Simulation of Middle Vessel Batch Reactive Distillation Column: Application to Hydrolysis of Methyl Lactate

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The middle vessel column (MVC) is a combination of a batch rectifier (conventional column) and a batch stripper (inverted column). Therefore it is possible to obtain a light and a heavy fraction simultaneously from the top and the bottom of the column while an intermediate fraction may also be recovered in the middle vessel. Several researchers in the past have proposed the esterification of lactic acid (impure) with alcohol to obtain lactate ester which is then separated by distillation. To the best of our knowledge, simulation of middle vessel batch reactive distillation column for hydrolysis system has not yet been explored. In this work, the hydrolysis reaction of methyl lactate to produce lactic acid (LA) is carried out in a middle vessel column with fixed batch time while control variables are treated as a piecewise constant reflux ratio (multiple time intervals) and a single reboil ratio. For MVC, the LA being the heaviest in the reaction mixture, reflux and reboil ratios policy plays an important role to achieve high purity of LA.

1. Introduction

The use of conventional batch distillation for some reactions would result in removal of reactants as the distillation proceeds thus lowering conversion and yield of product. Therefore, it is very important to select the right batch distillation column for each type of chemical reaction. Conventional batch distillation (CBD) is not suitable when all reaction products have higher boiling temperatures than those of the reactants. Inverted batch distillation (IBD) is suitable for such situation. For cases where some of the reaction products have higher and some lower boiling points than those of the reactants, then neither the conventional nor the inverted batch distillation are exactly suitable/efficient.

For such reaction schemes, the Middle Vessel Batch Distillation Column (MVC) will be the most suitable one because the light and heavy products can now be withdrawn simultaneously from the column, thus pushing the reaction further to the product side (Mujtaba, 2004). In MVC (Figure 1) the separation section is divided, as in the usual continuous distillation column, into rectifying and stripping sections, with a feed tray in the middle. This configuration was first mentioned by Robinson and Gilliland (1950) Hasebe et al. (1992); Mujtaba and Macchietto (1992); Barolo et al. (1996); and Greaves et al. (2003) reported further use of MVC.

Several researchers in the past have proposed the esterification of lactic acid (impure) with alcohol to obtain lactate ester which is then separated by distillation. Seo et al. (1999) investigated two reactions, esterification followed by hydrolysis for recovery of lactic acid by batch reactive distillation using cation exchange resin as a catalyst.

The distilled lactate ester is then hydrolyzed into pure lactic acid (Li et al, 2005). Kumar et al. (2006) explored and investigated a novel reactive distillation strategy involving experimental esterification and hydrolysis reaction for recovery of pure lactic acid. Edreder et al. (2010) considered a batch reactive distillation for hydrolysis reaction of methyl lactate to produce lactic acid. Recently, Edreder et al. (2011) considered optimal operation of conventional and inverted batch reactive distillations for hydrolysis of methyl lactate to produce lactic acid.

To the best of our knowledge, simulation of middle vessel batch reactive distillation column for hydrolysis system has not yet been explored.

In this work, simulation of simultaneous chemical reaction and separation in an MVC column using detailed dynamic model is considered for hydrolysis of methyl lactate to produce lactic acid for a given batch time while the control variables are treated as a piecewise constant reflux ratio (multiple time intervals) and single reboil ratio.
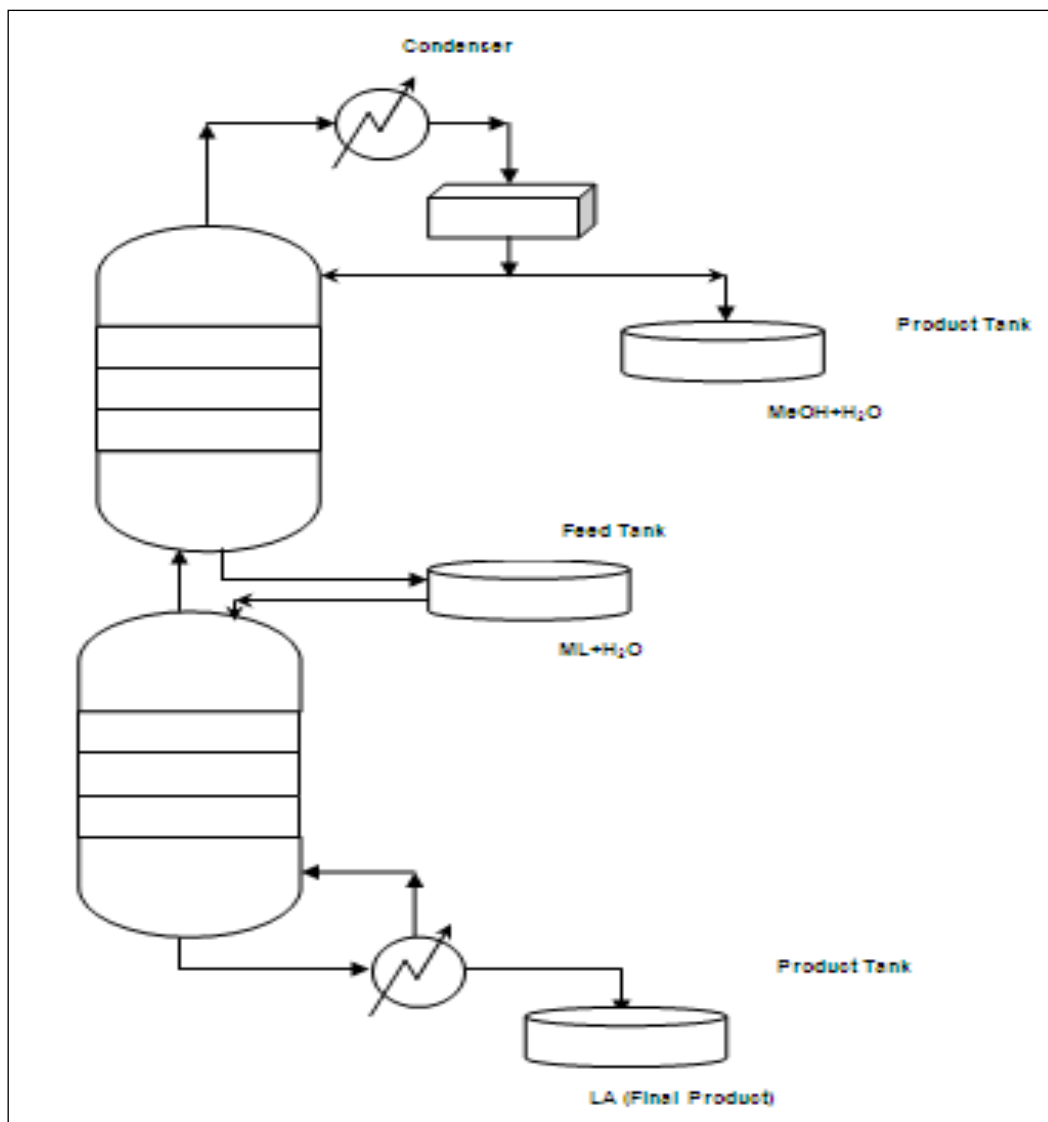

Figure 1. Middle vessel batch reactive distillation column

2. Process model

Referring to (Figure 1) for MVC column configuration, the reaction is modelled by detailed dynamic model. It includes mass and energy balances with constant molar holdup and rigorous thermodynamic properties. The model assumes negligible vapour holdup, adiabatic plates, constant molar holdup on plates and in the condenser, perfect mixing on trays, fast energy dynamics, constant operating pressure and total condensation with no sub-cooling and assuming no azeotrope formation. The model is developed within gPROMS (2004). Model equations for feed tank and feed plate are shown in Figure 2. Details can be found in Mujtaba (2004).

3. Hydrolysis of methyl lactate system

3.1 Problem specification

The feed tank location was $N_F = 5$ (stages numbered from the top down). The feed composition <Methyl Lactate (ML), Water (H_2O), Lactic acid (LA), Methanol (MeOH) is : <0.5, 0.50, 0.0, 0.0>. The other input data are presented in Table 1. The reaction products are LA (main product) and MeOH, the latter being the most volatile component and LA being the least volatile component in the reaction mixture.

3.2. Chemical reaction and kinetics

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

Methyl lactate (1) + Water (2) <=> Lactic acid (3) + Methanol (4)   (1)
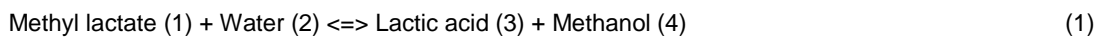
A quasi-homogeneneous (QH) activity ($a_i = \gamma_i x_i$) based kinetic model is used and can be written as:

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

3.3 Vapor-Liquid equilibrium (VLE)

K-values (VLE constants) are computed from (Eq. 3) where γ_i is computed from UNIQUAC equation, the vapor pressure (P^{sat}) of pure components has been obtained by using Antoine's equation. See Edreder et al. (2011) for more details

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

Table 1.Column specifications for hydrolysis of methyl lactate system

No of ideal stages*	= 10	Internal plate hold up (kmol)	= 0.0125
Feed Location	= 5	Condenser and reboiler hold ups (kmol)	= 0.10
Total fresh feed (kmol)	= 5	Vapour boil up rate (kmol/h)	= 2.50
		Column pressure (bar)	= 1.01325

*including reboiler and condenser

4. Simulation results

Here, simulation results using MVC for hydrolysis of methyl lactate have been obtained for given batch time 7.5 hrs. The reflux (multiple time intervals) and single reboil ratios have chosen as control variables and treated as a piecewise constant.
The switching time is at 2.5 h time interval indicated in Table 2. . Figure 3 shows the accumulated distillate, feed tank and bottom product composition profiles for the operation and the holdup profiles in

the distillate accumulator, feed tank and bottom product accumulator. It can be shown that conversion to product LA was 55 %.

Also 1.25 kmol of product LA with bottom product accumulated composition of 0.80 molefraction were obtained with no MeOH (most volatility component) and water existing in the bottom product accumulator. For MVC, the LA being the heaviest in the reaction mixture, reflux and reboil ratios policy plays an important role to achieve high purity of LA.
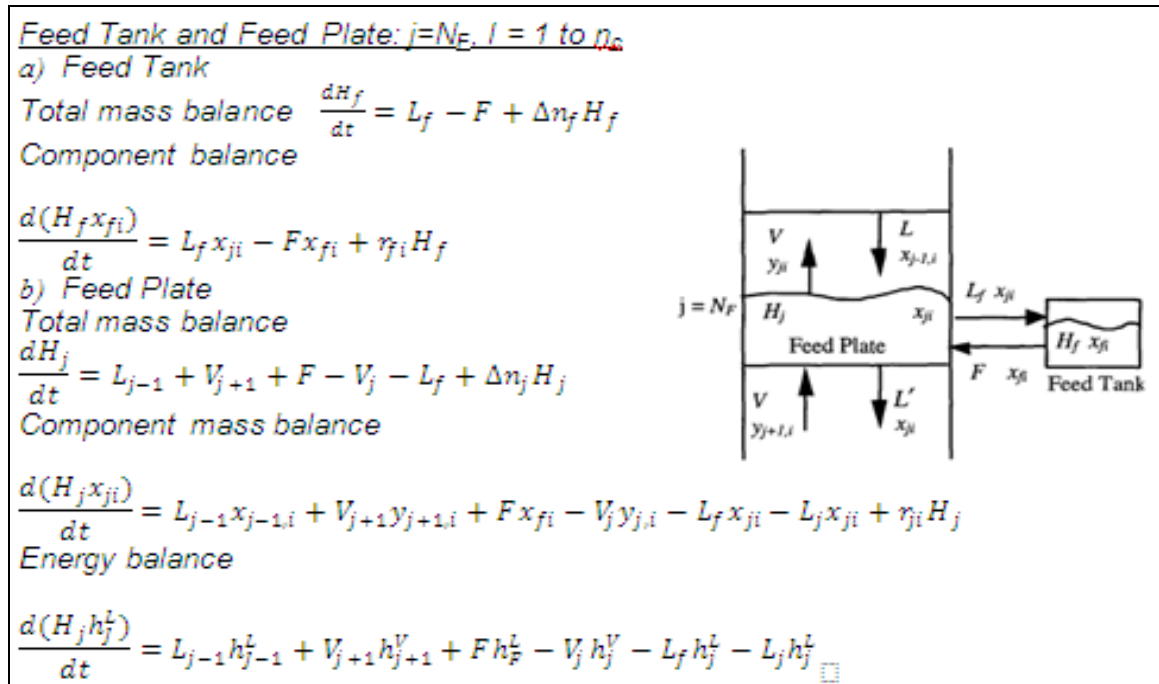
Feed Tank and Feed Plate: $j=N_F$, $I = 1$ to n_c

a) Feed Tank

Total mass balance $\quad \dfrac{dH_f}{dt} = L_f - F + \Delta n_f H_f$

Component balance

$$\frac{d(H_f x_{fi})}{dt} = L_f x_{ji} - F x_{fi} + r_{fi} H_f$$

b) Feed Plate

Total mass balance

$$\frac{dH_j}{dt} = L_{j-1} + V_{j+1} + F - V_j - L_f + \Delta n_j H_j$$

Component mass balance

$$\frac{d(H_j x_{ji})}{dt} = L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} + F x_{fi} - V_j y_{j,i} - L_f x_{ji} - L_j x_{ji} + r_{ji} H_j$$

Energy balance

$$\frac{d(H_j h_j^l)}{dt} = L_{j-1} h_{j-1}^l + V_{j+1} h_{j+1}^V + F h_F^l - V_j h_j^V - L_f h_j^l - L_j h_j^l$$

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

Table 2. Switching time and reboil and reflux ratios

Switching time, h	2.5	5.0	7.5
Reboil ratio	0.9206	0.9206	0.9206
Reflux ratio	0.700	0.800	0.900

5. Conclusions

In this work, simulation of middle vessel column involving the hydrolysis of methyl lactate reaction system is investigated. A detailed dynamic model in terms of mass and energy balances and thermodynamic properties within gPROMS modelling software was used. Piecewise constant reflux ratio (discretized into three control intervals) and single reboil ratio are considered over the batch time operation for this purpose. The results indicate that, study with middle vessel column would be interesting as both methyl lactate and water are mid-boiling components in the mixture. The reaction products methanol (lightest) and lactic acid (heaviest) can be withdrawn simultaneously from the top and bottom of the column in such case. Furthermore, theoretically, removal of both methanol and lactic acid in MVC should improve the conversion of the limiting reactant (methyl lactate or water) and will save operation time. Optimal operation of MVC for this system should be considered.
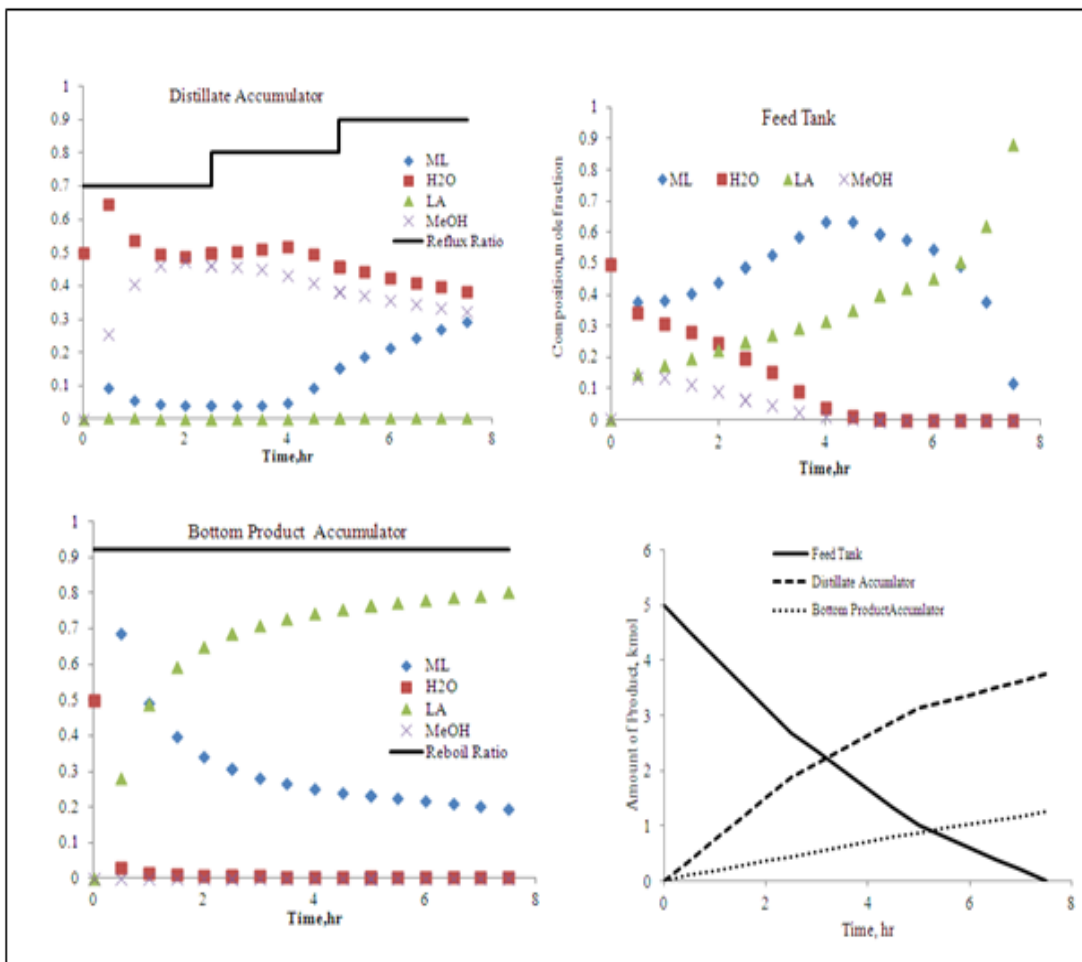
Figure 3. MVC with chemical reaction - composition and holdup profiles

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