Optimal High Purity Acetone Production in a Batch Extractive Distillation Column

P. Kittisupakorn, K. Jariyaboon, and W. Weerachaipichasgul

Abstract— **A waste solvent mixture of acetone-methanol in a pharmaceutical plant which is minimum-boiling azeotrope properties, it is difficult tasked to separate this liquid mixtures by conventional batch distillation. To achieve higher purity, a batch extractive distillation, combining the extraction and separation into a single stage, is widely carried out to separate this waste solvent mixture. The objective of this work is to study an approach to produce acetone with the purity of 94.0% by mole by a batch extractive distillation column. In the column operation, semi-continues mode has been proposed to improve purity of acetone. The total reflux start-up period is finished when the unit reaches its steady state and/or maximum purity. Water has been used as solvent. Dynamic optimization strategy is proposed after the total reflux start-up period is ended. The optimization problem is formulated to maximize the weight of distillate product for a given product specification, reboiler heat duty, and batch operating time. Simulation results show that 94.0% purity of the distillate product can be produced by the dynamic optimization programming with two or more time intervals. Besides, the higher time intervals results in the higher distillate product.**

Index Terms—**Minimum-boiling azeotrope, Batch extractive distillation, Dynamic optimization, High purity acetone**

I. INTRODUCTION

Batch distillation is widely applied mostly for the fine and specialty chemical and pharmaceutical industries for the purification of solvent and reagents, and for pollutants elimination from wastewaters. Moreover, the operation of the batch distillation is very attractive; the flexibility in purifying different mixtures under a variety of operational condition, and the separation multicomponent mixture in a single batch column. However, the mainly weakness of batch distillation is that the mixture can form an azeotrope; it cannot be separated by conventional distillation. As a result, alternative distillation methods must be used: azeotropic, extractive, salted and pressure-swing distillations. In industrial applications, extractive and azeotropic distillations are most frequently used but the extractive distillation is generally more flexible than azeotropic distillation, a greater variety of solvents and a wider range of operation conditions. Moreover, the concentration of solvents may be controlled by heat and material balances. However, the operation of extractive distillation for binary mixtures in continuous mode requires at least two columns in sequence, one for the separation step and the others for the solvent recovery step. Thus, it is not limited to any economic and/or environmental constraint.

The extractive distillation is operated into a batch mode called “Batch extractive distillation (BED)” that offers the advantages of both the batch and the extractive distillation. The BED operations are rather complex including the operation of batch distillation, the introduction of a solvent, the location of solvent feeding, and the feed flow rate of solvent, etc..Therefore, the BED process has been less studied.

However, due to the advantages of the BED, modeling of BED has been carried out to study its dynamic behavior [1]. The operations under constant reflux ratio and optimization of quantity and quality product in a fixed time with the smaller quantity of solvent have been proposed and studied in several research work [1],[2],[3], and [4]. Moreover, the BED process has been improved with a new operation. For examples, a batch distillation column combines with two reboilers for solving the problem of larger volume of the reboiler and higher heat duty in conventional batch extractive distillation [5], and the BED has been operated by a hybrid process [6].

In a pharmaceutical plant, a waste solvent mixture of acetone-methanol is formed an azeotrope with a minimum-boiling temperature of 55.24 ^{o}C at atmospheric pressure. This mixture can be separated by the BED using water as an entrainer. The production of acetone using the BED column, focused on optimization and control operations have been presented in [7], and [8]. Acetone (boiling point 56.14 ^{o}C) is an organic compound that is miscible with water. It is used widely as a solvent and in chemical industries. Methanol (boiling point 64.53 ^{o}C) is a polar liquid that applies to be an antifreeze, solvent, fuel, and as a denaturant for ethanol at room temperature.

The aim of this work is focused on a conventional BED for the separation of minimum azeotropes by rigorous mathematical models. To achieve the high product quality, dynamic optimization technique has been applied by successive quadratic programming (SQP) solving [9], [10], and [11]. The objective function of the optimization problem is to maximize the weight of distillate product with reboiler heat duty kept constant value along the operation time and the specified product purity is greater than 0.94.

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II. PROCESS AND THE MODEL

In a conventional batch extractive distillation as shown in Fig. 1, it consists of total twenty trays, including the condenser holdup tank (1st tray) and reboiler (20th tray). Rigorous nonlinear models considered the effect of heat and mass transfer operations and fluid flow on the plates are needed to represent realistic operation of the batch extractive distillation. The models of BED are derived from first principles with following assumptions: 1) constant molar holdup for condenser and internal plates, 2) total condensation without sub-cooling, 3) negligible vapor holdup, 4) perfect mixing of liquid and vapor on the plates, 5) negligible heat losses, 6) theoretical plates, 7) negligible pressure drop across the column, and 8) constant reboiler heat duty.

To achieve the mathematical models, the material and energy can be balanced around the reflux drum the internal plate, and the reboiler.

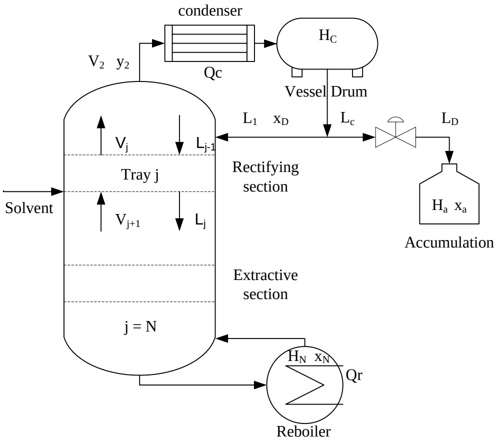

Fig. 1. Conventional batch extractive distillation

-- Condenser and Accumulator (*j =1; i = 1 to* n_c)

Accumulator

Total mass balance:

$$\frac{dH_a}{dt} = L_D \tag{1}$$

Component balance;

$$\frac{dH_a x_a}{dt} = L_D x_{Di} \tag{2}$$

$$L_D = L_c(1-R_f) \tag{3}$$

Condenser hold up tank

Total mass balance:

$$\frac{dH_c}{dt} = V_2 - L_c \tag{4}$$

Component balance;

$$\frac{dH_c x_{Di}}{dt} = V_2 y_{2i} - L_c x_{Di} \tag{5}$$

Energy balance:

$$\frac{dH_c h_1^L}{dt} = V_2 h_2^V - L_c h_1^L - Q_C \tag{6}$$

-- Internal Plates *(j = 2 to (N-1); i = 1 to* n_c*)*

Total mass balance:

$$\frac{dH_j}{dt} = L_{j-1} + V_{j+1} - L_j - V_j \tag{7}$$

Component balance:

$$\frac{dH_j x_{ji}}{dt} = L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} - L_j x_{ji} - V_j y_{ji} \tag{8}$$

Energy balance:

$$\frac{dH_j h_{ji}}{dt} = L_{j-1} h_{j-1}^L + V_{j+1} h_{j+1}^V - L_j h_j^L - V_j h_j^V \tag{9}$$

-- Entrainer feed Plate *(j =*N_F*; i = 1 to* n_c*)*

Total mass balance:

$$\frac{dH_j}{dt} = L_{j-1} + V_{j+1} - L_j - V_j + F \tag{10}$$

Component balance:

$$\frac{dH_j x_{ji}}{dt} = L_{j-1} x_{j-1,i} + V_{j+1} y_{j+1,i} - L_j x_{ji} - V_j y_{ji} + F x_F \tag{11}$$

Energy balance:

$$\frac{dH_j h_{ji}}{dt} = L_{j-1} h_{j-1}^L + V_{j+1} h_{j+1}^V - L_j h_j^L - V_j h_j^V + F h_F^L \tag{12}$$

-- Reboiler *(j = N; i =1 to* n_c *)*

Total mass balance:

$$\frac{dH_N}{dt} = L_{N-1} - V_N \tag{13}$$

Component mass balance:

$$\frac{d(H_N x_{Ni})}{dt} = L_{N-1} x_{N-1,i} - V_N y_{Ni} \tag{14}$$

Energy balance:

$$\frac{d(H_N h_N^L)}{dt} = L_{N-1} h_{N-1}^L - V_N h_N^V + Q_r \tag{15}$$

where y is a vapour mol fraction that can calculated by the vapour-liquid equilibrium as;

$$y_{j,i} = \gamma_{j,i} \frac{P_{s,j,i}}{P} x_{j,i} \tag{16}$$

where P is the column pressure , and $P_{s,j,i}$ is the vapour pressure of component i in plate j .

The vapor pressures $P_{s,j,i}(T)$ of the pure components are calculated by the Antoine equation as;

$$\log P_{s,j,i} = A - \frac{B}{T + C(°C)} \tag{17}$$

The liquid-phase activity coefficients γ are calculated using the NRTL model

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left[\tau_{ij} - \frac{\sum_m x_m \tau_{mj} G_{mj}}{\sum_k x_k G_{kj}} \right] \qquad (18)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \qquad (19)$$

$$\tau_{ij} = a_{ij} + (b_{ij} / T) \qquad (20)$$

where $\alpha_{ij} = c_{ij}$, $\tau_{ii} = 0$, and $G_{ii} = 1$. The vapour-liquid equilibrium relation can be used to compute bubble point temperature that $\sum_i^{Nc} y_{j,i} = 1$. Moreover, the other variables such as h^l, and h^v can be calculated using the relation of enthalpy respectively.

$$h_j^L = h_j^L (x_j, T_j, P) \qquad (21)$$

$$h_j^V = h_j^V (y_j, T_j, P) \qquad (22)$$

In this work, at the beginning of the batch operation, it is assumed that the reboiler, all the trays, and the reflux drum are filled with the liquid feed. Water as the entrainer is selected to perform the separation of acetone from methanol. The entrainer feed flow rate at the tray number 6 is kept constant during step 2 and 3 of the BED operation steps. The column specification, the Antoine coefficients, and NRTL model parameters are given in Table 1- Table 3.

TABLE I

COLUMN SPECIFICATIONS

No. of ideal stages (including reboiler and condenser)	20
Reboiler maximum capacity (kmol)	52
Entrainer feed flow rate (kmol/hr)	7
Feed composition (mol fraction, *x*)	
- Acetone	0.5
- Methanol	0.5
- Water	0.0
Column holdup (kmol)	
- Condenser (H_c)	0.1
- Internal plates(H_j)	0.5
Column pressure (bar)	1.013
Reboiler heat duty Q_r (MJ/h)	4E+2

TABLE II

ANTOINE COEFFICIENTS

	A	*B*	*C*
Acetone (A)	7.02447	$1.16000{\times}10^3$	$2.2400{\times}10^2$
Methanol (B)	7.878863	$1.47311{\times}10^3$	$2.2300{\times}10^2$
Water (E)	7.96681	$1.66821{\times}10^3$	$2.2800{\times}10^2$

TABLE III

NRTL PARAMETERS

Component, *i*	Aceton	Acetone	Methanol
Component, *j*	Methanol	Water	Water
a_{ij}	0	6.3981	-0.6930
a_{ji}	0	0.0544	2.7322
b_{ij}	101.8859	-1808.9900	172.9871
b_{ji}	114.1347	419.9700	-617.2690
c_{ij}	0.3	0.3	0.3

In this work, the BED separation steps are as follows:

1. Operation under total reflux without solvent feeding resulting in steady-state operation (azeotropic composition).
2. Operation under total reflux with solvent feeding until maximum purity of acetone (A) is reached.
3. Operation under various finite reflux with solvent feeding to withdraw acetone (A) until the desired purity of acetone is achieved.
4. Operation under finite reflux without solvent feeding to withdraw methanol (B) until the desired purity of methanol is achieved.

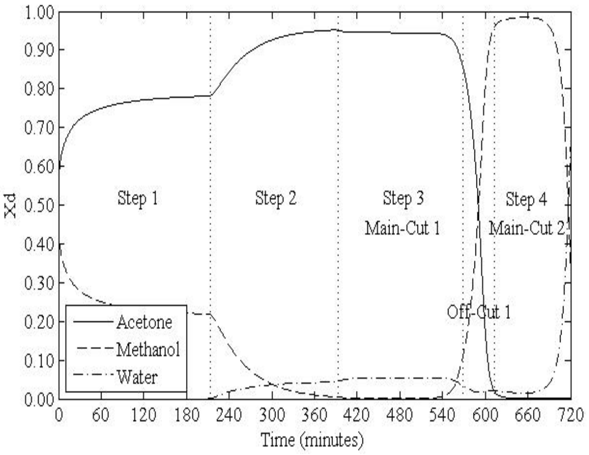

Fig. 2. Distillate composition profiles of acetone-methanol-water

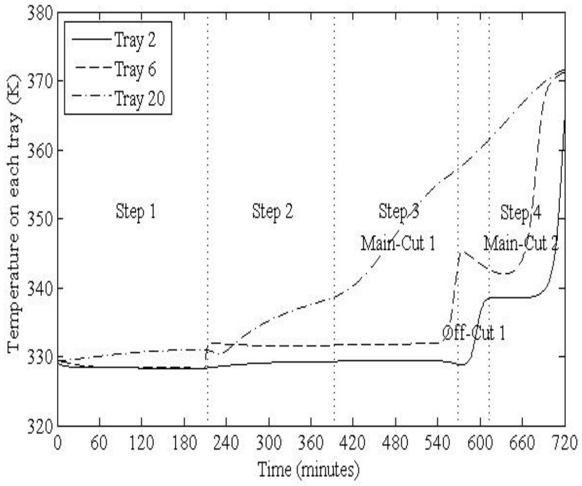

Fig. 3. Temperatures profile on each tray in BED column

In the step 1, the maximum value of $x_{d,A}$ is approached at the steady-state operation. In the experimental at atmospheric pressure, azeotropic composition and temperature are in the range between 74.94 - 81.60 mol% acetone, and 55.10 - 56.90 ^{o}C, respectively. While the predicted value of the azeotropic composition from the NRTL model is 77.75 mol% acetone and the temperature is 55.22 ^{o}C. Therefore, the NRTL model can precisely represent the actual system.

In the step 2 and 3, the entrainer (water) is charged into the column to break the azeotropic composition of acetone and methanol. The water has a greater affinity to methanol, the more polar of the pair, so the relative volatility of methanol is decreased. Acetone which is more volatile will go up to the top of the column and a methanol which is less volatile will be carried with the water toward the column bottom. In the rectifying section, due to the lack of methanol in this section, only the separation of acetone and water is performed. Pure acetone will preferably go to the top of the batch extractive distillation column. In the end of step 4, after the draw-off of the acetone product in the main cut period and a slop-cut period where the acetone in the column is completely depleted, the methanol product can be collected at the top of the column. The water can be collected at the bottom of the column.

III. DYNAMIC OPTIMIZATION PROBLEM FORMULATION

A conventional batch extractive distillation model described by the system of differential algebraic equation (DAEs) presented in the Eqs. (1) - (22) can be written as:

$$f(t,\dot{x},x,u,v)=0 \qquad (23)$$

With consistent initial conditions

$$f(t_0=0,\dot{x}_0,x_0,u_0,v)=0 \qquad (24)$$

where *x* is the set of all the variables (differential and algebraic), values are the time derivatives of the differential variables, *u* values are the time dependent control variables, *v* is a set of constant parameters, and *t* is the time. The function *f* is assumed to be continuously differentiable with respect to all arguments.

A dynamic optimization problem is formulated and solved using an optimal control algorithm. The optimization problem for the DAE system given by [1] is formulated as a nonlinear programming problem with the time-varying controls parameterized into a finite set of control parameters. Other optimization variables: time independent i.e., design parameters, initial conditions, and the final batch time, are optimized to give a maximum of a general objective function $f(t_0=0,\dot{x}_0,x_0,u_0,v)=0$ subject to any constraints as shown in Fig. 4. Details of the algorithm are in [9]-[15]. A robust code is used for DAE integration, with an efficient successive quadratic programming (SQP) method used for optimization of the finite number of parameters.

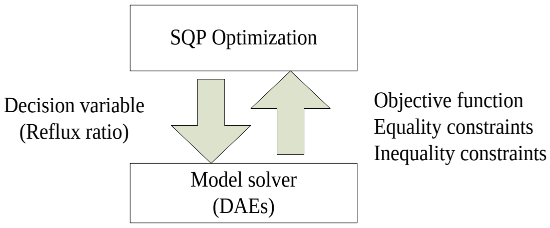

Fig. 4. Feasible path optimization strategy

In this work, a maximum distillate problem into step 3 of batch extractive distillation operation is considered to be an objective function subject to a given product purity constraints. The reflux ratio is selected as the decision variable to be optimized for the fixed batch time and reboiler heat duty to so as to maximize the weight of the distillate product. The optimization problem can be stated as follows:

Maximum Distillate Problem

Optimization problem formulation

Given:	the column configuration, solvent feed location, the feed mixture, solvent feed flow rate, reboiler heat duty
Determine:	the optimal internal reflux ratio
So as to:	maximize an objective function defined for the amount of distillate products in the accumulation
Subject to:	equality and inequality constraints

Mathematically, the problem can be written as:

$$\underset{R_f(t)}{Max} \quad Ha$$

Subject to

$$f(t,\dot{x},x,u,v)=0 \qquad \text{(Model equation)}$$

$$x_{a1} \geq 0.94 \qquad \text{(Inequality constraints)}$$

$$0 \leq R_f \leq 1 \qquad \text{(Inequality constraints)}$$

$$t_f = 3 \qquad \text{(Equality constraints)}$$

IV. RESULT AND DISCUSSIONS

A dynamic optimization problem for a batch extractive distillation process is transformed into a nonlinear programming (NLP) problem to be solved by a SQP-based optimization technique and developed process models are integrated by using the Gear's type method. The maximum weight of the distillate product with respect to variations of time intervals: 2, 4, 8 and 16 intervals have been carried out. The simulation results with different time intervals are shown in Fig. 5. Table 4 reports the distillate composition in accumulate and amount of the desired product at each time intervals. It has been found that at the final batch time, the maximum product is achieved in the case of 16 time intervals.

TABLE IV
SUMMARY OF THE OPTIMAL RESULTS

Interval	$xa_1(t_f)$	Product (kg)
1	0.94	477.48
2	0.94	477.48
4	0.94	493.84
8	0.94	508.20
16	0.94	511.25

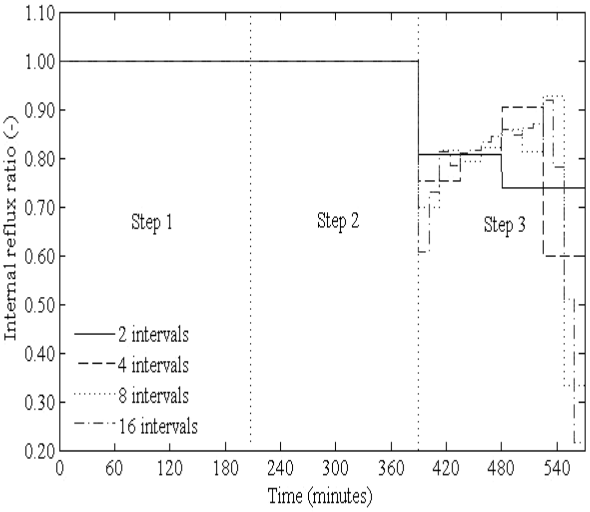

Fig. 5. Optimal reflux ratio profile:2, 4, 8 and 16 intervals

V. CONCLUSION

In this work, production of high purity acetone in the batch extractive distillation into step 3 is presented. The dynamic optimization strategy is incorporated to solve an optimization problem formulating with an objective function: to maximize the weight of distillate product for a given product specification, reboiler heat duty, entrainer feed, and batch operating time (3 hrs.). Ninety four percentages purity of the distillate product can be produced by an optimal reflux ratio profile with two or more time intervals. The increasing of time intervals results in the increasing of the distillate product.

Nomenclature:

h^L	Liquid enthalpy of component i at stage j (kJ / $kmol$)
h^V	Vapor enthalpy at stage j $(kJ/kmol)$
H	Molar holdup $(kmol)$
L	Molar liquid flow rate ($kmol$ / hr)
n_c	Number of component
Q_c	Condenser duty (kJ / hr)
Q_r	Reboiler duty (kJ / hr)
R_f	Internal reflux ratio
T	Temperature (K)
V	Molar vapor flow rate ($kmol$ / hr)
X	Liquid composition
y	Vapor composition

Subscripts:

i	Component number
j	Stage number
a	Accumulator
c	Condenser
D	Distillate

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