

The University of Bradford Institutional Repository

<http://bradscholars.brad.ac.uk>

This work is made available online in accordance with publisher policies. Please refer to the repository record for this item and our Policy Document available from the repository home page for further information.

To see the final version of this work please visit the publisher's website. Access to the published online version may require a subscription.

Link to publisher's version: <http://dx.doi.org/10.1016/j.cep.2016.07.009>

Citation: Aqar DY, Rahmanian N and Mujtaba IM (2016) Integrated Batch Reactive Distillation Column Configurations for Optimal Synthesis of Methyl Lactate. Chemical Engineering and Processing: Process Intensification. 108:197-211.

Copyright statement: © 2016 Elsevier, Ltd. Reproduced in accordance with the publisher's self-archiving policy. This manuscript version is made available under the [CC-BY-NC-ND 4.0 license](#).



Integrated Batch Reactive Distillation Column Configurations for Optimal Synthesis of Methyl Lactate

Dhia Y. Aqar, Nejat Rahmanian, Iqbal M. Mujtaba*

Chemical Engineering Division, School of Engineering, Faculty of Engineering and Informatics, University of Bradford, Bradford, BD7 1DP, UK

**Corresponding author I.M.Mujtaba@bradford.ac.uk*

Abstract

Although batch reactive distillation process outperforms traditional reactor-distillation processes due to simultaneous reaction and separation of products for many reaction systems, synthesis of Methyl lactate (ML) through esterification of lactic acid (LA) with methanol in such process is very challenging due to difficulty of keeping the reactants together when one of the reactants (in this case methanol) has the lowest boiling point than the reaction products. To overcome this challenge, two novel reactive distillation column configurations are proposed in this work and are investigated in detail. These are: (1) integrated conventional batch distillation column (i-CBD) with recycled methanol and (2) integrated semi-batch and conventional batch distillation columns (i-SBD) with methanol recovery and recycle.

Performances of each of these configurations are evaluated in terms of profitability for a defined separation task. In i-SBD column, an additional constraint is included to avoid overflow of the reboiler due to continuous feeding of methanol into the reboiler as the reboiler is initially charged to its maximum capacity. This study clearly indicates that both integrated column configurations outperform the traditional column configurations (batch or semi-batch) in terms of batch time, energy consumption, conversion of LA to ML, and the achievable profit.

Keywords: Dynamic Modelling; Optimization; Methyl Lactate; i-CBD; i-SBD; Esterification

1. Introduction

Batch reactive distillation process is extensively employed in the chemical industry, particularly for seasonal demand and/or low-volume production. The integration of reaction and distillation in a single vessel (reactive distillation) has offered a number of specific advantages over conventional process of chemical reaction followed by separation (Mujtaba and Macchietto, 1997). It can save the thermal heat consumption, reduce capital and operating costs, overcome

the chemical reaction equilibrium, and improve conversion and selectivity as compared to traditional operations of carrying out reaction and purification separately (Kao and Ward, 2015). The esterification reaction (e.g. synthesis of ethyl acetate) is a well-known operation and widely used reaction in several chemical industries such as pharmaceuticals, solvents of paints, adhesive agents, bio-plastics, personal-cares and chemical flavours, emulsifiers and pesticides, perfumery additive, detergents and surfactants, food, and synthesising a biodiesel from lower quality renewable sources (Edreder et al., 2008; and Toor et al., 2011).

The impure lactic acid esterification with multiple alcohols to produce lactate ester is an old-fashioned process. For instance, several researchers focused on the ethyl lactate production via esterification of lactic acid with ethanol (Engin et al., 2003; Zhang et al., 2004; Adams and Seider, 2008 and Delgado et al., 2010). Investigations on the reaction of LA with isopropanol to form isopropyl lactate were carried out by a limited number of works (Yadav et al, 2000; and Toor et al., 2011). However, the others have previously characterized lactic acid esterification with n-butanol to synthesize n-butyl lactate (Dassy et al., 1994; Kumar and Mahajani, 2007).

Most recently, Aqar et al. (2016) studied the esterification reaction of lactic acid with methanol producing methyl lactate. For a given separation task (desired amount of ML and its purity), they compared the performances of CBD and SBD columns in terms of total energy consumption or minimum operating time. Their results clearly indicated that SBD process with continuous additional feeding of methanol (the lightest component in the reaction mixture) offered much better performance than the CBD for ML synthesis. For example, the SBD process produced ML at a higher purity of 85% compared to maximum purity of 48% obtained using a CBD. However, recovery of methanol and its recycling were not considered in their work.

Due to the nature of the reaction system, in this work, recovery and recycling of methanol in an integrated manner are considered. We have proposed two new integrated configurations for the process (i) a CBD with recycling of distillate (containing high purity methanol) back into the reboiler as the process continues. We call this configuration i-CBD; (ii) an integrated SBD column and a methanol distillation column (called i-SBD). In the methanol distillation column, methanol is separated at higher purity than that is the case in i-CBD and is then fed together with fresh methanol into the i-SBD. While i-CBD does not create operational problem of reboiler overflow, i-SBD creates operational problem in terms of reboiler overflow which is managed by applying the strategy used in Aqar et al. (2016).

The performances of i-CBD and i-SBD are evaluated in terms of minimum energy consumption or minimum batch time. The piecewise-constant strategy for the optimization parameters (reflux ratios, methanol recycled rate (only for i-CBD), and methanol feed rate (for i-SBD) are used in the optimization study. A rigorous dynamic model based on mass and energy balances is presented and incorporated into the optimization within gPROMS (general PROcess Modelling System, 2015) software. The dynamic optimization case is converted to a nonlinear programming problem (NLP) and solved by Control Vector Parameterization (CPV) method using successive quadratic programming (SQP) based technique within gPROMS (more details about this approach can be found in Mujtaba, 2004).

2. Process models

2.1 Integrated conventional batch distillation (i-CBD) with recycled methanol

The model equations are developed with reference to the schematic diagram of i-CBD as depicted in Figure 1. The mathematical model involves unsteady state mass and energy balances with constant molar hold-up on all trays and in the total condenser, reaction taking place in the trays, in the condenser, and in the reboiler vessel. The column trays are numbered from the top to the bottom. See Aqar et al. (2016) for the list of assumptions considered in developing the process model. The i-CBD process model is exactly similar to the CBD column presented in Aqar et al (2016) except that the additional terms added to the system of equations to cater for recycled methanol-rich stream as presented below.

2.1.1 Condenser and Distillate Accumulator: j=1

- Accumulator Total Mole Balance:

$$\frac{dH_a}{dt} = D - S_{\text{MeOH}} \quad (1)$$

- Component Mole Balance:

a) Distillate Accumulator:

$$H_a \frac{dx_{ai}}{dt} = (D - S_{\text{MeOH}}) (x_{Di} - x_{ai}) \quad (2)$$

2.1.2 Partial Reboiler: j= N

- Total Mole Balance:

$$\frac{dH_N}{dt} = L_{N-1} + V_N + S_{\text{MeOH}} + \Delta n_N M_N \quad (3)$$

- Component Mole Balance:

$$H_N \frac{dx_N}{dt} = L_{N-1}(x_{N-1} - x_N) + V_N(y_N - x_N) + S_{\text{MeOH}}(x_a - x_N) + M_N r_N \quad (4)$$

- Energy balance:

$$0 = L_{N-1}(H_{N-1}^L - H_N^L) + V_N(H_N^V - H_N^L) + S_{\text{MeOH}}(H^a - H_N^L) + Q_r \quad (5)$$

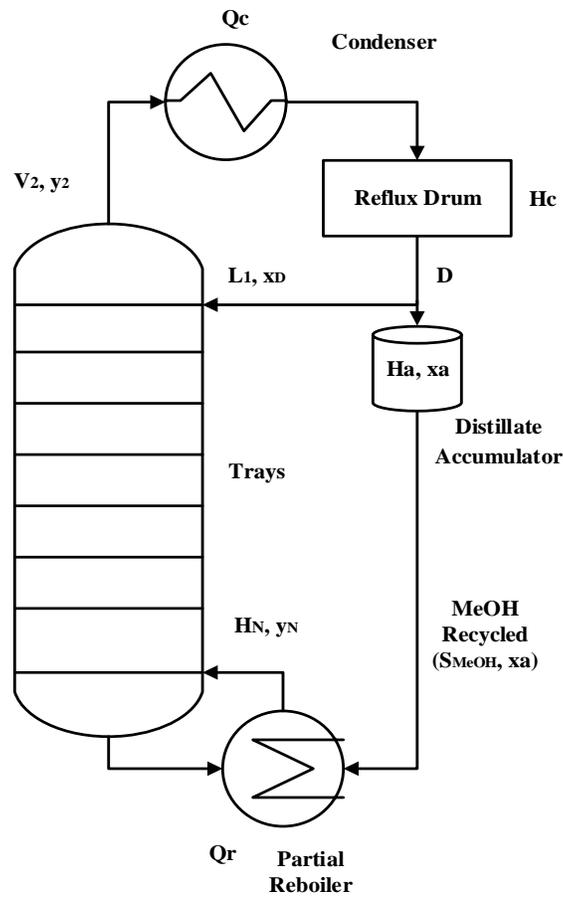


Figure 1: Schematic diagram for ML production using i-CBD.

2.2 Integrated semi-batch and conventional batch distillation columns (i-SBD) with methanol recovery and recycle

Figure 2 shows a SBD column without methanol recovery and recycle option as considered in Aqar et al. (2016).

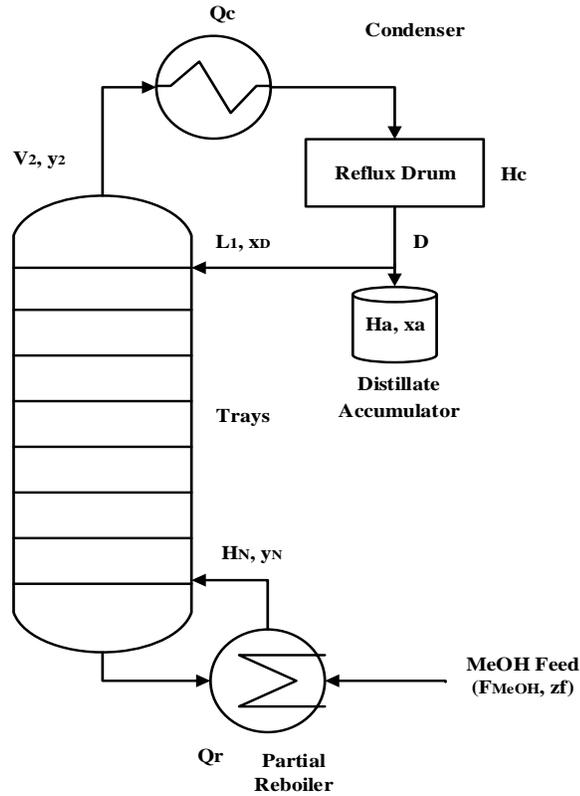


Figure 2: Schematic representation for ML production using SBD.

In the i-SBD configuration, the distillate accumulator from the SBD (Figure 2) is further processed in a CBD to recover methanol at a desired purity and mixed up with make-up methanol of the same quality before being fed to the next batch of SBD. The operation schedule for i-SBD process is displayed in Figure 3A which is translated in Figure 3B for easy understanding. Note, the operation time for CBD is assigned to be the same as the time operation of the SBD. Therefore, while the CBD is in operation for the first batch, SBD for the second batch will be in operation in parallel.

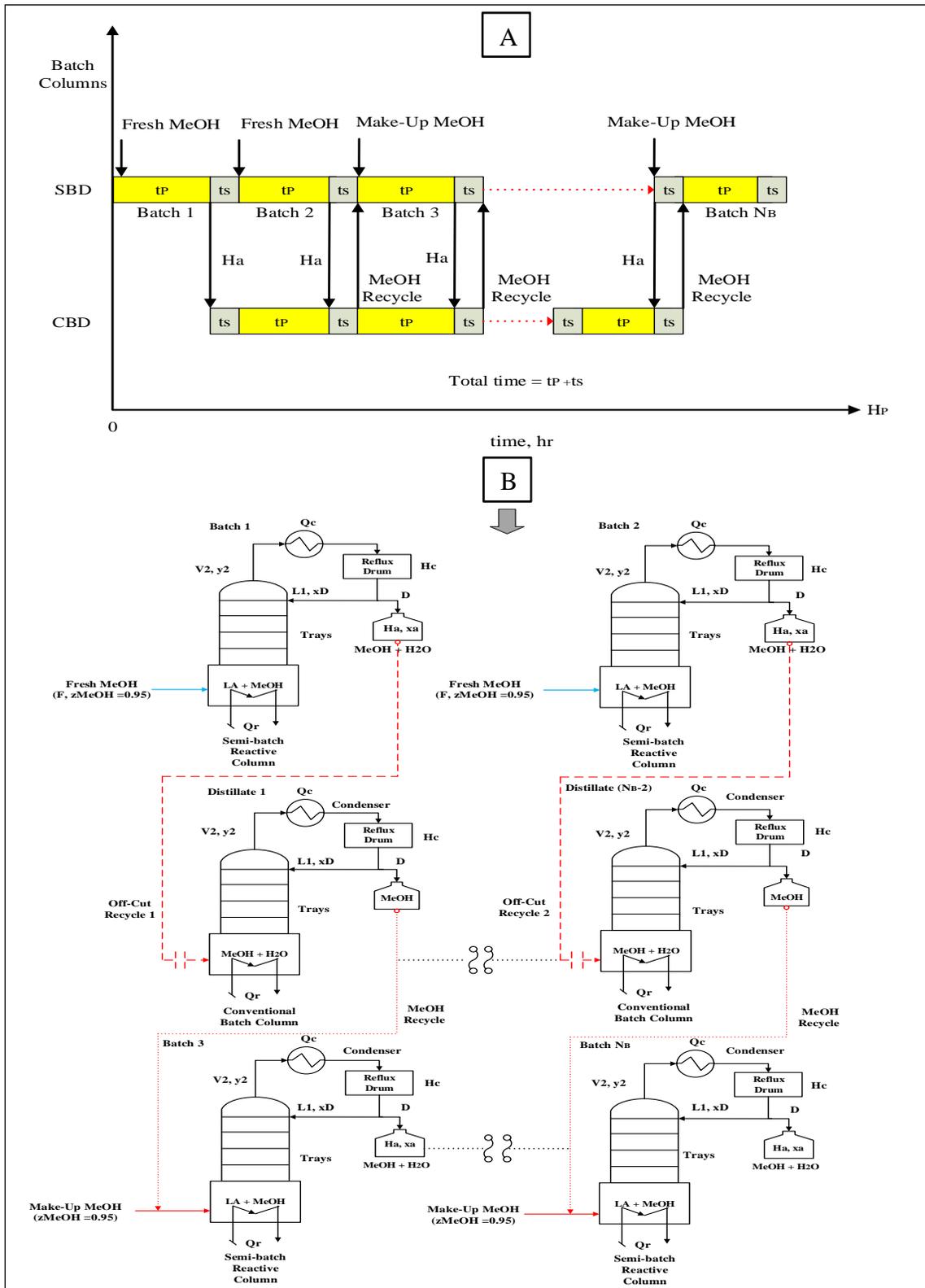
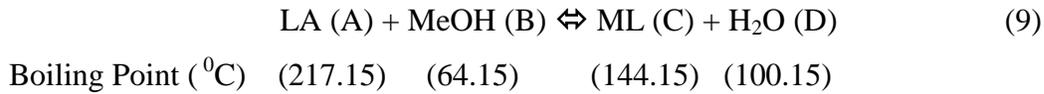


Figure 3: The operating strategy for SBD and i-SBD

When the CBD is done with the first batch of methanol recovery task, the feed for the second batch of CBD will be ready from the second batch of SBD. Note, the first two batch of SBD will not have recycled methanol. However, a pseudo-steady state operation will be in place after the second batch of SBD. Note, t_s is the combined set up time for SBD and CBD. For the SBD column, the model equations are same as those presented in Aqar et al. (2016). In contrast, the second column is a conventional batch distillation without any chemical reaction which is used to separate methanol at a desired purity. Note, the rigorous model without chemical reaction equations of the CBD can be found in Mujtaba (2004).

2.3 Kinetics of the reaction and phase equilibrium (VLE)

Methyl lactate is produced by the esterification of lactic acid and methanol via the reversible kinetic reaction together with the normal boiling temperature of each component is given by the following stoichiometric relationship:



The kinetic VLE models for the system are presented in detail in Aqar et al. (2016).

3. Operation Strategy

We considered *constant vapour load to condenser* strategy (as considered by Aqar et al., 2016) to operate both i-CBD and i-SBD. In this policy the reboiler duty (Q_{reb}) progressively increases to keep the constancy of the vapour load to the overhead condenser. This leads to the following equation for the evaluation of total energy consumption.

$$E_{\text{tot}} = \int_0^{t_p} Q_{\text{reb}} dt \quad (6)$$

or

$$\frac{dE_{\text{tot}}}{dt} = Q_{\text{reb}} \quad (7)$$

Note, this differential equation (7) is inserted to the mathematical model equation discussed above. The other variables constraints are discussed in the next section.

As discussed in Aqar et al. (2016), SBD column needs to be carefully operated to avoid reboiler overflow due to continuous feeding of methanol. With the injected methanol feed rate F_{MeOH} (kmol/hr) and the reflux ratio R (which controls the distillate rate, D , kmol/hr) need to be carefully regulated for a given condenser vapour load rate (V_L). Similarly to the reboiler overloading for the batch extractive distillation, where the excessive solvent was needed to be charged, which was analysed by Lang et al. (1994). Following constraint which sets the upper limit of R was considered by Aqar et al. (2016) to avoid the reboiler overflow.

$$R_{Max} = (1 - \frac{F_{MeOH}}{V_L}) \quad (8)$$

Note, the same condition will apply for the operation of SBD column of the i-SBD process.

4. Dynamic optimization problem formulation

In this work, the optimal operations of i-CBD, SBD column of the i-SBD process are determined based on minimum processing time for a given amount of ML product and desired purity. As the CBD column of the i-SBD process enjoys the same operation time as SBD, the optimal operation of CBD is determined based on maximization of the amount of methanol recovery for a given batch time and product purity. The optimization problem can be described as:

4.1 i-CBD and SBD Column (of i-SBD process)

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

Determine: Reflux ratio (R) and Recycle rate (S_{MeOH}) (for i-CBD)

Or, Reflux ratio (R_{SBD}) and Methanol feed (F_{MeOH}) (for SBD of i-SBD process)

So as to: Minimize the batch processing time

Subject to: Model equation, Process constraints

Mathematically the optimization problem (OP1) can be represented as:

Minimum Operating Time Problem

OP1 Min t_p

$R(t), S_{MeOH}(t)$ (for i - CBD)

Or,

$R_{SBD}(t), F_{MeOH}(t)$ (for SBD of i - SBD process)

subject to:

(10)

$$B_p = B_p^* \quad (\text{Inequality constraint})$$

$$x_p \geq x_p^* \quad (\text{Inequality constraint})$$

And $f(t, x', x, u, \Lambda)$ (Model equation, equality constraint)

With $f(t_0, x'_0, x_0, u_0, \Lambda_0) \Lambda_0$ (Initial condition, equality constraint)

Linear bound on $R(t)$, $S_{\text{MeOH}}(t)$, $R_{\text{SBD}}(t)$, and $F_{\text{MeOH}}(t)$ (Equality constraint)

Where B_p , x_p are the amount of bottom product and composition of ML at the end of processing time t_p in the reboiler drum, (B_p^* , and x_p^* denotes that they are specified).

4.2 CBD column (of i-SBD process)

Given: The column configuration the feed mixture, vapour load to the condenser, desired purity of the distillate product, fixed batch time

Determine: Reflux ratio (R_{CBD})

So as to: Maximize the amount of distillate product

Subject to: Model equation, Process constraints

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

Maximum Distillate Problem

$$\text{OP2} \quad \text{Max} \quad D_{\text{MeOH}} \quad R_{\text{CBD}}(t) \quad (11)$$

subject to:

$$t_p = t_p^* \quad (\text{Inequality constraint})$$

$$x_{\text{MeOH}} \geq x_{\text{MeOH}}^* \quad (\text{Inequality constraint})$$

Linear bound on $R_{\text{CBD}}(t)$ (Equality constraint)

Where, D_{MeOH} is the distillate amount of methanol, $R_{\text{CBD}}(t)$ is the reflux ratio as a function of time (t), x_{MeOH} is the purity of recovered methanol at the final time (t_p), (t_p^* , x_{MeOH}^*) are the specified final batch time and the specified composition of recovered methanol (which is recycled to SBD of the next batch).

The highly coupled set of differential-algebraic equations (DAEs) describing the process model acts as an equality constraint to the optimization problem.

5. Results and Discussions

5.1 i-CBD Column

The investigation has taken place in a batch distillation column with eight plates (excluding condenser and reboiler) with fixed overhead vapour condenser load (2.5 kmol/hr). The column configuration is kept the same as SBD for easy comparison (Aqar et al., 2016). Four percent of the initial feed is considered as the total column holdup (of which 50% is considered as condenser holdup and the rest equally divided is considered as the tray holdup). Similar strategy of holdup distribution was considered by several investigators in the past (see Mujtaba, 2004). The information described above together with other specifications is summarised in Table 1. The fresh feed is a mixture of <Lactic acid, Methanol, Methyl Lactate, Water> with respective composition of <0.5, 0.5, 0.0, 0.0>. At the beginning, plate and condenser holdups assume the same composition as the fresh feed. The column is then operated under total reflux for some time until it reaches the steady-state condition and the column composition profiles are thus established. The production period starts from this point (considered $t = 0$ in all case studies presented later) onward. This strategy of column initialization was used in the past by Cuille and Reklaitis (1986).

Table 1. Column specifications and operating conditions i-CBD.

Variable	Specifications
Total number of Trays*	8
Column pressure (throughout)	1.013 (bar)
Initial feed charged	5 (kmol)
Condenser Vapor Load	2.5 (kmol/hr)
Holdup on the condenser drum	0.1(kmol)
Holdup on trays	0.0125 (kmol)
Catalyst loading per stage	25 (g)

*excluding condenser and reboiler

Note, the limitations of ML synthesis using CBD column (with specifications same as in Table 1) have been discussed in detail in our recent work (Aqar et al., 2016). It was noted that using

CBD maximum ML purity achieved was around 0.50 (mole fraction) with conversion of LA of about 55% for varying bottom product amount.

Two case studies are examined here one with single reflux interval and the other with two reflux intervals. Note that, the purity of ML product specification is changed from 0.70 to 0.90 mole fraction in each case while the amount of bottom product remains the same at 2.3 kmol.

5.1.1 Optimal Operation using Single Reflux Interval (RV=1)

The optimal operating policy for the i-CBD system are summarised in Table 2, including the optimal reflux ratio profile, optimal recycle rate of methanol, minimum production time, conversion of LA into ML, the total energy consumption, and the total amount of methanol recycled over the production time. As can be seen, the optimal reflux ratio, and the operating time with the energy usage rate, gradually increase with increasing ML purity. Increasing production time obviously helped increasing the conversion of LA into ML. Clearly i-CBD column yielded a higher purity of ML (0.9 mole fraction), converted more lactic acid (93.11%) compared to those obtained by CBD column (Aqar et al., 2016). Note, the total amount of methanol recycled (S_{tot}) is computed by multiplying the methanol recycle rate by the production time as shown below:

$$S_{tot} = S_{MeOH} \times t_P \quad (12)$$

Table 2. Optimal Operation results for i-CBD using RV = 1.

X_{ML}^*	Optimal Reflux Ratio, R	Optimal Methanol Recycle Rate, S_{MeOH} kmol/hr	Minimum Production time, t_P , hr	Conversion of LA (%)	Total energy, E_{tot} , GJ	Total Amount of Recycled MeOH, S_{tot} kmol
0.70	0.543	0.925	12.33	77.38	1.191	11.40
0.75	0.628	0.782	18.34	80.75	1.723	14.34
0.80	0.703	0.645	27.52	84.36	2.528	17.77
0.85	0.726	0.620	41.34	88.73	3.730	25.62
0.90	0.751	0.586	71.86	93.11	6.377	42.09

Table 3 shows the reboiler and distillate mole fraction profiles at the end of the production time for each product purity. It is noted that mainly methyl lactate and the unreacted LA are remained in the still pot, while the distillate accumulator (Figure 1) contains methanol and some water. The mole fraction of ML in the distillate accumulator was seen to be negligible (as it is heavier). Note that the distillate amount is 2.7 kmol for all ML purities (by mass balance).

Figure 4 displays the reboiler and the distillate accumulator composition profiles for the ML purity ($x_{ML}^* = 0.90$). Note that there is a sharp increase in minimum production time and thus total energy consumption and total amount of methanol recycle (Table 2) to increase the ML purity from 0.85 to 0.90 (molefraction). For this case, the column needs to operate at even a higher reflux ratio to suppress the travel of ML up the column further, resulting in lower distillate rate to distillate accumulator, lower methanol recycle rate from the accumulator (Table 2) but longer time to meet the product specification.

Table 3. The reboiler and distillate composition profiles at several purities of ML using $RV = 1$.

Purity of ML	x_{LA}	x_{MeOH}	x_{H_2O}	* x_{LA}	* x_{MeOH}	* x_{ML}	* x_{H_2O}
0.70	0.244	0.020	0.036	1.67E-4	0.637	0.023	0.339
0.75	0.208	0.018	0.024	1.06E-4	0.706	0.016	0.278
0.80	0.169	0.017	0.014	7.66E-5	0.778	0.012	0.210
0.85	0.122	0.016	0.012	5.90E-5	0.830	0.009	0.161
0.90	0.076	0.015	0.009	5.27E-5	0.886	0.006	0.108

* The composition in the distillate accumulator (molefraction).

Using the results of Table 2, the overall profit of the process is calculated. Note, all prices of chemical reactant reaction (LA, and MeOH) are taken from (Alibaba Trade, 2016). From Alibaba Trade (www.alibaba.com/trade), March 2016 the price of methyl lactate for 99% purity is found to be 572.61 \$/kmol. We apply exponential trend to determine product prices at other purities. Based on the trend used in the past by Mujtaba and Greaves (2006) the price of ML at 90% purity is calculated to be 239.99 \$/kmol. The prices for the reactants (LA, and MeOH) and methyl lactate at different ML composition values are given in Table 4.

The profit function equations and parameters are taken from Miladi and Mujtaba (2004) and can be found in the Appendix. The number of batches produced over the year, total yearly product, annual capital investment cost, utility cost, and the profit are presented in Table 5. As the ML composition and batch time increase (Table 2), the number of batches and total annual production reduce gradually. It is also clear from Table 5 that using one interval i-CBD process is more profitable at product purity case ($x_{ML}^* = 0.90$) as compared to others ML purities. This is because a higher profit (18,704 \$/yr) with the highest purity constraint makes a higher priced product (239.99 \$/kmol) than a lower priced product (see Table 4). Note, for all product quality requirements which the annualized capital cost and the operating cost remained the same.

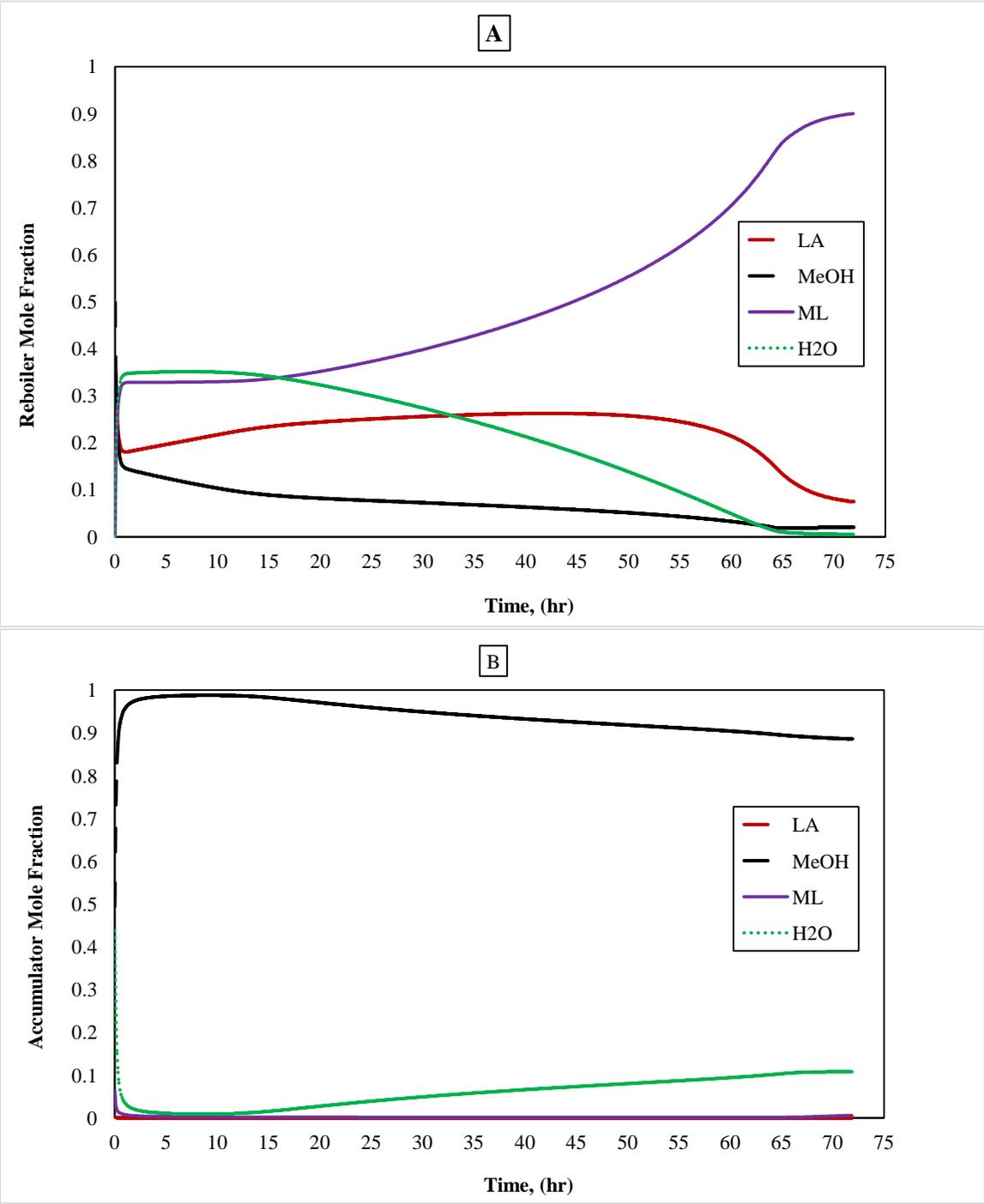


Figure 4: The reboiler and accumulator composition profiles of i-CBD, $RV = 1$ ($X_{ML}^* = 0.9$).

Table 4. The costs of reactant and product reaction.

The cost parameters	Price (\$/kmol)
Methanol Reactant Cost at 100% purity	12.83
Methanol Charge Cost at 95% purity	12.19
Lactic Acid Reactant Cost at 100% purity	9.10
Methyl Lactate Cost at 70% purity	75.25
Methyl Lactate Cost at 75% purity	89.89
Methyl Lactate Cost at 80% purity	115.99
Methyl Lactate Cost at 85% purity	158.65
Methyl Lactate Cost at 90% purity	239.99

Table 5. Profit results of Optimal Operation for different ML purities for i-CBD using RV = 1.

Purity of ML	Number of Batches, N_B batch/yr	Total Yearly Product, kmol/yr	Annualized Capital Cost, \$/yr	Operating Cost, \$/yr	Profit, \$/yr
0.70	623.4	1434	29751.9	450	9347
0.75	424.6	977	29751.9	450	11031
0.80	285.5	657	29751.9	450	14658
0.85	191.2	440	29751.9	450	18610
0.90	110.6	254	29751.9	450	18704

5.1.2 Optimal Operation using Two Reflux Intervals (RV=2)

For the five purities considered, the optimum reflux ratio and methanol recycle rate profiles, optimal switching time, final production time, total thermal energy rate, the maximum conversion ratio, and the total amount of methanol recycled using two-reflux intervals are given in Table 6. For two control intervals policy, the total methanol recycled quantity (S_{tot}) can be estimated from the following equation:

$$S_{tot} = S_1 \times t_1 + S_2 \times t_2 \quad (13)$$

Compared with one reflux interval i-CBD column, the production time is cut down by about 40%, the total energy consumption is decreased by 38%, and the conversion of LA is improved 37% for ML purity of 0.90. Clearly two-reflux intervals offer better operational flexibility and shorter production time and thus heat consumption (Figure 5). It also decreases the total amount of methanol recycled (by almost 73%). At lower ML purity, the column operates at low reflux ratio in the first interval and then at higher reflux ratio in the second interval. However, at higher ML purity requirement, it reverses i.e. the column operates at higher reflux ratio in the first

interval and operating at lower reflux in the second interval. In the first interval methanol is removed from the column at high purity but is not recycled leading to higher LA composition in the reboiler and possibly having backward reaction (see Figure 6A). In the second interval methanol is recycled converting most of the LA and producing ML.

Table 6. Optimal Operation results for i-CBD using $RV = 2$.

X_{ML}^*	Reflux Ratios for both Intervals, R_1, R_2	MeOH Recycle Rates for both Intervals, S_1, S_2 , kmol/hr	First Time Interval, t_1 , hr	Second Time Interval, t_2 , hr	Batch Time, t_p , hr	Total Energy, E_{tot} , GJ	Conversion of LA (%)	Total Amount Recycled, S_{tot} kmol
0.70	0.422, 0.778	1.14, 0.42	8.46	0.77	9.24	0.915	77.40	9.96
0.75	0.565, 0.739	0.83, 0.67	10.75	3.48	14.23	1.382	80.79	11.26
0.80	0.637, 0.926	0.79, 0	23.14	0.11	23.25	2.155	84.39	18.29
0.85	0.922, 0.705	0, 0.73	12.99	14.80	27.82	2.640	89.35	10.77
0.90	0.974, 0.540	0, 1.09	33.18	10.10	43.29	3.961	93.46	11.11

Table 7. The reboiler and distillate composition profiles at several purities of ML using $RV = 2$.

Purity of ML	X_{LA}	X_{MeOH}	X_{H_2O}	$*X_{LA}$	$*X_{MeOH}$	$*X_{ML}$	$*X_{H_2O}$
0.70	0.277	0.007	0.016	2.04E-4	0.586	0.027	0.387
0.75	0.215	0.020	0.015	2.51E-4	0.628	0.025	0.347
0.80	0.164	0.022	0.014	8.00E-5	0.730	0.021	0.249
0.85	0.115	0.024	0.011	2.25E-4	0.788	0.019	0.193
0.90	0.049	0.045	0.006	7.44E-5	0.892	0.015	0.093

* The composition in the distillate tank (mole fraction).

For each case (presented in Table 6), Table 7 shows the final composition of the bottom product and of the distillate accumulator. Figure 6 presents the dynamics of the reboiler and the distillate accumulator compositions for 0.90 of ML purity, respectively.

Table 8 highlights the profitability of i-CBD operation for each purity specification for 2 reflux ratio intervals. It can be seen that the profitability of the i-CBD operation is improved from 57% to 63% compared to the profit obtained using one control interval. This is a reflection of the increase in product purity from 0.70 to 0.90.

Table 8. Profit results of Optimal Operation for different ML purities for i-CBD using $RV = 2$.

Purity of ML	Number of Batches, N_B batch/yr	Total Yearly Product, kmol/yr	Annualized Capital Cost, \$/yr	Operating Cost, \$/yr	Profit, \$/yr
0.70	821.6	1890	29751.9	450	21919
0.75	543.1	1249	29751.9	450	22537
0.80	336.9	775	29751.9	450	22733
0.85	282.5	650	29751.9	450	41908
0.90	182.7	420	29751.9	450	50609

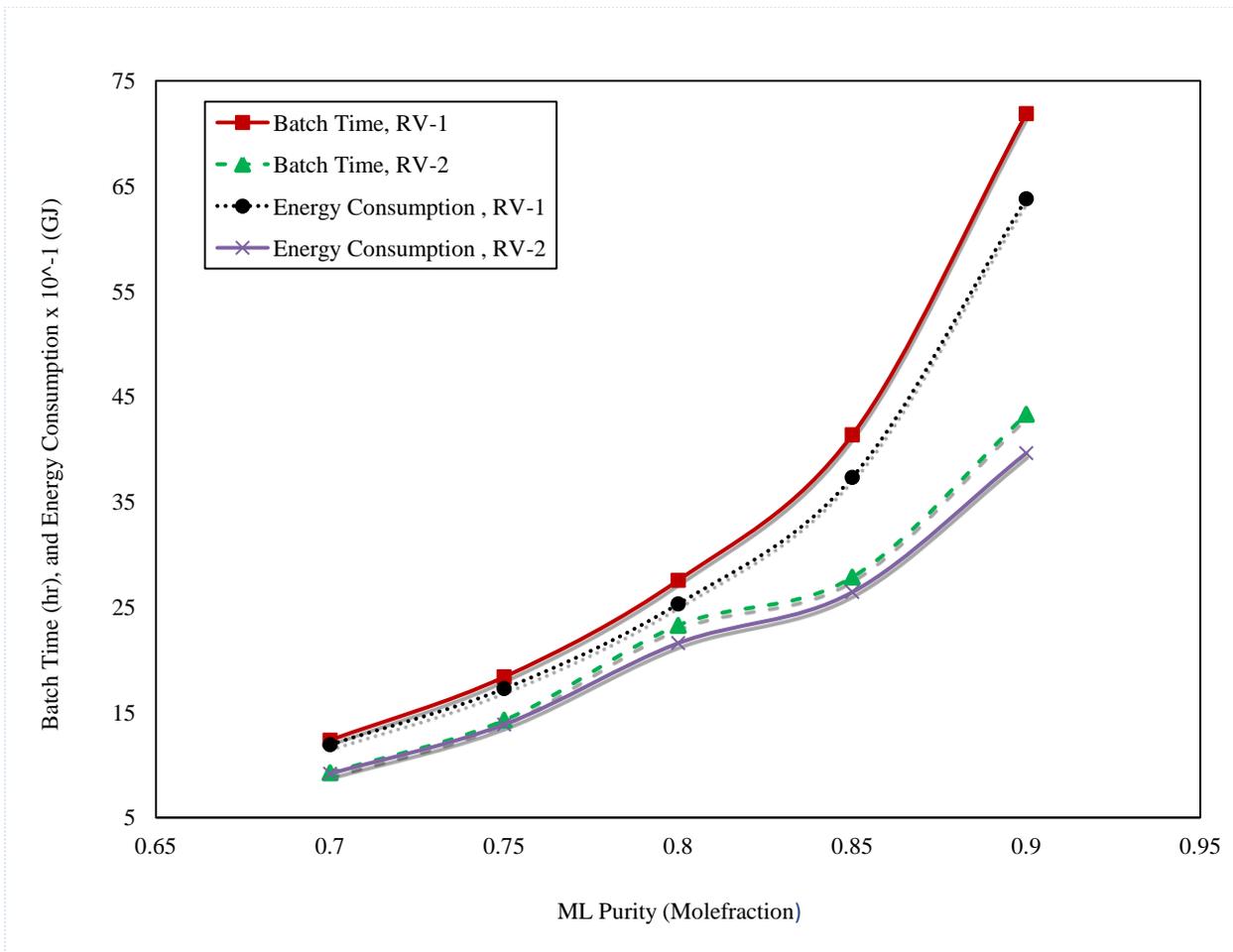


Figure 5: The final batch time and total thermal heat consumption profile for i-CBD.

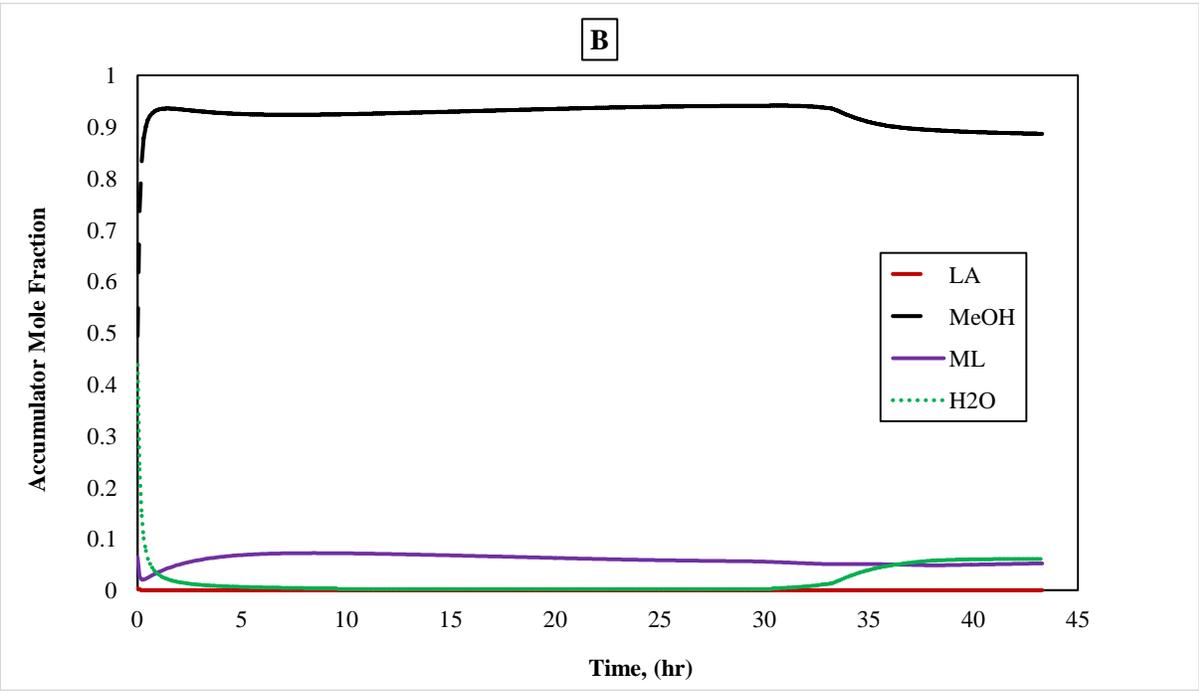
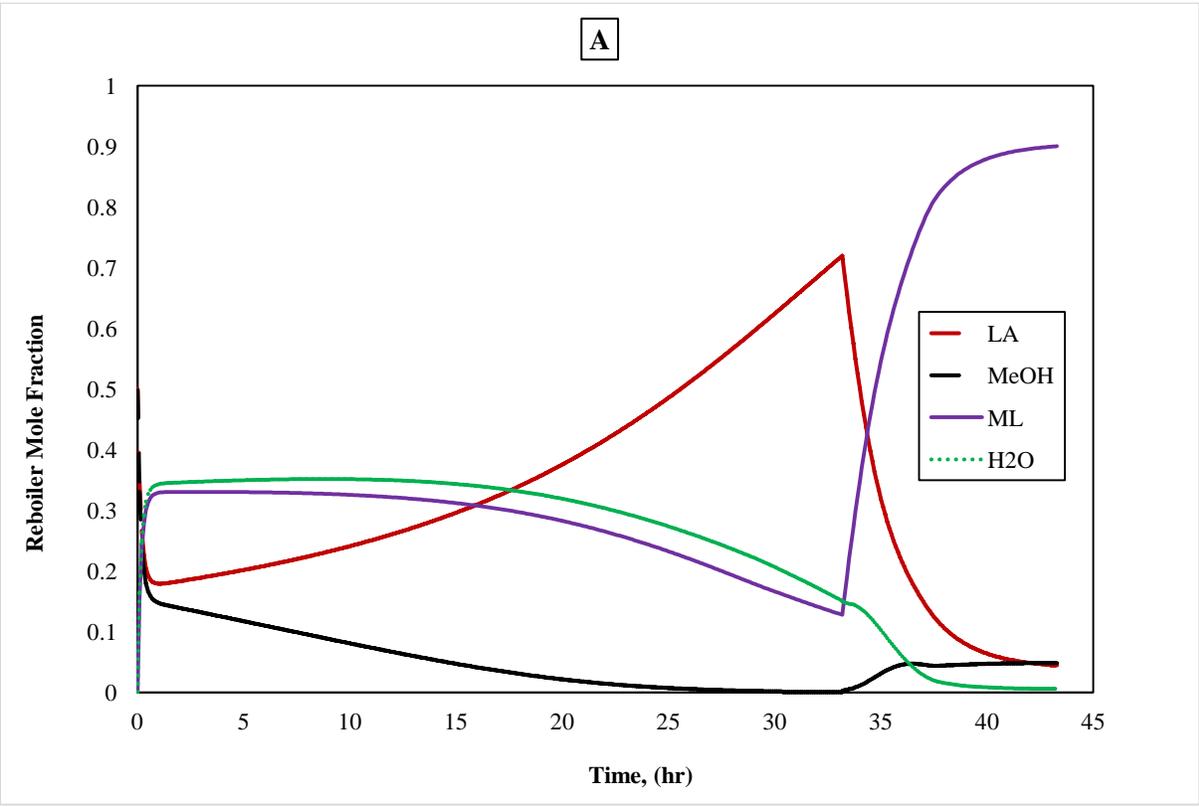


Figure 6: The reboiler and accumulator composition profiles of i-CBD, $RV = 2$ ($X_{ML}^* = 0.9$).

5.2 SBD Column

Most recently Aqar et al. (2016) suggested semi-batch distillation (SBD) column with continuous feeding of methanol for ML synthesis with maximum ML purity of 0.85 mole fraction. The purpose of studying SBD column again in this paper is to make a direct comparison of the performance by SBD column with i-SBD column (presented in the later part) where the maximum purity of ML is set to 0.90 mole fraction. Note, the problem specifications of SBD process and the holdup distribution assumptions are the same as those for i-CBD column (see section 4.1) and the composition of methanol fed stream is 0.95 mole fraction. Note, the difference in specifications in this work and in SBD of Aqar et al. (2016). They considered pure external methanol feed while this work considered external methanol feed is 95% pure (the remainder is water) which is the composition of the recovered (and recycled) methanol from the CBD of i-SBD. Also, the bottom product amount is set as 2.3 kmol in this work compared to 2.5 kmol and the column initialization of this work is different to Aqar et al. (2016).

Here, two case studies are considered. Case 1 uses single reflux interval while case 2 uses multiple reflux intervals for reflux ratio.

5.2.1 Case 1: Optimal Operation using Single Reflux Interval (RV=1)

Table 9 displays optimal reflux ratio and methanol feed rate profiles, maximum allowable reflux ratio, minimum batch time, total energy consuming, and maximum conversion (%) of LA to ML, as well as total amount of methanol feed rate for different bottom product purities of ML. For all cases, the amount of bottom product to be achieved is set at 2.3 kmol (same as i-CBD column). It can be observed that as the purity of ML increases from 0.70 to 0.90 mole fraction, final batch time, heat consumption rate and the MeOH feed rate increase together with the total amount of methanol fed and conversion of LA except the case with 0.90 mole fraction. For the last case, there is a sharp increase in reflux ratio and production time leading to higher total energy consumption and total amount of methanol fed (although methanol fed rate decreased for this case).

Note, the maximum reflux ratio (R_{Max}) is computed from different values of the optimal methanol feed rate. For all cases, the values of R_{Max} are greater than actual reflux ratio ensuring no overflowing of reboiler.

Table 9. Optimal Operation results for SBD column using $RV = 1$.

X_{ML}^*	Optimal Methanol Feed, F_{MeOH} kmol/hr	Optimal Reflux Ratio, R	Maximum Reflux Ratio, R_{Max}	Batch Time, t_p , hr	Total energy E_{tot} , GJ	Conversion of LA (%)	Total Amount of Fed MeOH, F_t kmol
0.70	0.68	0.493	0.727	4.60	0.471	77.84	3.13
0.75	0.82	0.463	0.672	5.18	0.518	81.05	4.25
0.80	1.01	0.415	0.595	6.00	0.582	86.72	6.07
0.85	1.15	0.421	0.540	9.06	0.836	92.12	10.4
0.90	0.97	0.571	0.614	25.1	2.222	95.30	24.3

At the end of the batch, the bottom mole fraction, the accumulator mole fraction, and its corresponding amount for different ML purities are shown in Table 10. As can be seen that in the bottom product mainly contains ML with some unreacted lactic acid, while, it is mainly methanol and water in the distillate accumulator. Note, the distillate amount increases with increasing the ML composition due to increasing methanol feed and fixed bottom product amount (set to 2.3 kmol for all cases).

Table 10. The reboiler and distillate accumulator composition profiles and the accumulator amount at several purities of ML for SBD column using $RV = 1$.

Purity of ML	x_{LA}	x_{MeOH}	x_{H2O}	$*x_{LA}$	$*x_{MeOH}$	$*x_{ML}$	$*x_{H2O}$	H_a , kmol
0.70	0.259	0.016	0.025	2.46E-4	0.615	0.031	0.353	5.83
0.75	0.204	0.023	0.023	1.83E-4	0.647	0.028	0.324	6.95
0.80	0.143	0.036	0.021	1.25E-4	0.688	0.026	0.285	8.77
0.85	0.090	0.042	0.018	5.87E-5	0.781	0.025	0.193	13.12
0.90	0.048	0.042	0.010	4.14E-5	0.837	0.018	0.144	26.97

* The composition in the distillate tank (mole fraction).

The composition profiles of the reboiler and the distillate drum of SBD operation at product purity constraint ($x_{ML}^*=0.9$) are given in Figure 7-A and B for single interval strategy, respectively. It can be noticed from Figure 7-A that the composition of water (as the second light boiler) increases from zero and reaches to the higher value and then falls down to almost zero (due to strip off in the distillate receiver, Figure 7-B). Lactic acid as the heaviest boiling component is almost consumed through the reaction with methanol (in the bottom receiver) and producing higher LA conversion rate at the end of reaction (Figure 7-A, Table 9). In the still pot

drum, the composition of both the reactant elements, namely lactic acid and methanol, progressively decreases as long as the reaction continues. In the same operating time, ML starts moving up and finally, the bottom tank is enriched with methyl lactate having a maximum achievable purity of 0.9.

For each ML product composition specifications, the results in terms of number of batches (N_B), total yearly product (TYP), and annual capital cost (ACC), and operating cost (OC) for SBD column, as well as the profit (Profit) are provided in Table 11. As the number of batches (N_B) reduces with increasing the operating time (t_p) total production rate (TYP) decreases. As the product purity specification increases from (0.70 to 0.85 mole fractions) together with cost of ML product, the annual revenue increases progressively and are better than i-CBD in most cases. However, note, for 0.90 of product purity, there is a sharp reduction in the profit due to significant increase in the operating time and the cost of total amount of charged methanol (see Table 9). This makes SBD uncompetitive (compared to even the profit obtained by i-CBD) at higher product purity and hence the proposed i-SBD configuration.

Table 11. Profit results of optimal operation for different ML purities for SBD using $RV = 1$.

Purity of ML	Batch Time, hr	Number of Batches, N_B batch/yr	Total Yearly Product, kmol/yr	Product Amount, kmol/batch	Annualized Capital Cost, \$/yr	Operating Cost, \$/yr	Profit, \$/yr
0.70	4.59	1569.4	3610	2.3	29751.9	450	9427
0.75	5.18	1408.0	3238	2.3	29751.9	450	33584
0.80	5.99	1231.1	2831	2.3	29751.9	450	72197
0.85	9.06	836.9	1925	2.3	29751.9	450	77184
0.90	25.14	312.0	718	2.3	29751.9	450	15524

5.2.2 Case 2: Optimal Operation using Two Reflux Interval ($RV=2$)

Table 12 summarizes the optimum reflux ratio and methanol feed rate and profiles, optimal switching time, final operating time, the thermal heat consumption, the LA conversion and the total amount of fed methanol using two reflux intervals policy. It is evident from Table 12 that two reflux interval policy caused a reduction in the production time, the energy consumption, the amount feed of methanol and the LA conversion compared to one reflux interval. For 0.90 mole fraction purity the savings in the total amount of methanol, the batch time and the energy are about 67 %, 68 % and 66 % respectively compared to RV-1 policy (Case 1).

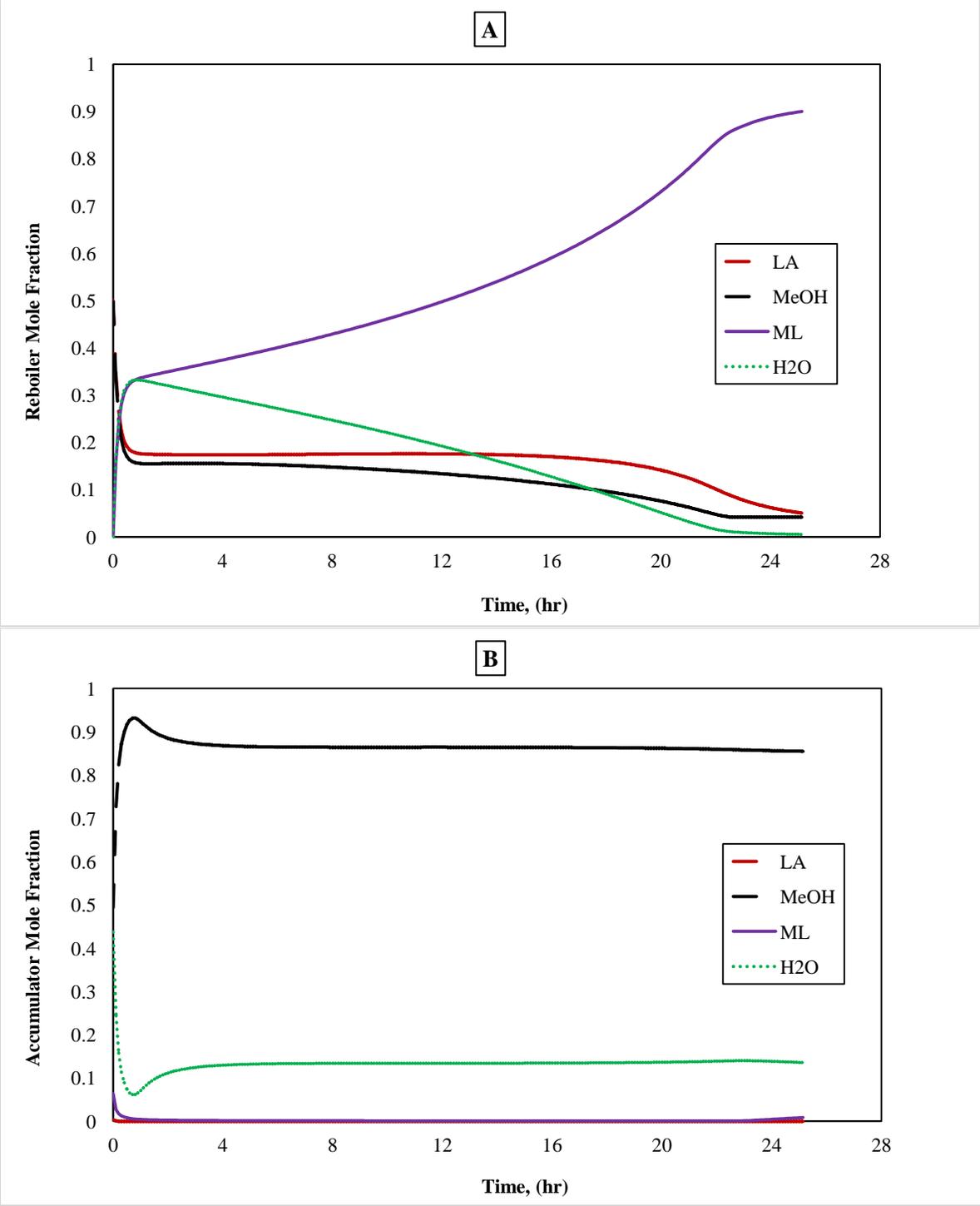


Figure 7: The reboiler and accumulator composition profiles of SBD, $RV = 1$ ($X_{ML}^* = 0.9$).

Figure 8 compares the batch time and energy consumption for all ML purities for both single and two-reflux operation policies. Note, the column runs at low reflux ratio in the first time interval for each ML purity consideration to drive water up the column, whereas, and the column operates at higher reflux ratio in the second interval to keep both chemical reactants (LA and MeOH) in the reaction zone to allow further reaction and to satisfy the specified purity. For all the purity conditions, the R_{Max} values are larger than the optimal values of (R_1 and R_2) preventing the reboiler overflow as shown in eq. (8).

Table 12. Optimal Operation results for SBD column using $RV = 2$.

X_{ML}^*	Reflux Ratios, R_1, R_2	MeOH Charge Rates, F_1, F_2 kmol/hr	First Time Interval, t_1 , hr	Second Time Interval, t_2 , hr	Batch Time, t_p , hr	Total Energy, E_{tot} , GJ	Conversion of LA (%)	Total Amount of Fed, F_t kmol
0.70	0, 0.494	0.36, 1.11	1.17	1.22	2.39	0.274	79.13	1.78
0.75	0.184, 0.718	1.19, 0	2.94	0.28	3.22	0.336	81.15	3.50
0.80	0.252, 0.889	1.19, 0	3.92	0.19	4.11	0.413	86.92	4.69
0.85	0.231, 0.715	1.41, 0	4.80	0.34	5.13	0.493	92.91	6.76
0.90	0.288, 0.660	1.20, 0.81	4.37	3.61	7.98	0.750	95.45	8.14

The reboiler and distillate composition profiles and corresponding amount of distillate for different ML purities are shown in Table 13. As can be seen, mainly ML and little unreacted lactic acid are left in the reboiler, whilst distillate accumulator contains mainly methanol and water. Note, the distillate amount in two reflux operation is less than that resulted in one reflux operation due to less amount of external methanol being required in the SBD in the latter case.

The results of Tables 12 and 13 are used to calculate the profitability of two reflux operation and these are presented in Table 14. For all ML purities, the profit for two reflux operation is much better than that of one reflux operation (Table 11). For the 0.9 of ML purity case, comparison of the maximum profit using RV-2 with those obtained using the RV-1 policy shows 94 % more profit due to low batch time required to achieve the desired purity specifications.

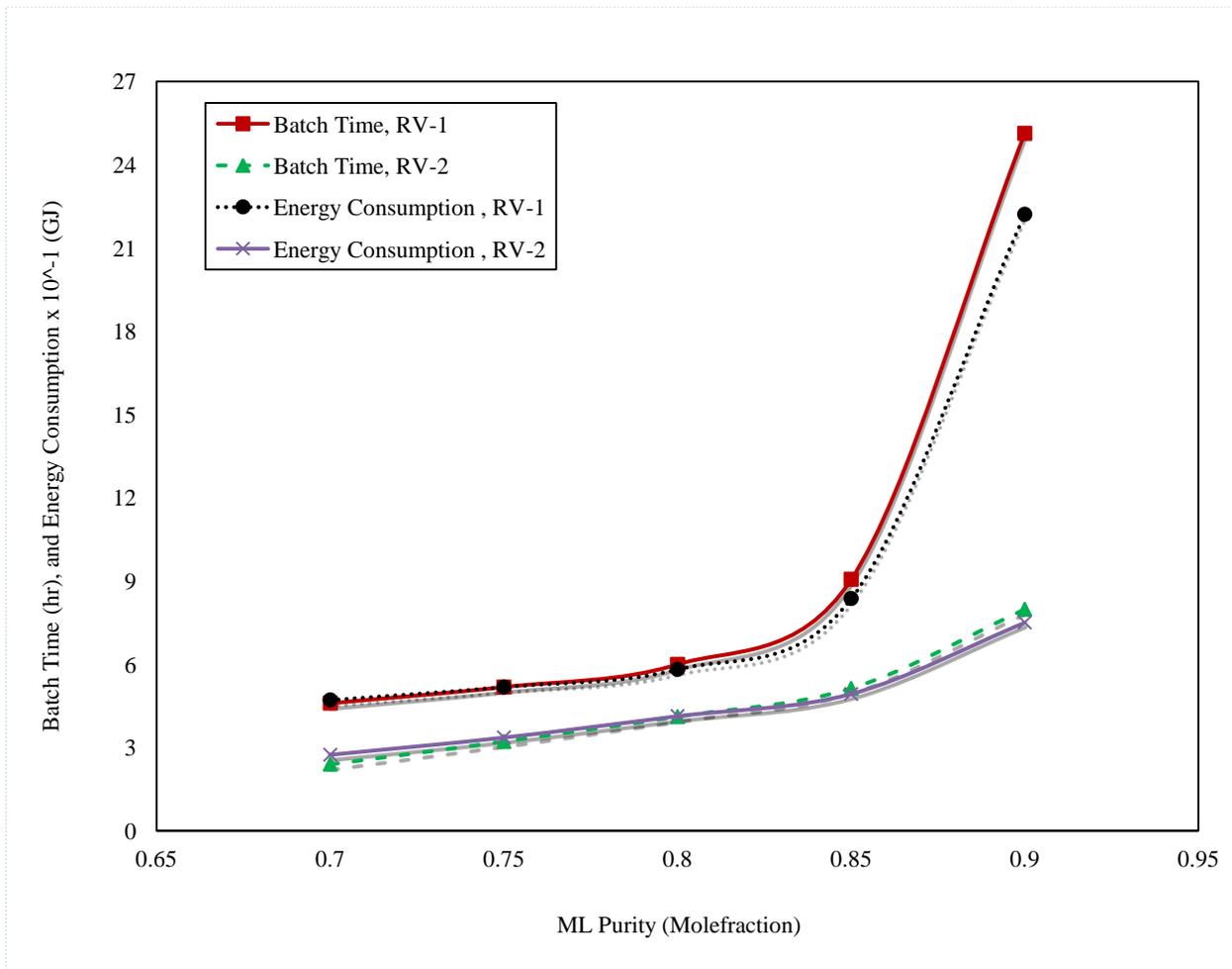


Figure 8: The final batch time and total thermal heat consumption profile for SBD.

Table 13. The reboiler and distillate accumulator composition profiles and the accumulator amount at several purities of ML for SBD column using RV = 2.

Purity of ML	X_{LA}	X_{MeOH}	X_{H_2O}	* X_{LA}	* X_{MeOH}	* X_{ML}	* X_{H_2O}	H_a , kmol
0.70	0.218	0.038	0.044	4.03E-3	0.478	0.075	0.447	4.48
0.75	0.211	0.020	0.019	2.46E-4	0.616	0.040	0.344	6.20
0.80	0.168	0.015	0.017	1.84E-4	0.646	0.036	0.318	7.39
0.85	0.135	0.008	0.006	1.12E-4	0.710	0.021	0.269	9.46
0.90	0.087	0.007	0.006	1.13E-4	0.712	0.019	0.269	10.8

* The composition in the distillate tank (molefraction).

Table 14. Profit results of Optimal Operation for different ML purities for SBD using $RV = 2$.

Purity of ML	Number of Batches, N_B batch/yr	Total Yearly Product, kmol/yr	Annualized Capital Cost, \$/yr	Operating Cost, \$/yr	Profit, \$/yr
0.70	2764.7	6359	29751.9	450	85320
0.75	2151.7	4949	29751.9	450	87081
0.80	1733.9	3988	29751.9	450	143234
0.85	1420.2	3266	29751.9	450	215269
0.90	943.3	2170	29751.9	450	293497

5.3 Performance of i-SBD Column

The feasibility of the i-SBD column (Figure 3) as an integrated process is discussed here in detail. The ML synthesis reaction takes place in SBD only. The CBD recovers methanol from the distillate of SBD at 0.95 mole fraction purity and which is fed back into the SBD column together with make-up methanol (same purity). Note, the column specifications and operating variables for both columns of i-SBD unit are the same as those in Table 1 except that the total number of stages (excluding condenser and partial reboiler) and vapour load to condenser in the CBD column are 4-plates and 1.5 kmol/hr respectively. Two scenarios are considered here, scenario 1 is with single reflux control interval, and scenario 2 is with two reflux intervals. As before, the ML product composition is varied from 0.70 to 0.90 mole fraction in each scenario with the reboiler product amount being kept constant at 2.3 kmol so that comparison of performances of i-SBD can be made with i-CBD and SBD in terms of maximum profit.

5.3.1 Scenario 1: Optimal Operation using Single Reflux Interval ($RV=1$)

The results of SBD column are the same as those presented in Tables 9-11. However, parts of these results are shown in Table 15 together with those obtained for CBD for convenience.

As can be seen from Table 15, increasing ML purity increases the amount of methanol fed to the CBD with higher composition of methanol (see Table 10) and thus increases the amount of methanol recovered from the CBD. As the methanol feed composition of the CBD increases, it reduces the reflux ratio (as the separation becomes easier). Since the total amount of methanol fed to SBD increases, the amount of make-up methanol also increases for the SBD column. Note, the make-up of methanol amount is calculated using the following form:

$$\text{Make-Up}_{\text{MeOH}} = F_{\text{MeOH}} - D_{\text{MeOH}} \quad (14)$$

Table 15. Optimal Operation results for i-SBD column using $RV = 1$.

SBD (1 st) Column			CBD (2 nd) Column			i-SBD Column		
X_{ML}^*	Optimal Methanol Feed, F_{MeOH} kmol/hr	Optimal Reflux Ratio, R_{SBD}	Total Amount of Fed MeOH, F_t , kmol	Feed Loading Amount, kmol	Optimal Reflux Ratio, R_{CBD}	Distillate Amount of MeOH, D_{MeOH} , kmol	Make-Up MeOH, kmol	Batch Time, t_p , hr
0.70	0.68	0.493	3.13	5.83	0.549	3.11	0.02	4.59
0.75	0.82	0.463	4.25	6.95	0.506	3.84	0.41	5.18
0.80	1.01	0.415	6.07	8.77	0.446	4.99	1.08	5.99
0.85	1.15	0.421	10.4	13.12	0.367	8.60	1.82	9.06
0.90	0.97	0.571	24.3	26.97	0.369	23.8	0.50	25.14

Table 16 shows the profitability of single reflux i-SBD operation. The results in Table 16 clearly show that the use of i-SBD system is significantly more profitable than both i-CBD and SBD columns in terms of using one reflux interval. For example, for the scenario with 0.9 mole fraction of ML the i-SBD system gave 78% and 82% higher annual profits compared to that of the i-CBD and SBD columns, respectively.

5.3.2 Scenario 2: Optimal Operation using Two Reflux Intervals ($RV=2$)

Similar to Table 15, Table 17 summarises the results for two reflux operation. The trend of the results of each column is qualitatively similar to those presented in Table 15. Figure 9 shows the make-up amount of methanol for different range of the product (ML) purity for both $RV=1$ and $RV=2$ policies. It can be observed that, the total make-up methanol amount achieved is 62% at ML purity of 90 % compared to that obtained by using the single-reflux policy.

Table 18 gives the summary of profitability of i-SBD process for two reflux operation. The profit of i-SBD operation with two reflux ratio intervals is about 75% more compared to the single reflux i-SBD operation due to low operating time and quantity of MeOH make-up charge which are required to achieve the product specification (0.9 molefraction). For all product purities, the annual capital and the utility costs of the i-SBD operation remained the same for both scenarios.

Table 16. Profitability for i-SBD using RV = 1.

Purity of ML	Total Annualized Capital Cost, \$/yr	Total Operating Cost, \$/yr	Profit, \$/yr
0.70	47685.7	720	50718
0.75	47685.7	720	81238
0.80	47685.7	720	128800
0.85	47685.7	720	146710
0.90	47685.7	720	87691

Table 17 .Optimal Operation results for i-SBD column using RV = 2.

1 st Column (SBD)				2 nd Column (CBD)			i-SBD Column	
X_{ML}^*	MeOH Charge Rates, F_1, F_2 kmol/hr	Reflux Ratios, $R_{SBD1}R_{SBD2}$	Total Amount of Fed, F_t kmol	Feed Loading Amount, kmol	Reflux Ratio, R_{CBD}	Distillate Amount, D_{MeOH} , kmol	Make-Up MeOH, kmol	Batch Time, t_p , hr
0.70	0.36, 1.11	0, 0.494	1.78	4.48	0.691	1.11	0.67	2.39
0.75	1.19, 0	0.184, 0.718	3.50	6.20	0.495	2.44	1.06	3.22
0.80	1.19, 0	0.252, 0.889	4.69	7.39	0.461	3.32	1.37	4.11
0.85	1.41, 0	0.231, 0.715	6.76	9.46	0.392	4.69	2.07	5.13
0.90	1.20, 0.81	0.288, 0.660	8.14	10.8	0.430	6.82	1.32	7.98

Table 18. Profit results of Optimal Operation for different ML purities for i-SBD using RV = 2.

Purity of ML	Total Annualized Capital Cost, \$/yr	Total Operating Cost, \$/yr	Profit, \$/yr
0.70	47685.7	720	104494
0.75	47685.7	720	132760
0.80	47685.7	720	188653
0.85	47685.7	720	278156
0.90	47685.7	720	353681

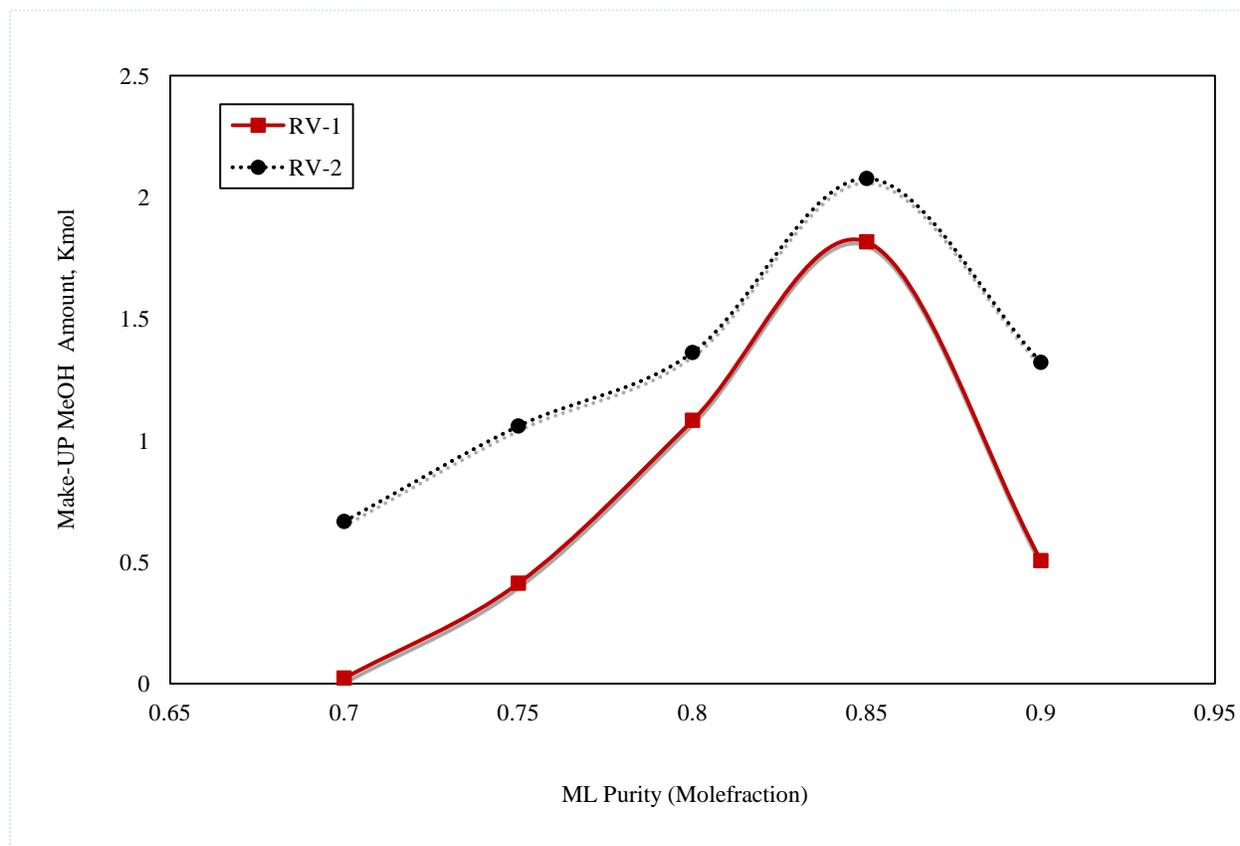


Figure 9: The Make-Up methanol amount for i-SBD.

5. Conclusions

In this work ML synthesis via the esterification of LA is considered. Due to large variation in boiling points between the chemical reactants, the efficacy of performing batch reactive column is a quite limited because of the depletion of methanol from the reaction zone. The reverse reaction is activated as the operation progresses due to the loss of methanol reactant (one of the forward reaction reactants), causing a significant reduction in the conversion level of LA into ML. In order to face this type of the challenging problem, two novel batch reactive column configurations are proposed here and they are: (1) i-CBD column and (2) i-SBD column. The performances of these configurations are evaluated in terms of profitability under single and multi-reflux operation mode. A detailed dynamic model for the process is incorporated in the optimisation framework within gPROMS and the optimization problem is solved for different values of ML purity ranging from 0.70 to 0.90 molefraction. Piecewise constant reflux ratio, methanol recycled rate strategy (for i-CBD only), and methanol feed rate strategy (for both SBD,

and i-SBD) are considered. Clearly, the integrated batch distillation operations are found to outperform the classical batch operations (CBD or SBD columns) to achieve higher ML purity constraints with lower batch time and energy usage, and higher annual profit. Also, the optimization results for a given separation task illustrate that using multi-reflux intervals is more attractive policy compared to a single reflux interval in terms of batch time and energy savings, and highest achievable revenue in the i-SBD operation. For instance, the batch time and total energy savings achieved are 68 % and 66 % and the maximum achievable profit improvement is about 75% at ML purity of 0.9 molefraction compared to that obtained by using single reflux interval policy. Also, i-SBD outperforms i-CBD in many respect.

Notation

ACC	Annualised capital cost (\$/yr)
C_{LA}	Cost of reactant lactic acid (\$/kmol)
C_{MeOH}	Cost of reactant methanol (\$/kmol)
$C_{MeOH\ Charge}$	Cost of methanol charge (\$)
$C_{Make-Up\ MeOH}$	Cost of makeup methanol (\$)
C_{ML}	Cost of methyl lactate (\$/kmol)
C_R	Cost of reactant (\$/kmol)
CVP	Control vector parameterisation
D	Distillate product (kmol)
DAEs	Differential algebraic equations
E_{tot}	Total Energy Consumption (GJ)
F_{MeOH}	Methanol feed rate (kmol/hr)
H_L, H_V	Liquid, vapor enthalpy (kJ/kmol)
L	Liquid rate in the column (kmol/hr)
H_a, H_C	Accumulator and condenser holdup respectively (kmol)
H, H_N	Stage and re-boiler holdup respectively (kmol)
N	Number of stages
N_B	Number of batches/yr
OC	Operating cost/year (\$/batch)
OP	Optimisation

P	The net Profit for different column schemes (\$/yr)
Q_C, Q_{reb}	Condenser or reboiler duty (kJ/hr)
R_1, R_2	Reflux ratio in time interval 1, and 2 for i-CBD
R_{SBD1}, R_{SBD2}	Reflux ratio in time interval 1, and 2 for semi-batch column of i-SBD
R, R_{Max}	Reflux ratio and maximum reflux ratio
R_{MeOH}	Recycled Methanol rate from the SBD to CD column in i-SBD (kmol/hr)
RV	Number of control intervals
S_{MeOH}	Recycled Methanol rate (kmol/hr)
S_1, S_2	Recycled Methanol rate in time interval 1, and 2 for i-CBD (kmol/hr)
SQP	Successive quadratic programming algorithm
t, t_p	Batch time, final batch time (h)
t_1, t_2	Length of interval 1, and 2 and (hr)
V	Vapor flow rate in the column (kmol/hr)
x	Liquid composition (mole fraction)
x_a	Accumulated distillate composition (mole fraction)
x_D	Instant distillate composition (mole fraction)
y	Vapor composition (mole fraction)

Greek Letters

Superscripts and subscripts

i	Component number
j	Plate number
Δn	Change in moles due to chemical reaction

6. References

- Adams, T. A. & Seider, W. D. (2008). Semicontinuous distillation for ethyl lactate production. *AIChE Journal*, 54, 2539-2552.
- Aqar, D. Y., Rahmanian, N. & Mujtaba, I.M. (2016). Methyl Lactate Synthesis using Batch Reactive Distillation: Operational Challenges and Strategy for Enhanced Performance. *Separation and Purification Technology*, 158, 193–203.
- Alibaba Trade, (2016). Available at: <http://www.alibaba.com/trade> (Accessed On: 30 March 2016).
- Cuille, P.E. & Reklaitis, G.V. (1986). Dynamic simulation of multicomponent batch rectification with chemical reactions, *Computers & Chemical Engineering*, 10, 389-398.

- Dassy, S., Wiame, H. & Thyron, F. C. (1994). Kinetics of the liquid phase synthesis and hydrolysis of butyl lactate catalysed by cation exchange resin. *Journal of Chemical Technology and Biotechnology*, 59, 149-156.
- Delgado, P., Sanz, M. T., Beltrán, S., & Núñez, L. A. (2010). Ethyl lactate production via esterification of lactic acid with ethanol combined with pervaporation. *Chemical Engineering Journal*, 165, 693-700.
- Edreder, E.A., Emtir, M.M, Mujtaba, I.M. (2008). Improving the maximum conversion of ethanol esterification, *Chemical Product and Process Modeling*, The Berkeley Electronic Press, vol. 3, Issue 1, Art. 36.
- Engin, A., Haluk, H., & Gurkan, K. (2003). Production of lactic acid esters catalyzed by heteropoly acid supported over ion-exchange resins. *Green Chemistry*, 5, 460-466.
- gPROMS, (2015). gPROMS Advanced User Guide. Process Systems Enterprise Ltd., London.
- Kao, Y.-L. & Ward, J. D. (2015). Batch Reactive Distillation with Off-Cut Recycling. *Industrial & Engineering Chemistry Research*, 54, 2188-2200.
- Kumar, R. & Mahajani, S. M.(2007). Esterification of lactic acid with n-butanol by reactive distillation. *Industrial & Engineering Chemistry Research*, 46, 6873-6882.
- Lang, P., Yatim, H., Moszkowics, P. & Otterbein, M. (1994). Batch extractive distillation under constant reflux ratio. *Computers & chemical engineering*, 18, 1057-1069.
- Mujtaba, I. & Greaves, M. (2006). Neural Network Based Modelling and Optimisation in Batch Reactive Distillation. *INSTITUTION OF CHEMICAL ENGINEERS SYMPOSIUM SERIES*, Institution of Chemical Engineers; 1999, 868.
- Mujtaba I.M, Macchietto S., (1997). Efficient optimisation of batch distillation with chemical reaction using polynomial curve fitting techniques, Mujtaba I.M, Macchietto S., (1997). Efficient optimisation of batch distillation with chemical reaction using polynomial curve fitting techniques, *Ind. Eng. Chem. Res.*, 36, pp 2287.
- Mujtaba, I.M. (2004). *Batch distillation: Design and operation*. London: Imperial College Press.
- Toor, A. P., Sharma, M., Thakur, S. & Wanchoo, R. K. (2011). Ion-exchange resin catalyzed esterification of lactic acid with isopropanol: a kinetic study. *Bulletin of Chemical Reaction Engineering & Catalysis*, 6, 39-45.
- Yadav, G. D. & Kulkarni, H. B. (2000). Ion-exchange resin catalysis in the synthesis of isopropyl lactate. *Reactive and Functional Polymers*, 44, 153-165.
- Zhang, Y., MA, L. & Yang, J. (2004). Kinetics of esterification of lactic acid with ethanol catalyzed by cation-exchange resins. *Reactive and Functional Polymers*, 61, 101-114.

Appendix

The profit function (\$/yr) can be defined as:

$$P_{i-CBD} (\$/yr) = (C_{ML} B_f - C_R B_0 - OC) \times N_B - ACC \quad (15)$$

$$P_{SBD} (\$/yr) = (C_{ML} B_f - C_R B_0 - OC - C_{MeOH \text{ Charge}}) \times N_B - ACC \quad (16)$$

$$P_{i-SBD} (\$/yr) = (C_{ML} B_f - C_R B_0 - OC_{i-SBD} - C_{MakeUP_{MeOH}}) \times N_B - ACC_{i-SBD} \quad (17)$$

$$OC (\$/batch) = \left(\frac{K_3 V_L}{A_P} \right) \times (t_p + t_s) \quad (18)$$

$$OC_{i-SBD} (\$/batch) = OC_{SBD} + OC_{CBD} \quad (19)$$

$$N_B \text{ (batch / yr)} = \frac{(H_p / \text{yr})}{(t_p + t_s)} \quad (20)$$

$$\text{ACC} (\$/\text{yr}) = K_1 (V_L)^{0.5} (N)^{0.8} + K_2 (V_L)^{0.65} \quad (21)$$

$$\text{ACC}_{i\text{-SBD}} (\$/\text{yr}) = \text{ACC}_{\text{SBD}} + \text{ACC}_{\text{CBD}} \quad (22)$$

$$\text{TYP} \text{ (kmol/yr)} = N_B \times B_f \quad (23)$$

$$C_R = C_{LA} + C_{\text{MeOH}} \quad (24)$$

$$C_{\text{MeOH Charge}} (\$) = F_t \times C_{\text{MeOH}} \times z_{\text{MeOH}} \quad (\text{For SBD column}) \quad (25)$$

$$C_{\text{MakeUP}_{\text{MeOH}}} (\$) = (F_t - D_{\text{MeOH}}) \times C_{\text{MeOH}} \times z_{\text{MeOH}} \quad (\text{For i-SBD column}) \quad (26)$$

Where, OC is operating cost (\$/batch), N_B (batch/yr) is the total number of batches produced per year, ACC is Annualised capital cost (\$/yr), TYP is Total Yearly Product (kmol/yr), Constant for annualised capital costs equation (K_1) = 1500; Constant for annualised capital costs equation (K_2) = 9500; Utility costs coefficient constant for operating cost equation (K_3) = 180; the operating cost constant (A_p) = 8000; setup time (t_s) = 0.5 hr; Production horizon (H_p) = 8000 hr/yr.