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Significant Profitability Improvement for Methyl Decanoate Production using Different Types of Batch Distillation Columns

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Esterification of fatty acid (Decanoic Acid) is a common practice in the chemical industries, which can be widely used in several applications such as lubricants agent, plasticizers in polymer industries, pharmaceutical and food industries, solvents for inks and paint removal, and detergents. Methyl decanoate (MeDC) as fatty ester is an important chemical component. Reactive distillation columns have been successfully employed in many reaction systems where reaction and separation takes place simultaneously. In this paper, the performance of esterification of decanoic acid to produce MeDC is considered using the newly developed integrated conventional batch (i-CBD) and semi-batch distillation processes (SBD). The performances of these column configurations are evaluated in terms of profitability via minimisation of production time for a given separation task. Additional operational constraints into SBD column are posed in the optimisation problem to avoid overflowing of still pot at any time of the process due to continuous feeding of methanol into the bottom of column as the reboiler is initially charged to its full capacity. The optimization results clearly demonstrate that the SBD system is more attractive operation in terms of batch time and energy consumption savings, maximum conversion level and higher annual profit as compared to the i-CBD column.

1. Introduction

The investments in fatty acid alkyl esters (biodiesel) as biodegradable fuels produced from renewable resources are increasingly receiving attention in recent years due to the global warming problems and the economic issues. A large number of scholars (Karacan and Karacan, 2015) have previously studied the esterification of fatty acids (such as dodecanoic, and oleic acids) with methanol to form fatty methyl ester with only few (Machado et al., 2011) looking at methyl decanoate synthesis by the esterification of decanoic acid with methanol which is the main focus of this study. Batch operation is becoming more important in numerous chemical plants as the trend to specialty, low-scale production of high-added value chemicals continues. The integration of reaction and separation into one operation unit (reactive distillation) can reduce the capital investment, operational costs, and environment emissions as well as the energy consumption, improved productivity and selectivity. A number of studies (Edreder et al., 2009) discussed optimal design and operation polices of batch distillation column under fixed product demand scenario and strict purity considerations. More recently, Aqar et al. (2016a) presented new integrated batch reactive distillation columns for optimal synthesis of methyl lactate. For a defined separation task, they compared the performances of each of these column (i-CBD and i-SBD) configurations in terms of profitability. Their results visibly indicated that the i-SBD system provides much better performance than the i-CBD for methyl lactate synthesis. In this work, the performances of i-CBD and SBD processes for MeDC synthesis in terms of maximum profit function via minimizing processing batch time are determined by formulating and solving an optimization problem incorporating a detail dynamic model for the process. The dynamic optimization case is transformed into a nonlinear programming problem (NLP) and is solved utilizing Control Vector Parameterization (CVP) and Successive Quadratic Programming (SQP) based optimization approach available within gPROMS software. The product

amount and its purity are used as constraints and the reflux ratios, and methanol recycle rate (only for the i-CBD) and methanol feed rate (for the SBD system) are optimized.

2. Column configurations and process models

With reference to two column configurations (i-CBD and SBD) shown in Figure 1, the detailed dynamic model (Aqar et al., 2016) includes mass and energy balance equations, column holdup, rigorous thermodynamic properties, and chemical reaction on the trays, in the reboiler and in the condenser is used here. The process model assumes no vapour holdup, constant molar holdup on the trays and in the condenser, no heat loss, perfect mixing on all trays, fast energy dynamics, constant column pressure and total condensation with no sub-cooling. Note, further details can be found in Mujtaba (2004).

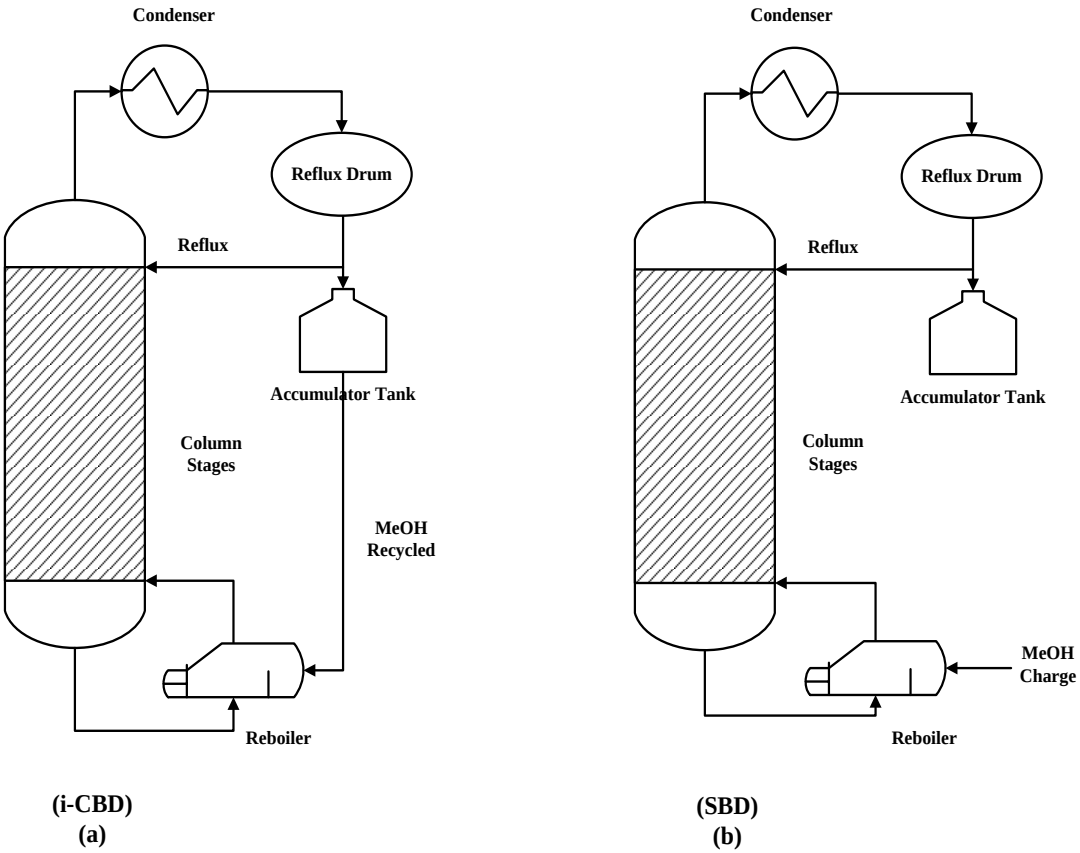

Figure 1: Schematic diagram of two column configurations for producing methyl decanoate: (a) the integrated conventional (i-CBD), and (b) semi-batch distillation (SBD)

3. Optimization problem formulation

In this study, the optimum operations of i-CBD and SBD columns are evaluated in terms of maximum yearly revenue for a given product amount and desired purity of MeDC.

3.1 Maximum Profit Problem

The optimization problem can be described as follows:

Given: The i-CBD/SBD column configurations, the feed composition, the condenser vapour load, The product purity and the amount of bottom product (methyl decanoate)

Optimize: The reflux ratio ($R_{i\text{-}CBD}$), and the MeOH recycle rate (S_{MeOH}) profiles (for i-CBD)

Or, the reflux ratio (R_{SBD}), and the MeOH feed rate (F_{MeOH}) profiles (for SCBD)

So as to maximise: The profit

Subject to: Process constraints (reboiler overflowing, etc.), Model equations (Equality and inequality constraints)

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

OP1 Max P

$R_{i\text{-}CBD}(t)$, $S_{MeOH}(t)$ (For i-CBD Column)

Or (1)

$R_{SBD}(t)$, $F_{MeOH}(t)$ (For SBD Column)

Subject to :

$B = B^*$ (Inequality Constraints) (2)

$x^*_{MeDC} - \varepsilon \leq x_{MeDC} \leq x^*_{MeDC} + \varepsilon$ (Inequality Constraints) (3)

The profit function equations and constants for both i-CBD and SBD systems can be shown as:

$P_{i\text{-}CBD} = (C_{MeDC} B - C_R B_0 - OC) \times N_B - ACC$ (4)

$P_{SBD} = (C_{MeDC} B - C_R B_0 - OC - C_{MeOH\ Charge}) \times N_B - ACC$ (5)

OC (The operating cost, \$/Batch) = $(\frac{K_3 V_C}{A_P}) \times (t_f + t_s)$ (6)

N_B (Number of Batches, Batch/ yr) = $\frac{(P_H\ /\ yr)}{(t_f + t_s)}$ (7)

ACC (Annual Capital Cost, \$/ yr) = $K_1 (V_C)^{0.5} (N)^{0.8} + K_2 (V_C)^{0.65}$ (8)

TYP (Kmol/ yr) = $N_B \times B$ (9)

Where, K_1 =1500; K_2 = 9500; K_3 = 180; the operating cost constant (A_P) = 8000; setup time (t_s) = 0.5 hr; P_H = 8000 hr/yr (Miladi and Mujtaba, 2004). Since the number of plates (N) and the vapor load to condenser (V_C) kept constant, the annual capital cost (ACC) is also fixed. For a given separation task (given product amount and purity of product per batch), the minimization of batch time will increase the number of batches (N_B) and thus will increase the profitability. Therefore, the maximum profit problem can be converted to minimum batch time problem as shown below.

3.2 Minimum Batch Time Problem

The optimization problem can be described as follows:

Given: The i-CBD/SBD column configurations, the feed composition, the condenser vapour load, The product purity and the amount of bottom product (methyl decanoate)

Optimize: The reflux ratio ($R_{i\text{-}CBD}$), and the MeOH recycle rate (S_{MeOH}) profiles (for i-CBD)
Or, the reflux ratio (R_{SBD}), and the MeOH feed rate (F_{MeOH}) profiles (for SCBD)

So as to minimise: The operating batch time

Subject to: Process constraints (reboiler overflowing, etc.), Model equations (Equality and inequality constraints)

Mathematically, the optimization problem (OP2) can be stated as follow:

OP2 Min t_f

$R_{i\text{-}CBD}(t)$, $S_{MeOH}(t)$ (For i-CBD Column)

Or (10)

$R_{SBD}(t)$, $F_{MeOH}(t)$ (For SBD Column)

Subject to :

$B = B^*$ (Inequality Constraints) (11)

$x^*_{MeDC} - \varepsilon \leq x_{MeDC} \leq x^*_{MeDC} + \varepsilon$ (Inequality Constraints) (12)

Where B, x_{MeDC} are the amount of bottom product (2.4 kmol for both columns), and purity of methyl decanoate at the final batch time t_f (denotes that the B^*, x^*_{MeDC} are specified). R_{SBD} (t) and $R_{i\text{-}CBD}$ (t) are the optimal reflux ratio profiles for both columns (SBD and i-CBD) which are optimized and ε is small positive numbering the order of 10^{-3}. Note, all prices of reactant were taken from (Alibaba Trade, 2016) and the prices of methyl decanoate at other purities are estimated based on the exponential trend method used in (Aqar et al., 2016b).

The costs of chemical reaction (DeC and MeOH) and product (MeDC) at various product purities values are tabulated in Table 1. Note also, the calculations of operational constraints policy in terms of overloading of reboiler (B, x_{MeDC}) for the SBD column are similar to those used in (Aqar et al., 2016b).

Table 1: The prices of feed and product

Pure MeOH Reactant Price	12.84	MeDC Price at 92.5% Purity	250
MeOH Charge Price at 95% Purity	12.20	MeDC Price at 95.0% Purity	280
Pure DeC Reactant Price	87.00	MeDC Price at 96.5% Purity	335
MeDC Price at 90.0% Purity	240.0	MeDC Price at 97.5% Purity	380

4. The synthesis of methyl decanoate system

4.1 Problem description

The case study is implemented in a 10-plates batch column (including a total condenser and a reboiler) with the condenser vapour load, V_C = 2.5 kmol/hr. The column stages are numbered from the top down. Four percent of the initial feed is the total column holdup. Fifty percent of this total holdup is taken as the condenser holdup and the rest is taken as the plate holdup (equally divided). This strategy of column holdups has been applied for both columns (i-CBD and SBD). Note, the same strategy is used for the catalyst loading distribution. The total initial amount of feed is 5 kmol with the feed composition < DeC, MeOH, MeDC, H_2O > is : <0.5, 0.5, 0.0, 0.0>, respectively.

4.2 Chemical reaction and kinetics

The esterification reaction of decanoic acid (DeC) with methanol (MeOH) forms methyl decanoate (MeDC) and water (H_2O) together with the boiling points of the components can be expressed as follows:

$$\underset{\text{B.P (K)}}{\underset{543.15}{\text{DeC (1)}} + \underset{337.15}{\text{MeOH (2)}} \Leftrightarrow \underset{505.15}{\text{MeDC (3)}} + \underset{373.15}{H_2O\ (4)}} \tag{13}$$

The modified Langmuir-Hinshelwood-Hougen-Watson (LHHW) activity ($a_i = \gamma_i x_i$) based kinetic model is used (taken from Steinigeweg and Gmehling, 2003) and can be written as:

$$-r = M_{Cat}\left(3.1819 \times 10^6 \exp\left(\frac{72230}{RT}\right) \times \left(\frac{a_1 a_2}{(2.766\, a_4)^2}\right) - 3.5505 \times 10^5 \exp\left(\frac{71900}{RT}\right) \times \left(\frac{a_3}{2.766\, a_4}\right)\right) \tag{14}$$

4.3 Vapour-liquid equilibrium (VLE)

K-values (VLE constants) are calculated from (Eq. 15) where γ_i is calculated from the NRTL method, the saturated vapor pressure (P^{sat}) for each pure substances is estimated by using Antoine's equation. The NRTL binary interaction parameters were taken from Aspen HYSYS package and Antoine coefficients were taken from Steinigeweg and Gmehling (2003). The vapor enthalpies are computed using empirical equations from Aspen HYSYS (2016) and the liquid enthalpies were computed by subtracting enthalpy of vaporization from the vapor enthalpies.

$$K = \left(\frac{\gamma_i P_i^{sat}}{P}\right) \tag{15}$$

5. Results and discussions

i-CBD process: Table 2 summarizes the optimal operation strategy, including methanol recycle rates, reflux ratios, total amount of recycled methanol, the operating time, heat usage rate, the conversion rate of DeC, the number of batches, and annual production rate, as well as the maximum achievable profit for the i-CBD column. As can be noted form Table 2 that increasing the quality of MeDC product increases all reflux ratios, and the processing-batch time together with total energy consumption, and the total amount of methanol recycled to column. Clearly, increasing the operating time can lead to increase the conversion ratio of DeC into MeDC. It can be noticed also from Table 2 that as the product composition and production time increase, the number of batches produced over the year and total yearly product progressively decrease (see Eqs. 7 and 9). As the bottom product purity constraint increases form (0.90 to 0.975 mole fractions) together with price of MeDC product, the annual profit increases progressively. However, note, for 0.975 of product purity, there is a sharp decrease in the product revenue due to huge increase in the production batch time and reflux ratio (although the recycle rate of methanol reduces). This makes i-CBD uncompetitive process (compared to others) at higher MeDC quality and hence the suggested SBD mode.

SBD mode: For the five product purities considered, the summary of optimization results including optimal methanol feed rates and reflux ratios profiles, maximum reflux ratios, total amount of charged methanol, the

operating batch time, total thermal heat rate, the conversion rate of DeC, the number of batches, and annual production rate, and the net profit for the SBD column are presented in Table 3. It is clear form Table 3 that the use of SBD mode caused big savings in the operating batch time and the total energy demand, and higher improvement in the DeC conversion and the process revenue as compared to the i-CBD operation (Table 2). For instance, at 0.975 mole fraction purity the reductions in the batch processing time, and the thermal energy requirement are almost 81.16%, and 81.57%, and the improvement in conversion rate is about 0.79%, as compared to i-CBD column. It is seen form Table 3 that the total annual product demand upgraded is about 79.30% at product purity of 97.50% compared to that obtained by the i-CBD operation. In addition, for the 0.975 of MeDC composition case, comparison of the maximum yearly profit for the SBD column with those obtained using i-CBD reveals 80.06% more profit due to low production time and thermal heat demanded to achieve the desired purity requirements. Clearly, the SBD is found to outperform the i-CBD operation in many respects. Figure 2 compares the processing batch time for all MeDC mole fractions for both column configurations. For i-CBD column up to 0.965 purity of MeDC, the increasing product value dominates over the batch time. Beyond 0.965 purity, the batch time dominates over the product value thereby reducing the profitability. In such circumstances, probably higher number of column trays are necessary. Note, the values of total annualized capital cost and total operating cost remained the same for all MeDC purity (both columns) which are 32198 $/yr and 450 $/yr, respectively. It can be observed from Table 3 for each MeDC purity specification that the values of maximal reflux ratios (R_{Max}) are found to be larger than normal reflux ratios ensuring no overflowing of still pot.

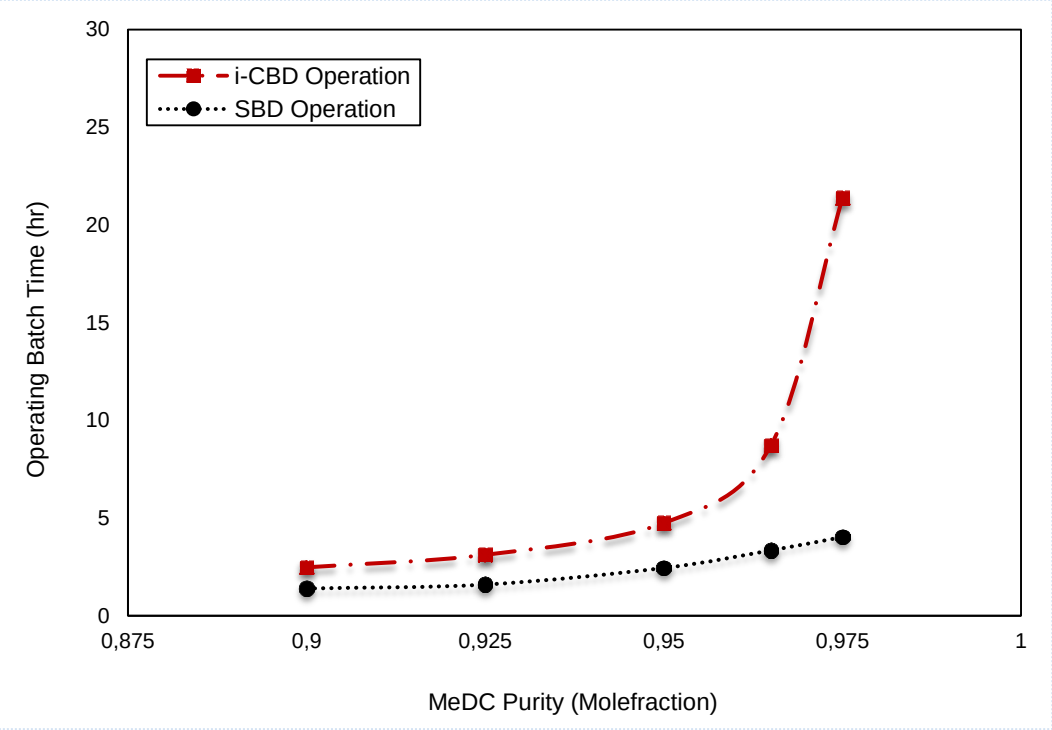

Figure 2: The final operating time profile for both i-CBD and SBD systems

Table 2: Summary of optimization results for i-CBD column

Purity of MeDC	0.90	0.925	0.950	0.965	0.975
Recycle Rate, S_{MeOH}, kmol/hr	1.26	1.28	1.11	0.91	0.86
Reflux Ratio, $R_{i\text{-}CBD}$	0.107	0.180	0.355	0.526	0.612
Total MeOH Amount, S_t, kmol	3.13	3.99	5.25	7.94	18.40
Batch Time, t_f, hr	2.48	3.12	4.75	8.72	21.40
Heat Usage, Q_{Tot}, mkJ	0.233	0.293	0.446	0.822	1.992
Conversion of DeC, %	93.00	95.14	96.86	98.00	98.72
Number of Batches, N_B, batch/yr	2688	2211	1525	867	366
Total Yearly Product, kmol/yr	6450	5306	3659	2081	878
Annual Profit, $/yr	173675	190147	230784	231672	118332

Table 3: Summary of optimization results for SBD column

Purity of MeDC	0.90	0.925	0.950	0.965	0.975
Feed Rate, F_{MeOH}, kmol/hr	0.78	0.70	1.35	1.32	1.19
Reflux Ratio, R_{SBD}	0.00	0.118	0.069	0.185	0.286
Maximum Reflux Ratio, R_{Max}	0.689	0.720	0.462	0.472	0.524
Total Fed Amount, F_t, kmol	1.09	1.12	3.29	4.42	4.79
Batch Time, t_f, hr	1.39	1.60	2.44	3.35	4.03
Heat Usage, Q_{Tot}, mkJ	0.130	0.143	0.225	0.305	0.367
Conversion of DeC, %	93.00	94.51	98.50	99.32	99.51
Number of Batches, N_B, batch/yr	4223	3818	2716	2079	1767
Total Yearly Product, kmol/yr	10136	9162	6520	4990	4241
Annual Profit, $/yr	235626	300044	327672	488928	593531

6. Conclusions

In this study, the synthesis of methyl decanoate via esterification of decanoic acid is investigated in different types of batch reactive distillation processes. The performances of i-CBD and SBD systems in terms of profitability are determined using model-based methods where a rigours process model is embedded with the dynamic optimization problem in gPROMS modelling software. Piecewise constants reflux ratios and methanol recycle rate profiles (only for i-CBD), and methanol feed rate (for SBD column) are considered. The results indicate that the employment of SBD operation is more promising option and quite interesting compared to the i-CBD system in terms of minimum batch time and thus energy consumption, highest conversion of DeC, and maximum achievable profit improvement. As an example, the operating time and thus energy usage rate are saved by an average 81.16%, and 81.57%, and the highest achievable conversion and maximum revenue are improved by almost 0.79% and 80.06% respectively at product purity of 0.975 mole fraction compared to that obtained by the i-CBD mode.

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