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Methyl Lactate Synthesis using Batch Reactive Distillation: Operational Challenges and Strategy for Enhanced Performance

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Abstract

Batch reactive distillation is well known for improved conversion and separation of desired reaction products. However, for a number of reactions, the distillation can separate the reactants depending on their boiling points of them and thus not only reduces the benefit of the reactive distillation but also offers operational challenges for keeping the reactants together. Methyl lactate (ML) synthesis via the esterification of lactic acid (LA) with methanol in a reactive distillation falls into this category and perhaps that is why this process has not been explored in the past. The boiling points of the reactants (LA, methanol) are about 490 K and 337 K while those of the products (ML, water) are 417 K and 373 K respectively. Clearly in a conventional reactive distillation (batch or continuous) methanol will be separated from the LA and will reduce the conversion of LA to ML significantly.

Here, first the limitations of the use of conventional batch distillation column (CBD) for the synthesis of ML is investigated in detail and a semi-batch reactive distillation (SBD) configuration is studied in detail where LA is the limiting reactant and methanol is continuously fed in excess in the reboiler allowing the reactants to be together for a longer period. However, this poses an operational challenge that the column has to be carefully controlled to avoid overflow of the reboiler at any time of the operation. In this work, the performance of SBD for the synthesis of ML is evaluated using model based optimization in which operational constraints are embedded. The results clearly demonstrate the viability of the system for the synthesis of ML.

Keywords: Dynamic Modelling, Optimization, Methyl Lactate, Conventional Reactive Distillation, Semi-Batch Reactive Distillation, Esterification

1. Introduction

Since lactic acid (LA) can be manufactured easily by fermentation or by chemical synthesis from many carbohydrates, the conversion of LA into its esters is worth studying (Filachione et al., 1945). Methyl lactate (ML) is a clear and colorless liquid having a characteristic odor (cool mint). ML is a useful product as chiral pharmaceuticals and agrochemicals, green solvent, cleaning agent, plasticizer agent, or intermediate and its two functional groups can be utilized to prepare numerous derivatives. In general, it constitutes a powerful component which has good possibilities of application at industrial levels, food industries, personal-care and cosmetic (makeup, shampoos, hair dyes and colors, etc.) applications (Ullmann's Encyclopedia, 1985; Gelbard, 2005; and Acton, 2013).

The global market for lactate ester products were 2505 kilotons in year 2013 and are expected to be around 3569.6 kilotons by year 2020. Lactate esters accounted for 30% of total market volume in 2013 and emerged as the leading product segment. Increasing demands for lactate esters are expected to have a positive influence on the market growth (Grand View Research, 2015). There are several reaction schemes which can be used to produce ML and some of these are listed in Table 1.

Table 1. Several proposed reaction schemes for methyl lactate production.

| Reaction Scheme | Reference |
|---|---------------------------|
| $LA + MEOH \rightleftharpoons ML + H_2O$ | (Sanz et al., 2004) |
| $EL + MEOH \rightleftharpoons ML + ETOH$ | (Özen, 2004) |
| $AmL + MEOH \Rightarrow ML + AM$ | (Filachione et al., 1945) |
| $AgL + CH_3Cl \Rightarrow ML + AgCl$ | (Özen, 2004) |
| $GLA \text{ or } DHA \Rightarrow HC \Rightarrow ML$ | (West et al., 2010) |

The esterification process of LA (impure) with many alcohols to yield lactate ester is not new. For example, studies on esterification reaction of LA with ethanol to form ethyl lactate (EL) were investigated by Zhang et al. (2004) and Delgado et al. (2007). Adams and Seider (2008) proposed a semi-batch reactive distillation (SBD) process for the production of EL from ethanol and LA. Yadav et al (2000) and Toor et al (2011) studied the esterification of LA with isopropanol to synthesize isopropyl lactate. A number of researchers also discussed the reaction

of LA with n-butanol to produce n-butyl lactate (Charles and Gabriel, 1928; Dassy et al., 1994; Kumar and Mahajani, 2007).

In the past, purification of impure LA has been considered in reactive distillation (batch or continuous) as a two-step process: esterification of impure LA into ML followed by hydrolysis of methyl lactate into pure lactic acid (Kim et al., 2000; Kumar et al., 2006 a; Kumar et al., 2006 b). However, the main focus of their study was the production of lactic acid and not the methyl lactate (see Figure 1). Also interestingly, although some of these work mentioned the requirement of removal of large amount of water in the esterification step (due to dilute LA feed and subsequent production of water) before the separation of ML for the hydrolysis step, no one appreciated the difficulty of keeping methanol and the LA together in the reboiler to enhance the conversion of LA to ML. To overcome the water removal problem, Thotla and Mahajani (2009) proposed a reactive distillation configuration with water side draw using both continuous and semi-batch columns, for the esterification step to enhance the conversion of LA. However, they also did not appreciate the difficulty of keeping methanol and the LA together in the system which could further enhance the conversion of LA.

With the above backdrop, it is attempted to focus again at the esterification step in detail with the objective of enhanced production and recovery of ML rather than focusing on the purification of LA which has already received quite a bit of attention in recent years (Edreder et al., 2011; Mujtaba et al., 2012). Here, first, the limitations of CBD column are explored for the synthesis of ML. Then the enhancement of the conversion of LA into ML is looked at by continuously feeding methanol into a SBD column and dealt with the operational challenge due to this mode of operation. The ultimate aim was to obtain the best operational strategy of SBD for the synthesis of ML. Note, like others the recovery of water is not attempted or suggested before the recovery of ML. Rather, the proposed strategy will produce ML and water simultaneously in the reboiler and in the distillate. To achieve the above the model based techniques are adopted. A detailed dynamic model based on mass and energy balances is considered and incorporated into the optimization framework within gPROMS (general PROcess Modeling System, 2013) software. The performance of SBD is evaluated in terms of minimum batch time and energy consumption for the production of ML. In order to avoid overloading of the reboiler due to additional methanol feeding, an operation constraint is added into the optimization framework. The dynamic optimization problem was transformed to a nonlinear programming problem and

solved by using Control Vector Parameterization (CPV) technique using efficient sequential quadratic programming (SQP) method within gPROMS (further details about this technique can be found in Mujtaba, 2004). Reflux ratio and methanol feed rate are considered as the control variables of the system and piecewise-constant control strategy is used in the optimization study.

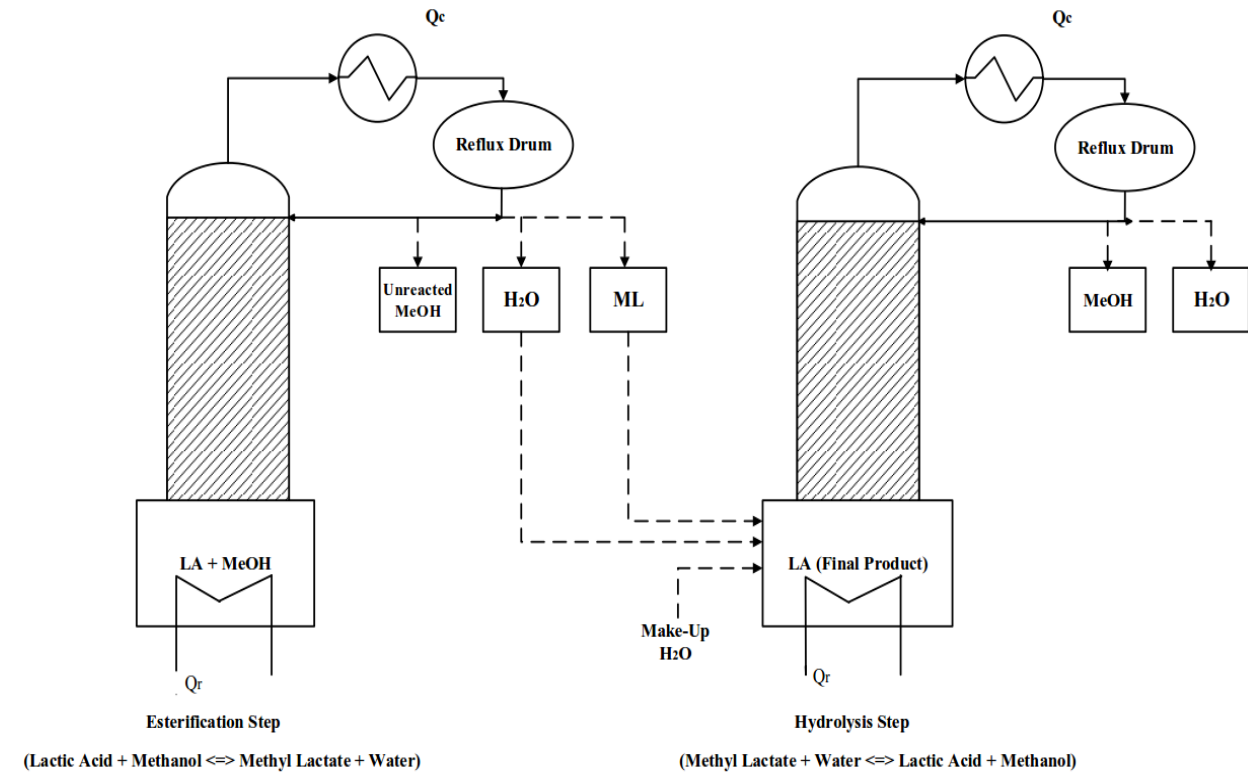


Figure1. Schematic flow diagram of batch operation of Lactic acid production.

2. Operation modes and energy consumption

Mujtaba (2004) reported different modes to operate batch distillation column: (A) Constant vapor boil-up rate mode, (B) Constant reboiler duty mode and (c) Constant condenser vapor load rate mode. For each mode, Mujtaba et al. (2012) suggested the following equations to calculate the total energy consumption in the column:

$$\text{Mode A: } Q_T = V \int_0^{t_f} \lambda_r dt \quad (1)$$

$$\text{Mode B: } Q_T = Q_r \times t_f \quad (2)$$

$$\text{Mode C: } Q_T = \int_0^{t_f} Q_r dt \quad (3)$$

Where λ_r is the heat of vaporisation which changes with time as the reboiler composition changes. In this work, the operation mode (C) is considered when the vapor load to the condenser (V_C) is kept constant. Note the reboiler heat duty (Q_r) gradually increases in this mode to maintain the constant vapour boil-up rate and vapour load to the condenser. This mode of operation has been widely used by others in the past. Nad and Spigel (1987) maintained this constancy of vapour load in their experimental column by making an enthalpy balance around the condenser system with appropriate control to adjust the heat load to the reboiler. Wakge and Reklaitis (1999) also used this operation mode. Further details on this type of operation can be found in Mujtaba (2004). Differentiation of Equation (3) gives:

$$\frac{dQ_T}{dt} = Q_r \quad (4)$$

The above differential equation is added to the model equations presented in the next section. Q_T at the end of batch time (t_f) will give the total energy consumption of the process.

3. Process model

With reference to the SBD column configuration shown in Figure 2, the model equations are presented here. The model contains mass and energy balances with constant molar holdup, chemical reaction on the stages, in the reboiler and in the total condenser and rigorous thermodynamic properties. The column stages are counted from the top down. The main model assumptions are (a) negligible vapor holdup, (b) no heat loss (adiabatic process), (c) constant a molar hold-up on all stages and in the condenser vessel, (d) perfect mixing on all column stages, (e) fast energy dynamics, (f) constant operating pressure and total condensation with no sub-cooling. The model equations of semi-batch reactive distillation which describe the physical and chemical process are presented below:

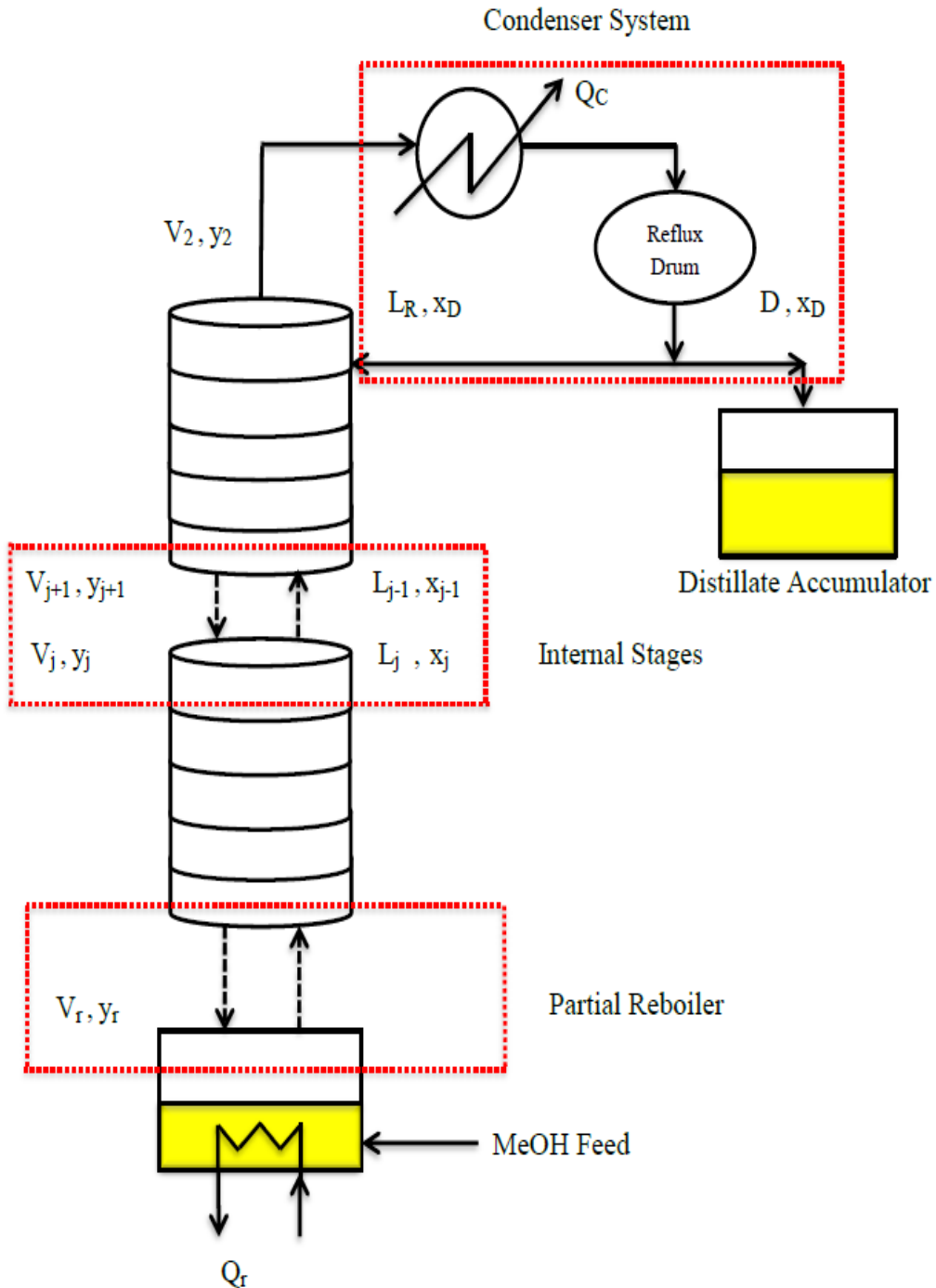


Figure 2: Schematic diagram of Semi-Batch Distillation Column (SBD) showing stream parameters.

3.1. Condenser System and Distillate Accumulator: $j=1$

- Distillate Accumulator Total Mass Balance:

$$\frac{dM_a}{dt} = D \quad (5)$$

- Component Mass Balance:

a) Distillate Accumulator:

$$M_a \frac{dx_{ai}}{dt} = D (x_{Di} - x_{ai}) \quad (6)$$

b) Condenser Holdup Tank:

$$M_C \frac{dx_{ai}}{dt} = V_2 y_2 - (V_2 + \Delta n_1 M_C) x_{Di} + r_{i1} M_C \quad (7)$$

- Energy Balance:

$$0 = V_2 H_2^V - (V_2 + \Delta n_1 M_C) h_1^L - Q_C \quad (8)$$

- Physical Properties and other equations:

$$h_1^L = h_1^L(x_{D1}, T_1, P) \quad (9)$$

$$T_1 = T_1(x_{D1}, P) \quad (10)$$

$$r_{i1} = r_{i1}(k_e, x_{Di}) \quad (11)$$

$$\Delta n = \sum r_{i1} \quad (12)$$

$$L_1 = R (V_2 + \Delta n_1 M_C) \quad (13)$$

$$D = (1 - R) (V_2 + \Delta n_1 M_C) \quad (14)$$

3.2. Internal Stages: j= 2 to N-1

- Total Mass Balance:

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j M_j \quad (15)$$

- Component Balance:

$$M_j \frac{dx_j}{dt} = L_{j-1} x_{j-1} + V_{j+1} y_{j+1} - L_j x_j - V_j y_j \quad (16)$$

- Energy Balance:

$$0 = L_{j-1} H_{j-1}^L + V_{j+1} H_{j+1}^V - L_j H_j^L - V_j H_j^V \quad (17)$$

- Phase Equilibrium Relation:

$$y_{i,j} = K_{i,j} x_{i,j} \quad (18)$$

- Restrictions:

$$\sum y_{i,j} = 1 \quad (19)$$

- Relations Defining Physical Properties and Chemical Reactions:

$$K_{i,j} = K_{i,j}(y_{i,j}, x_{i,j}, T_j, P) \quad (20)$$

$$H_{i,j}^L = H_{i,j}^L(x_{i,j}, T_j, P) \quad (21)$$

$$H_{i,j}^V = H_{i,j}^V(y_{i,j}, T_j, P) \quad (22)$$

$$r_{i,j} = r_{i,j}(k_e, x_{i,j}) \quad (23)$$

$$\Delta n_j = \sum r_{i,j} \quad (24)$$

3.3. Partial Reboiler: j=N

- Total Mass Balance:

$$\frac{dM_N}{dt} = L_{N-1} + V_N + F + \Delta n_N M_N \quad (25)$$

- Component Mass Balance:

$$M_N \frac{dx_N}{dt} = L_{N-1}(x_{N-1} - x_N) + V_N(y_N - x_N) + F(x_f - x_N) + M_N r_N \quad (26)$$

- Energy balance:

$$0 = L_{N-1}(H_{N-1}^L - H_N^L) + V_N(H_N^V - H_N^L) + F(H^f - H_N^L) + Q_r \quad (27)$$

- The conversion of lactic acid into methyl lactate (%):

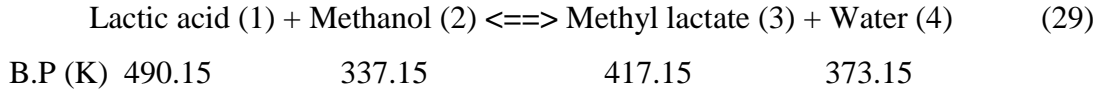
$$\text{LA Conversion (\%)} = \frac{\text{Moles of LA reacted}}{\text{Moles of LA feeded}} \times 100 \quad (28)$$

Note, the other equations for the partial reboiler are similar to the internal stages equations (18-24) where j replaced by N. Further details on some of the thermos-physical and kinetic equations are provided in the following sections. Note, the CBD process model will be exactly same as the SBD process model presented above except that the additional feed (F) terms to the reboiler equations will be zero.

4. The ML kinetic model

The esterification of LA and hydrolysis of LA ester kinetic studies are very important for the proper design of batch reactive operation. Several investigators have explored only the kinetics of LA esterification with methanol in the past (Choi et al., 1996; Seo and Hong, 2000; Sanz et al., 2002; Kumar et al., 2006b; and Jiang et al., 2010. Sanz et al. (2004) studied the kinetic

behaviour of LA esterification and ML hydrolysis by analysing three different models, the quasi-homogeneous (QH), the Langmuir-Hinshelwood (LH), and the Eley-Rideal (ER) models. The synthesis of ML was carried out via esterification of LA with methanol (MeOH) (Equation 29) over an acid catalyst such as the cation-exchange resin Amberlyst 15. Boiling point temperature of each components are also shown in Equation 29.



A quasi-homogeneous (QH) activity ($a_i = \gamma_i x_i$) based on kinetic model is used and can be written as:

$$-r_{ML} = m_{cat} \left[1.16 \times 10^6 \exp\left(\frac{-48.52}{RT}\right) a_{LA} a_{MeOH} - 1.65 \times 10^5 \exp\left(\frac{-50.91}{RT}\right) a_{ML} a_{H_2O} \right] \quad (30)$$

The QH model considers catalysis of liquid-phase reactions by ion-exchange resins close to homogeneous catalysis based on the Helfferich approach. This model provides a good description for the kinetic behavior of the global system where one of the reactants or the solvent is highly polar; therefore, this model is used in this study.

5. Vapor-liquid equilibrium (VLE)

K-values (VLE constants) are calculated from (Eq. 36) where γ_i is computed from UNIQUAC equation. The enthalpy of component in vapour phase can be computed using empirical equations is given by Aspen HYSYS[®] (HYSYS, 2013):

$$h_{vi} = (a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + a_5 T^5) M_{wti} \quad (31)$$

$$H_{vi} = \sum y_{j,i} h_{vi} \quad (32)$$

Where, $a_0, a_1, a_2, a_3, a_4,$ and a_5 are the constants of vapour enthalpy taken from Aspen HYSIS[®] package. The liquid phase enthalpies were obtained by subtracting the latent heat from the vapour enthalpies:

$$H_{Li} = \sum x_{j,i} (H_{vi} - \lambda_i) \quad (33)$$

The heat of vaporization (the latent heat) can be written as follow:

$$\lambda_i = \lambda_{bi} \left(\frac{1 - T_{r1}}{1 - T_{r2}} \right)^{0.38} \quad (34)$$

The vapour-liquid phase equilibrium (the activity coefficients) was computed using the UNIQUAC model with the binary interaction parameters are given in Sanz et al. (2003) are summarized in the Appendix. The vapour phase was assumed to be ideal.

The vapour pressure (P_i^{sat}) of pure components has been obtained by using Antoine's equation:

$$\text{Log } P_i^{\text{sat}} = A - \frac{B}{T + C} \quad (35)$$

Where A, B, C are the constants for the Antoine equations and T is the temperature in Kelvin. All physical and thermodynamic properties of pure components and Antoine constants were taken from Sanz et al. (2003) and are listed in Appendix.

$$K = \gamma_i \frac{P_i^{\text{sat}}}{P} \quad (36)$$

6. Formulation for optimization problem

In this case study, the aim of the optimization problem of the CBD/SBD column is to minimize the operating time for a given amount of desired product (ML) and purity of product.

The optimization problem can be described as:

- Given: The CBD/SBD column configuration, the feed composition, condenser hold-up, distillate rate, a separation task (i.e. obtain the product with desired purity specification for a key product component).
- Optimize: the reflux ratio (R_t), and the feed rate (F) profiles (for SBD only)
- So as to minimize: the batch operating time.
- Subject to: Process constraints (reboiler overloading, etc.), Model equations (Equality and inequality constraints)

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

$$\text{OP1} \quad \min \quad t_f \\ R(t) \text{ and/or } F(t)$$

subject to:

Process Model Equations (equality constraints)

$$M_N = M_N^* \quad (\text{Inequality constraint}) \quad (37)$$

$$x_{ML} = x_{ML}^* + \varepsilon \quad (\text{Inequality constraint}) \quad (38)$$

Other operational constraints (next section)

Where M_N , x_{ML} are the amount of product and composition of ML at the final time t_f in the reboiler, (M_N^* , x_{ML}^* are specified). $R(t)$ is the time dependent reflux ratio profile and $F(t)$ is the feed rate profile of methanol (in case of SBD) which are optimized and ϵ is small positive number of the order of 10^{-3} . The model equations of the CBD/SBD column in the form of differential algebraic equations (DAE) (see Section 3) are the equality constraints to the optimisation problem.

6.1 Operation constraints for SBD

At the beginning of the process, the feed mixture is fed into the reboiler to its maximum capacity as a full reboiler charge strategy. The batch distillation column will overflow if the reflux ratio R (which governs the distillate rate, D , kmol /hr) and the feed flow rate F (kmol/hr) are not carefully regulated for a given vapor load to the condenser (V_c). To avoid reboiler overloading the following constraint must be satisfied as suggested by Mujtaba (1999):

$$D \geq F \quad (39)$$

Where, $D = V_c(1 - R)$ (40)

This leads to: $R \leq (1 - \frac{F}{V_c})$ and $R = (1 - \frac{F}{V_c})$ (41)

For a given the methanol feed rate with fixed condenser vapor load (V_c) the above inequality constraints on the reflux ratio (R) must be satisfied to prevent reboiler overloading (see equation, 41). The productivity can be further developed and the reboiler will be able to accommodate more reactant if the actual reflux ratio is lower than R_{Max} for some time (Mujtaba, 1999). Note, Lang et al. (1994) also provided analysis of reboiler overloading for batch extractive distillation system, where additional solvent was required to be fed.

7. Results and Discussions

7.1 Lactic acid conversion in a single stage CBD

It has been generally accepted that a reactive distillation performs better than a batch reactor followed by distillation in terms of conversion of limiting reactant, the higher reaction rates, enhanced conversion and selectivity, heat integration advantages and the lower operating costs

(Tadé and Tian, 2000). Edreder (2010) also provided this evidence for a number of reaction schemes. To be sure that this is the case for the LA esterification considered in this work, the esterification reaction is simulated in a single stage batch reactive distillation (acting as a batch reactor) with total reflux for 5 hours. The simulation result is shown in Figure 3. Note, the system gets to the steady state after half an hour with a maximum LA conversion of 62%. Figure 4 presents the dynamics of the reboiler composition of the representative CBD reactive column. It is evident from the figure that the product (ML) response takes nearly 0.5 hour to reach a steady state with a maximum purity of ML of 0.34 (mole fraction).

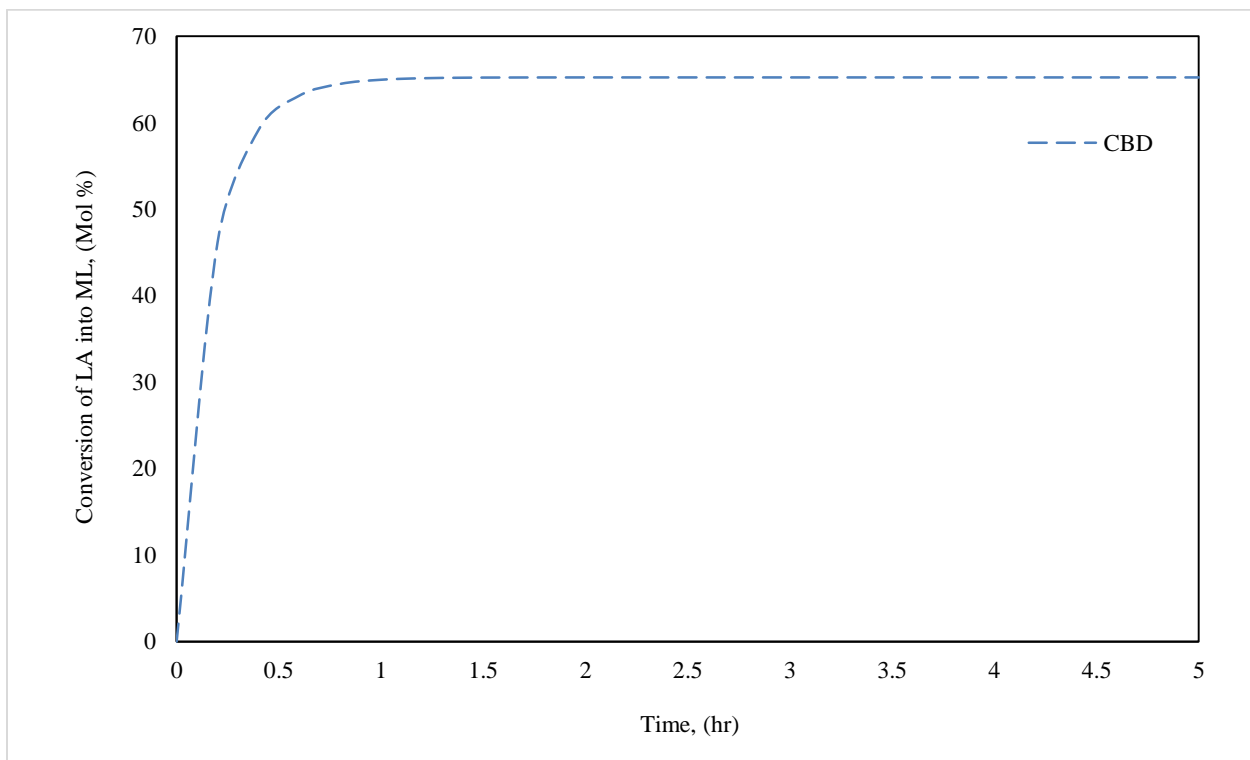


Figure 3: Dynamic response of Lactic Acid conversion at ($V_c = 2.5$ & $R = 1$).

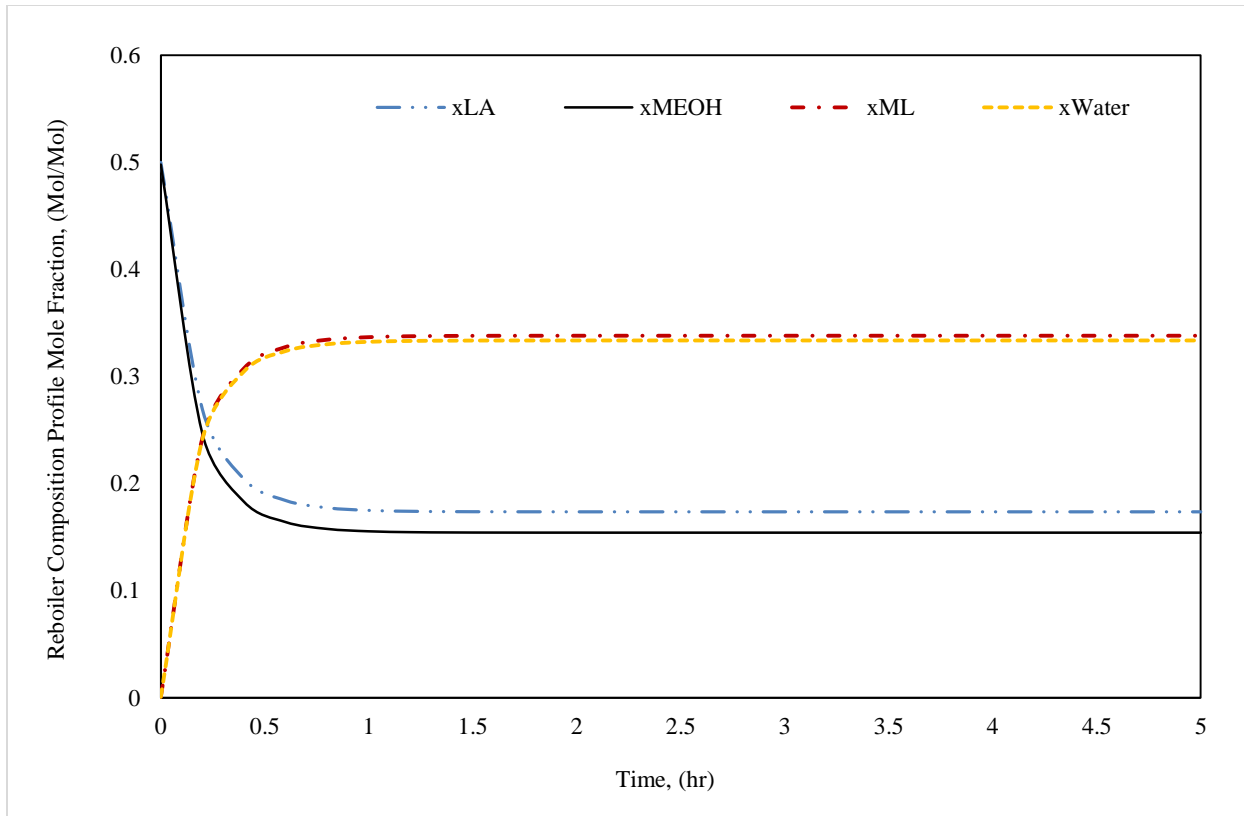


Figure 4: The reboiler composition profile at ($V_c = 2.5$ & $R = 1$).

7.2 Limitations of CBD for ML synthesis

Here, the limitations of CBD for ML synthesis are explored in detail via simulation. The column and the feed specifications used in this work (chosen arbitrarily) for the CBD are given in Table 2. The process investigation is performed in a ten stages column (including both condenser and reboiler drums) with (2.5 kmol/hr) of vapour load to the condenser (V_C). The total column holdup (including condenser) was assumed to be 4% of the total charged feed. Half of this total holdup is for condenser and the other half is for the stages (equally divided). Similar distributions of column hold-up were used by many researchers in the past as noted in Mujtaba (2004).

The capacity of the reboiler is 5 kmol and the feed mole fraction < Lactic acid (1), Methanol (2), Methyl Lactate (3), Water (4) > is: <0.5, 0.5, 0.0, 0.0>. At the beginning of process ($t=0$), the plates and the condenser compositions are initialized to those of the initial feed composition. Ideally, these compositions should have been the compositions achieved after the start-up period (Mujtaba, 2004). However, for the sake of convenience of numerical calculations the above assumption is made. Since LA is very heavy and almost non-volatile, and due to small amount of plate and condenser holdup (Table 2), the column composition profiles are established in few

minutes of the operation compared to that taken for the reboiler composition profile. Due to very large reboiler holdup (compared to plates and condenser) the reboiler takes about 30 minutes (Figure 4) to establish the composition profile. The assumption made in this work will have little impact on the composition of the distillate product tank (0.003-0.01 molefraction, Table 8 and 9).

The CBD column is simulated using 3 different reflux ratios (Table 3). The results are analyzed based on a given reboiler product amount which is 2.5 kmol. For different reflux this amount is achieved at different batch time as shown in Table 3. Figure 5 shows that for all reflux ratios, the conversion of LA to ML increases with batch time initially, goes through a peak and then drops down quite significantly. It is clear that due to distillation, methanol is removed as a distillate product (at higher rate at lower reflux values) leaving behind considerable amount of ML and water in the reboiler (almost equal amount of both at higher reflux) to activate the reversible reaction producing LA and methanol (Figure 6). At lower reflux ratio, some of the water is also removed with methanol (more ML at the reboiler than water) thereby restricting the reversible reaction to some extent leading to more overall conversion of LA compared to higher reflux case (Figure 5, Table 3) and leaving more ML at the reboiler (Figure 6).

Table 2. Column specifications for esterification of LA& MEOH system

| | |
|---|--|
| Number of Stages (including reboiler and condenser) | 10 |
| Total pressure (bar) | 1.013 |
| Initial Reboiler Charge (kmol) | 5 |
| Feed Composition (mole fraction) | LA = 0.5, MEOH = 0.5 H ₂ O = 0.0, ML = 0.0 |
| Condenser Vapor Load (kmol/hr) | 2.5 |
| Condenser hold-up (kmol) | 0.1 |
| Internal stage hold-up (kmol) | 0.0125 |
| The catalyst loading in each plate (g) | 25 |

Note, when the single stage column is run at total reflux (Figure 3), methanol is not removed from the system and the reaction systems gets to the equilibrium with much higher conversion of LA (62%) compared to those observed at finite reflux ratio (Figure 5).

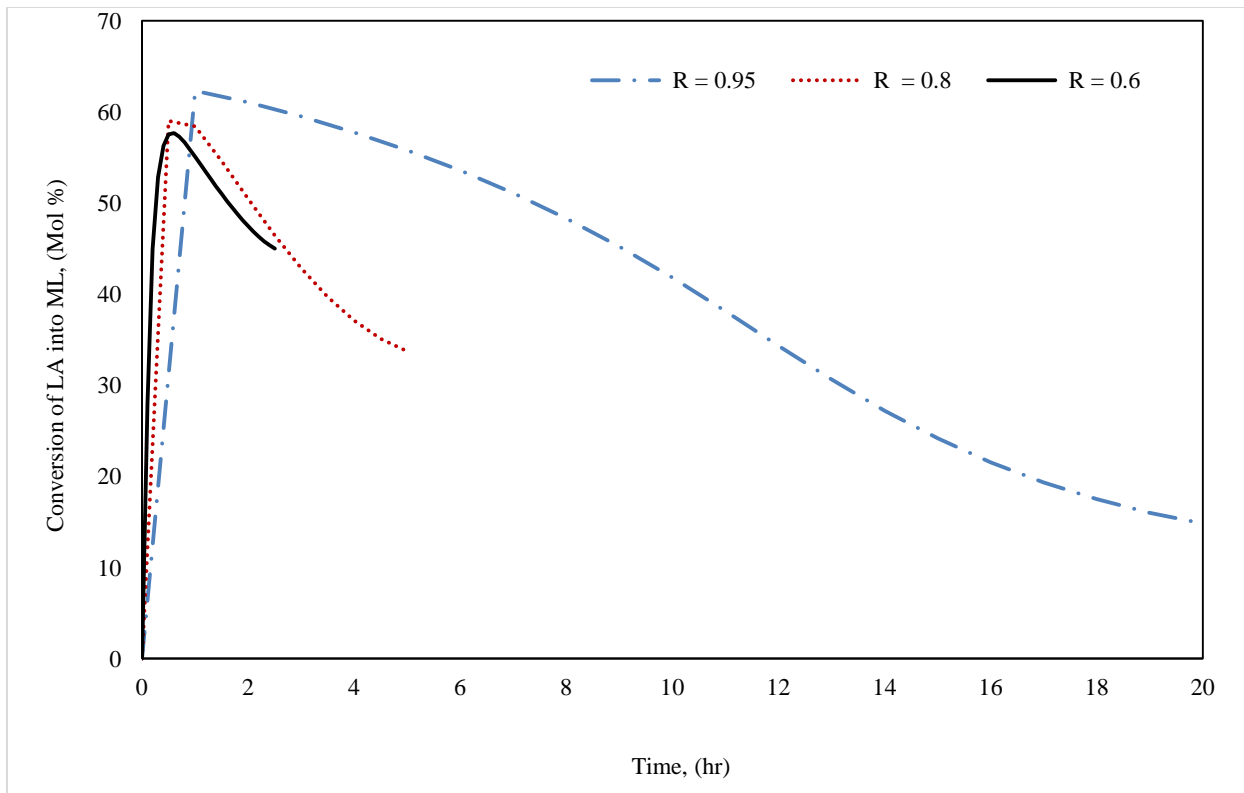


Figure 5: Dynamic response of LA conversion at different reflux ratios ($R = 0.95, 0.8$ and 0.6).

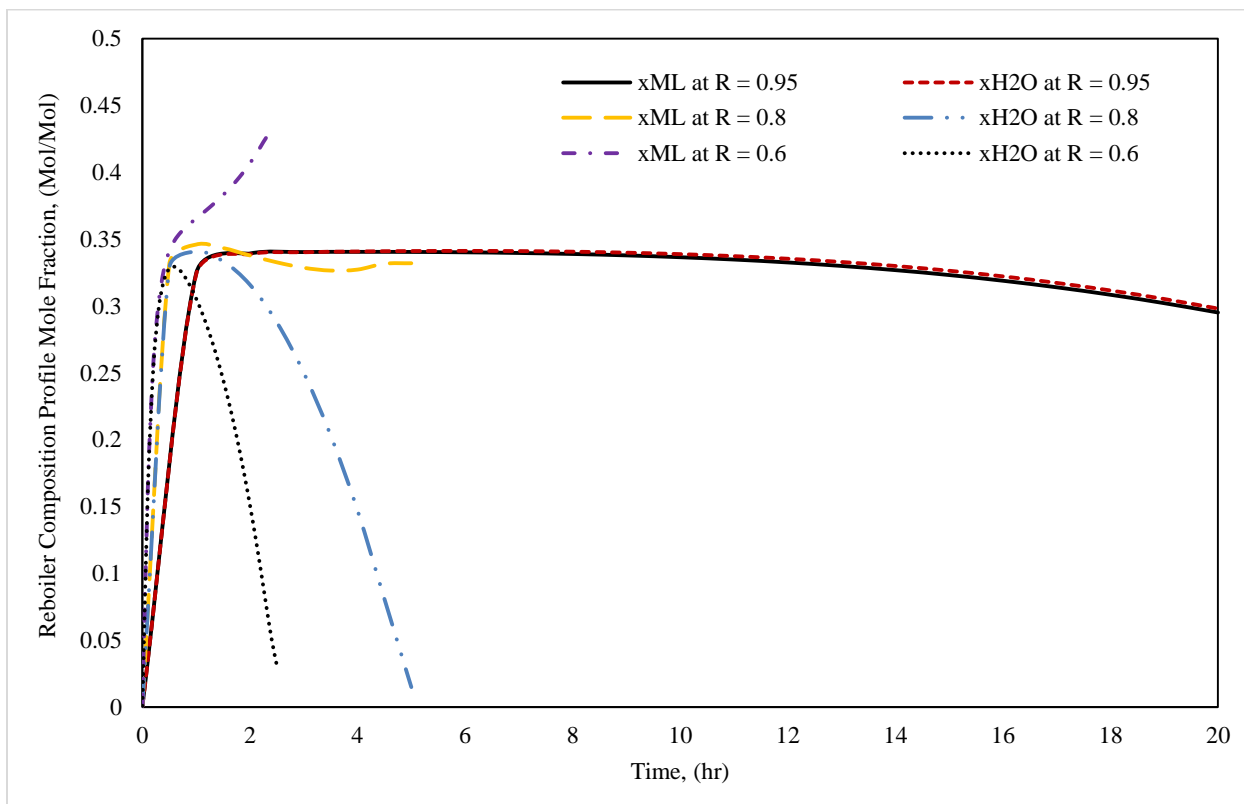


Figure 6: The composition profile of H_2O and ML in the reboiler.

Table 3: The Simulation results summary.

| Reflux Ratio | Distillate rate, L_D (kmol/hr) | Conversion of LA (%) | operating time, t_f (hr) | Total energy, Q_T (m kJ) |
|--------------|----------------------------------|----------------------|----------------------------|----------------------------|
| 0.95 | 0.125 | 14.83 | 20 | 1.887 |
| 0.8 | 0.5 | 33.72 | 5 | 0.526 |
| 0.6 | 1 | 44.99 | 2.5 | 0.292 |

It will be interesting to evaluate the performance of the same CBD column discussed above in terms of minimum batch time for different purity of ML but for a given amount of reboiler product which is 2.5 kmol. Table 4 summarises the optimisation results in terms of optimal reflux ratio, conversion of LA, minimum operating time, the total energy consumption and total amount of ML for a range of product purity (0.40 to 0.49) at equimolar molar ratio (LA: MeOH) of initial feed. The results of Table 4 indicated that all reflux ratio, operating batch time and thermal energy consumption decrease with increasing the desired product purity and the product amount (as expected based on simulation results presented earlier) and also it is impossible to obtain a high conversion of LA using a conventional batch reactive column. Note, no results were obtained at product purity of 0.49 mole fractions. This is due to reversible reaction being active and loss of methanol due to distillation.

The results presented above so far confirms why CBD is not at all suitable for ML synthesis and considered in the past as a potential manufacturing route.

Table 4. Summary of optimization results using CBD column at equimolar molar ratio.

| Purity of ML, x_{ML}^* (mole fraction) | Optimum Reflux Ratio | Conversion of LA (%) | Minimum batch time, t_f (hr) | Total energy, Q_T (m kJ) | Total Amount of ML, kmol |
|--|----------------------|----------------------|--------------------------------|----------------------------|--------------------------|
| 0.40 | 0.673 | 41.99 | 3.06 | 0.345 | 1 |
| 0.44 | 0.555 | 46.42 | 2.24 | 0.168 | 1.1 |
| 0.48 | 0.230 | 55.50 | 1.30 | 0.175 | 1.2 |
| 0.49** | --- | --- | --- | --- | --- |

** not achievable

7.3 Semi-Batch Distillation Column (SBD)

Here it is explored SBD column as a potential and feasible candidate for ML synthesis.

7.3.1 Separation Strategy

With the start of the operation, the chemical reaction will begin and ML and water will be produced. Having water as the next boiling component after methanol, it will start travelling up the column after methanol.

Methyl lactate will tend to be near the vicinity of the reboiler due to high boiling point. Instead of separating ML in the distillate tank after the separation of methanol and water, it is decided to collect unreacted methanol and the reaction product water in one distillate tank. Methyl lactate product can remain in the reboiler and it can be purified to the desired specification by converting more and more of the LA. In the bottom product tank, therefore, it will be a mixture of mainly ML and unconverted LA. The distillate product will be mainly a mixture of methanol and water which can be further separated into methanol and water and methanol can be recycled back into the reboiler. Note, however, separation of methanol is beyond the scope of this paper.

Two cases are studied here, one (Case-1) with single time interval strategy of operation (STI = 1) and the other (Case-2) with two time intervals (TTI = 2). Both reflux ratio and methanol feed rate will be optimized within these intervals together with the length of the intervals.

7.3.1.1 Case-1: Single Interval Operation

For different product purity specifications, the optimization results (optimal reflux ratios, optimal methanol rates, maximum reflux ratios, conversion of LA to ML, minimum final batch time, the total energy consumption and total methanol feed amount) are summarized in Table 5. It can be noticed from these results that the operating batch time, the conversion level and the total energy consumption, increase gradually with increasing the product compositions (unlike those observed in a CBD column). This is obvious as higher purity of ML dictates more conversion of LA. This can only be achieved by having higher reflux ratio and more methanol feed but at the expense of more batch time and thus more energy consumptions.

Also note, in all cases R_{max} is calculated for different values of feed rate of methanol. Also note, in all cases optimum reflux ratio is found to be less than R_{max} thus satisfy the reboiler overloading condition. According to Eq. (41), the R_{max} reduces when the feed rate increases. It can be seen also that the total feed amount (F_t) which is estimated from the optimal feed rate (F) multiplying by the production batch time (see equation 42) increases when the product purity demand increase.

$$F_t = F \times t_f \quad (42)$$

It is clear from Table 5 that higher operation time and higher reflux ratio with higher total feed amount are required at 0.85 of ML composition as compared to others to satisfy the product specification. A comparison of the results between the conversion of LA using SBD column in Case-1 and the CBD column conversion (Table 4) shows that for the same amount of reboiler product (2.5 kmol) SBD column can produce ML at a much higher purity (0.85 compared to 0.48) and can convert more LA (91% as opposed to only 55.5%).

Table 5. Optimal reflux ratio and methanol feed using STI = 1 (Case-1)

| x_{ML}^* | Optimum Feed Rate, kmol/hr | Optimum Reflux Ratio | Maximum Reflux Ratio | Conversion of LA (%) | t_f , (hr) | Q_T , (m kJ) | Total Amount of Injected Methanol, kmol |
|------------|----------------------------|----------------------|----------------------|----------------------|--------------|----------------|---|
| 0.70 | 1.07 | 0.230 | 0.573 | 77.26 | 2.79 | 0.294 | 2.99 |
| 0.75 | 1.18 | 0.257 | 0.530 | 81.89 | 3.51 | 0.353 | 4.13 |
| 0.80 | 1.26 | 0.286 | 0.496 | 86.45 | 4.58 | 0.441 | 5.76 |
| 0.85 | 1.31 | 0.326 | 0.475 | 91.31 | 6.47 | 0.596 | 8.49 |

At this stage, it will be interesting to investigate the effect of excess methanol in the CBD (as it was the case for SBD above). For the first case in Table 5, the total lactic acid feed was 2.5 kmol and total methanol feed was 5.49 kmol (2.5 kmol initial charge + 2.99 additional methanol feed) which made a ration of LA:MeOH = <0.313, 0.687>. Optimisation of CBD similar to those presented in Table 4 were carried out. In terms of ML purity in the reboiler and the conversion of LA the results were no better than those presented in Table 4, reconfirming the limitation of CBD even with excess methanol.

7.3.2.2 Case-2: Two Intervals Operation

Table 6 shows the optimizations results in terms of minimum batch time, the optimal both reflux ratio and methanol feed for each operating time, optimal length period for each interval, total minimum batch time, the total energy consumption, total methanol amount, and the maximum conversion using two reflux ratio intervals to achieve the product purity (case-2). It is indicated from Table 6 that significant reductions in batch time (i.e. 18-35.5%), total energy consumptions (i.e. 11.15-28.91%), and higher improvements in LA conversion (i.e. 3.5-75%) using two control intervals as compared to one control interval SBD column.

However, more methanol feed and high reflux ratio as control variables at multi-control intervals are needed to consume all the LA from the bottom. As illustrated also in case-2, the optimal values of both reflux ratios (R_1 , and R_2) are still lower than R_{max} meaning the reboiler is never overflowed (see also Figures 14 and 15). It can be realized from Table 6 for each purity specification that the distillation column operates with lower reflux ratio for the first interval to push water up to the accumulator tank.

While, higher reflux ratio and higher batch time are needed in the second time interval to retain LA and methanol in the reaction region to have further reaction and to achieve the product (ML) purity. In case-2, the total methanol feed is calculated using the following form:

$$F_t = F_1 \times t_1 + F_2 \times t_2 \quad (43)$$

Where, t_2 is the second batch time interval obtained from the following equation:

$$t_2 = t_f - t_1 \quad (44)$$

As a comparison between case-1 and case-2, more of total methanol quantities (F_t) are saved at using two time intervals as control variable for the process (reduction by about 55.4 % compared with the single time interval). For comparison, using dynamic optimization strategy with two time intervals can drive quickly the purity of bottom product to the desired purity specification. It is obviously shown from the results that the distillation column carried out at the lower reflux ratio for single and two intervals to meet the product specifications. Table 7 gives the percent of time, thermal heat savings, and the process conversion improvements when the STI policy is used as opposed to TTI policy.

Both the total thermal heat consuming and the batch time profiles for different range of the product (ML) purity for both STI and TTI policies and it indicates considerable reductions in production batch time and total energy consumption are possible for the same product purity in case of multi-time intervals strategy as presented in Figures 7 and 8. It can be seen that, the minimum time and the maximum heat savings achieved are 35.5 % and 28.91% at ML purity of 85 % compared to that obtained by using the STI policy. It can be also observed from Figure 9 that the conversion has obviously upgraded using two reflux policy as a control variable compared to that using the one policy.

Two interval strategy is found to outperform single time interval strategy to achieve higher products purity requirements with lower operating time and energy consumption and higher conversion rate. This fact is shown in a better way in Figures 7, 8 and 9 in terms of minimum

final batch time and energy consumption and maximum conversion as function of methanol feed rate and reflux ratio policy and the ML purity specifications.

Table 6. Optimal reflux ratio and methanol feed using TTI = 2 (Case-2)

| x_{ML}^* | R_1, R_2 | $F_1, F_2,$ kmol/hr | t_1, hr | t_f, hr | t_2, hr | $Q_T,$ mKJ | Total Amount Feed, kmol | Conversion of LA (%) |
|------------|--------------|------------------------|------------------|------------------|------------------|---------------|----------------------------------|----------------------------|
| 0.70 | 0.124, 0.427 | 0.06, 1.22 | 1 | 2.31 | 1.31 | 0.262 | 1.66 | 77.29 |
| 0.75 | 0.166, 0.441 | 0, 1.23 | 1.01 | 2.72 | 1.71 | 0.299 | 2.09 | 81.99 |
| 0.80 | 0.189, 0.465 | 0, 1.24 | 1.08 | 3.29 | 2.21 | 0.349 | 2.75 | 86.71 |
| 0.85 | 0.210, 0.481 | 0.004, 1.25 | 1.14 | 4.17 | 3.03 | 0.424 | 3.79 | 92.00 |

Table 7. Batch time, energy savings, and conversion improvements by SBD with different product purity

| x_{ML}^* | Time Saving % | Energy Saving % | Conversion Improvement % |
|------------|---------------------|-----------------------|--------------------------------|
| 0.70 | 18 | 11.15 | 3.5 |
| 0.75 | 22.6 | 15.33 | 12.2 |
| 0.80 | 28 | 20.83 | 29.9 |
| 0.85 | 35.5 | 28.91 | 75.0 |

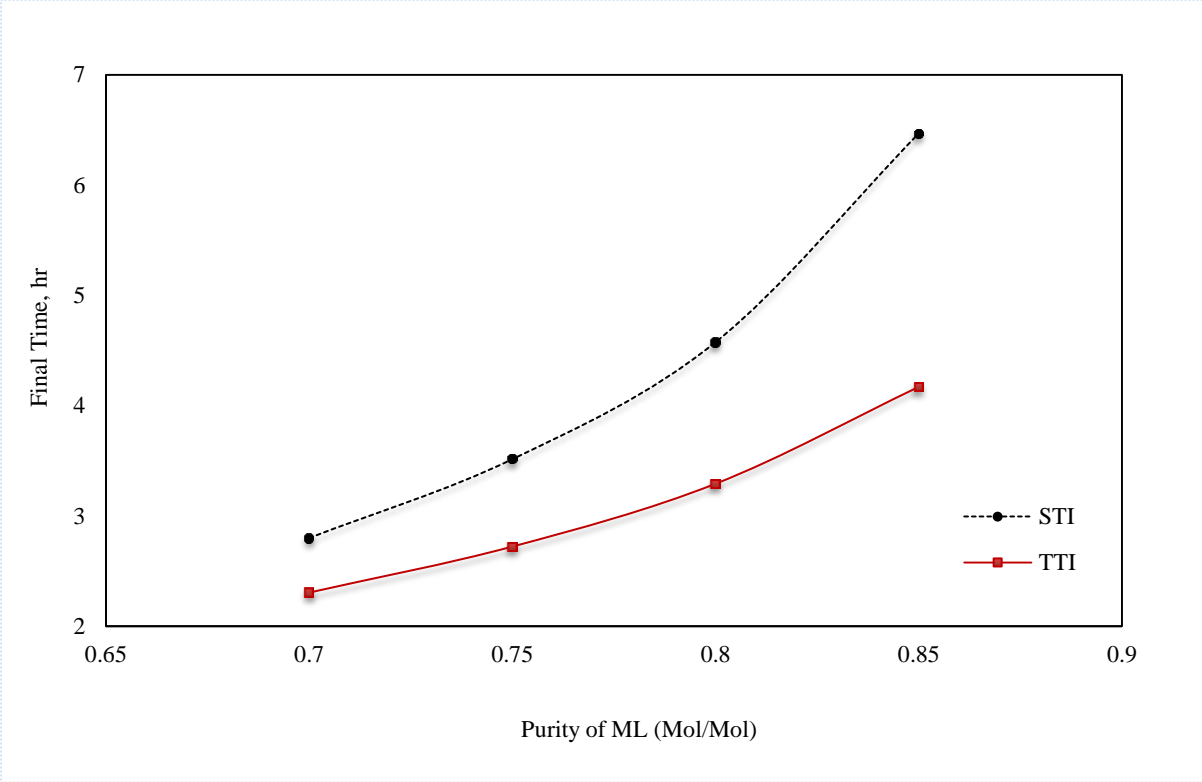


Figure 7: The optimum operating time profile

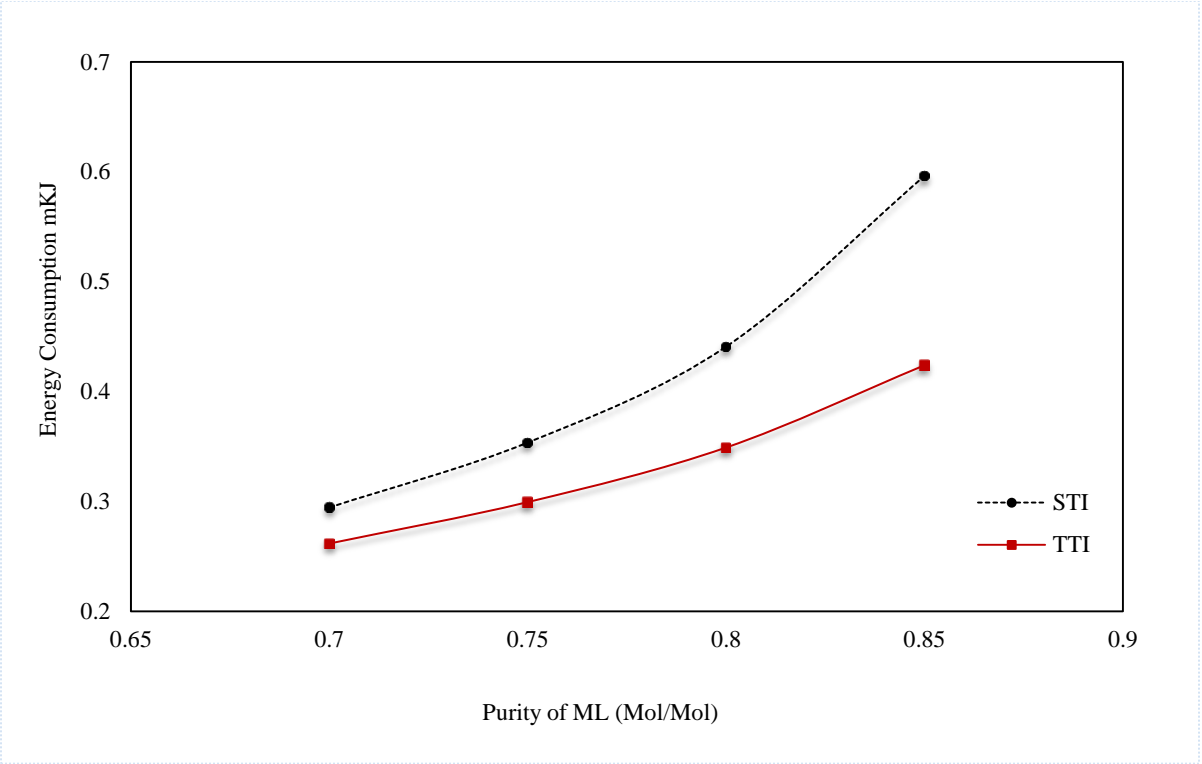


Figure 8: The total thermal heat consumption profile.

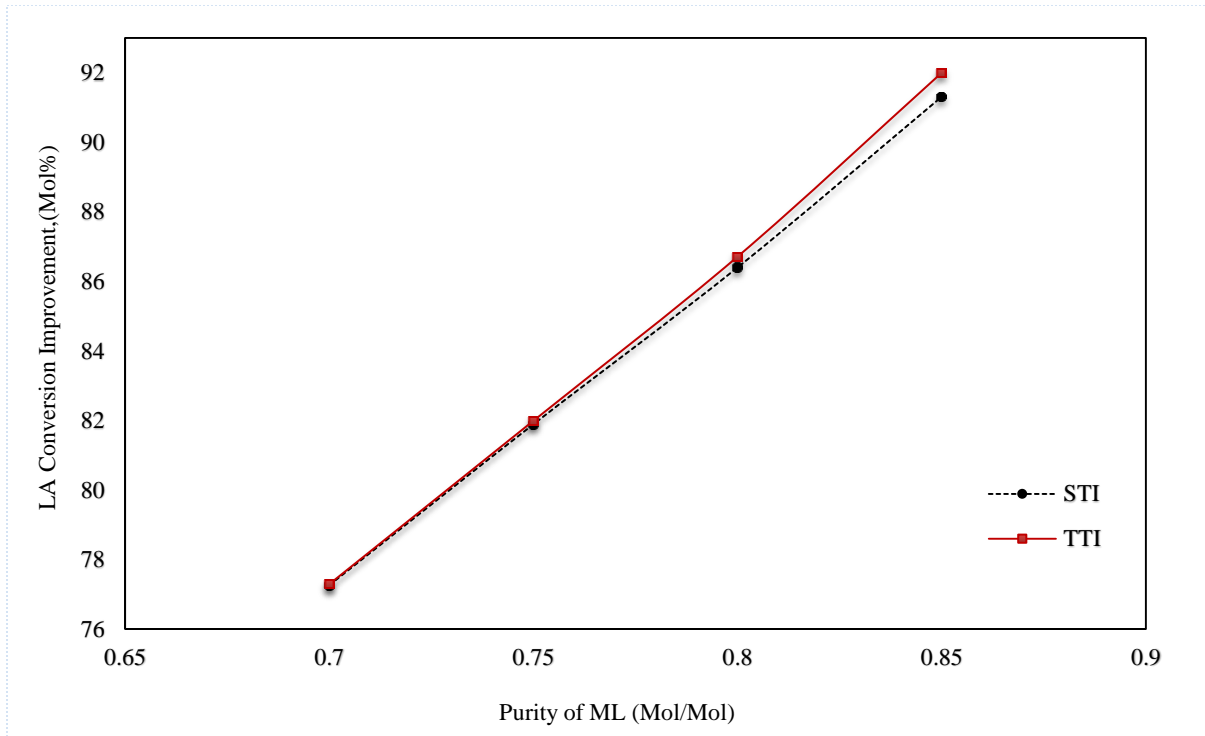


Figure 9: The optimum LA conversion profile.

Tables 8 and 9 present the optimization results, the distillate amount and its composition (in the accumulator tank), the reboiler mole fractions, respectively for different product purities at the end of the batch time using both time interval policies. Note, in the accumulator it is mainly methanol and water methyl lactate is mainly in the reboiler with the remaining unconverted lactic acid. Furthermore, note the distillate amounts in case-2 are lower than those obtained in case-1 due to less amount of methanol being fed in semi-continuous mode in case-2. Note, the reboiler amount is fixed at 2.5 kmol for both cases.

Table 8. Distillate amounts, and Distillate and Reboiler composition profiles at Multiple Purities of ML using STI = 1 (Case-1)

| Purity of ML | D, kmol | x_{LA} | x_{MEOH} | x_{ML} | x_{Water} | * x_{LA} | * x_{MEOH} | * x_{Water} |
|--------------|---------|----------|------------|----------|-------------|------------|--------------|---------------|
| 0.70 | 5.38 | 0.006 | 0.612 | 0.031 | 0.351 | 0.188 | 0.051 | 0.061 |
| 0.75 | 6.52 | 0.005 | 0.661 | 0.022 | 0.312 | 0.145 | 0.064 | 0.041 |
| 0.80 | 8.16 | 0.004 | 0.708 | 0.016 | 0.272 | 0.121 | 0.052 | 0.027 |
| 0.85 | 10.0 | 0.003 | 0.768 | 0.006 | 0.223 | 0.075 | 0.061 | 0.014 |

* The composition in the reboiler (molefraction)

Table 9. Distillate amounts, and Distillate and Reboiler composition profiles at Multiple Purities of ML using TTI = 2 (Case-2)

| Purity of ML | D, kmol | x_{LA} | x_{MEOH} | x_{ML} | x_{Water} | * x_{LA} | * x_{MEOH} | * x_{Water} |
|--------------|---------|----------|------------|----------|-------------|------------|--------------|---------------|
| 0.70 | 4.05 | 0.010 | 0.492 | 0.046 | 0.452 | 0.194 | 0.051 | 0.055 |
| 0.75 | 4.49 | 0.009 | 0.514 | 0.033 | 0.444 | 0.156 | 0.055 | 0.039 |
| 0.80 | 5.14 | 0.007 | 0.545 | 0.027 | 0.421 | 0.115 | 0.059 | 0.026 |
| 0.85 | 6.18 | 0.006 | 0.596 | 0.023 | 0.375 | 0.076 | 0.062 | 0.012 |

* The composition in the reboiler (molefraction)

The mixture composition profiles in the reboiler and in the accumulator at product purity (* $x_{ML} = 0.8$) are illustrated in Figures 10 and 11 for single time interval and in Figures 12 and 13 for two time intervals. Note, the methanol feed rate is shown in Figure 10 and 12 as the horizontal dashed-line. It can be noticed from Figure 10 and 12 that the mole fraction of water (2nd boiling component) rises from zero and reaches the maximum value and then falls down to almost zero (due to removal in the accumulator, Fig. 11 and 13). More ML is produced as the batch progresses and stays in the reboiler (as the second heavier boiling product).

The mole fraction of methanol reactant is decreased with increasing time because of its highest volatility component and gathered in the distillate receiver (accumulator, Figure 11 and 13). Further LA is consumed gradually with increasing the operating time due consumption by reaction with methanol. A higher reflux ratio with longer operation time is needed to retain the reactants (LA and methanol) in the reaction section. The ML reached the desired purity quicker for two interval cases than the one interval cases.

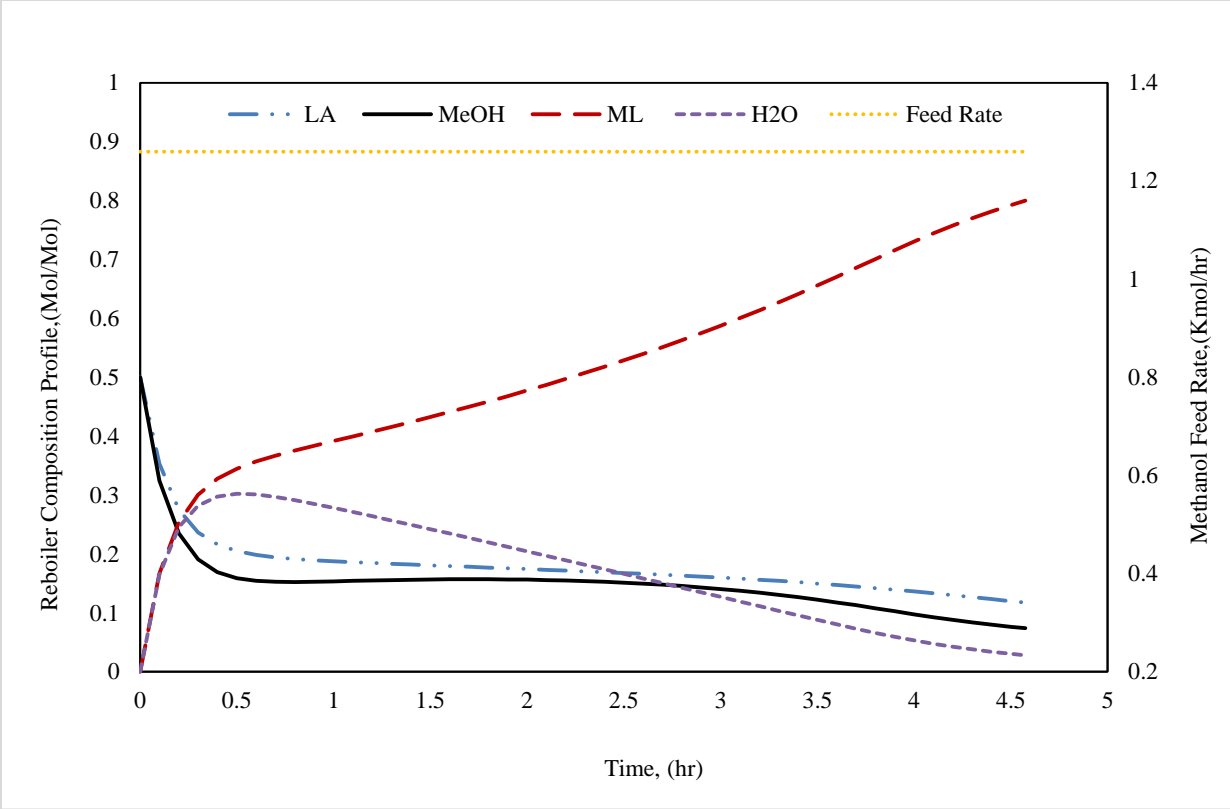


Figure 10: The Mixture Composition in the Reboiler and Feed Rate profile for Single Time Interval.

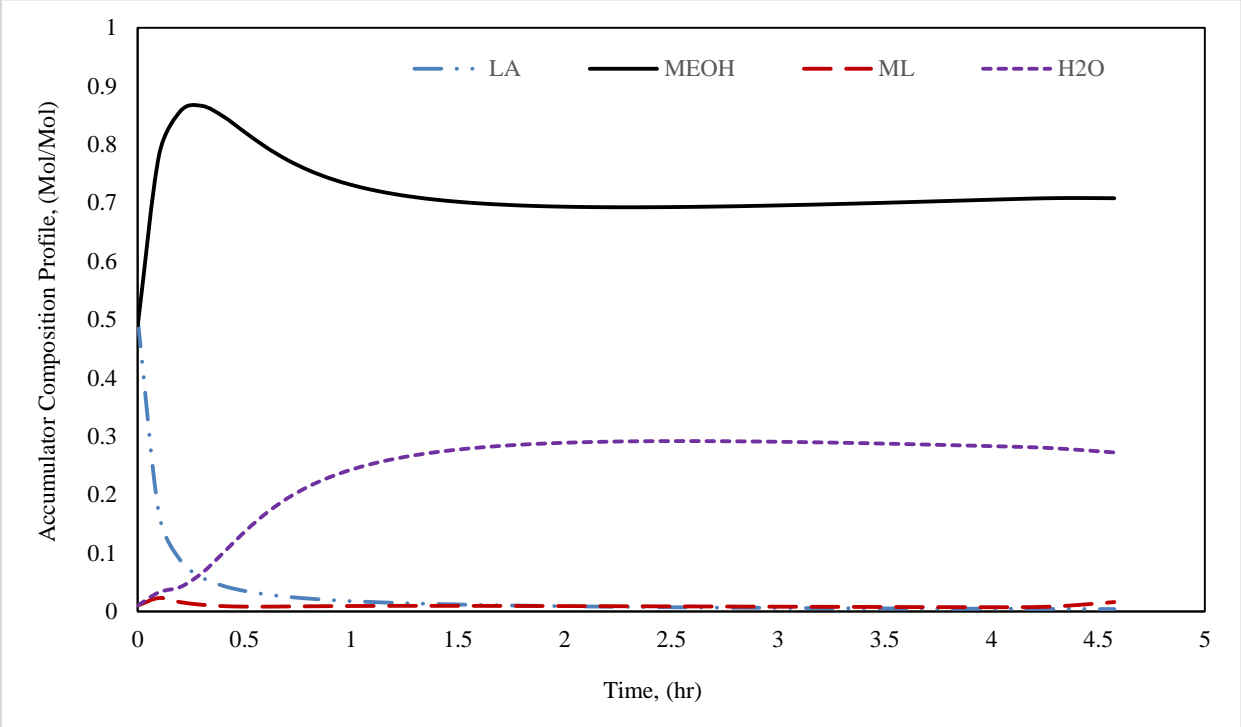


Figure 11: The Accumulator Composition profile for Single Time Interval.

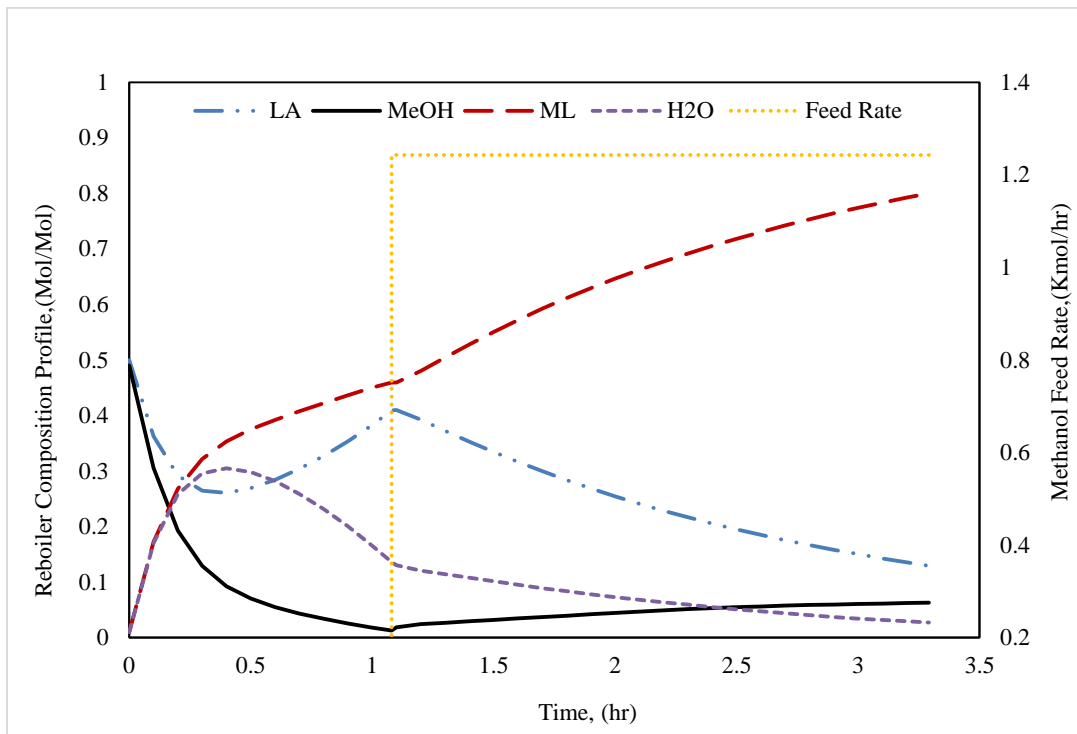


Figure 12: The mixture composition in reboiler and feed rate profiles for Two Time Intervals.

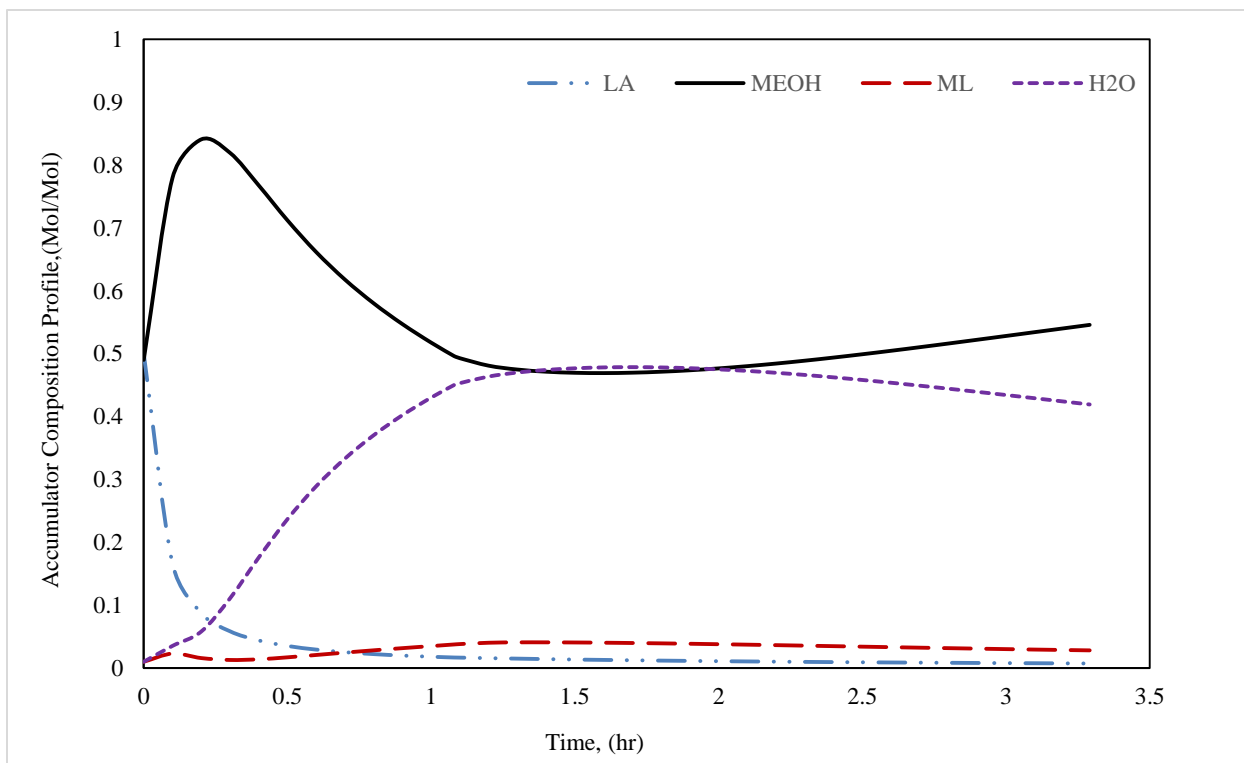


Figure 13: The Mixture Composition in Accumulator profile for Single Time Intervals.

Figures 14 and 15 show the total reboiler holdup profile for Case 1 and 2 at multiple product purities. It clearly shows that at any point of time, the holdup is always below the maximum capacity of the reboiler (5 kmol) ensuring no column flooding for both cases.

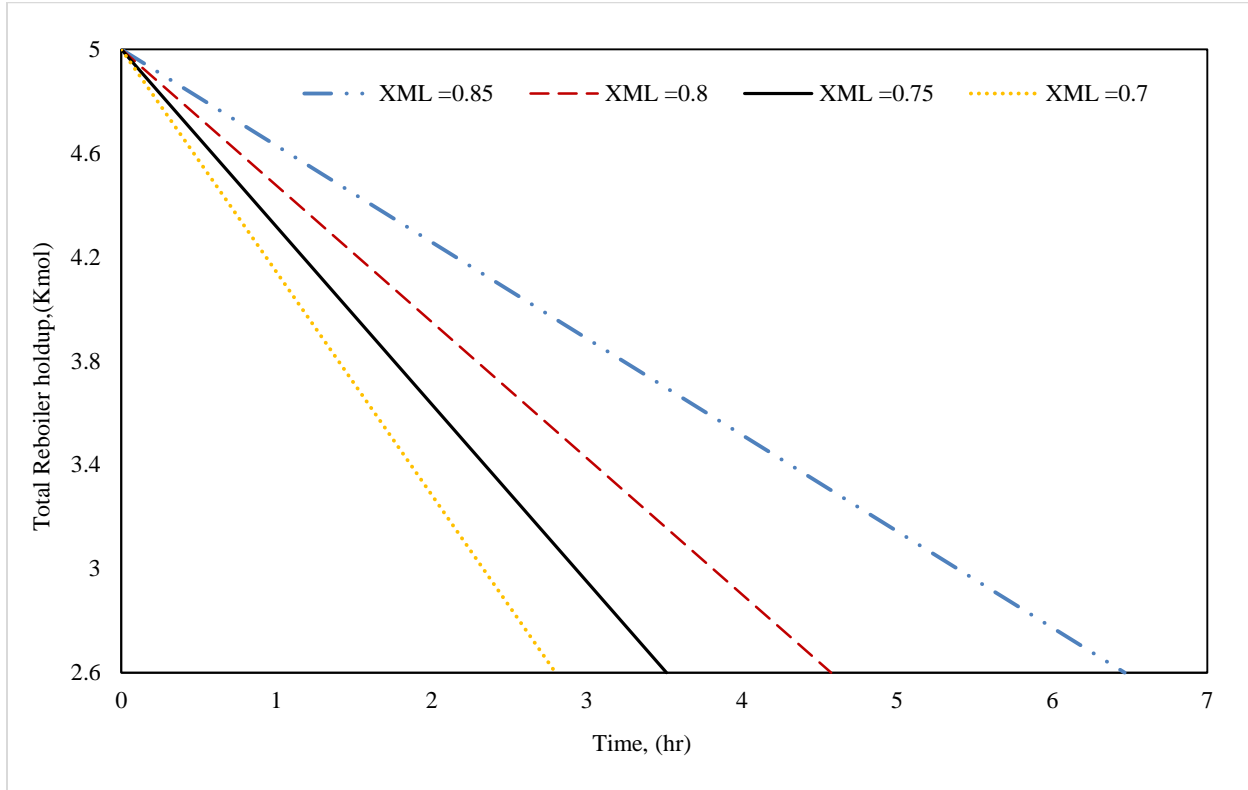


Figure 14: The total reboiler holdup profile for Case-1.

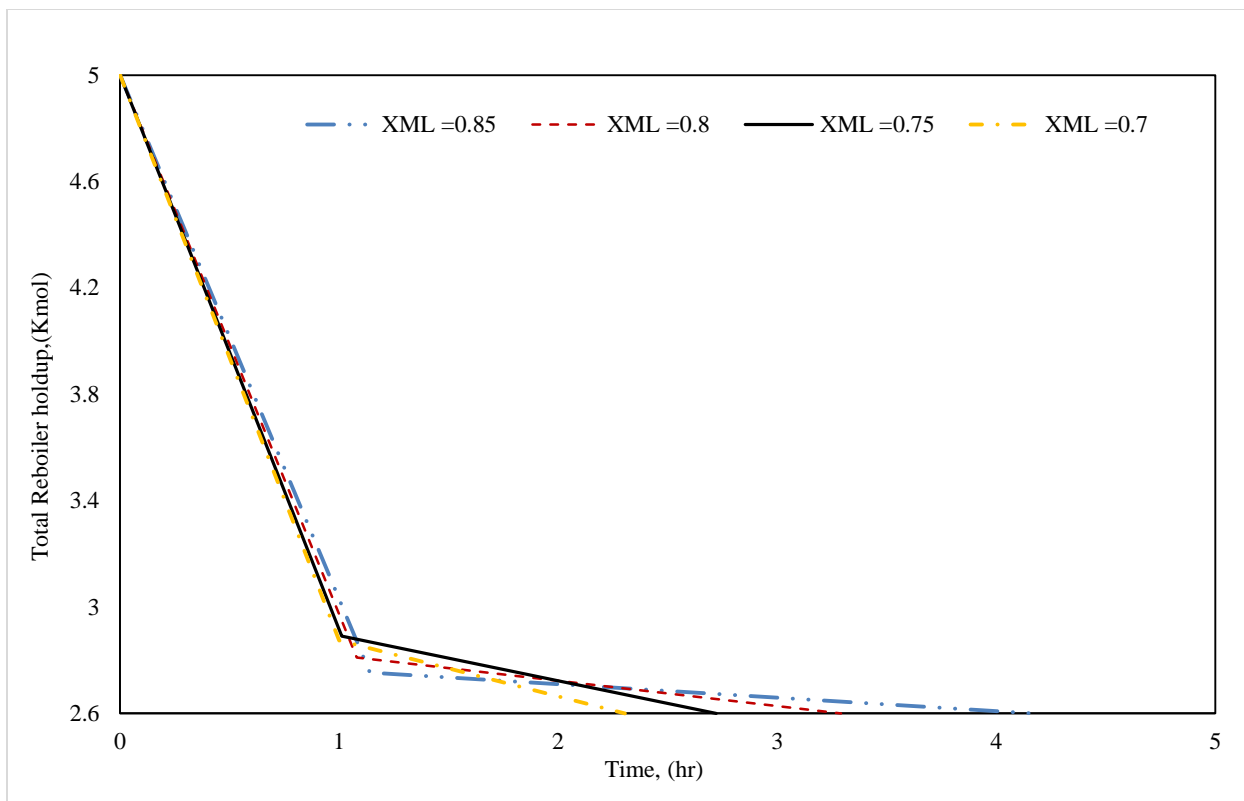


Figure 15: The total reboiler holdup profile for Case-2.

8. Conclusions

In this study, synthesis of ML via the esterification of LA is considered in a conventional (CBD) and semi-batch reactive distillation (SBD) columns. Due to separation of methanol from LA in a distillation column because of the wide difference in boiling points between the reactants, the use of CBD column is restricted. With the removal of methanol (one of the reactants of the forward reaction), the reversible reaction is activated along the process reducing conversion of LA to ML drastically. Therefore, use of SBD column is suggested where methanol is continuously fed into the reboiler to enhance interaction between the reactants and to improve the conversion of LA to ML. Operating constraints are put in place to avoid overloading of the reboiler drum due to continuous methanol feed. Instead of separating ML (the desired product) in a sequential manner (unreacted methanol, water, ML) in the distillate tank, ML is collected as the bottom product together with any unreacted LA.

The performances of the CBD and the proposed SBD column are evaluated in terms of minimum batch time using model based techniques where a detailed model of the process is developed

using gPROMS Model Builder 3.7.1 and is embedded within the optimization framework. A series of minimum time optimisation problems was solved with multi values of ML purity ranging from 0.7 to 0.85 compositions and the effect of time dependant reflux ratio and feed rate operation strategies on the batch time and energy consumption are evaluated. Clearly SBD column outperforms CBD column significantly. Also, the optimization results for a given separation task illustrate that use of two time intervals is more effective policy compared to a single interval in terms of batch time and energy savings in the SBD column.

Nomenclature

| | |
|------------------|--|
| B_{ij}, B_{ji} | Binary interaction parameters for UNIQUAC equation |
| CVP | Control vector parameterisation |
| D | Distillate product (kmol) |
| DAE | Differential algebraic equations |
| F | Methanol feed rate (kmol/hr) |
| H_L, H_V | Liquid, vapor enthalpy (kJ/kmol) |
| K | Vapor-liquid equilibrium constant |
| k_e | Pre-exponential factor for the esterification reaction |
| L | Liquid rate in the column (kmol/hr) |
| M_{wi} | Molecular weight of each component |
| M_a, M_C | Accumulator and condenser holdup respectively (kmol) |
| M, M_N | Stage and re-boiler holdup respectively (kmol) |
| m_{cat} | The catalyst weight (kg of catalyst) |
| N | Number of stages |
| NCI | Number of control intervals |
| OP1 | Optimisation |
| P | Pressure (bar) |
| P^{sat} | Vapor pressure of pure component i |
| Q_C, Q_r | Condenser or reboiler duty (kJ/hr) |
| Q_T | Total Energy Consumption (mkJ) |
| R_1, R_2 | Reflux ratio in time interval 1, and 2 |
| R, R_{Max} | Reflux ratio and maximum reflux ratio |

| | |
|------------------|--|
| r_{ML} | Reaction rate of Methyl Lactate ($\text{kmol (kg of catalyst)}^{-1} \text{ min}^{-1}$) |
| SQP | Successive quadratic programming algorithm |
| T | Temperature (K) |
| T_{r1}, T_{r2} | Reference Temperatures (K) |
| t, t_f | 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

| | |
|----------------|---|
| ϵ | Small positive numbering the order of 10^{-3} |
| i | Component number |
| j | Stage number |
| λ_i | Latent heat of vaporisation (kJ/kmol) of component |
| λ_r | Latent heat of vaporisation (kJ/kmol) of the reboiler mixture |
| λ_{bi} | Latent heat (kJ/kmol) of component at normal boiling point |
| γ_i | Activity coefficient of component i |
| Δn | Change in moles due to chemical reaction |

Abbreviations

| | |
|--------------------|------------------|
| AgCL | Silver Chloride |
| AgL | Silver Lactate |
| AM | Acetamide |
| AmL | Ammonium Lactate |
| CH ₃ CL | Methyl Chloride |
| DHA | Dihydroxyacetone |
| ET | Ethyl Lactate |
| GLA | Glyceraldehyde |
| HC | Hemiacetal |

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Appendix

Table 10. Binary interaction parameters for UNIQUAC Model (Sanz et al., 2003)

| Components | b_{ji} (K) | b_{ij} (K) |
|-----------------------|--------------|--------------|
| LA-MEOH | 17.14 | 322.59 |
| LA-ML | -302.09 | 367.14 |
| LA-H ₂ O | -26.1 | -84.80 |
| MEOH-ML | 866.6 | -164.4 |
| MEOH-H ₂ O | -192.6 | 325.0 |
| ML-H ₂ O | 325.31 | -20.05 |

Table 11. Physical and thermodynamic properties, Antoine constants, and the area and volume parameters of the UNIQUAC model (Sanz et al., 2003)

| Physical Properties | LA | MEOH | ML | H ₂ O |
|-----------------------|---------|---------|---------|------------------|
| T _C (K) | 627.0 | 512.6 | 584.0 | 647.3 |
| λ_b (KJ/kmol) | 54670 | 35290 | 38177 | 40651 |
| M _{wt} | 90.08 | 32.04 | 104.11 | 18.02 |
| r | 5.27432 | 1.4311 | 5.95005 | 0.92 |
| q | 4.47617 | 1.4320 | 5.01723 | 1.39970 |
| A | 7.51107 | 7.21274 | 7.24147 | 7.0436 |
| B | 1965.7 | 1588.63 | 2016.46 | 1636.909 |
| C | -91.021 | -32.599 | 30.4 | -48.230 |