# Optimisation of Semi-Batch Reactive Distillation Column for the Synthesis of Methyl Palmitate

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## Abstract

Synthesis of methyl palmitate (MP) has not been considered in the past using a reactive distillation process (continuous or batch) due to the challenge of keeping the reactants palmitic acid (PA) and methanol (MeOH) together in the reactive zone. MeOH, being the lightest in the reaction mixture, travels up the distillation column as distillation proceeds and will be removed from the system via the distillate in a conventional batch reactive distillation (CBRD) column and thus will limit the conversion of PA. Therefore, in this work semi-batch reactive distillation (SBRD) column is proposed where additional methanol will be fed at the bottom of the column in a continuous mode allowing the chemical reaction to continue. However, as water ($H_2O$) is one of the reaction products and is the second lightest component in the mixture, it will travel up the column next and will be removed in the distillate tank. Also due to wide difference in the boiling points of the reaction products and due to diminishing amount of water in the reboiler, the backward reaction will not be a dominating factor and therefore ignored in this work. With this backdrop, optimal performance of the SBRD column is evaluated in terms of conversion of PA to MP and energy consumption via minimization of the operating batch time for a wide range on MP purity.

Keywords: SBRD; Kinetics Modelling; Optimization, Batch Time, Methyl Palmitate

# 1. Introduction

A number of investigators considered the continuous reactive distillation systems in the past, which are widely employed in chemical and petrochemical applications. However, the batch-wise operation has attracted more attention due to growing demand for the high-value-added products, and the specialty fine chemicals, as well as the pharmaceutical products (Parhi et al., 2020; 2021). It is more appropriate for low volume production and more flexible process with low yearly cost with respect to the continuous reactive distillation mode (Kao and Ward, 2015). Methyl palmitate (MP) is a clear colourless liquid and low melting solid having a characteristic odour with a molecular weight of 270.45 kg/kmol, and melting point of 302 K. It is a fatty acid alkyl ester, which naturally occurs in a number of palm plants. In general, methyl palmitate is formed via the esterification of palmitic acid and MeOH or alcoholysis of palm oil plus vacuum distillation process (Lewis et al., 2016). It can be utilized extensively in several applications such as adhesives, emulsifiers, toilet soap and personnel cares, solvents for paint, detergents, resins, flavours, lubricants, and animal feeds (Yaakob and Bhatia, 2004; Saravanan et al., 2016; Auto Market News, 2021).

The esterification of fatty acid (palmitic acid) with a number of alcohols to produce palmitate esters is an industrially important class of reactions especially with an increasing interest in biodiesel as a renewable energy resource (Thotla and Mahajani, 2009). Beula and Sai (2013) investigated the synthesis of ethyl palmitate by the esterification of palmitic acid with ethanol. The production of isopropyl palmitate via the esterification of palmitic acid with isopropanol in reactive distillation (RD) modes was previously studied by a number of scholars (Bhatia et al., 2006; Bhatia et al., 2007; Chen et al., 2012; Chen et al., 2016; Zhang et al., 2015).

The production of methyl palmitate via the esterification reaction of palmitic acid with methanol was conducted only in a batch reactor employing the Amberlyst-15 catalyst by Yaakob and Bhatia (2004). The effects of operating parameters such as the total amount of

catalyst weight, the molar feed quantity of alcohol to fatty acid, the water inhibition, the reaction temperature, and the agitator speed were examined in their work. They found that the experimental data matched the simulation data fairly well. Note also, only about 55% of the maximum conversion rate of carboxylic acid was achieved.

Three kinetic models such as Langmuir-Hinshelwood-Hougen-Watson (LW), Eley-Rideal (ER), and pseudo-homogeneous (PH) were explored by Srilatha et al. (2011) to investigate experimentally the reaction rate behaviour of the formation of methyl palmitate utilizing 12-tungstophosphoric acid as catalyst in a batch reactor system. It was found that the LW model provided the good fitting for the methyl palmitate manufacture. Saravanan et al. (2015) employed a batch reactor for the synthesis of methyl palmitate from the esterification of palmitic acid (PA) and methanol (MeOH) over the mesoporous sulfated zirconia as a catalyst using pseudo-homogenous (PH) model. However, note, to the best of our knowledge, only the batch reactor was used to form methyl palmitate (MP) through the esterification process of methanol with palmitic acid in all the previous investigations. The excess alcohol (methanol) in the feed mixture has been employed to enhance the conversion of palmitic acid to methyl palmitate.

However, no reported studies in literature have utilized either continuous or batch reactive distillation operations for the synthesis of methyl palmitate from the reaction mixture. In the present study, we have developed a new kinetic model based on the experimental data available in the literature. Reflux ratio and feed rate of methanol are optimized in order to minimize the batch time for a given amount and purity of the desired product, MP.

## 2. Semi-Batch Distillation Column and Process Modelling

Figure 1 illustrates schematic diagrams of the SBRD column. The rigorous mathematical model is based on the following assumptions.

- No vapour holdup on the plates and ideal vapour phase

- No heat transfer to the surroundings and fast energy dynamics
- Perfect mixing and phase equilibria on all column plates
- Constant pressure throughout (1 atm)
- No sub-cooling with total condensation and no azeotrope formation
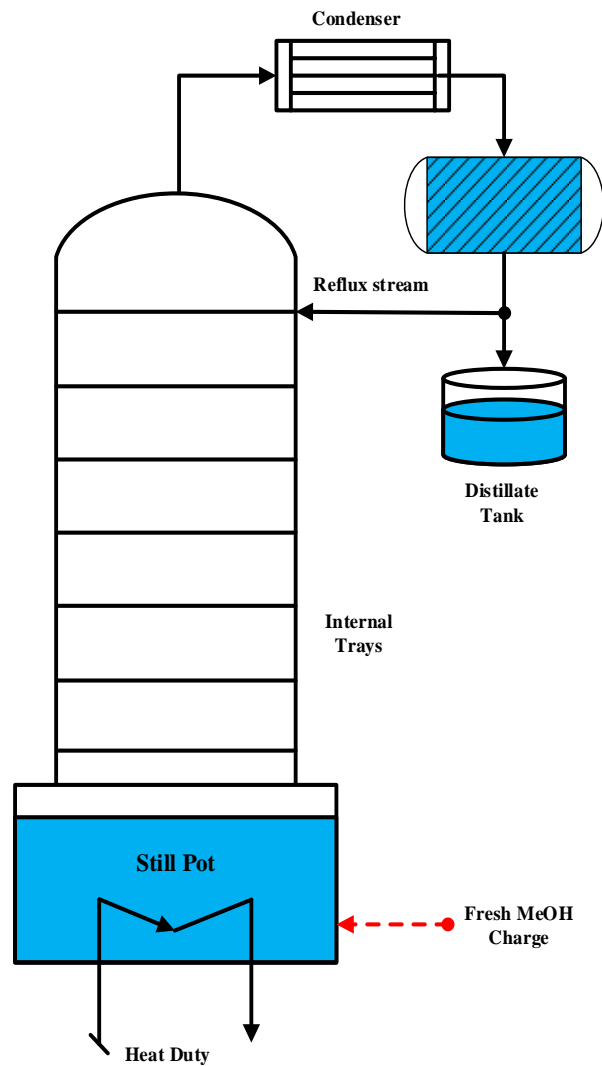- Chemical reaction taking place only in the still pot.



Figure 1: Semi-batch batch reactive distillation (SBRD) for the synthesis of methyl palmitate.

## Reflux Drum and Distillate Receiver: j=1

- Total Mass Balance of Distillate Accumulator:

$$\frac{dH_a}{dt} = L_D \qquad (1)$$

- Component Mass Balance of Reflux Drum and Distillate Receiver:

a) Distillate Receiver:

$$H_a \frac{dx_{ai}}{dt} = L_D (x_{Di} - x_{ai}) \tag{2}$$

b) Reflux Drum Hold-up Tank:

$$H_R \frac{dx_{ci}}{dt} = V_C y_2 - (V_C + \Delta n_1 H_R) x_{Di} + r_{1i} H_R \tag{3}$$

- Energy Balance:

$$0 = V_C H_2^V - (V_C + \Delta n_1 H_R) H_1^L - Q_c \tag{4}$$

- Physical Properties and other equations:

$$H_1^L = H_1^L (x_{D1}, T_1, P) \tag{5}$$

$$T_1 = T_1(x_{D1}, P) \tag{6}$$

$$r_{1j} = r_{1j} (k_e, x_{Di}) \tag{7}$$

$$\Delta n_1 = \sum r_{1j} \tag{8}$$

$$L_1 = R (V_2 + \Delta n_1 H_R) \tag{9}$$

$$L_D = (1 - R) (V_C + \Delta n_1 H_R) \tag{10}$$

## 2.2. Internal trays: j= 2 to N-1

- Total Mass Balance:

$$0 = L_{j-1} + V_{j+1} - L_j - V_j + \Delta n_j H_j \tag{11}$$

- Component Balance:

$$H_j \frac{dx_j}{dt} = L_{j-1} x_{j-1} + V_{j+1} y_{j+1} - L_j x_j - V_j y_j + H_j r_{ji} \tag{12}$$

- Energy Balance:

$$0 = L_{j-1} H_{j-1}^L + V_{j+1} H_{j+1}^V - L_j H_j^L - V_j H_j^V \tag{13}$$

- Equilibrium:

$$K_{j,i} = \frac{y_{j,i}}{x_{j,i}} \tag{14}$$

- Restrictions:

$$\sum y_{j,i} = 1 \tag{15}$$

- Relations Defining Physical Properties and Chemical Reactions:

$$K_{j,i} = K_{j,i} ( y_{j,i}, x_{j,i}, T_j, P) \tag{16}$$

$$H_{j, i}^L = H_{j, i}^L (x_{j, i}, T_j, P) \tag{17}$$

$$H_{j, i}^V = H_{j, i}^V (y_{j, i}, T_j, P) \tag{18}$$

$$r_{j,i} = r_{j,i} (k_e, x_{j,i})$$  (19)

$$\Delta n_j = \sum r_{j,i}$$  (20)

**2.3. <u>Pot Drum: j= N</u>**

- Total Mass Balance of Reboiler:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + \Delta n_n H_n$$  (21)

- Component Mass Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n (y_n - x_n) + H_n r_n$$  (22)

- Energy balance:

$$0 = L_{n-1} (H_{n-1}^L - H_n^L) - V_n (H_n^V - H_n^L) + Q_{heat}$$  (23)

**<u>Partial Reboiler: j= N</u>**

- Total Mass Balance:

$$\frac{dH_n}{dt} = L_{n-1} - V_n + F_{MeOH} + \Delta n_n H_n$$  (24)

- Component Mass Balance:

$$H_n \frac{dx_n}{dt} = L_{n-1}(x_{n-1} - x_n) - V_n (y_n - x_n) + F_{MeOH} (x_{fi} - x_n) + H_n r_n$$  (25)

- Energy balance:

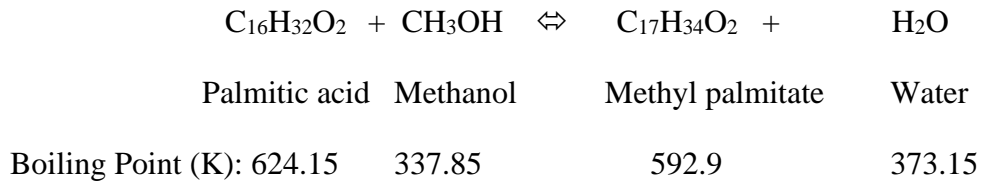$$0 = L_{n-1} (H_{n-1}^L - H_n^L) - V_n (H_n^V - H_n^L) + F_{MeOH} (H^f - H_n^L) + Q_{heat}$$  (26)

**2.1 Kinetic modelling and phase equilibria for the synthesis of methyl palmitate**

**2.1.1 Chemistry and kinetic model**

New kinetic analysis has been carried out for the experimental data for the production of methyl palmitate via esterification reaction of methanol and palmitic acid using the Amberlyst-15 catalyst (Yaakob and Bhatia, 2004). The reaction was carried out with a feed ratio of MeOH to PA equal to 4, catalyst loading equal to 5 g per each litre of the limiting reactant, and reaction temperature between 343 and 373 K.

Yaakob and Bhatia (2004) considered esterification of palmitic acid as reversible reaction (shown below) and evaluated temperature dependent reaction constants for both forward and backward reaction using the experimental data in a batch reactor.

$$C_{16}H_{32}O_2 \; + \; CH_3OH \quad \Leftrightarrow \quad C_{17}H_{34}O_2 \; + \qquad H_2O$$

| Palmitic acid | Methanol | Methyl palmitate | Water |
|---|---|---|---|
| Boiling Point (K): 624.15 | 337.85 | 592.9 | 373.15 |

In batch reactive distillation, considered in this case, methyl palmitate is the second heavy component and water is the second light component (Huber et al., 2009). With distillation and reaction proceeding simultaneously water produced will be quickly separated from methyl palmitate due to very wide boiling point difference between the two, therefore reversible reaction rate will be almost negligible. Therefore, in this work we only considered forward reaction. However, similar argument can be put forward for the forward reaction as methanol being the lightest will also be separated from palmitic acid due to distillation. However, SBRD operation considered in this work will allow additional methanol to the reboiler is considered so that the forward reaction is dominant and continue to take place as long as palmitic acid is in the system.

Xu et al. (2016) measured the vapour-liquid equilibrium (VLE) data for binary system (methanol + methyl palmitate) by determining experimentally their saturated pressures and the compositions. They found out that no azeotrope was formed in binary mixture (methanol + methyl palmitate). According to DeGarmo et al. (1992), the formation of azeotrope in reactive distillation operation is usually overcome due to its ability to achieve a high conversion ratio of fatty acids by removing the products immediately from the reaction region, and by eliminating the azeotropic forming components in reaction (Chen et al., 2012, Zhang et al., 2015; and Aqar et al., 2017a; 2019). Perhaps, this could be the main cause why the azeotrope formation was not taken into consideration by a number of investigators in their works (Yaakob and Bhatia, 2004; Srilatha et al., 2011; Saravanan et al., 2015, 2016). Based on these literatures, we have not considered azeotropes in this work.

### 2.1.1.1 Reaction Rate Model

The suggested kinetic model assumes an elementary forward esterification reaction of palmitic acid (A) as limiting reactant with methanol (B) to yield methyl palmate (C) and water (D) Equation (27). The reaction rate kinetic model is shown equation (28), where k is the forward reaction rate coefficient and follow the Arrhenius law (Eq. 29)

$$C_A + C_B \xrightarrow{k} C_C + C_D \tag{27}$$

$$-r_A = k\ C_A\ C_B \tag{28}$$

$$k = k_o\ e^{-\frac{E}{RT}} \tag{29}$$

Where: $k_o$ is an Arrhenius constant, E (kJ/kmol) is the activation energy of reaction rate, R is the gas constant (8.314 kJ/kmol. K), and T is the absolute temperature for the chemical reaction in K. In general, the amount of unconverted limiting reactant ($C_A$) is given by equation (30). For reactions in liquid phase, no notifiable change in volume, in this case, $\varepsilon_A$ equal to zero leading to equation (31). Where, $C_{Ao}$ is the initial concentration of palmitic acid, $x_A$ is the reaction conversion and $\varepsilon_A$ is the molar volume ratio of the system by divided the system without conversion over the system with the complete conversion of the limiting reactant. The derivative of Eq.31 is shown in Eq. 32:

$$C_A = \frac{C_{Ao}(1-x_A)}{1+\varepsilon_A x_A} \tag{30}$$

$$C_A = C_{Ao}(1-x_A) \tag{31}$$

So, the concentration of methanol could be written as in Eq. 32 which can be obtained from the stoichiometric calculation for the reaction mentioned in equation (27).

$$C_B = C_{Bo} - (C_{Ao}.x_A) \tag{32}$$

The initial concentration of the reactant is 4 kmol of methanol for each mole of palmitic acid, and there were no product materials. Therefore: $C_{Ao}=1$, $C_{Bo}=4$, $C_{Co}=C_{Do}=0$, and equations 31 and 32 become:

$$C_A = 1 - x_A \tag{33}$$

$$C_B = 4 - x_A \tag{34}$$

Substitution of equations 29, 33 and 34 in Eq. 28, gives:

$$-r_A = k_o e^{-\frac{E}{RT}}(1-x_A)(4-x_A) \tag{35}$$

## 2.1.1.2 Regression and Results

Generalized reduced gradient optimization algorithm was used to minimise the sum of the squared error between the actual reaction rates (Yaakob and Bhatia, 2004) and calculated reaction rates using Eq. 37 (Lente, 2015; Levenspeil, 1999). Figure 2 shows the experimental data of Yaakob and Bhatia which are used in this work. Yaakob and Bhatia used the Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic model in their work. The LHHW kinetic model assumed that both oil and alcohol molecules are adsorbed onto the catalyst surface. The final stage of the mechanism involves the de-sorption of both products, MP, and water. This model assumed that surface reaction is the rate-controlling step. This assumption might be accurate in batch reactor but not in reactive distillation. In reactive distillation process, both reactant and products materials exist in vapour and liquid phases that causing an apparent homogeneity and then the apparent homogeneous model becomes more suitable than LHHW model. Apparent homogeneous reaction means that the reaction behaves like a homogeneous reaction (all reactants, products and catalyst are in the same phase). Here, all mass transfer resistances of the diffusion steps are assumed very low (quick steps) and thus neglected. Use of the apparent homogeneous model will simplify the simulation and will give results with

acceptable accuracy. In this work, the apparent homogeneous model was used successfully to describe the reaction rate with the $R^2$ value of 0.8918 with confidence level of 95% (Table 1).
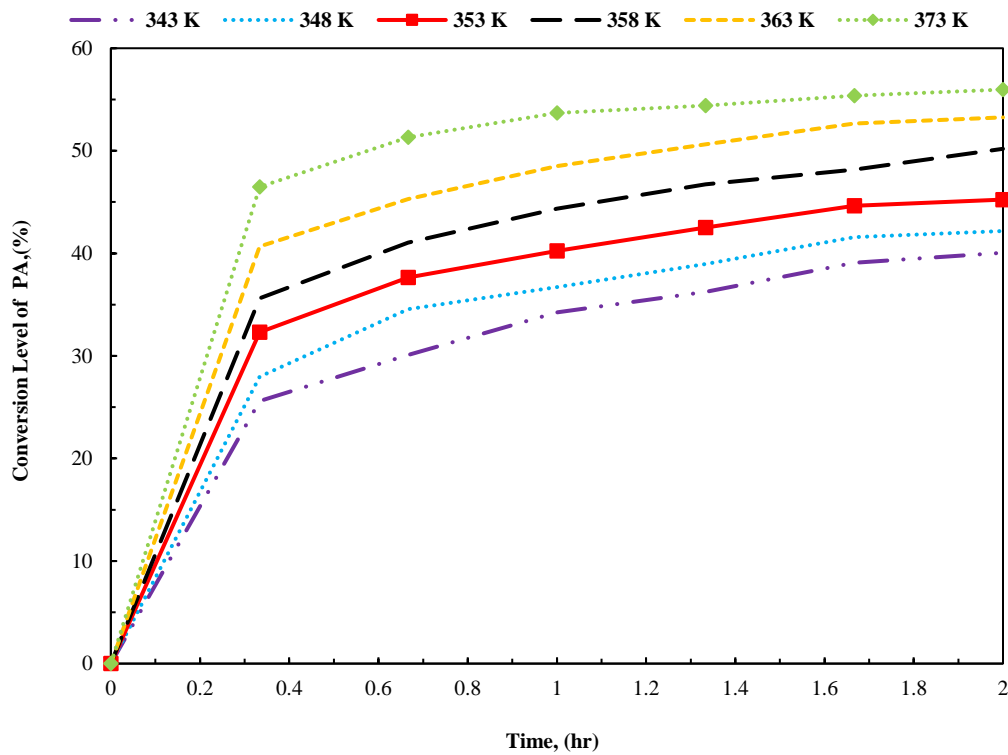


Figure 2: Experimental conversion profile of palmitic acid at different temperatures with excess methanol (adapted from Yaakob and Bhatia (2004)).

Where: $R^2$ is the correlation coefficient and calculated by:

$$R^2 = \frac{\sum_{i=1}^{n}\left(r_{cal} - \overline{r_{\exp}}\right)^2}{\sum_{i=1}^{n}\left(r_{cal} - \overline{r_{\exp}}\right)^2 + \sum_{i=1}^{n}\left(r_{cal} - r_{\exp}\right)^2} \tag{36}$$

Where $r_{cal}$ and $r_{exp}$ are the calculated and experimental values (from the reaction rate model), respectively. i denotes to the current number of the experiment, and n is the total number of the experimental data.

| Table 1: Kinetic analysis regression results | | |
|---|---|---|
| **Constant** | **Value** | **Units** |
| $k_0$ | 3654 | L mol$^{-1}$ hr$^{-1}$ |
| E | 30526.263 | J/mol |
| $R^2$ | 0.8918 | - |
| Standard Error | 0.0027 | - |
| Observations | 42 | - |
| Confidence level | 95 | % |

**2.1.2 Phase equilibria (VLE)**

Note that, the calculations of vapour and liquid molar enthalpies and the phase equilibria for the methyl palmitate system are the same as those presented in our earlier work for methyl lactate system (Aqar et al., 2017b). The saturated pressure of the vapor ($P^{sat}$) of each component is computed as a function of absolute temperature from the Antoine's form:

$$Log_{10}P_i^{sat} = A + \frac{B}{CT} + D \log_{10}T + ET^F \tag{37}$$

Where A, B, C, D, E, F are the regression constants for the Antoine's form and T is the absolute temperature in Kelvin. For this reaction system, the binary interaction parameters of the NRTL method (Table A.1) and the Antoine coefficients (Table A.2) were taken from the data bank of Aspen Plus. Note also, all coefficients for the molar vapour enthalpy and the latent heat of vaporization for all pure components are taken from Aspen HYSYS (2018), Yaws (1997), and Holland (1981), respectively. Note, no azeotrope formation was found from the calculations of VLE properties.

## 3. Strategy for Initial Charge to the Column

Mujtaba (1999) noted two strategies in this mode of operation as far as charging of the initial feed mixture is concerned: (a) Full reboiler charge (b) Partial reboiler charge.

3.1 Full reboiler charge:

In this strategy the feed mixture is charged in the reboiler (at the beginning of the process) to its maximum capacity. In the context of this research, for a given condenser vapour load $V_C$, if the reflux ratio R (which governs the distillate rate, $L_D$) and the solvent feed rate $F_{MeOH}$ are not carefully controlled the column will be flooded. To avoid the column flooding the following constraints were suggested in Mujtaba (2004).

$$L_D \geq F_{MeOH} \qquad\qquad (38)$$
$$L_D = V_c(1-R) \qquad\qquad (39)$$

3.2 Fractional reboiler charge:

In this strategy the feed mixture is charged to a certain fraction of the maximum capacity. The column can operate at a reflux ratio greater than $R_{max}$ for some period until the reboiler level reaches to its maximum capacity. In this strategy the column is underutilized and but can be useful when an existing column is oversized for the task in hand. In, Rodriguez-Donis et al. (2003), the initial feed charge was one fifth of the reboiler capacity. In this work we used full reboiler capacity and therefore added Equations (38) and (39) as additional constraints to the optimization problem.

## 4. Optimization Framework

In the present study, the dynamic optimisation formulations for SBRD operations can be represented as follows:

| | |
|---|---|
| Given: | The batch configuration, feed concentration, condenser load, desired quantity of MP product and concentration consideration. |
| Optimize: | Reflux ratio ($R_{SBRD}$), MeOH charged ($F_{MeOH}$) |
| So as to minimize: | The overall operation batch time |
| Subject to: | Model equations (inequality constraints), Operational constraints |

It has been well-established in the literature that for a defined product quantity and concentration, the minimization of operating batch time results in maximum number of batches

of the desired product. In this work, the main goal is to reduce $t_{Batch}$ under this operating condition and therefore a single objective optimization is considered. For this one-objective problem, operating variables (reflux ratio and feed rate of methanol) are the continuous type of decision variables to be optimized.

Mathematically, the dynamic optimization problem (OP) can be expressed as:

$OP$          $Min$       $t_{Batch}$

            $R(t), F_{MeOH}(t)$

*Subject to :*

$$f(t, \dot{x}(t), x(t), u(t), v) = 0; \; [t_0 \quad t_{Batch}] \qquad (Process\ model)$$

$$f(t_0, \dot{x}_0, x_0, u, v) = 0; \qquad\qquad\qquad (Initial\ condition)$$

$$P_{MP} \geq P_{MP}^* \qquad\qquad\qquad (Inequality\ constraints)$$

$$x_{MP} \geq x_{MP}^*) \qquad\qquad\qquad (Inequality\ constraints)$$

$$L_D \geq F_{MeOH} \qquad\qquad\qquad (Flooding\ constraints)$$

$$L_D = V_c(1-R) \qquad\qquad\qquad (Flooding\ constraints)$$

*Linear bound on*   $R(t), F_{MeOH}(t)$        *(Inequality Constraints)*

$f(t, \dot{x}(t), x(t), u(t), v) = 0$ represents the process model of a SBRD configuration shown in section 2, which is expressed by Eqs. 1-26, where $t$ is the independent variable (operating batch time), $x(t)$ gives the set of all ordinary differential equations and algebraic variables, $\dot{x}(t)$ is the derivative of all differential variables, u(t) denotes the optimization variables, and $v$ represents the time invariant variables. The production batch time under a certain consideration $[t_0 \quad t_{Batch}]$, and $f$: is the mathematical function, which is assumed to be continuously differentiable as a function of all its variables (Mujtaba, 2004). $P_{MP}$, and $x_{MP}$ are the quantity of bottom product in still pot and concentration of MP at the operating batch time $t_{Batch}$ in the bottom tank ($P_{MP}^*$ and $x_{MP}^*$ are specified). $R$ is the time dependent reflux ratio, $F_{MeOH}$ is the feed rate of methanol which are controlled in the optimization study. Note, the process model for SBRD column is described by a number of non-linear differential and algebraic equations

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(DAEs), which acts as the inequality constraints to the dynamic optimization case. The model resulted in 49 Differential Equations and 1178 Algebraic Equations. The optimization problem incorporates detailed model of the SBRD column and is converted into nonlinear programming (NLP) problem using piecewise constant Control Vector Parameterisation (CVP) technique (Vassiliadis et al., 1994) which is solved employing a successive quadratic problem (SQP) method within gPROMS software (2019) (gPROMS Model Builder 5.1.0).

# 5. Problem Statement

The production of methyl palmitate (MP) from palmitic acid (PA) and methanol is a feasible biofuel choice, since both precursors can be obtained from biomass. The RD (Reactive Distillation) technology is a viable operation, and it is anticipated that the continuous methanol feed to the still pot in the SBRD column, will increase the contact of methanol and acid and thus will enhance the reaction conversion. The main focus of this work will be to convert more and more acid, so that the bottom product (MP) is rich in the desired product. The production of methyl palmitate is carried out in an eight plates distillation column (excluding overhead condenser and still pot) with 2.5 (kmol/hr) of the vapor load to the condenser ($V_C$). Column plates are counted from the top-down; topmost plate is Stage 1 and bottommost plate is Stage 8. 5 kmol of total initial amount loaded into the pot drum at the beginning of the process. Note that the number of plates refers to the number of theoretical plates or ideal trays (chosen arbitrarily). The total holdup of distillation column is assumed to be four percent of the total feed quantity. 50% of the total column holdup is placed in the reflux drum and the rest is equally divided on the all-column plates (Aqar et al., 2016; 2021). The compositions of reflux drum and plates are assumed initially to be similar to the fresh feed composition in the still drum at the beginning of the operation (Aqar et al., 2018). Note, usually for non-reactive batch distillation, the batch distillation column starts operating in close operation mode under total reflux until the column profile is established (Logsdon and Biegler; 1993; Mujtaba, 2004)..

However, for the reactive batch distillation process considered in this work, the model equations being solved at time t=0, calculate the column temperature profiles which are basically, the boiling point temperatures at each location of the column (e.g. reboiler, stages, condenser holdup tank, etc.). The chemical reaction starts from time t=0 and also the production phase for all case studies starts from the initial time t = 0 onward. Batch distillation operation usually runs at the one of the specific column distillation modes: (A) fixed vapor load to the condenser, (B) fixed heat supplied to the still pot, (C) fixed vapor boil-up rate and (D) fixed distillate rate. In the present study, the constant vapour load rate to the reflux drum (Mode C) is employed to operate all batch reactive distillation columns. The still pot heat duty ($Q_{heat}$) progressively changes with the operating batch time to keep the constancy of the vapour load to the condenser drum. The mode of constant condenser vapour load is used here to run SBRD, as employed by a number of scholars in the past (Kao and Ward, 2014; Wajge and Reklaitis, 1999) for the computing the total energy consumption rate. The constancy of condenser vapour load rate was kept in the batch configurations by operating them at constant reflux ratio and making mass/energy balances around the reflux drum with appropriate control tools to calculate the reboiler heat duty. Note, the total energy usage for this reaction system is computed utilizing the following equation (Aqar et al., 2021):

$$Q_{tot} = \int_{0}^{t_{Batch}} Q_{Heat} \, dt \tag{40}$$

The differentiation of Equation (42) gives:

$$\frac{dQ_{tot}}{dt} = Q_{Heat} \tag{41}$$

The above differential equation was added to the process model equation shown in section 2 which calculates the total reboiler duty at the end of batch time. Note, the column energy efficiency ($\eta_{energy}$) can be computed using:

$$\eta_{energy} = Q_{tot} / (\text{Amount of Methyl Palmitate product in the reboiler}) \tag{42}$$

## 6. Results and Discussions

The total feed into the reboiler is 5 kmol. The feed composition expressed in molefraction are <0.50 PA, 0.50 MeOH, 0.0 MP and 0.0 $H_2O$> the maximum product amount in the reboiler to be accomplished is set as 2.5 kmol.

Table 2 shows the optimum process results for SBRD operation in terms of methanol feed rate, reflux ratio, maximum reflux ratio, minimum operating batch time, and the total energy demand, the PM conversion rate, and the process productivity, as well as the energy efficiency for various product concentration considerations (molefraction of 0.800 to 0.950).

Note that, the maximum reflux ratio ($R_{Max}$) is calculated using the optimum feed rate of MeOH. In all cases, it can be seen from Table 2 that, the feed rate, actual reflux ratio, operating batch time, and energy usage, increase progressively with increasing purity of the desired product.

Note again that synthesis of methyl palmitate (MP) has not been considered in the past using a reactive distillation process due to the challenge of keeping the reactants palmitic acid (PA) and methanol (MeOH) together in the reactive zone. For the same reason, conventional batch distillation column is not suitable for this type of chemical reaction. Hence, we have used semi-batch reactive distillation column to address the limitation.

Also, note that Yaakob and Bhatia (2004) achieved only 55% conversion of the acid in the laboratory batch reactor study. In the absence of any other studies of this reaction system, the results in Table 2 are compared with that of Yaakob and Bhatia (2004) in terms of conversion to acid.

Table 2 clearly shows that synthesis of MP is indeed possible in a semi-batch reactive distillation column at a very high purity (up to 0.95 molefraction) and with a very high conversion of acid. With a MP purity of 0.8 molefraction, the acid conversion can be as high 84% (52% improvement). With a MP purity of 0.95 molefraction, the acid conversion can be

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as high 99% (80% improvement compared to that obtained by Yaakob and Bhatia (2004). Table 2 notes that with the increase of purity, the methanol feed rate increases.

Increasing the methanol feed rate decreases $R_{max}$ to avoid column flooding. Note, as the purity increases, the differences between ($R_{max}$-R) decreases. This clearly indicates that the column has to operate a close to the $R_{max}$ as purity increases and thus leading to increase in batch time and energy consumption. Note, for all the MP purity cases, the maximum reflux ratio ($R_{Max}$) is higher than the actual reflux ratio preventing the flooding of the still tank. Also note, in all cases $R_{max}$ is computed for different values of MeOH feed rate as shown below.

$$R_{Max} = \left(1 - \frac{F_{MeOH}}{V_C}\right) \tag{43}$$

Figures 3 and 4 present the dynamics of the pot drum and the distillate tank concentrations at the equimolar feed ratio for 0.950 of MP quality, respectively. Note, the total amount of distillate was 13.61 kmol at 0.950 of MP purity. The still pot temperature profiles of formation of methyl palmitate ($x^{*}_{MP} = 0.950$ molefraction) at the equimolar feed amount are presented in Figure 5.

It was observed that the reboiler temperature increases progressively with the operating time at the initial period due to the increasing amount water, and methyl palmitate concentrations. After a certain period as the lightest component (methanol) is separated from the pot tank, the heaviest component (palmitic acid) is stayed in the reboiler, therefore the reaction temperature starts to increase. Figure 6 shows the reflux ratio and fresh charge rate of methanol for different range of the product (MP) purity for SBRD column.
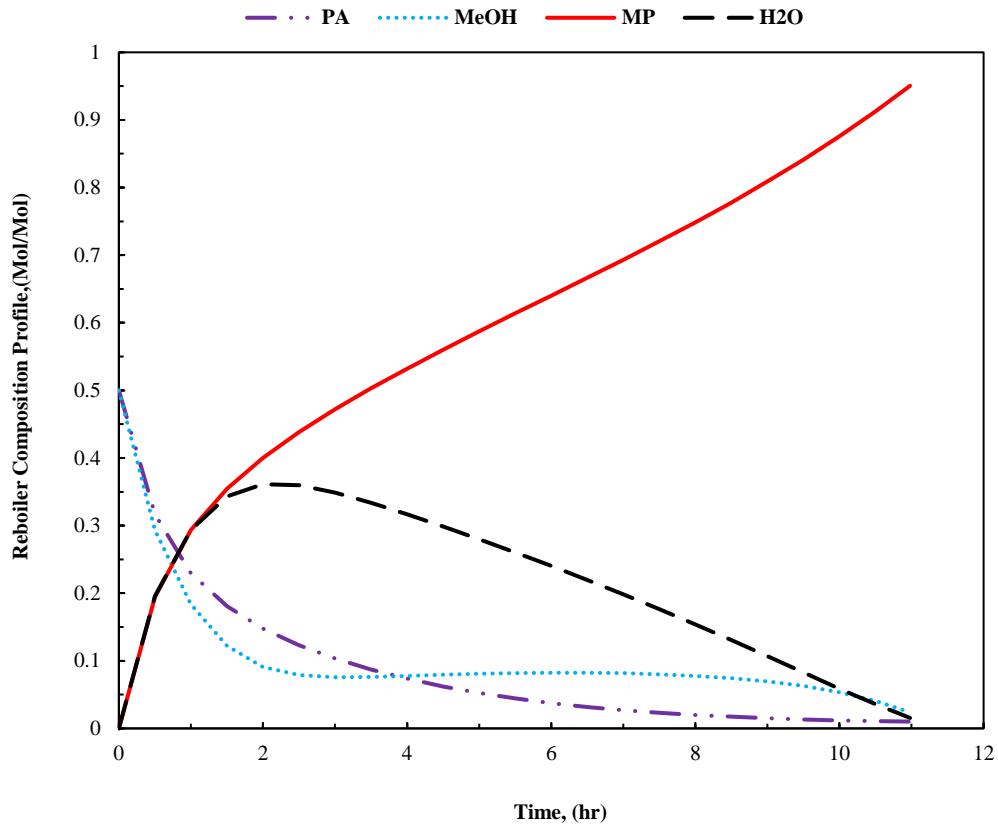
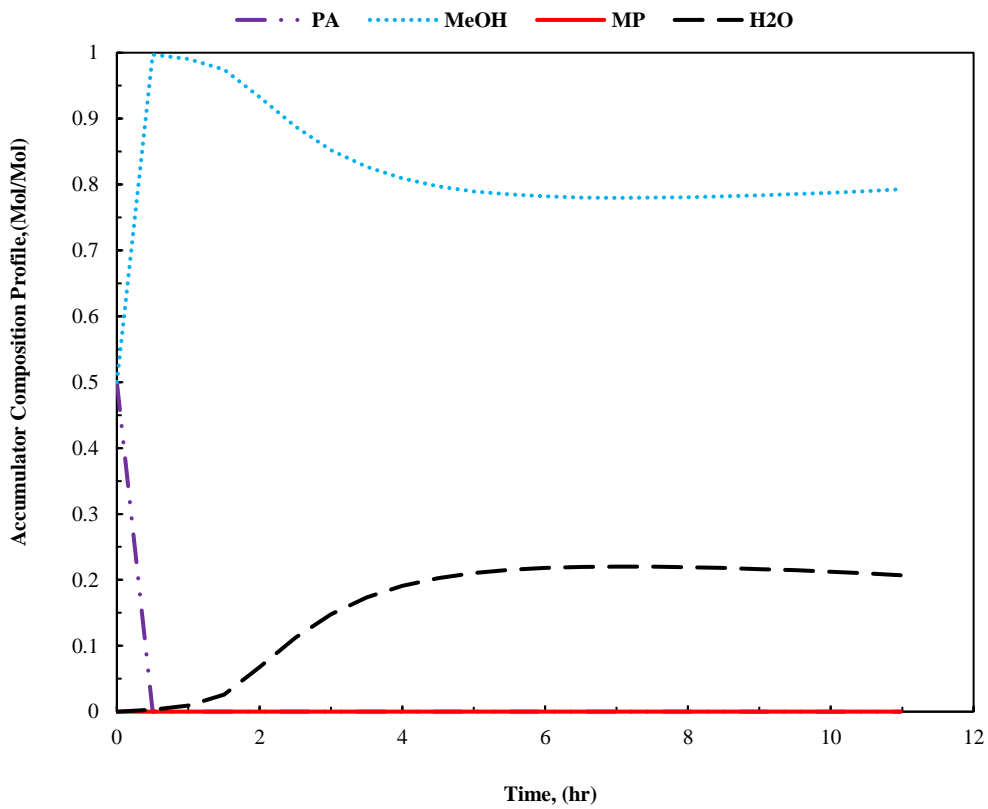Figure 3: The still pot composition of SBRD for MP system ($x_{MP}^{*}= 0.95$).



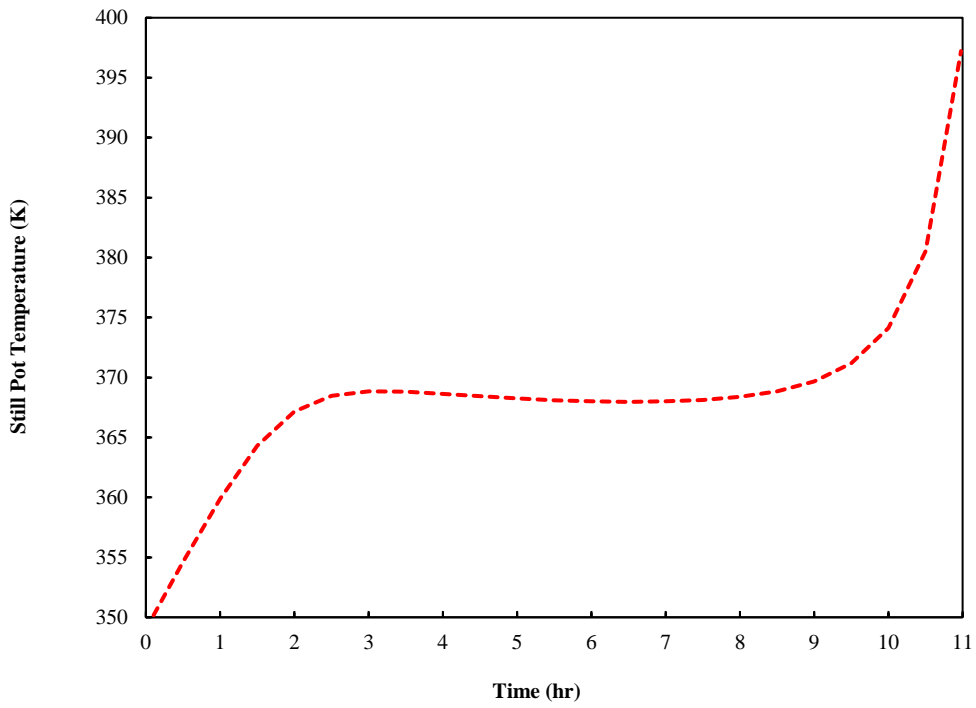Figure 4: The accumulator composition of SBRD for MP system ($x_{MP}^{*}= 0.95$).

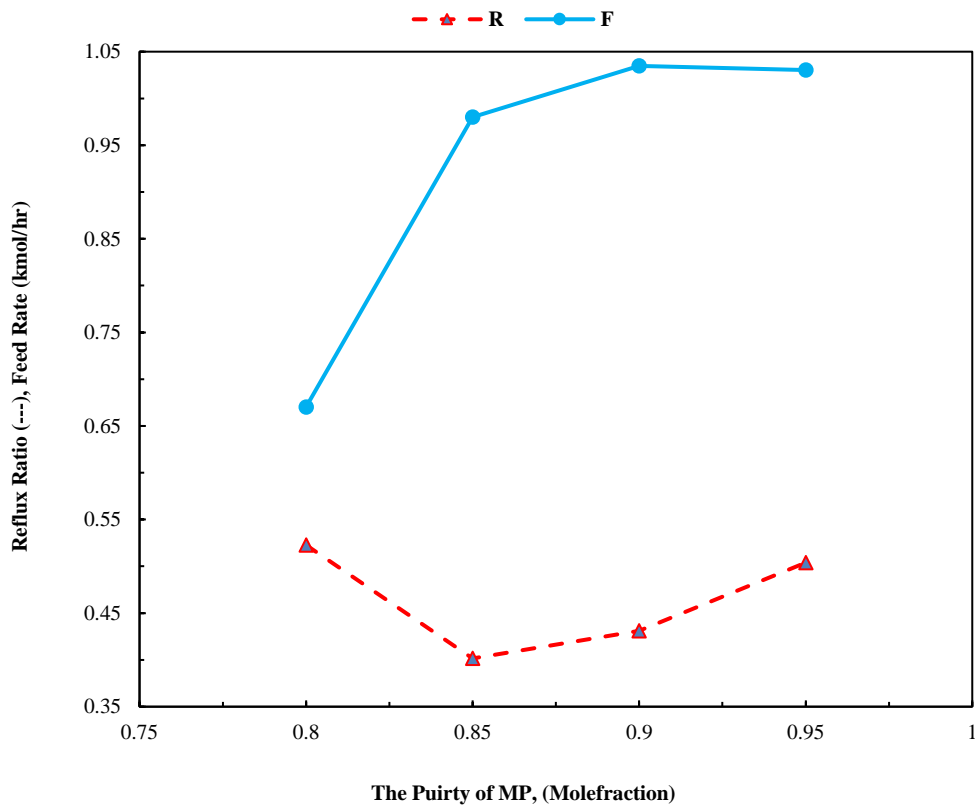18

Figure 5: The still pot temperature for MP system.



Figure 6: The reflux ratio and feed rate of fresh methanol versus the product purity of MP.

# 7. Conclusions

The synthesis of methyl palmitate (MP) by the esterification reaction of palmitic acid (PA) with additional MeOH is only explored in the past utilizing batch reactors but the employment of batch reactive distillation process has not been explored yet. However, a continuous distillation column or a conventional batch reactive distillation (CBRD) column are not suitable for this purpose as the methanol being the lightest in the reaction mixture will be separated from the top of the distillation column as distillation proceeds thus will limit the conversion of PA. Therefore, in this work semi-batch reactive distillation (SBRD) column is proposed where additional methanol is fed at the bottom of the column in a continuous mode to allow the chemical reaction to proceed.

The optimal performance of SBRD is determined in terms of minimum batch time for a given separation task (amount of MP and quality). A rigorous model for the operation is incorporated into the optimisation dynamic problem within gPROMS model builder and the optimization problem is solved for different ranges of MP quality constraints and column flooding constraints. Piecewise constant reflux ratio and methanol feed rate are considered which are optimised. For different MP qualities, the improvement in the conversion of PA ranges from 52-80% compared to that reported in the literature. Although batch time and energy consumption increase with the MP quality, energy efficiency (energy consumption per kmol of product) improves with the MP quality.

## Nomenclature

| | | |
|---|---|---|
| $a_i$ | Activity of component i | - |
| $B_{Pr}$ | The product amount in the reboiler drum | kmol |
| CBRD | Convectional batch reactive distillation | - |
| $C_i$ | Concentration of component i | Mol/lit |
| DAEs | Differential algebraic equations | - |

| | | |
|---|---|---|
| $F_{MeOH}$ | Methanol feed rate (kmol/hr) | - |
| $H^L$, $h^V$ | Liquid, and vapour enthalpy | kJ/kmol |
| $H_a$, $H_C$ | Accumulator and condenser holdups | kmol |
| $H$, $H_N$ | Trays and reboiler holdups, respectively | kmol |
| K | Vapour–liquid equilibrium | - |
| L | Liquid flow rate | kmol/hr |
| $L_D$ | Distillate rate | kmol/hr |
| $m_{cat}$ | The catalyst weight | g |
| NLP | Nonlinear programming problem | - |
| OP | Optimisation problem | - |
| $Q_C$, $Q_{heat}$ | Condenser duty and reboiler heat duty | kJ/hr |
| R | Reflux ratio | - |
| $r_i$ | Reaction rate | - |
| SQP | Successive quadratic programming algorithm | - |
| SBRD | Semi-batch reactive distillation | - |
| $t_{Batch}$ | Processing batch time | hr |
| $V_C$ | Vapour Load | kmol/hr |
| x | Liquid concentration | molefraction |
| $x_A$ | The reaction conversion | - |
| $x_a$ | Accumulated distillate concentration | molefraction |
| $x_D$ | Instant distillate concentration | molefraction |
| y | Vapor concentration | molefraction |

## Greek Letters

*Superscripts and subscripts*

| | |
|---|---|
| i | Component number |
| j | Plate number |
| $\Delta n$ | Change in moles due to reaction. |
| $\varepsilon_A$ | The molar volume ratio |

# Abbreviations

| | |
|---|---|
| PA | Palmitic Acid |
| MP | Methyl Palmitate |
| MeOH | Methanol |
| $H_2O$ | Water |

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# Appendix

Table A.1 NRTL Binary Parameters for Esterification of Palmitic Acid System.

| Component i | Component j | $A_{ij}$ (cal/mol) | $A_{ji}$ (cal/mol) | α |
|---|---|---|---|---|
| | | **Methyl Palmitate** | **System** | |
| PA | MeOH | -224.118 | 692.913 | 0.3 |
| PA | MP | -142.728 | 297.196 | 0.3 |
| MP | MeOH | 70.152 | 944.338 | 0.3 |
| H$_2$O | MeOH | 367.67 | -112.992 | 0.3 |
| H$_2$O | PA | 4393.02 | 547.274 | 0.3 |
| H$_2$O | MP | 5313.81 | 1037.19 | 0.3 |

$\alpha_{ij} = 0.0$ and $A_{ij} = 0.0$ when i = j

Table A.2 Antoine Parameters for the MP system.

| Antoine Coefficients | **Methyl** PA | **Palmitate** MeOH | **System** MP | H$_2$O |
|---|---|---|---|---|
| A [--] | 62.0161 | 59.8373 | -61.8807 | 65.9278 |
| B [K] | -11660.1 | -6282.89 | -6033.71 | -7227.53 |
| C [K$^{-1}$] | 0.0 | 0.0 | 0.0 | 0.0 |
| D [K$^{-1}$] | -6.11606 | -6.37873 | 12.8029 | -7.17695 |
| E [K$^{-1}$] | 1.65937E-6 | 4.61746E-6 | -1.47867E-5 | 4.0313E-6 |
| F [K$^{-2}$] | 2.0 | 2.0 | 2.0 | 2.0 |

A, B, C, D, E, F are the regression coeffieicents for each component

Table 2: Summary of optimization results for SBRD column with equimolar and excess feed cases

| Product Quality of MP | Feed Rate, $F_{MeOH,}$ kmol/hr | Reflux Ratio, R | Reflux Ratio, $R_{Max}$ | $R_{Max} - R$ | Batch time, $t_{Batch}$, hr | Energy Usage, GJ | Energy Efficiency, (GJ/kmol) | Conversion of Acid (%) |
|---|---|---|---|---|---|---|---|---|
| 0.800 | 0.670 | 0.523 | 0.732 | 0.209 | 4.40 | 0.044 | 0.017 | 84.00 |
| 0.850 | 0.980 | 0.402 | 0.608 | 0.206 | 4.46 | 0.044 | 0.018 | 89.00 |
| 0.900 | 1.035 | 0.431 | 0.586 | 0.155 | 5.93 | 0.058 | 0.023 | 94.00 |
| 0.950 | 1.030 | 0.504 | 0.588 | 0.084 | 10.98 | 0.103 | 0.041 | 99.00 |