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Comparison of Conventional and Middle Vessel Batch Reactive Distillation Column: Application to Hydrolysis of Methyl Lactate to Lactic Acid

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Comparison of optimal operation between conventional batch reactive distillation column (CBRD) and middle-vessel batch reactive column (MVBRD) for the production of lactic acid via hydrolysis of methyl lactate has not been considered in the past. Therefore, it is the main focus in this work. A dynamic optimization problem incorporating a process model is formulated to minimize the batch time subject to constraints on the amount and purity of lactic acid. Control variables (reflux ratio or/and a reboil ratio) are treated as a piecewise constant. Optimization results indicate that MVBRD is more effective than CBRD in terms of saving in batch time which can be as high as of 20 %.

1. Introduction

Generally, in the conventional batch reactive distillation column (CBRD), a feed is charged into a reboiler or reactor at the bottom of the column. While in the inverted batch reactive distillation column (IBRD), a feed is charged to the condenser drum. The combination of these configurations is described as the middle-vessel batch reactive column (MVBRD). The feed mixture is loaded into the middle vessel, where the reaction takes place, between the two separation sections and the products are simultaneously obtained from the top and the bottom of the column. This configuration was first mentioned by Robinson and Gilliland (1950). The esterification of lactic acid (impure) with alcohol to obtain lactate ester and then hydrolyzed into pure lactic acid have proposed in the past (Choi and Hong, 1999). Kim et al. (2000) utilized a batch reactive distillation with esterification and hydrolysis for the recovery of lactic acid using experiments and simple modelling to obtain optimum design and effective operation. Kumar et al. (2006) explored and investigated a novel reactive distillation strategy involving experimental esterification and hydrolysis reaction for recovery of pure lactic acid. Edreder et al. (2011) considered optimal operations of CBRD and IBRD columns to produce lactic acid by hydrolysis of methyl lactate. Recently 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. In this work a comparative study of the performance of CBRD and MVBRD is presented for hydrolysis reaction of methyl lactate to produce lactic acid (main product) and methanol. The hydrolysis process is modelled using detailed mass and energy balances within gPROMS modelling software. Dynamic optimisation problem is formulated to minimise batch time. Product amount and purity are used as constraints while optimising the reflux ratio for CBRD operation and both the reflux and reboil ratios for MVBRD.

2. Process model

With reference to the CBRD column configuration shown in Figure 1, the model includes column holdup, rigorous phase equilibria, and chemical reaction on the plates, in the reboiler and in the condenser. The detailed model equations are given in Edreder et al. (2011) although Figure 1 shows typical model equations for the reboiler. Referring to Figure 2 for MVBRD column configuration, the model equations for

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the rectifying section are the same as those presented for CBRD, while the reboiler equations are same as the inverted batch distillation column. Model equations for feed tank and feed plate are shown in Figure 2. More details can be found in Mujtaba (2004).

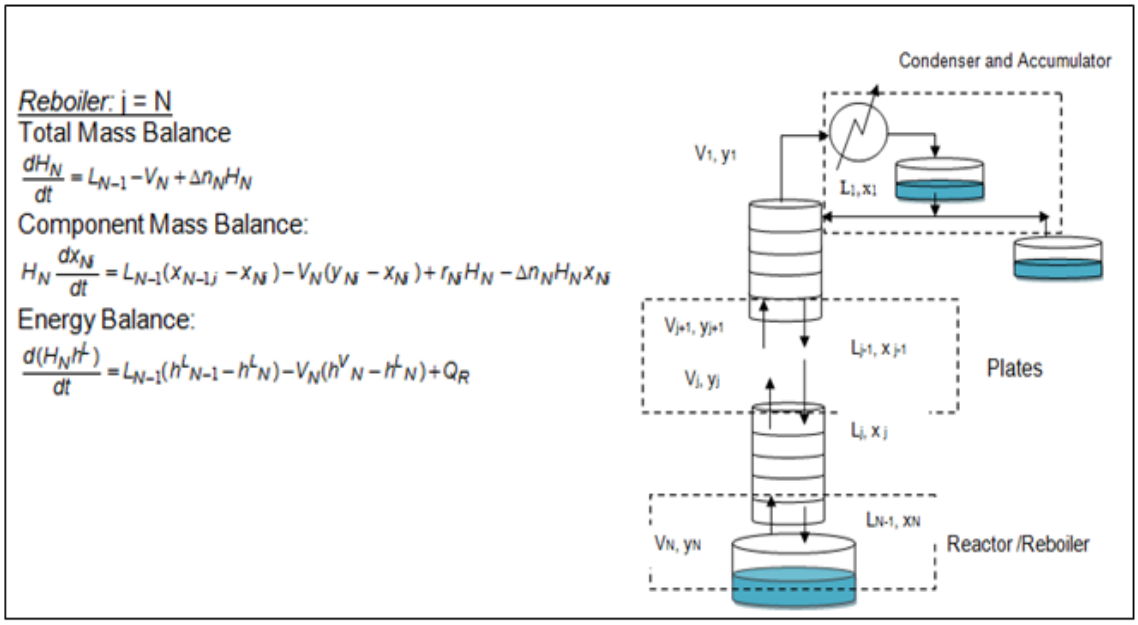

Figure 1: CBRD column and Reboiler model equations

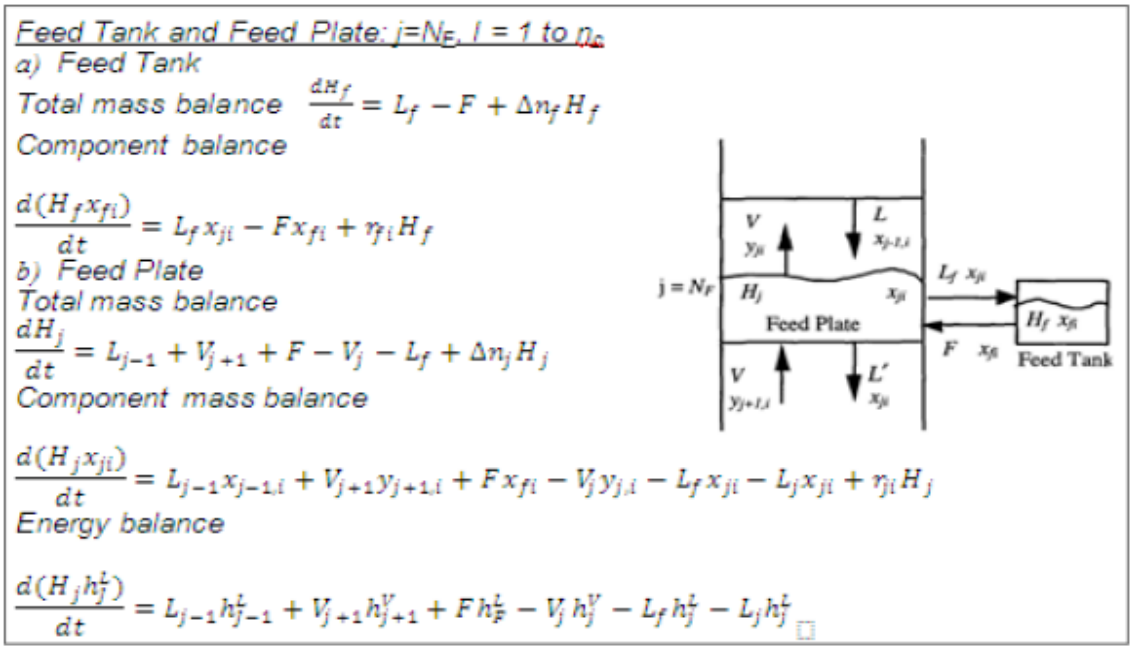

Figure. 2: Configuration and model equations for feed tank and feed plate

3. Optimisation problem formulation

The optimal operation of both CBRD and MVBRD in terms of minimum operating time for given product and purity of main product is investigated herein and can be stated as:

OP2 $\min \; t_f$

$R(t)/or\ and\ Rb$ (1)

$subject\ to$:

$B = B^*$ (Inequality constraint)

$x_3 = x_3^* \pm \varepsilon$ (Inequality constraint)

$and\ \ f(t, x', x, u, \upsilon) = 0$ (Model Equation, equality constraint)

$with\ f(t_0, x'_0, x_0, u_0, \upsilon) = 0$ (Initial condition, equality constraint)

Linear bound on R (Equality constraint)

Where B, x_3 are the amount of bottom product (2.5 kmol) and composition of lactic acid at the final time t_f, (denotes that the B and x^*_3 are specified). *R(t)* is the reflux ratio profile and Rb is reboil ratio which are optimized and ε is small positive numbering the order of 10^{-3}. The control variables u represent time dependent decision variables while v is the set of constant parameters and t is the time.

The optimisation problem is formulated and solved using Control Vector Parameterization (CVP) and Successive Quadratic Programming (SQP) technique in gPROMS modelling software

In words, find the optimal reflux ratio R (for CBRD column) or reflux ratio R and reboil ratio Rb (for MVBRD column) which minimises the total operating time (t_f).

4. Case study

4.1 Specifications

The feed composition <Methyl Lactate (ML), Water (H_2O), Lactic acid (LA), Methanol (MeOH) is : <0.5, 0.50, 0.0, 0.0> for both processes. The other input data are presented in Table 1

Table 1: Column specifications for hydrolysis of methyl lactate system

No of ideal stages*	10	Internal plate hold up (kmol)	0.0125
Feed Location (For MVBRD)	5	Condenser and reboiler hold ups (kmol)	0.10
Total fresh feed (kmol)	5	Vapour boil up rate (kmol/h)	2.50
		Column pressure (bar)	1.013

*including reboiler and condenser

4.2 Chemical reaction and kinetics

The hydrolysis reaction of methyl lactate together with the boiling temperature of the components can be shown below:

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

B.P (K) 417.15 373.15 490.15 337.15

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

$$-r = 1.65 \times 10^5 \exp\left(\frac{-50.91}{RT}\right) a_1 a_2 - 1.16 \times 10^6 \exp\left(\frac{-48.52}{RT}\right) a_3 a_4 \quad (3)$$

The reaction products are lactic acid (LA) and methanol (MeOH), with LA being the main product.

4.3 Vapor-liquid equilibrium (VLE)

K-values (VLE constants) are computed from (Eq. 4) where γi is computed from UNIQUAC equation, the vapor pressure (P^{sat}) of pure components has been obtained by using Antoine's equation. The UNIQUAC binary interaction parameters and Antoine parameters were taken from Sanz et al. (2003). Vapor phase enthalpies are calculated using empirical equations from formulation Holland (1981) and the liquid phase enthalpies were calculated by subtracting heat of vaporization from the vapor enthalpies.

$$K = \gamma_i P_i^{sat} / P \quad (4)$$

4.4 Optimization results

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 2. The reflux and reboil ratios are defined over single control interval and are assumed piecewise constant control type. An

optimization result in terms of minimum operating time is shown graphically in Figure 3 for different product purity using CBRD and MVBRD columns.

Table 2 Optimal reflux or and reboil ratios and batch time for both processes

x_3^*	CBRD		MVBRD		
	Reflux Ratio	t_f(h)	Reflux Ratio	Reboil Ratio	t_f(h)
0.70	0.8638	7.37	0.8530	0.8362	6.68
0.75	0.9020	10.20	0.8796	0.8586	8.28
0.80	0.9330	14.88	0.9204	0.8926	11.98

*mole fraction of LA

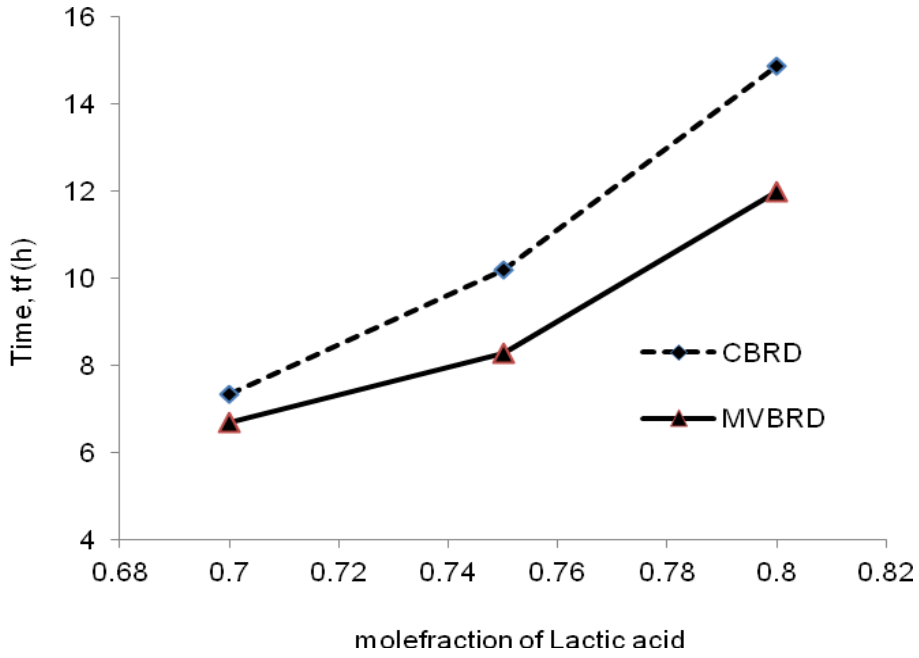

Figure 3. Optimum operating time vs. purity specification (both CBRD and MVBRD)

It can be seen from Table 2 that the optimal reflux ratio increases with increasing product purity for both CBRD and MVBRD processes. The results also show that the batch time increases gradually with increasing product purity using both processes (Figure 3). For the same product purity, a significant reduction in batch time is possible when the process is operated by MVBRD column. For example, for product purity 0.75 molefraction, a batch time reduction of 18.8 % is achieved compared to that using CBRD. Furthermore the MVBRD column has indeed a shorter batch time than the CBRD column. It is indicated that MVBRD is more effective than CBRD in terms of saving in batch time (20 % saving is noted for some cases).

Figures (4a & 4b) present bottom product composition profile for MVBRD and the reboiler composition profile for CBRD at product purity of 0.8. From Figure 4a, it can be noticed that the lower boiling product (methanol) is not present in the bottom tank, while in Figure 4b, it can be seen that the composition of methanol rises from zero reaching its maximum value and then gradually falls to zero in the reboiler. The rise in mole fraction is due to high rate of reaction initially in the reboiler. Methyl lactate decreases with time due to consumption by reaction with water. As batch time increases more lactic acid has been produced in order to meet product specification.

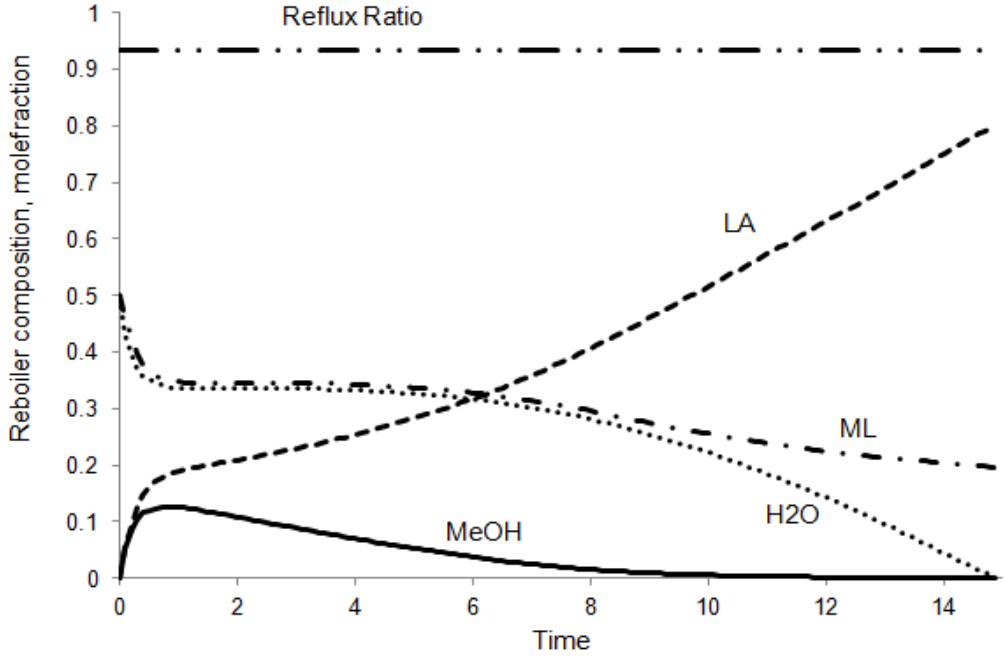

Figure 4a. Bottom product composition and reboil ratio profiles (MVBRD) at 80 % purity

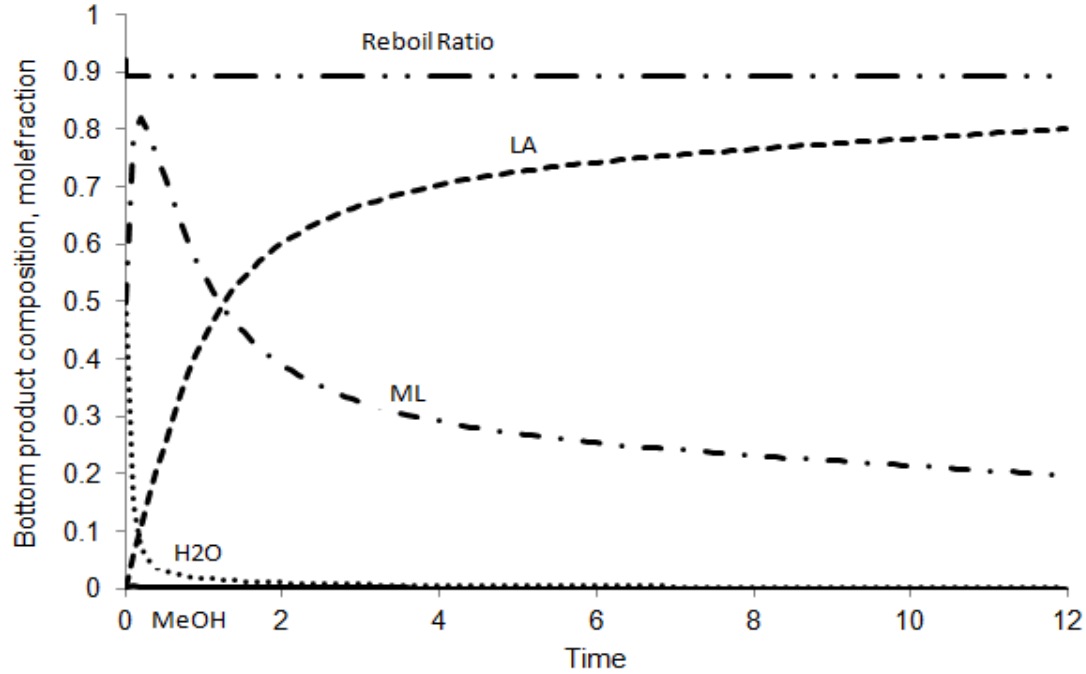

Figure 4b. Reboiler composition and reflux ratio profiles (CBRD) at 80 % purity

5. Conclusions

In this study, the performances of conventional and middle vessel batch reactive distillation columns in terms of minimum batch time are evaluated for the production of lactic acid via hydrolysis reaction of methyl lactate. A dynamic optimization problem incorporating a process model is formulated to minimize the batch time subject to constraints on the amount and purity of lactic acid. Piecewise constant reflux ratio profile and a single interval reboil ratio are considered as a control variable for CBRD and MVBRD

respectively. The results indicate that, middle vessel column is more efficient and quite interesting as both methyl lactate and water are mid-boiling components in the mixture and therefore removal of both methanol and lactic acid in MVBRD column has improved the conversion and reduced the batch time (maximum of 20 % saving in batch time could be achieved).

Notation

MVBRD	Middle-vessel batch reactive column
CBRD	conventional batch reactive distillation column
H_j, H_N	plate and reboiler holdup respectively (kmol)
h^L, h^V	liquid, vapour enthalpy (kJ/kmol)
L, V	liquid, vapour flow rates in the column (kmol/h)
N	number of plates
Q_C, Q_R	condenser or reboiler duty (kJ/h)
T, P	temperature (K), pressure (bar)
K	vapour-liquid equilibrium constant
r	reaction rate
t	batch time (h)
x, y	liquid or vapour composition (mole fraction)
LA	Lactic acid
MeOH	Methanol
ML	Methyl Lactate
H_2O	water
R, Rb	reflux and Reboil ratio
SQP	Successive quadratic programming algorithm
VLE	Vapour-liquid equilibrium
CVP	control vector parameterisation
u	The control variables represent time dependent decision variables
v	the set of constant parameters and t is the time
Superscripts and subscripts	
i	component number
j	stage number
ε	small positive numbering the order of 10^{-3}
Δn	change in moles due to chemical reaction
γ_I	Activity coefficient of component *i*

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