

Optimal Operation of Batch Reactive Distillation Process Involving Esterification Reaction System

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The performance of batch reactive distillation process involving the esterification of acetic acid with methanol to produce methyl acetate and water is considered in this work. Two cases studies with varying amount of the reactants are considered. The reflux ratio (single time interval) is selected as the control variable to be optimised (treated as piecewise constant) for different but fixed batch time ranging from 5 to 15 h, so as to maximise the conversion of methanol subject to product purity of methyl acetate. The dynamic optimisation problem is converted to a nonlinear programming problem by Control Vector Parameterization (CVP) technique and is solved by using efficient SQP method. The optimisation results show that as the methanol and methyl acetate are wide boiling, the separation of methyl acetate is easier without losing much of methanol reactant. The conversion improves by 6.4 % due to sufficient amount of acetic acid being reacted with methanol. Moreover an excess of acetic acid leads to high operation temperature and therefore high reflux operation (to reduce loss of methanol from the top of the column) to maximise the conversion.

1. Introduction

Methyl acetate (MeAc) is one of the carboxylic acid ester that is an industrially important chemical. It is widely used as a solvent in glues, nail polish removers. It is also used in the manufacture of a variety of polyesters such as photographic film base. MeAc is produced by the reversible esterification reaction of methanol (MeOH) with acetic acid (AA) (Mekala and Goli, 2014). The integration of chemical reaction and separation processes in one unit operation results in batch reactive distillation. It allows significant capital and operational cost savings, especially in the case of equilibrium limited reactions, such as esterification and etherification reactions. Wajge and Reklaitis (1999) demonstrated rigorous model within the reactive batch distillation optimisation (RBD OPT) to simulate batch reactive distillation for the production of MeAc by esterification of MeOH and AA using total and different reflux ratio values. For column operation with 10 stages at 18 h the composition of MeAc in the accumulated distillate was found 0.75 molefraction.

Kirbaslar et al. (2001) carried out the esterification of AA with MeOH in batch and continuous packed bed reactive distillation column to produce high purity of MeAc using Amberlyst 15 as catalyst. The rate data was correlated with a second-order kinetic model based on homogeneous reaction. Elgue et al. (2002) presented the dynamic optimisation of MeAc synthesis. They considered two types of optimisation problems: the first minimising the operating time necessary to obtain the desired reactant conversion and the second minimising an objective function which is a combination of operating time and conversion. They showed that a significant total reflux operation time (more than 15 min) is required for high conversion of reactant in the first type. For the second type it was shown that a total reflux time of about 23 min is required if the conversion is privileged and only further operating time would allow reaching higher conversion. Tang (2005) studied esterification of AA with different alcohols ranging from C₁ to C₅ produce different range of products like MeAc, ethyl acetate, iso-propyl acetate and amyl acetate. Liu et al. (2006) focused their study into the comparison of esterification of AA with MeOH using heterogeneous and homogeneous acid catalysis. Edreder et al. (2008) studied optimal

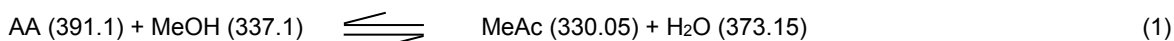
operation of conventional batch reactive distillation process (synthesis of ethyl acetate). Different cases with varying feed composition (including cases with no water in the feed) and maximum conversion problem were considered and solved with varying fixed batch time. Edreder et al. (2010, 2013) considered conventional and nonconventional column configurations and a number of reaction systems such as esterification and hydrolysis reactions.

Recently, Kamath et al. (2014) presented the comparison of simulation of continuous reactive distillation column for MeAc production. Different configurations included traditional process (reactor followed by several distillation column) were investigated. The optimization of design and operation parameters (i.e number of stages, feed location points, number of reaction stages and reflux ratios) were studied. Mekala and Goli (2014) studied the esterification of AA with MeOH to produce MeAc in an isothermal stirred batch reactor in the presence of different catalyst. The feed mole ratio was varied from 1: 1 to 1: 4. The effect of temperature, catalyst concentration, agitation speed, size of catalyst particle and reactant concentration on the AA conversion was investigated. A second-order kinetic rate equation was proposed to fit the experimental data. The AA conversion was increased with increases in AA to MeOH ratio in the feed. Later, the developed kinetic rate equation was used by the authors for the simulation of reactive distillation process.

The research work concerning the use of a batch reactive distillation column to produce MeAc is very limited compared to continuous reactive distillation. This work focuses on the optimisation of batch reactive distillation process in terms of maximum conversion for MeOH esterification process in conventional batch reactive distillation column with varying feed composition and subjected to a given product purity of MeAc. The optimisation problem is formulated and solved with different fixed batch time. Piecewise constant reflux ratio as a control variable (single time interval) is investigated and optimised.

2. Methanol esterification process

The column configuration considered in this work is shown in Figure 1. The reversible reaction scheme together with the boiling temperatures (K) of the components for esterification of MeOH and AA to produce MeAc and H₂O are:



MeAc as main product has the lowest boiling temperature in the mixture and therefore has the highest volatility. Controlled removal of MeAc by distillation will improve the conversion of the reactants by shifting the chemical equilibrium further to the right side. This will also increase the yield proportionately.

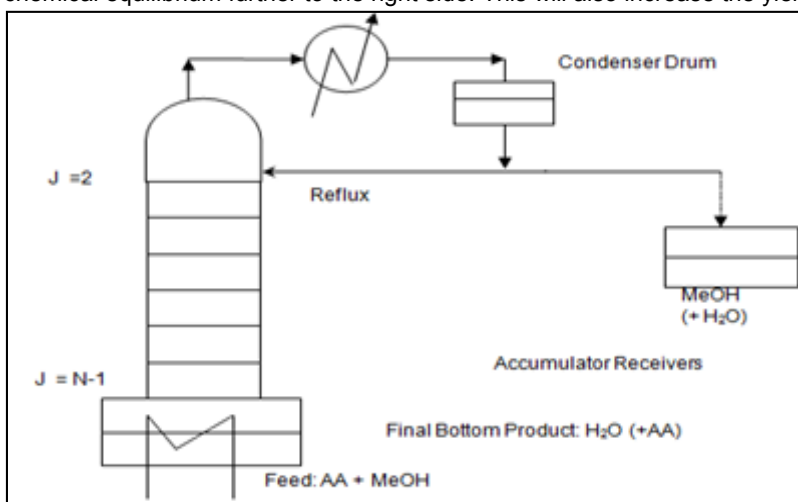


Figure 1: Methanol esterification process

3. Model equations and reaction kinetics

The model equations include mass and energy balances, column holdup, rigorous phase equilibria, chemical reaction on the plates, in the reboiler and in the condenser. Model equations for reboiler are shown in Figure 2. Details of the model except the reaction kinetics can be found in Edreder et al. (2008).

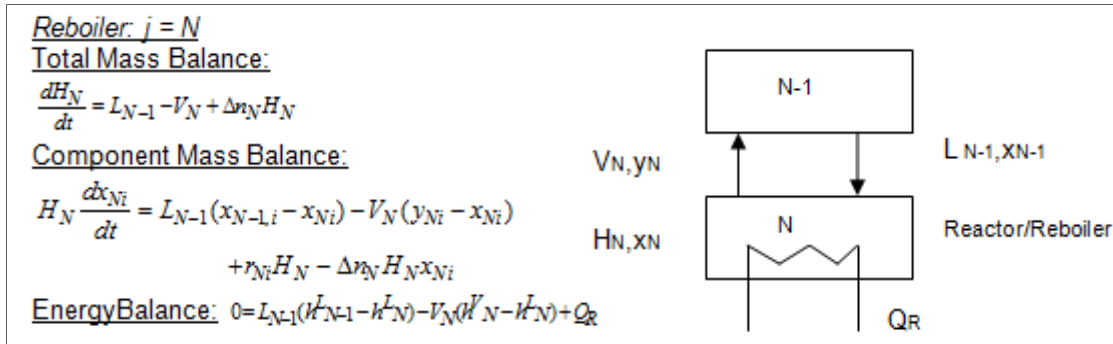


Figure 2: Configuration and model equations for the reboiler

In this work, pseudo-homogeneous activity based kinetic model (in the presence of solvated protons as a catalyst) was taken from Popken et al. (2001) and can be written as:

$$-r(\text{mol g}^{-1} \text{s}^{-1}) = k_1 a_{AA} a_{MeOH} - k_2 a_{MeAc} a_{H_2O} \quad (2)$$

With

$$k_1 = 2.961 \times 10^4 \text{ mol g}_{cat}^{-1} \text{ s}^{-1} \exp\left(\frac{-49190 \text{ J mol}^{-1}}{RT}\right) \quad (3)$$

$$k_2 = 1.348 \times 10^6 \text{ mol g}_{cat}^{-1} \text{ s}^{-1} \exp\left(\frac{-69230 \text{ J mol}^{-1}}{RT}\right) \quad (4)$$

Where a_i is the activity of each component ($a_i = \gamma_i x_i$). γ is the activity coefficient of component i which is calculated using non-random two-liquid (NRTL) equation.

4. Optimisation problem

Mathematically the optimisation problem *OP1* can be written as:

$$\begin{aligned} \text{OP1} \quad & \text{Max } X \\ & R(t) \end{aligned} \quad (5)$$

subject to :

$$t = t_f^*$$

$$x_p = x_p^* + \varepsilon \quad (\text{Inequality constraint})$$

$$\text{and } f(t, x', x, u, v) = 0 \quad (\text{Model Equation, equality constraint})$$

$$\text{with } f(t_0, x'_0, x_0, u_0, v) = 0 \quad (\text{Initial condition, equality constraint})$$

Where X is the conversion of limiting reactant to product, $R(t)$ is the reflux ratio as a function of time (t) and x_p is the composition of product at final time t_f , x_p^* is the desired composition of product and ε is a small positive number in the order of magnitude of 10^{-3} . The function f represents dynamic process model (Mujtaba, 2004). The dynamic optimisation problem is converted to a nonlinear programming problem by CVP technique and is solved by using efficient SQP technique in gPROMS modelling software (gPROMS 2004).

5. Case study

Here, two cases are used to study the effect of feed change on the maximum conversion of MeOH to MeAc. The optimisation problem OP1 is considered and solved with varying fixed batch time t_f (between 5 to 15 h) and given product MeAc purity 0.7 molefraction in the distillate as assumed in Edreder et al (2008). A single piecewise constant reflux ratio level is optimised over the batch time of operation.

5.1 Specifications

The two cases are considered in a 10 stages column (including condenser and reboiler) with vapour load equal 2.5 kmol/h. The total column holdup is 4 % of the initial feed (50 % is taken as the condenser hold up and the rest is equally divided in the plates) and the reboiler capacity is 5 kmol. The feeds <AA, MeOH, MeAc, H₂O> are: Case 1<2.5, 2.5, 0.0, 0. 0>, Case 2 - <3.0, 2.0, 0.0, 0.0>. Case 2 has proportionally more AA than in Case 1. Stage compositions, product accumulator compositions, reboiler compositions are initialised to those of the feed compositions.

5.2 Results

Table 1 shows the maximum conversion (%) of MeOH to produce MeAc, optimal reflux ratio profile and the corresponding amount of distillate product (kmol) for different batch times in both cases. Note optimisation results for Case 2 are shown in the brackets.

Table 1: Maximum conversion, reflux ratio profile and distillate product (Case 1 and Case 2) (in brackets)

| t_f , h | Max. Conversion % | Reflux Ratio | Distillate, kmol |
|-----------|-------------------|---------------|--------------------|
| 5.0 | 79.5 (85.1) | 0.765 (0.798) | 2.94 (2.52) |
| 5.0 | 77.09 | 0.918 | 1.025 (Simulation) |
| 7.5 | 81.3 (86.6) | 0.839 (0.863) | 3.02 (2.57) |
| 10.0 | 82.2 (87.4) | 0.878 (0.896) | 3.05 (2.59) |
| 12.5 | 82.8 (87.7) | 0.902 (0.917) | 3.07 (2.60) |
| 15.0 | 83.1 (88.0) | 0.918 (0.930) | 3.08 (2.61) |

Case 1 indicates that at $t_f = 5$ h, the column can be operated at low reflux ratio to remove acetate as quickly as possible and increase conversion as shown in Table 1. However it is done at the expense of losing MeOH and reducing the amount of distillate. Higher reflux ratio operation (ex. $R = 0.918$ which is optimum reflux ratio at $t_f = 15$ h) at low batch time ($t_f = 5$ h) reduces the conversion and amount of product. With longer batch time, the column exhibit more freedom to remove acetate by operating at higher reflux while retaining MeOH as much as possible for further reaction. This improves not only the conversion but the amount of product as well at a given purity. It was not possible to simulate the column for 15 h using low reflux ratio ($R = 0.765$). The maximum allowable operating time is 8.5 h (the reboiler gets empty after that time). It was seen that at low reflux operation with longer batch time would lower the conversion and would not produce the distillate at the required purity. The results of Case 2 show that a similar trend to those observed in Case 1. As a comparison, at the same operating time, it can be seen that the lower reflux ratio is lower in Case 1 than in Case 2. This allows more distillate product withdrawn in Case 1 than that achieved in Case 2.

5.3 Comparison between the two case studies

With respect to conversion: Figure 3 shows the maximum conversion achieved for both cases. It can be seen that the conversion has been improved by 6.4 % in Case 2 because there is sufficient amount of AA left in the column to react with MeOH compared to that in Case 1 (Figure 4). Also, at time $t = 0$ it is assumed that the reboiler content is at its bubble point. With more AA for Case 2, the boiling point for Case 2 at $t = 0$ was higher compared to that in Case 1 (see Figure 5) and this enhances the rate of reaction and therefore conversion. Figure 3 also shows the maximum conversion profile achieved under total reflux operation (where no product is withdrawn). This scenario is close to the situation when the column operates as the reactor only without distillation. It can be noticed from Figure 3 that an improvement in conversion is achieved for the two cases

when compared to the conversion achieved under total reflux operation. Figure 4 shows the AA composition profile at $t_r = 15$ h for both Cases 2. AA composition gradually decreases until $t = 3$ h and then kept at the same value with increasing the time for Case 1. In Case 2 it gradually increases due to no further reaction (no MeOH available).

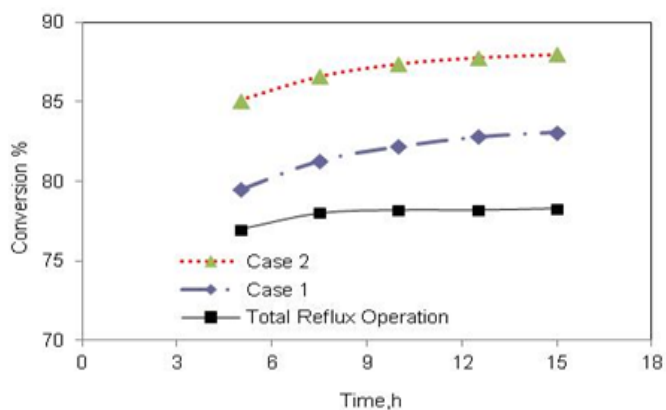


Figure 3: Maximum conversion vs. batch time for different cases

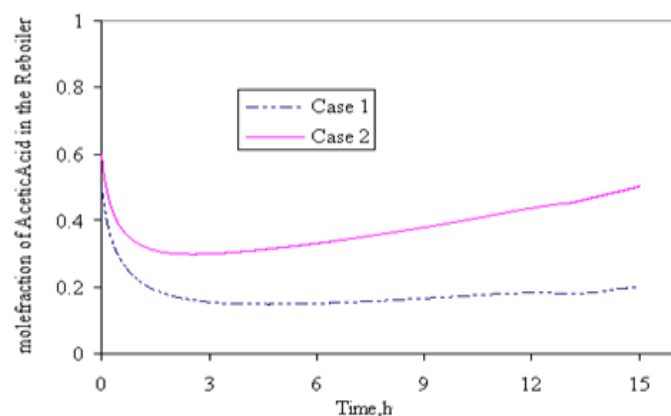


Figure 4: Reboiler composition profiles for AA in both cases ($t_r = 15$ h)

With respect to reboiler temperature time profiles: the reboiler temperature profile for both cases at operation time 15 h and product purity 0.7 (as an example) is shown in Figure 5. Similar trends can be observed in both Cases.

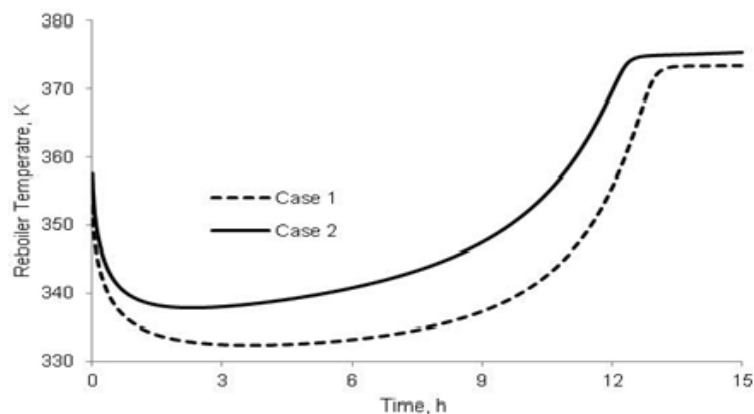


Figure 5: Reboiler temperature profile for both cases ($t_r = 15$ h).

In Case 2 higher temperature operation is noticed due to more AA in the feed. Higher temperature of the reboiler at initial time is noticed which decreases gradually with time in both cases. The decrease in

temperature is due to more volatile components produced by the reaction. After a certain time as the lighter components are distilled off, the heavier components are left in the reboiler, therefore the temperature begins to increase

6. Conclusions

Optimal operation of batch reactive distillation column involving the esterification process of AA with MeOH to produce MeAc and H₂O was considered. Two cases are studied with varying amount of reactants. The model equations in terms of mass and energy balances and thermodynamic properties within gPROMS modelling software were used. Optimisation problem was formulated to optimize the reflux ratio (assumed piecewise constant with a single time interval) while maximizing the conversion of MeOH to MeAc for different but fixed batch time t_r (between 5 and 15 h) and for given product purity ($X_{\text{MeAc}} = 0.7$). The dynamic optimisation problem is converted to a nonlinear programming problem by CVP technique and is solved by using efficient SQP method. Since MeOH and MeAc are wide boiling system which indicates easy separation of MeAc without losing much MeOH reactant (compared to ethanol esterification system). The optimisation results show that excess AA (Case 2) leads to high temperature operation and therefore high reflux operation in order to maximise the conversion.

Nomenclature

| | |
|---|---|
| H_j, H_N : plate and reboiler holdup (kmol) | h_L, h_V : liquid, vapour enthalpy (kJ/kmol) |
| L, V : liquid, vapour flow rates (kmol/hr) | N : number of plates |
| Q_C, Q_R : condenser or reboiler duty (kJ/hr) | T, P : temperature (K), pressure (bar) |
| K : vapour-liquid equilibrium constant | r : reaction rate |
| t : batch time (h) | x, y : liquid or vapour composition (mole fraction) |
| R, R_b : reflux and reboil ratio | u : The control variables represent time dependent decision variables |
| | v : the set of constant parameters |

Superscripts and subscripts

Δn : change in moles due to chemical reaction

i : component number

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