_{j-1} + V_{j+1} h^V_{j+1} - L_j h^L_j - V_j h^V_j$

Equilibrium: $y_{ij} = K_{ij} x_{ij}$

Restrictions: $\sum y_{ij} = 1$

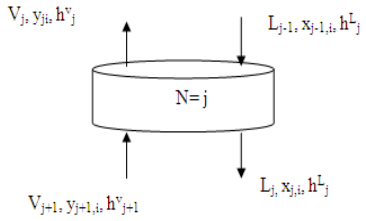

Fig. 1. Configuration and model equations for typical plate (N = j).

The model assumes negligible vapor holdup, adiabatic plates, constant molar holdup on plates and in the condenser, perfect mixing on trays, fast energy dynamics, constant operating pressure and total condensation with no sub-cooling and assuming no azeotrope formation. Model equations for typical plates are shown in Fig. 1.

2.1 Chemical Reaction and Kinetics

The hydrolysis reaction of methyl lactate can be expressed as follows:

Methyl lactate (1) + Water (2) <=> Lactic acid (3) + Methanol (4) (1)

A quasi-homogeneneous (QH) activity ($a_i = \gamma_i x_i$) based kinetic model is used (taken from Sanz et al., 2004) and can be written as:

$$-r = 1.65 \times 10^5 \exp\left(\frac{-50.91}{RT}\right) a_1 a_2 - 1.16 \times 10^6 \exp\left(\frac{-48.52}{RT}\right) a_3 a_4 \quad (2)$$

2.2 Vapor-Liquid Equilibrium (VLE)

K-values (VLE constants) are computed from (Eq. 3) where γ_i is computed from UNIQUAC equation, the vapor pressure (P^{sat}) of pure components has been obtained by using Antoine's equation.

$$K = \gamma_i P_i^{sat} / P \quad (3)$$

3. Optimization Problem Formulation

The minimization of batch time is selected which will directly minimize the total energy consumption of the process. Therefore, an optimal reflux ratio policy will be chosen so that a given amount of lactic acid product with a given purity can be achieved in minimum time. Here three cases are studies. Case 1, single reflux ratio is used, yielding an optimal constant reflux ratio policy. Case 2 and Case 3, multiple reflux ratio (piecewise constant) strategy is used. Within each interval the reflux ratio together with the switching time from one to next interval are optimized. The optimization problem can be described as:

given:	the column configuration, the feed mixture, vapor boil-up rate, product purity, amount of bottom product.
determine:	optimal reflux ratio which governs the operation
so as to minimize:	the operation time.
subject to:	equality and inequality constraints (e.g. model equations).

Mathematically the problem can be stated as:

$$\begin{aligned} &\text{Min} && t_f \\ &\text{R(t)} \\ &\text{s.t} \\ &&\text{Process Model Equation} && \text{(equality constriants)} \\ &&B = B^* && \text{(inequality constraint)} \\ &&x_3^* - \varepsilon \le x_3 \le x_3^* + \varepsilon && \text{(inequality constraint)} \end{aligned} \quad (4)$$

Where B, the amount of bottom product (B^*= 2.4 kmol for all cases) and x_3 is the composition at the final time t_f, (denotes that the B and x_3 are specified), R(t) is the reflux ratio profile which is optimized. ε =0.001. The dynamic optimization problem is converted to nonlinear programming problem by Control Vector Parameterization (CVP) technique and is solved by using efficient SQP method (Mujtaba, 2004) within gPROMS.

4. Case Study

The feed composition <Methyl Lactate (1), Water (2), Lactic acid (3), Methanol (4)> is: <0.48, 0.52, 0.0, 0.0>. The other input data are shown in Table 1.

Table 1: Column specifications for hydrolysis of methyl lactate system

No of ideal stages (including reboiler and condenser)	= 10	Internal plate hold up (kmol)	= 0.0125
Column pressure (bar)	= 1.013	Condenser hold up (kmol)	= 0.10
Total fresh feed (kmol)	= 5	Condenser vapor load (kmol/hr)	= 2.50

5. Results and Discussions

Case 1 (NCI = 1): the results in terms of optimal reflux ratio, minimum batch time and conversion of methyl lactate to lactic acid are summarized in Table 2. It can be seen from Table 2 that the column operated at shorter batch time and reflux ratio to produce lactic acid at 0.8 mole fraction purity. With increasing product purity more time is required to satisfy the product specifications therefore the reflux ratio will be increased. Comparison of the results with those obtained by Edreder et al. (2010) shows that with excess water in the feed, the recovery rate is significantly higher. For example, with purity 0.925 mole fraction, the recovery rate was 0.0068 (kmol of lactic acid produced per kmol of methyl lactate feed per hr). In this work, the recovery rate for the same case is found to be 0.025 which is significantly higher.

Case 2 (NCI = 2): optimization results are summarized. It can be seen from Table 2 that the column operates at lower reflux ratio in the first interval, helping the methanol to escape from the top of the column since it has the lowest boiling temperature. Furthermore it can be seen from Table 2 that when the purity of product increases more reactants was 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). Therefore the column will be running using more than two time intervals.

Case 3 (NCI =3): Optimization results are summarized in Table 2. It can be noticed that with 3 reflux intervals, the lactic acid product purity of 0.999 mole fraction was possible to achieve and the recovery rate is found to be 0.027at product purity of 0.975, while in the same case by Edreder et al., 2010 the recovery rate is found to be 0.018. Moreover this results indicate that more effective to run the column at 3 time intervals which can be significantly enhance the product purity.

4.1 Comparison between single and multi reflux ratio strategy

The results in Figure 2 show that, more effective way to operate the column is by using multi reflux intervals rather than single reflux ratio interval in terms of saving the operating time which directly affects the operating cost in the column. As an example the operating time has been saved by an average 11.4 % and by 25.4 % using two and three time intervals respectively for the range of the purity from 0.8 to 0.925. Moreover

multi-reflux operation enjoys more freedom to balance between the conversion and product purity (as can be seen in Cases 2-3). In all cases, it is found that excess water in the feed improves the recovery rate of lactic acid significantly compared to those obtained by Edreder et al. (2010).

Table 2: Summary of optimization results using single and Multi time intervals

Case 1: NCI=1 interval

x_{purity}	R	t_f(hr)	Conv.%
0.800	0.912	11.83	77.8
0.850	0.939	17.05	82.6
0.900	0.961	26.44	87.3
0.925	0.970	34.94	89.6
0.950*	*	*	*

Case 2: NCI= 2 intervals

x_{purity}	t_1,R_1	t_f ,R_2	Conv. %
0.800	9.06,0.901	11.54,0.941	77.8
0.850	12.3,0.925	16.08,0.966	82.6
0.900	14.46,0.941	22.05,0.975	87.7
0.925	19.29,0.953	27.55,0.985	90.0
0.950	18.46,0.955	31.19,0.983	92.6
0.975	12.07,0.941	34.75,0.986	95.2
0.990	10.07,0.933	48.38,0.991	96.4

Case 3: NCI= 3 intervals

x_{purity}	t_1,R_1	t_2,R_2	t_f ,R_3	Conv. %
0.800	2.96,0.828	5.42,0.934	9.78,0.878	77.9
0.850	2.44,0.820	1.70,0.906	12.78,0.948	82.8
0.900	2.09,0.828	13.79,0.956	21.15,0.987	87.7
0.925	6.42,0.909	2.71,0.954	21.28,0.972	90.6
0.950	7.02,0.906	5.40,0.976	26.32,0.982	93.1
0.975	14.0,0.947	18.95,0.985	34.80,0.989	95.2
0.990	8.11,0.923	10.73,0.977	38.89,0.991	97.1
0.999	10.77,0.936	20.60,0.985	55.70,0.998	97.8

Note, the (*) represents no results are obtained.

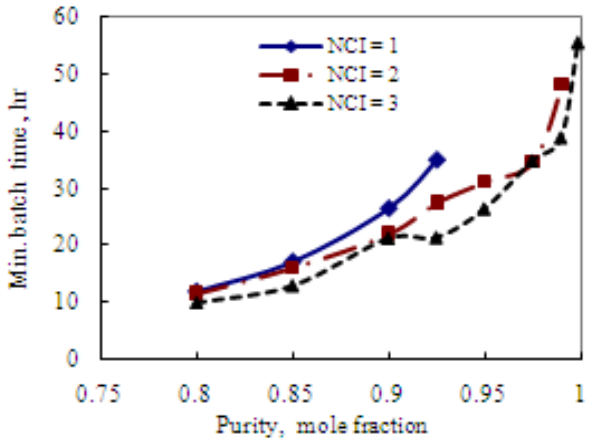

Fig.2. Total minimum operating time as a function of purity specification

5. Conclusions

In this work, optimal operation of batch reactive distillation column involving the hydrolysis process of methyl lactate acid producing high purity of lactic acid and methanol was considered. A detailed dynamic model in terms of mass and energy balances and thermodynamic properties within gPROMS modeling software was used. Optimization problem was formulated to minimize the operation time while optimizing the reflux ratio (single and multi interval time) subject to satisfaction of the amount and purity of the lactic acid product. Piecewise constant reflux ratio profile was considered for the process. It can be seen from the results that the increasing of water amount in the feed leads to achieve high purity of lactic acid (99.9 mol %). Finally, a comparison of operating scenarios shows that the batch time saving when the column operates with multi-reflux policy. Finally, it is found that excess water in the feed enhances the recovery rate of lactic acid significantly.

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