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Synthesis of Methyl Decanoate using Different Types of Batch Reactive Distillation Systems

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Abstract

Methyl Decanoate (MeDC) is a Fatty Acid Methyl Ester (FAME) and is an important chemical compound with global production of 31 million tons per year. However, synthesis of methyl decanoate (MeDC) via esterification of Decanoic Acid (DeC) with methanol by reactive distillation is operationally challenging due to difficulty of keeping the reactants together in the reaction zone as methanol being the lightest component in the mixture can separate itself easily from the other reactant deteriorating significantly the conversion of DeC using either conventional batch or continuous distillation column. This is probably the main reason for not applying the conventional route for MeDC synthesis. Whether Semi-batch Distillation column (SBD) and the recently developed Integrated Conventional Batch Distillation column (i-CBD) offer the possibility of revisiting such chemical reactions for the synthesis of MeDC is the focus of this paper. The minimum energy consumption (Q_{tot}) as the performance measure is used to evaluate the performances of each of these reactive column configurations for different range of methyl decanoate purity and the amount of product. It is observed that the use of i-CBD column provides much better performance than SBD column in terms of the production time and the maximum energy savings when excess methanol is used in the feed. However, the SBD column is found to perform better than the i-CBD column when both reactants in the feed are in equal amount. Also, the optimization results for a given separation task show that the performance of two-reflux intervals strategy is superior to the single-reflux interval in terms of operating batch time, and energy usage rate in the SBD process at equimolar ratio.

Keywords: Energy Usage, Optimization, Methyl Decanoate, CBD, i-CBD, SBD, Esterification

1. Introduction

The continuous reactive distillation columns are studied by a number of scholars and extensively used in chemical industries. The batch reactive distillation operations have received more considerations due to increasing seasonal demands for specialty chemicals, high-value added fine products, biochemical products and pharmaceuticals. Compared with the continuous reactive distillation operation, it is more flexible process with low investment cost and suitable for low-volume production.¹ Methyl decanoate (MeDC) also known as methyl caprate is a FAME (biodiesel) formed from capric acid (DeC) and methanol. It is a single compound representative for FAME biodiesels because of its long alkyl chain found in biodiesel. FAME is an alternative source of fossil fuels, organic, biodegradable and non-toxic fuel source with properties similar to petroleum-diesel that is produced mainly from renewable biomass sources (such as vegetable oils, animal fats or even waste oils from the food industry). The synthesis of biodiesel consisting of fatty esters, as one of the renewable energy source and key product of the chemical process industry, has significantly received more attention in research over the last 15 years due to its potential for reducing global warming, and reducing energy demand and greenhouse gas emissions.^{2, 3} It is very widely used in many industrial applications such as important chemical intermediates, plasticizers in polymer processing, solvents, personal-cares and cosmetics, emulsifiers, stabilizers, resins, flavorings, surfactants, lubricants, food and pharmaceutical industries, and detergents.⁴⁻⁸

The global markets for FAME biodiesel products were 22.5 million-ton in year 2011 and are about 31 million-ton in year 2016.⁹ In general, biodiesels consisting of fatty acid methyl esters (FAME) are traditionally synthesized by two main routes: the trans-esterification of Tri-alkyl Glycerides (TAG) with an alcohol (usually methanol) resulting in a long-chain mono-alkyl ester and glycerol (by-product), or the esterification of Free Fatty Acids (FFA) with methanol to produce fatty acid alkyl ester (biodiesel) and water (by-product) using homogeneous or heterogeneous reaction systems as summarized in Table 1.

Table 1. Several proposed reaction schemes for biodiesel production

Reaction Scheme	Reference
$\text{TAG} + 3 \text{ MeOH} \rightleftharpoons 3 \text{ FAME} + \text{Glycerol}$	(8, 10-13)
$\text{FFA} + \text{MeOH} \rightleftharpoons \text{FAME} + \text{H}_2\text{O}$	(14-16)

Esterification operation of fatty acids with many alcohols to yield fatty acid alkyl esters is a common practice in the chemical industry. The manufacturing of fatty acid alkyl esters (biodiesel) by reactive separation is a promising option to overcome the equilibrium limitations inherently associated with conventional distillation operations. The thermodynamically limited reactions (such as esterification, hydrolysis, transesterification, and etherification) are very important and appropriate for reactive distillation.

The esterification process of fatty organic acids (such as decanoic, dodecanoic, and oleic acids) with several alcohols, ranging from methanol, ethanol, and propanol to 2-ethyl hexanol using reactive distillation column is not new. For instance, investigations on esterification reaction of oleic acid with methanol to produce methyl oleate were studied by several researchers.¹⁷⁻²¹ Jeromin et al.²² compared the continuous process with a batch reactive distillation process for the esterification of different fatty acids with methanol in a tray column. Schleper et al.²³ and Bock et al.²⁴ discussed the esterification of fatty acid with 2-propanol in a tray reactive column. However, the others have previously discussed the reaction of lauric (dodecanoic) acid with methanol to produce methyl dodecanoate using thermally coupled reactive distillation columns.^{25, 26} In the past, the esterification of decanoic Acid (DeC) with methanol (MeOH) has been conducted only in Continuous Reactive Distillation (CRD) by a limited number of investigators^{27, 19} to synthesize methyl decanoate (MeDC). Steinigeweg and Gmehling²⁷ proposed a heterogeneously catalysed reactive distillation operation for the synthesis of methyl decanoate via the esterification of decanoic acid with methanol based on experimental and simulation studies at feed molar ratio of (DeC:MeOH) = <0.341:0.659>. However, they achieved a lower conversion and product purity (fatty acid methyl ester) of 42.99% and 0.314 mole fraction, respectively compared to higher conversion and purity target in this work. Recently, Machado et al.¹⁹ simulated a reactive distillation column for the esterification of decanoic acid with methanol using Amberlyst 15 catalyst and the stoichiometric molar ratio of reactants same as used by Steinigeweg and Gmehling²⁷. The simulation results were compared and validated with experiential data available in literature and obtained 42.99% of DeC conversion and 0.386 mole fraction of MeDC. Also interestingly, although their work mentioned the importance of synthesizing of MeDC in the esterification step, no one achieved higher purity of the decanoic acid methyl ester and conversion rate of DeC even with an excess amount of methanol. This is due to the fact that they did not appreciate the difficulty of keeping the both reactants (methanol and the DeC) together in the still pot to enhance the conversion of DeC to MeDC.

The use of batch reactive distillation for the synthesis of MeDC is non-existent. In this work, batch reactive distillation is considered to see if an improved conversion of DeC, recovery of MeDC, and productivity are possible. Conventional batch distillation column (CBD) together with recently developed configurations²⁸ such as i-CBD and SBD columns for the synthesis of methyl lactate are employed in this work. The performances of i-CBD and SBD operations are measured in terms of minimum energy requirement. Also note, the earlier authors²⁷ used excess methanol in the feed in continuous reactive distillation to enhance the conversion of the fatty acid. In this work, it will also be investigated if excess methanol in the feed is actually required when operated in batch reactive distillation columns.

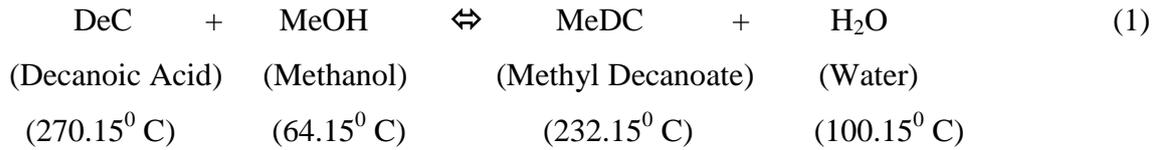
A detailed dynamic model for the process is incorporated within the optimization framework and reflux ratios and methanol recycled rate (only for i-CBD), and methanol feed rate (for SBD) are optimized while minimizing the energy consumption. gPROMS software²⁹ (gPROMS Model Builder 4.1.0) is used for both model building and optimization. The dynamic optimization problem is transformed into a nonlinear programming problem (NLP) and solved by using Control Vector Parameterization (CVP) technique using successive quadratic programming (SQP) algorithm within gPROMS³².

2. Process model

The mathematical model equations are developed with reference to the different column configurations (such as CBD, i-CBD, and SBD) as shown in parts a, b, and c of Figure 1. They consist of unsteady-state mass and energy balances with constant molar holdup on all stages including the condenser, rigorous thermodynamic (chemical and physical) properties, and chemical reaction on the trays, in the total condenser, and in the still pot drum. The plates are numbered from the top down of the column. Note, the list of main assumptions made in developing the model and the main model equations can be found in Aqar et al.^{28,30}.

2.1 Kinetics modelling and thermodynamic aspects

Steinigeweg and Gmehling²⁷ explored the kinetic behaviour of DeC esterification and MeDC hydrolysis by examining two kinetic models, the pseudo-homogeneous (PH), the Langmuir-Hinshelwood-Hougen-Watson (LHHW) models. The production of methyl decanoate (MeDC) by esterification of decanoic acid (DeC) with methanol (MeOH) over an acid catalyst such as a strong acidic ion-exchange resin (Amberlyst-15) through the reversible reaction scheme together with the boiling temperatures of the components is accomplished by the following stoichiometric equation:



A pseudo-homogeneous (PH) activity ($a_i = \gamma_i x_i$) based on kinetic model is employed and can be written as:

$$-r_{\text{DeC}} = M_{\text{cat}} \left\{ 9.1164 \times 10^5 \exp\left(\frac{-68710}{RT}\right) a_{\text{DeC}} a_{\text{MeOH}} - 1.4998 \times 10^4 \exp\left(\frac{-64660}{RT}\right) a_{\text{MeDC}} a_{\text{H}_2\text{O}} \right\} \quad (2)$$

The PH model is not complicated, has fewer parameter constants, and has a good representation for the kinetic behaviour of the system; therefore, this kinetic model²⁷ is used in this work. Note, Machado et al.¹⁹ also used this kinetic model for their simulation studies of continuous reactive distillation column.

Note, all the phase equilibrium equations (VLE) for the synthesis of methyl decanoate are same as those presented in the previous work.³⁰ The saturation vapour pressure (P^S) of the pure substances has been obtained by using Antoine's equation:

$$\text{Log } P_i^S = C_1 - \frac{C_2}{T + C_3} \quad (3)$$

Where C_1 , C_2 , C_3 are the regression coefficients (with appropriate units) for the Antoine equations and T is the temperature in Kelvin. The Antoine's equation coefficients used in this work were taken from Steinigeweg and Gmehling²⁷ and are given in Table 2.

Table 2. Antoine Parameters for Eq. (3) (Steinigeweg and Gmehling²⁷)

Antoine Coefficients	DeC	MeOH	MeDC	H ₂ O
C_1	6.11877	7.20587	6.14032	7.19621
C_2	1593.22	1582.27	1590.66	1730.63
C_3	-156.557	-33.424	-115.835	-39.724

The liquid-activity coefficients (the vapour-liquid equilibrium) were calculated using the NRTL method with the binary interaction parameters are taken from Aspen HYSYS V8.8 package³¹ are listed in Table 3. The ideal vapour phase was assumed.

Table 3. NRTL Binary Parameters for Esterification of Decanoic Acid System

Component i	Component j	A_{ij} (cal/mol)	A_{ji} (cal/mol)	α_{ij}	α_{ji}
DeC	MeOH	705.64	- 311.53	0.3	0.3
DeC	MeDC	816.25	- 415.08	0.3	0.3
MeDC	MeOH	1105.97	156.86	0.3	0.3
H ₂ O	MeOH	- 233.02	740.34	0.3	0.3

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

3. Optimization problem

The optimization problems can be described as follows:

Given: The i-CBD/SBD column configurations, the feed composition, condenser vapour load and desired amount of MeDC product and its purity specification.

Optimize: Reflux ratio (R) (for CBD Column)
 Or, Reflux ratio (R), and Recycle rate (S_{MeOH}) (for i-CBD Column)
 Or, Reflux ratio (R_{SBD}), and the feed rate (F_{MeOH}) (for SBD Column)

To minimize: The thermal energy usage

Subject to: Model equations (equality constraints), Operation constraints (reboiler overflowing, linear bounds on optimization variables, etc.)

Mathematically the optimization problem (OP1) can be represented as follow:

$$\begin{aligned}
 \text{OP1} \quad & \text{Min} \quad Q_{\text{tot}} \\
 & R_{\text{CBD}}(t) \quad \quad \quad (\text{For CBD Column}) \\
 & \text{Or} \\
 & R_{\text{i-CBD}}(t), S_{\text{MeOH}}(t) \quad \quad \quad (\text{For i-CBD Column}) \quad (4) \\
 & \text{Or} \\
 & R_{\text{SBD}}(t), F_{\text{MeOH}}(t) \quad \quad \quad (\text{For SBD Column})
 \end{aligned}$$

Subject to :

$$B_p = B_p^* \pm \varepsilon \quad \quad \quad (\text{Inequality Constraints})$$

$$x_p = x_p^* \pm \varepsilon \quad \quad \quad (\text{Inequality Constraints})$$

Where Q_{tot} is the total heat consumption equation (5), B_p , and x_p are the product amount (MeDC) in the bottom tank and its composition at final time, (B_p^* , and x_p^* are the specified amount of product and its purity). $R_{\text{CBD}}(t)$, $R_{\text{i-CBD}}(t)$, and $R_{\text{SBD}}(t)$ are the time dependent reflux ratios, $S_{\text{MeOH}}(t)$ is the recycle rate of methanol (in case of i-CBD column), and F_{MeOH}

(t) is the methanol feed rate profile (for SBD column) which are optimized. ε is a very small value of the order of 10^{-3} . Note, the model equations of the i-CBD/SBD column are described by the highly coupled set of differential-algebraic equations (DAEs) acting as equality constraints to the optimization problem. Note, the calculations of operating constraints strategy in terms of reboiler overload problem (B_P, x_P) for the SBD operation will be the same as that was considered in Aqar et al.^{28, 30}. Note also, the thermal energy usage is computed using the following mode of energy consumption:

$$Q_{\text{tot}} = Q_{\text{Heat}} \times t_p \quad (5)$$

4. Results and Discussions

4.1 The performance of CBD column for MeDC synthesis

The synthesis of methyl decanoate is taken place in a 20 tray batch distillation column including total condenser and reboiler with a 5 kmol of total feed charged to the reboiler with the following composition in molefraction: 0.341 decanoic acid, 0.659 methanol, 0.0 methyl decanoate, and 0.0 water. The column plates are calculated from top down, stage 1 being the total condenser and stage N the reboiler. The total column holdup is four percent of the initial feed charge (of which 50% of this total holdup is placed in the condenser drum and the other half is distributed on the stages (equally divided). Many authors have used the similar distributions of column hold-up in the past as outlined in Mujtaba³². The information described above together with other feed specifications and operating conditions used in this work for the CBD column is presented in Table 4.

Note, the column specifications and the operating conditions (including reboiler heat duty and weight of catalyst) are kept the same as those available in the literature^{27, 19} for comparison purpose. The compositions of condenser and all trays are initialized to the fresh feed compositions at the beginning of process. Then, the composition profiles of batch column are established after the column reached the steady-state under total reflux start-up procedure for 5 hrs. Then (designated as $t = 0$) the production period for all case studies begins. Note, Cuille and Reklaitis³³ used similar column initialization policy in the past.

Table 4. Column specifications and operating conditions for esterification of DeC and MeOH system

Variable	Specifications
Total number of theoretical Plates*	20
Column pressure (throughout)	1.013 (bar)
Initial feed charged	5 (kmol)
Feed Composition (mole fraction)	DeC = 0.341, MeOH = 0.659 MeDC = 0.0, H ₂ O = 0.0
Total Catalyst Amount	3.792 (Kg)
Heat supplied to the reboiler, Q _r	754 (W)

*including total condenser and reboiler. Assumes 100% plate efficiency

With the start of the process, methanol and water will tend to move up the column as they are lighter and decanoic acid and methyl decanoate being heavier will be near the bottom of the column. It will be interesting to evaluate the performance of the CBD column (Figure 1a) in terms of minimum heat consumption for different quality of MeDC but for a given amount of reboiler product (mainly MeDC) which is kept constant at 2.2 kmol. The optimization results in terms of optimum reflux ratio, final batch time, the total energy requirement, total product amount, and the conversion rate of DeC for a range of desired product purity specifications (0.35 to 0.42) are summarized in Table 5. The results of Table 5 showed that all reflux ratio, processing batch time, heat usage, total amount of MeDC, and DeC conversion increase gradually with increasing the purity of the product. Also, it can be indicated that it is difficult to achieve a high conversion level of DeC into MeDC using a conventional batch distillation process. Note, at purity of 0.41, the distillation column was operating at higher reflux ratio compared to others and it was not possible to achieve methyl decanoate at composition > 0.42 using conventional batch distillation process. This is due to the reversible reaction being active and quick removal of methanol reactant from DeC in the reboiler drum because of the wide gap in boiling points between the chemical reactants. Note, in this work, the reflux ratio is defined as the internal reflux ratio ($R = \frac{L}{V_C}$) bounded between 0 (= zero reflux) and 1 (= total reflux) as opposed to external reflux ratio ($r = \frac{L}{D}$) bounded between 0 (= zero reflux) and ∞ (= total reflux).

Note, however, for the same feed composition (i.e. with excess methanol) in a continuous reactive distillation Steinigeweg and Gmehling²⁷ achieved even a lower conversion and

product purity (42.99% and 0.314 molefraction). There is no doubt that CBD offers slightly better conversion and purity.

Table 5. Optimal Operation results for the MeDC production for CBD column at <DeC= 0.341, MeOH= 0.659>

Product Quality, X_{MeDC}^*	Optimal Reflux Ratio	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	Total Product Amount, kmol	Conversion of DeC (%)
0.350	0.421	79.5	0.216	0.77	43.07
0.370	0.571	100.4	0.273	0.81	45.53
0.390	0.674	126.3	0.343	0.86	48.03
0.410	0.834	232.7	0.632	0.90	50.49
0.420	--- ^a	--- ^a	--- ^a	--- ^a	--- ^a

^a Not Achievable

Table 6 presents the optimization results, the still pot and distillate mole fraction, respectively for each product quality at the end of the operating batch time. As seen, mainly methanol and some water are accumulated in the distillate receiver while the reboiler contains more unreacted DeC, methyl decanoate and water. The mole fractions of DeC and MeDC in the accumulator was noticed to be negligible (as they are heavier components). Note that the amount of the distillate accumulator is found to be 2.6 kmol for all MeDC product purity considerations (by mass balance).

Table 6. The still pot and distillate composition profiles at several purities of MeDC using CBD column

Purity of MeDC	X_{DeC}	X_{MeOH}	$X_{\text{H}_2\text{O}}$	* X_{DeC}	* X_{MeOH}	* X_{MeDC}	* $X_{\text{H}_2\text{O}}$
0.350	0.441	0.002	0.207	1.25E-4	0.972	2.68E-3	0.025
0.370	0.422	0.003	0.206	9.25E-5	0.964	1.98E-3	0.034
0.390	0.403	0.003	0.205	7.07E-5	0.950	1.51E-3	0.049
0.410	0.384	0.003	0.204	3.62E-5	0.930	7.69E-4	0.069

*The composition in the distillate accumulator (molefraction).

4.2 The performance of i-CBD and SBD columns for MeDC synthesis

The effect of feed molar ratio on the overall performance of i-CBD and SBD columns is investigated in detail in this work. Two case studies are considered here, one (Case A) with an excess methanol in the feed stream as used by Steinigeweg and Gmehling²⁷ in a continuous reactive distillation column, and the other one (Case B) without an excess methanol in the feed (equimolar ratio).

4.2.1 Case A: i-CBD column (Excess Methanol)

More recently Aqar et al. ²⁸ proposed an integrated conventional batch distillation column (i-CBD), where part of the distillate is recycled to the reboiler drum (Figure 1b). Note, the column specifications of i-CBD process and the holdup distribution strategy are the same as those for CBD column (see section 4.1).

The optimal results for the i-CBD operation are given in Table 7, including the optimal recycle rate, optimal reflux ratio, batch time, minimum heat usage, and total amount of recycled MeOH, as well as the DeC conversion for four product purities of MeDC. It can be realized from these results that the optimal recycle rate of methanol, the final production time and the total energy consumption with total methanol recycled amount, progressively increase with increasing MeDC compositions. Increasing batch time clearly assisted increasing conversion of DeC into MeDC. A comparison of the results between the conversion of DeC using i-CBD process and the CBD process conversion (Table 5) shows that for the same amount of reboiler product (2.2 kmol) i-CBD column can yield MeDC at a much higher purity (0.75 compared to 0.41) and can convert more decanoic acid (91.83% as opposed to only 50.49%). Note, the total amount of methanol recycle (S_{tot}) is calculated from the optimal recycle rate (S_{MeOH}) multiplying by the batch time as presented below:

$$S_{tot} = S_{MeOH} \times t_p \quad (6)$$

It is noted also from Table 7 that no results were obtained at product composition of 0.80 mole fractions due to small amount of reactants (decanoic acid and methanol) in the reboiler tank and the remaining reactants (especially methanol) are trapped in the internal plates and the condenser drum (see the still pot and the distillate accumulator composition profiles in Table 8).

Table 7. Optimal Operation results for the production of MeDC for i-CBD column at <DeC= 0.341, MeOH= 0.659>

Product Quality, X_{MeDC}^*	Optimal Recycle Rate, kmol/hr	Optimal Reflux Ratio	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Recycle Amount, kmol	Conversion of DeC (%)
0.65	0.05	0.089	198	0.537	9.87	79.51
0.70	0.05	0.109	253	0.686	13.39	85.58
0.73	0.05	0.089	305	0.827	17.35	89.35
0.75	0.06	0.087	359	0.975	21.21	91.83
0.80	--- ^a	--- ^a	--- ^a	--- ^a	--- ^a	--- ^a

^a Not Achievable

Table 8. The still pot and distillate composition profiles at several purities of MeDC using i-CBD column

Purity of MeDC	x_{DeC}	x_{MeOH}	x_{H2O}	* x_{DeC}	* x_{MeOH}	* x_{MeDC}	* x_{H2O}
0.65	0.158	0.031	0.161	3.87E-5	0.884	8.23E-4	0.115
0.70	0.112	0.036	0.152	2.82E-5	0.887	6.00E-4	0.112
0.73	0.082	0.044	0.144	2.20E-5	0.890	4.67E-4	0.109
0.75	0.063	0.049	0.138	1.75E-5	0.894	3.72E-4	0.105

*The composition in the distillate accumulator (molefraction).

4.2.2 Case B: SBD column (Excess Methanol)

The feasibility of semi-batch (SBD) column (Figure 1c) as a potential candidate for synthesizing MeDC is discussed here. The SBD system with continuous feeding strategy of methanol is suggested for methyl lactate production in our recent works^{28, 30} and the same strategy is used here. Note, the problem specifications for SBD column are similar to those used in the CBD column (see Table 4).

As before, the purity of MeDC in the reboiler is changed from 0.65 to 0.80 mole fraction in each case while the amount of bottom product being kept constant at 2.2 kmol so that comparison of performances of SBD column can be carried out with i-CBD in terms of minimum energy consumption rate at an excess of methanol reactant. Table 9 shows the optimizations results in terms of minimum energy consumption, the optimal methanol feed rates and reflux ratios profiles, maximum allowable reflux ratio, minimum batch time, the total energy usage rate, total methanol amount, and the maximum conversion for a different product purity. As before, the operation results in Table 9 evidently indicate that the production time, the total thermal heat consumption, and the conversion rate, increase gradually with increasing the MeDC mole fractions.

Note, although reflux ratio increased for this case, there is an increase in the total quantity of charged methanol leading to higher batch time and total heat consumption for 0.75 of product composition. As shown also in Table 9, the optimal values of all reflux ratios are smaller than R_{Max} ensuring no overloading of still pot for all the MeDC purity conditions. Note, the maximum reflux ratio (R_{Max}) has been obtained by the following equation, which is suggested by Mujtaba³⁴:

$$R_{Max} = \left(1 - \frac{F_{MeOH}}{V_C}\right) \quad (7)$$

However, higher operating time and higher amount of methanol fed are required to strip all the DeC from the bottom tank (see Table 10). Note also, it was found from Tables 7 and 9 that the performance of i-CBD operation outperformed the performance of SBD to achieve

the specified product requirements with lower batch time and thermal energy rate. For example, the savings in the batch time and total heat consumption are 27.18% at MeDC purity of 0.75 mole fraction compared to that obtained by using the SBD process. However, SBD system is better than i-CBD column in terms of maximum achievable conversion. It is realized that 3.25% of conversion rate of DeC can be upgraded at 0.75 of product purity as compared to that obtained by employing the i-CBD column. It was impossible to achieve a higher product purity at 0.80 of MeDC mole fraction.

Table 9. Optimal Operation results for the production of MeDC for SBD at $\langle \text{DeC} = 0.341, \text{MeOH} = 0.659 \rangle$

Product Quality, x_{MeDC}^*	Optimal Feed Rate, kmol/hr	Optimal Reflux Ratio	Maximum Reflux Ratio	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Charge Amount, kmol	Conversion of DeC (%)
0.65	0.06	0.046	0.232	231	0.627	12.92	83.49
0.70	0.06	0.099	0.244	295	0.799	16.48	88.61
0.73	0.06	0.043	0.147	410	1.112	26.11	93.63
0.75	0.06	0.149	0.234	493	1.339	28.37	94.91
0.80	--- ^a	--- ^a	--- ^a	--- ^a	--- ^a	--- ^a	--- ^a

^aNot Achievable

Table 10. The still pot and distillate composition profiles at several purities of MeDC using SBD column

Purity of MeDC	x_{DeC}	x_{MeOH}	$x_{\text{H}_2\text{O}}$	* x_{DeC}	* x_{MeOH}	* x_{MeDC}	* $x_{\text{H}_2\text{O}}$	H_a , kmol
0.65	0.127	0.058	0.165	3.73E-5	0.896	7.91E-4	0.103	15.72
0.70	0.088	0.059	0.153	2.88E-5	0.900	6.07E-4	0.099	19.28
0.73	0.049	0.091	0.130	2.04E-5	0.910	4.32E-4	0.090	28.91
0.75	0.039	0.073	0.137	1.68E-5	0.913	3.54E-4	0.086	31.17

*The composition in the distillate accumulator (molefraction).

Note, SBD case (Table 9) required higher batch processing time compared to i-CBD case (Table 7). Smaller amount of total methanol recycling was required for i-CBD compared to that for SBD. Since the desired product amount in the reboiler is fixed in both cases, removal of larger amount from the reboiler in the case of SBD required longer processing time.

4.2.3 Case C: i-CBD column (Equimolar feed)

As mentioned in the Introduction section, Steinigeweg and Gmehling²⁷ used excess methanol in the feed in their continuous reactive distillation column to enhance the conversion of the fatty acid. In the following, it is investigated if excess methanol in the feed is actually required when operated in batch reactive distillation columns. Here, two scenarios are examined. Scenario-A uses single-reflux control interval, whereas, Scenario-B uses two-

reflux intervals policy. Within each interval, the reflux ratio and the methanol recycled rate together with the length of intervals will be optimized. Note, the mole fraction of MeDC product is changed from 0.70 to 0.90 in each scenario while the reboiler product amount remains constant at 2.2 kmol.

4.2.3.1 One Control Interval (NCI=1)

With equimolar reactant ratio (DeC: MeOH) of initial feed charge and for different purity of MeDC (0.70 to 0.90 mole fraction) and the same amount of reboiler product (2.2 kmol), Table 11 presents the optimization results in terms of optimum recycle rate, optimum reflux ratio, final batch time, the thermal energy consumption rate, and total amount of MeOH recycled, as well as the conversion of DeC. As before, the results indicated that the batch processing time with minimum heat usage and total amount of methanol increase progressively with increasing desired product purity. Increasing the batch time also increases conversion of DeC. Comparing the results with those presented in Table 7 (i-CBD with excess methanol), the operating time and the total energy usage are reduced by about 58.83% for MeDC purity of 0.75. For MeDC purity of 0.90, there is a sharp increase in reflux ratio and batch time resulting in higher total heat usage requirement and total quantity of methanol recycle. This clearly establishes that with batch distillation configuration, use of excess methanol is not required as suggested by earlier authors^{27, 19} who used continuous reactive distillation for MeDC synthesis.

Table 11. Optimal Operation results for the production of MeDC for i-CBD column at equimolar ratio using NCI = 1

Product Quality, X_{MeDC}^*	Optimal Recycle Rate, kmol/hr	Optimal Reflux Ratio	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Recycle Amount, kmol	Conversion of DeC (%)
0.70	0.04	0.138	138	0.374	4.91	74.86
0.75	0.04	0.071	148	0.402	6.10	80.46
0.80	0.04	0.075	167	0.453	7.33	85.37
0.85	0.04	0.143	197	0.535	8.57	89.47
0.90	0.04	0.249	257	0.697	10.50	93.20

4.2.3.2 Two Control Intervals (NCI=2)

The optimal operating strategy for the i-CBD column are presented in Table 12, including the optimum recycle rate and reflux ratio profiles, optimum length period for each interval, final

batch time, minimum thermal heat consumption, total amount of MeOH recycle, and the maximum DeC conversion for different product purity considerations. It is seen from Table 12 that considerable reductions in the final production time and in total energy usage (by about 41.29%), the total methanol amount (by about 53.62%), and the conversion rate of DeC is upgraded by 4.5% at the 0.90 of MeDC composition case using 2-reflux control intervals as compared to single reflux control interval i-CBD column. Multi-control strategy for the i-CBD system is found to provide much better operational flexibility and lowers production time and thus energy usage to achieve higher MeDC purity constraints (Figure 2).

As seen from Table 12, at lower MeDC purity specification, the batch distillation column operates at higher possible reflux ratio in the first time interval to push water up to the distillate tank and operating at low reflux ratio in the second interval to retain both chemical reactants (DeC and MeOH) in the reaction zone to have further reaction to achieve the specified purity constraint. Unlike, the batch distillation column operates at the lower reflux ratio in the first interval and then at the higher reflux in the second interval at the higher MeDC purity consideration.

Table 12. Optimal Operation results for the production of MeDC for i-CBD column at equimolar ratio using $NCI = 2$

Product Quality, x_{MeDC}^*	Recycle Rates for intervals S_1, S_2	Reflux Ratios for intervals R_1, R_2	Batch Time Intervals t_1, t_2 , hr	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Recycle Amount, kmol	Conversion of DeC (%)
0.70	0, 0.05	0.265, 0.010	48.73, 56.54	105	0.286	2.58	77.24
0.75	0, 0.04	0.048, 0.240	43.01, 71.66	115	0.311	2.68	79.75
0.80	0, 0.05	0, 0.113	49.49, 72.44	122	0.331	3.58	86.60
0.85	0, 0.05	0.055, 0.143	43.80, 87.34	131	0.356	4.04	89.80
0.90	0, 0.05	0.058, 0.195	43.82, 107.0	151	0.409	4.88	93.62

The composition profiles in the reboiler and the distillate drum at the product purity constraint ($x_{MeDC}^* = 0.90$) are given in Figures 3 and 4 for one control interval operation and in Figures 5 and 6 for two control intervals operation. It can be seen from Figures 3 and 5 that the composition of water in the still pot rises from zero and reaches the higher value and then gradually falls down to almost zero due to its separation in the distillate tank (Figures 4 and 6). The mole fraction of methanol reactant is reduced rapidly with increasing the production batch time due to its highest relative volatility and the efficient removal of water, which

collected in the distillate accumulator (see Figures 4 and 6). At the end of the operation, there is still a few percent of DeC reactant at the bottom of the column because of consumption by reaction with methanol.

More MeDC (as the second heavier boiling component) is yielded as the operating time increases and retains in the still pot. As purity of product increases, higher reflux ratio and more batch time are demanded to keep both reactants together (DeC and MeOH) in the reaction zone. The methyl decanoate in the bottom tank reached the maximum achievable purity of 0.90 faster and shorter time for two-reflux operation strategy than single-control one.

4.2.4 The performance of SBD column with equimolar feed

The effect of initial feed ratio (equimolar ratio) on the SBD process efficiency is investigated in terms of minimum thermal energy consumption for each bottom product composition. Two scenarios are studied here. Single and two control intervals are used.

4.2.4.1 One Control Interval (NCI=1)

For different bottom product qualities of MeDC, the optimization results (optimal feed rates, optimal reflux ratios, maximum allowable reflux ratios, minimum final production time, the total energy consumption, methanol charge amount and maximum conversion (%) of DeC to MeDC) are displayed in Table 13. It can be seen from these results that as the purity of MeDC increases from 0.70 to 0.90 mole fraction, production batch time, total energy usage, and conversion level increase together with total methanol feed amount. The results in Table 13 clearly present that the use of SBD process outperforms i-CBD process in terms of batch processing time and heat usage savings to achieve higher MeDC purity specifications at an equimolar ratio except the conversion of DeC (only slight improvement by i-CBD). For example, the operation time and thermal energy expense using the SBD operation (in case of product purity 0.90 mole fraction) are saved by an average 30.40% compared to that obtained by the i-CBD operation (Table 9).

For all case studies, the R_{Max} is computed from different values of feed rate of methanol. Also note, in all cases the maximum reflux ratio (R_{Max}) is found to be greater than the current reflux ratio avoiding reboiler overflowing condition. It can be concluded that use of an excess methanol in the feed mixture could not significantly improve the performance of SBD process in terms of production time and thermal heat minimizations, and maximum achievable MeDC purity.

Table 13. Optimal Operation results for the production of MeDC for SBD column at equimolar ratio using NCI = 1

Product Quality, x_{MeDC}^*	Optimal Feed Rate, kmol/hr	Optimal Reflux Ratio	Maximum Reflux Ratio	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Charge Amount, kmol	Conversion of DeC (%)
0.70	0.04	0.076	0.362	116	0.316	4.11	74.66
0.75	0.03	0.228	0.441	137	0.373	4.27	78.55
0.80	0.03	0.242	0.431	151	0.409	4.91	83.26
0.85	0.03	0.267	0.429	169	0.458	5.66	87.78
0.90	0.04	0.125	0.286	179	0.485	7.92	93.03

4.2.4.2 Two Control Interval (NCI=2)

For the five MeDC purities considered, the optimal methanol feed rate and reflux ratio profiles, optimal length period, final batch processing time, heat usage rate, the total amount of methanol charged, the maximum conversion of DeC using two-reflux intervals policy are presented in Table 14.

Compared with one reflux interval SBD operation, the operation time and the total thermal heat consumption are decreased by about 31.90% for MeDC quality of 0.90. It is evident from Table 14 that two-reflux strategy caused a huge reduction in the processing batch time and the energy usage compared to one reflux policy. It can be also observed that, more methanol in feed are saved at using two-control operation (reduction by about 58.16% compared with the single control interval policy). This obviously reveals the advantage of using multi-control intervals policy. This fact is illustrated in a better manner in Figure 7 in terms of total operating batch time and minimum heat consumption for all MeDC purities for both single-reflex operation, and two-reflux operation policies. It can be seen from Table 14 that the column operates at lower reflux ratio for the first interval for each product purity requirement to drive water up to the top of column. Whilst, higher reflux ratio and higher methanol feed rate are demanded to keep both reactants (DeC and MeOH) in the reactive zone to have further chemical reaction and to meet the specified product quality in the second time interval. Note, the optimal values of (R_1 and R_2) are still lower than the maximum reflux ratio (R_{Max}) values meaning the reboiler is never overflowed. Visibly 2-control intervals strategy provides better operational flexibility and shorter batch-processing time and thus

thermal energy consumption. The composition profiles of the reboiler and the distillate accumulator of SBD system at product purity specification ($x_{\text{MeDC}}^* = 0.90$) are displayed in Figures 8 and 9 for single-control interval strategy, and in Figures 10 and 11 for two-control intervals strategy.

Table 14. Optimal Operation results for the production of MeDC for SBD column at equimolar ratio using $\text{NCI} = 2$

Product Quality, x_{MeDC}^*	Feed Rates for intervals F_1, F_2	Reflux Ratios for intervals R_1, R_2	Batch Time Intervals t_1, t_2 , hr	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Charge Amount, kmol	Conversion of DeC (%)
0.70	0, 0.04	0, 0.129	49.34, 41.04	90	0.245	1.78	75.85
0.75	0, 0.05	0.01, 0.123	49.83, 45.89	96	0.260	2.11	80.65
0.80	0, 0.05	0, 0.116	49.27, 53.19	102	0.278	2.55	85.33
0.85	0, 0.04	0, 0.204	49.58, 61.34	111	0.301	2.74	88.85
0.90	0, 0.05	0, 0.215	49.80, 71.92	122	0.330	3.32	92.99

Note, although in this work only two reflux intervals are considered, more than 2 control intervals can be used and further savings in batch processing time is expected in such cases.

4.3 The choice of kinetic model

Although Steinigeweg and Gmehling²⁷ and Machado et al.¹⁹ and this work used PH kinetic model, Steinigeweg and Gmehling²⁷ noted that sorption effect of water is neglected in the kinetic model and with rising water content in the bulk liquid, the reaction rate can slow down and therefore can increase the batch processing time as observed in this work.

4.4 Batch processing time

In all cases presented earlier in this section required a large batch processing time. This is due to the use of low reboiler heat duty (less than 754 W) and small amount of catalyst (3.792 kg) used by original researchers^{19,27} as mentioned earlier. The effect of these parameters on the batch processing time is shown in this section for two of the cases reported in earlier section (Table 11 for i-CBD and Table 13 for SBD). For this purpose, we used reboiler heat duty of 86 kW and catalyst amount of 430 Kg. The results are provided in Tables 15 and 16, respectively.

Table 15 summarizes optimal methanol recycle rate and reflux ratio profiles, minimum batch time, total energy consuming, and total amount of methanol recycle rate, as well as maximum conversion (%) of DeC to MeDC for different bottom product purities of MeDC. As before,

the amount of bottom product to be achieved is set at 2.2 kmol for all cases. It can be observed that as the purity of MeDC increases from 0.70 to 0.90 mole fraction, reflux ratio, final batch time, and heat consumption rate increase together with the total amount of methanol recycled and conversion of DeC.

Comparing the results with those shown in Table 11 (i-CBD with the less heat duty and small catalyst amount), the processing batch time is significantly reduced by about 96.56% for MeDC purity of 0.90. However, the i-CBD operation with the less heat duty and small catalyst amount provided a better performance than the i-CBD operation with the higher heat duty and larger catalyst amount in terms of maximum achievable conversion of DeC.

Table 15. Optimal Operation results for the production of MeDC for i-CBD column at equimolar ratio

Product Quality, x_{MeDC}^*	Optimal Recycle Rate, kmol/hr	Optimal Reflux Ratio	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Recycle Amount, kmol	Conversion of DeC (%)
0.70	1.64	0.682	2.33	0.718	3.82	74.16
0.75	1.31	0.771	4.10	1.266	5.37	78.40
0.80	1.12	0.815	6.01	1.855	6.73	82.72
0.85	1.11	0.824	7.05	2.173	7.79	87.10
0.90	1.04	0.841	8.85	2.731	9.17	91.45

The optimization results (including optimal MeOH feed rates, optimal reflux ratios, maximum reflux ratios, minimum batch time, the thermal heat demand, MeOH charge amount and maximum conversion rate (%) of DeC) for different product compositions of MeDC, are reported in Table 16. It can be realized from the results in Table 16 that as the quality of MeDC increases from 0.70 to 0.90 mole fraction, final batch time, total energy usage, and total MeOH feed amount increase together with maximum achievable conversion. The results in Table 16 visibly indicate that the employment of SBD column with higher energy supplied to the still pot and larger amount of catalyst outperforms those obtained in Table 13 in terms of only production batch time saving to fulfil higher MeDC quality constraints. As an example, with 0.90 mole fraction of MeDC, the batch time using the SBD process is cut down by an average 95.97% as compared to that obtained by the SBD operation at lower heat duty and mass of catalyst (Table 13). However, the conversion to DeC was slightly better for the case presented Table 13.

Table 16. Optimal Operation results for the production of MeDC for SBD column at equimolar ratio

Product Quality, x_{MeDC}^*	Optimal Feed Rate, kmol/hr	Optimal Reflux Ratio	Maximum Reflux Ratio	Final Batch time, t_p , hr	Heat Usage, Q_{tot} , GJ	MeOH Charge Amount, kmol	Conversion of DeC (%)
0.70	1.33	0.680	0.771	1.70	0.524	2.26	73.92
0.75	1.04	0.800	0.835	3.95	1.219	4.11	78.24
0.80	1.03	0.815	0.842	4.86	1.500	5.00	82.64
0.85	0.93	0.844	0.862	6.82	2.103	6.32	86.99
0.90	0.98	0.840	0.856	7.21	2.223	7.10	91.40

5. Conclusions

In the past, synthesis of methyl decanoate has been carried out in a continuous reactive distillation column only resulting in the poor product purity and conversion. In this work, for the first time, the performances of different types of batch reactive column configurations are evaluated in terms of minimum energy usage under single and multi-reflux intervals modes for the synthesis of MeDC through the esterification reaction of DeC. It is found that the efficacy of using CBD column is restricted due to separation of methanol from DeC in the reactive region because of large difference in boiling points between the chemical reactants. Hence, the backward reaction is being activated as the process progresses due to the removal of methanol (one of the reactants of the forward reaction elements), causing a severe decrease in the DeC conversion. To overcome these limitations and to enhance the conversion of limiting reactant DeC, two alternative of batch reactive operation configurations are investigated here and they are: (1) i-CBD column and (2) SBD column.

A detailed dynamic model for the process is developed using gPROMS Model Builder 4.1.0 and is embedded within the optimization framework and the optimization problem is solved for different values of MeDC composition ranging from 0.70 to 0.90 mole fraction. Piecewise constant reflux ratio, methanol recycle rate (for i-CBD column), and methanol feed rate (for SBD column) on the final batch time and thermal energy consuming are estimated. The results indicate that the i-CBD mode is found to outperform the SBD column when excess methanol is used in the feed, whereas, at an equimolar ratio case, the SBD operation outperforms i-CBD process to satisfy the specified product considerations with the lower

operating time and thermal energy consumption. Note also, the optimization results for a given separation task demonstrate that the use of two-control operation can significantly improve the operation efficiency and achieve great time and thermal heat savings compared to the use of single-control interval in both i-CBD and SBD systems for an equimolar ratio. Note, for both i-CBD and SBD operations significant savings in the batch processing time can be achieved with the higher heat duty and larger amount of catalyst. Finally note, as used by the earlier authors²⁷ use of excess methanol in the feed will be necessary in continuous reactive distillation to enhance the conversion of the fatty acid.

Nomenclature

A_{ij}, A_{ji}	Binary interaction parameters for UNIQUAC method	cal/mol
a_i	Activity of component i	-
B_p	The product amount in the reboiler drum	kmol
CBD	Convictional batch distillation	-
CRD	Continuous reactive distillation	-
CVP	Control vector parameterisation	-
DAEs	Differential algebraic equations	-
F_{MeOH}	Methanol feed rate	kmol/hr
F_1, F_2	Methanol feed rate in time interval 1, and 2 for SBD	kmol/hr
H_a	Accumulator holdup amount	kmol
i-CBD	Integrated conventional batch distillation	-
M_{cat}	The catalyst loading	Kg
NCI	Number of control intervals	-
NLP	Nonlinear programming problem	-
OP1	Optimisation	-
P^S	Vapour pressure of pure substance	kPa
Q_{Heat}	Reboiler heat duty	W
Q_{tot}	Total Energy Consumption	GJ
R_{CBD}	Reflux ratio for CBD	-
R_{i-CBD}	Reflux ratio for i-CBD	-
R_{SBD}	Reflux ratio for SBD	-

R_{Max}	Maximum reflux ratio	-
r_{DeC}	Reaction rate	mol/g.s
S_{MeOH}	Recycled Methanol rate	kmol/hr
SBD	Semi-batch distillation	-
SQP	Successive quadratic programming algorithm	-
t_1, t_2	Length of interval 1, and 2	hr
t_p	Batch processing time	hr
V_c	Vapour load the condenser	kmol/hr

Abbreviations

DeC	Decanoic Acid
H ₂ O	Water
MeDC	Methyl Decanoate
MeOH	Methanol

6. References

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Figure 3: The reboiler composition profiles of i-CBD column for single-control interval strategy

$$(X_{\text{MeDC}}^* = 0.90).$$

Figure 4: The accumulator composition profiles of i-CBD column for single-control interval strategy

$$(X_{\text{MeDC}}^* = 0.90).$$

Figure 5: The reboiler composition profiles of i-CBD column for multi-control interval strategy

$$(X_{\text{MeDC}}^* = 0.90).$$

Figure 6: The accumulator composition profiles of i-CBD column for multi-control interval strategy

$$(X_{\text{MeDC}}^* = 0.90).$$

Figure 7: The optimal operating batch time and total energy consumption profile.

Figure 8: The reboiler composition profiles of SBD column for single-control interval strategy ($X_{\text{MeDC}}^* = 0.90$).

Figure 9: The accumulator composition profiles of SBD column for single-control interval strategy

$$(X_{\text{MeDC}}^* = 0.90).$$

Figure 10: The reboiler composition profiles of SBD column for multi-control intervals strategy

$$(X_{\text{MeDC}}^* = 0.90).$$

Figure 11: The accumulator composition profiles of SBD column for multi-control intervals strategy

$$(X_{\text{MeDC}}^* = 0.90).$$

Figure 1

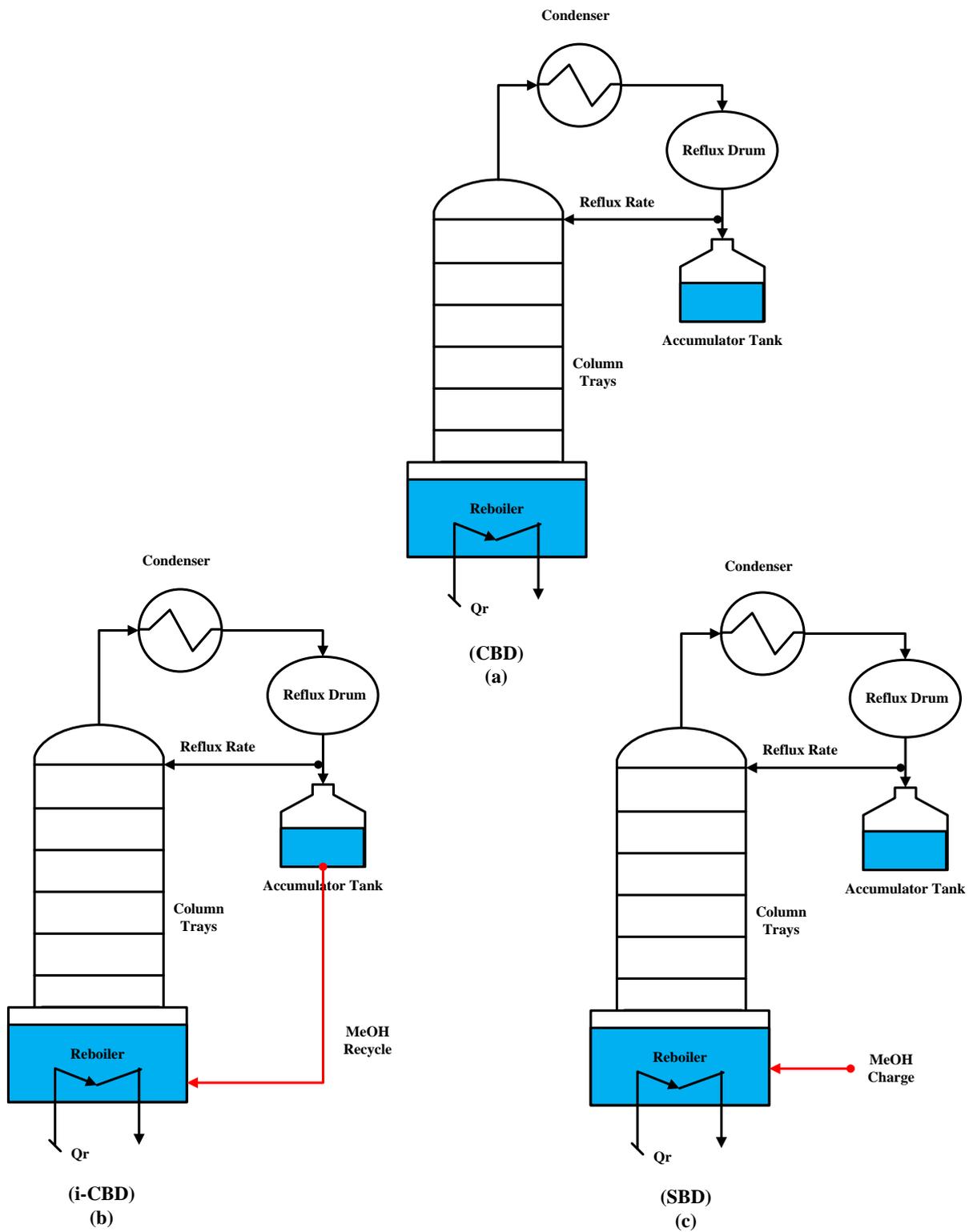


Figure 2

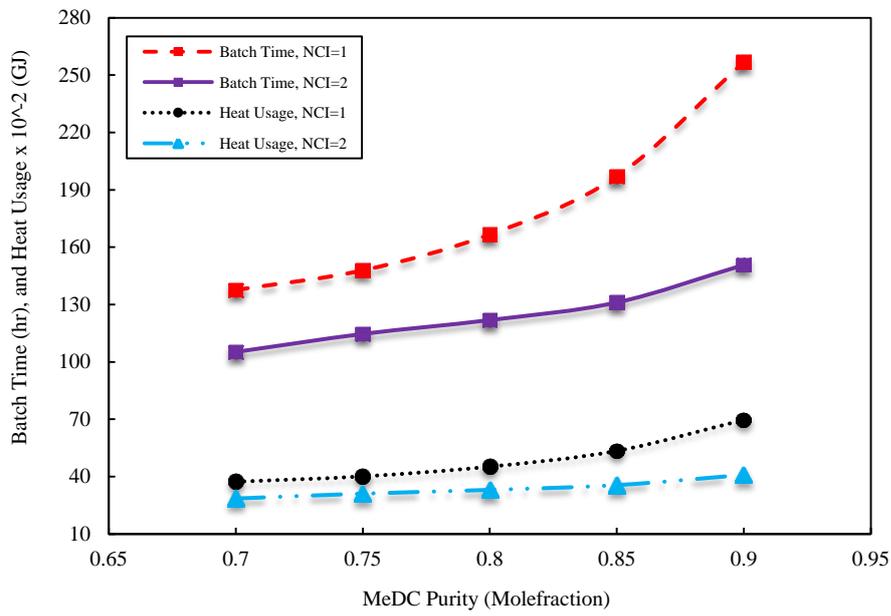


Figure 3

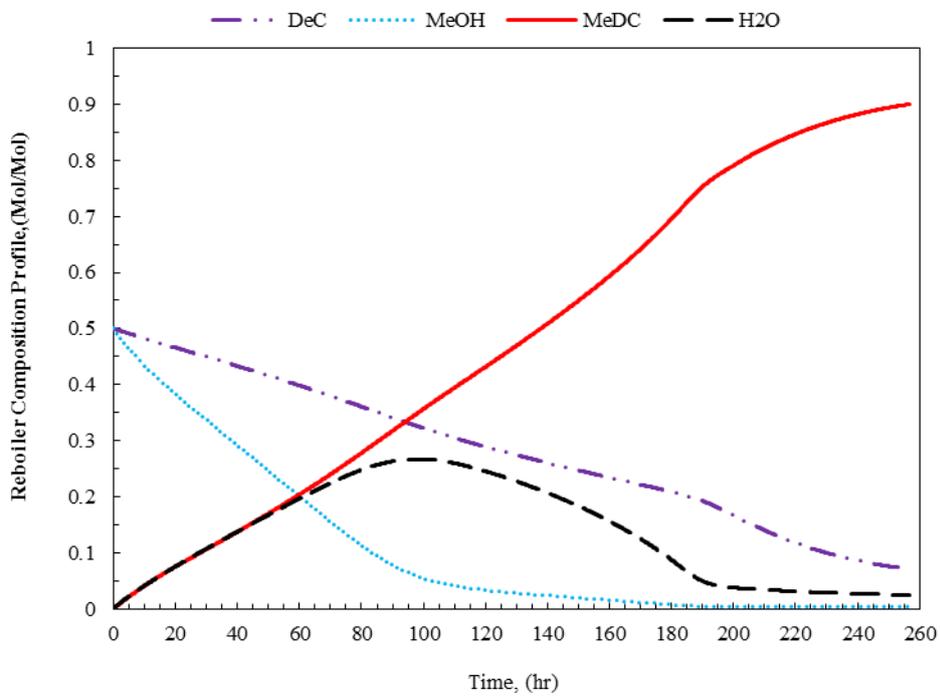


Figure 4

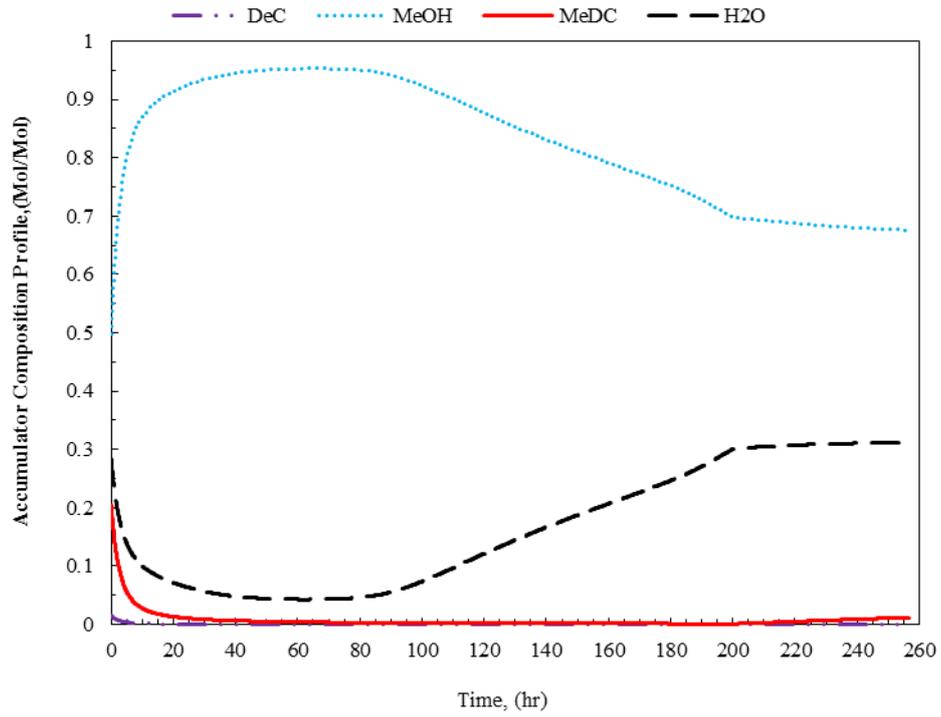


Figure 5

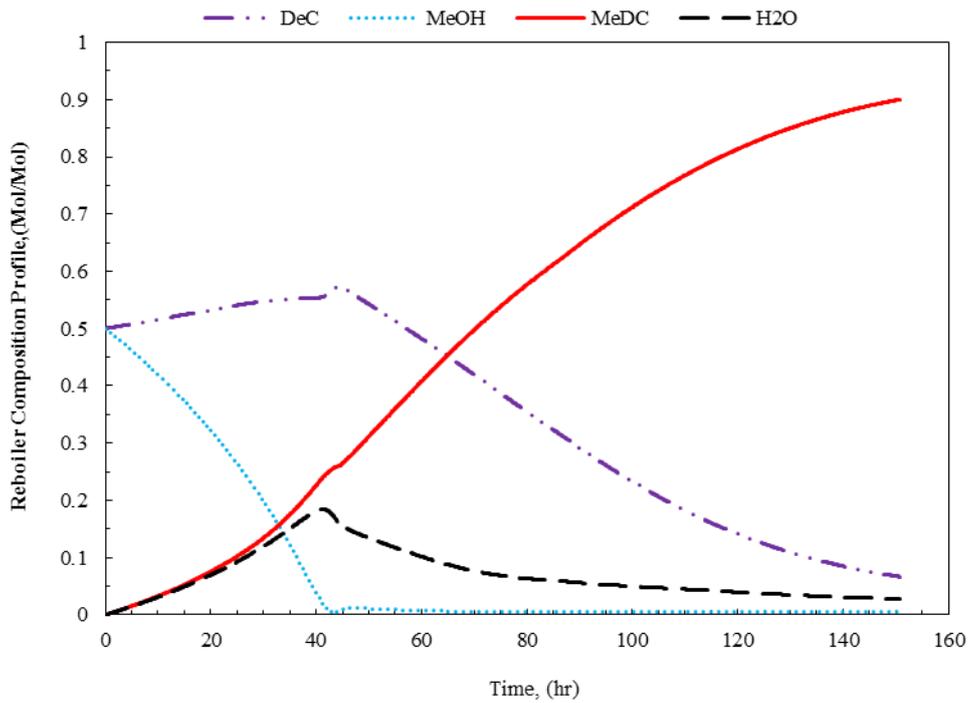


Figure 6

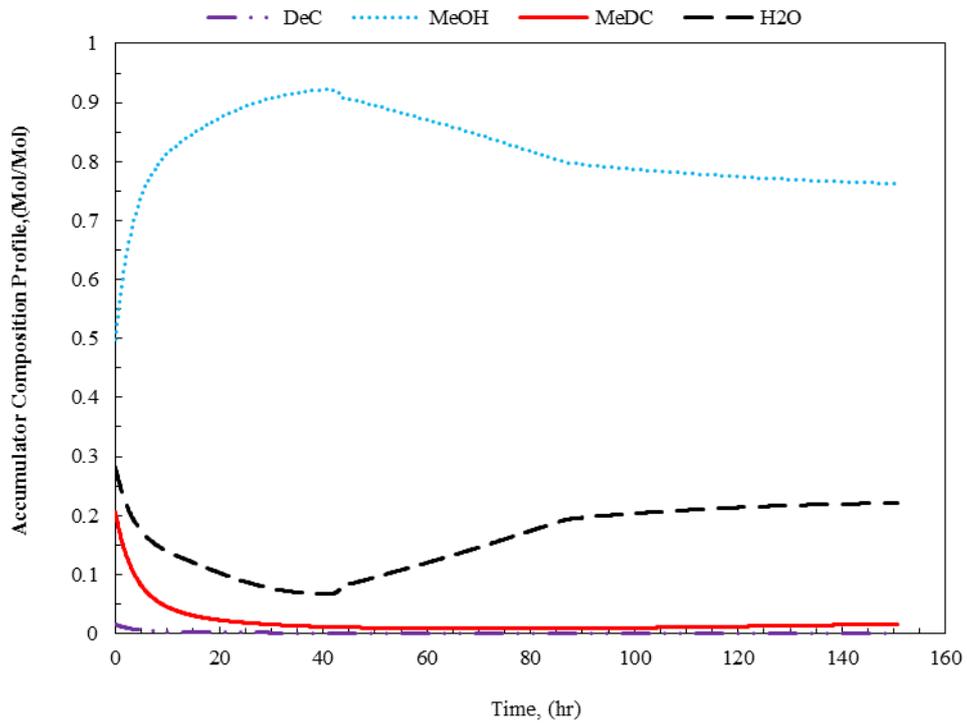


Figure 7

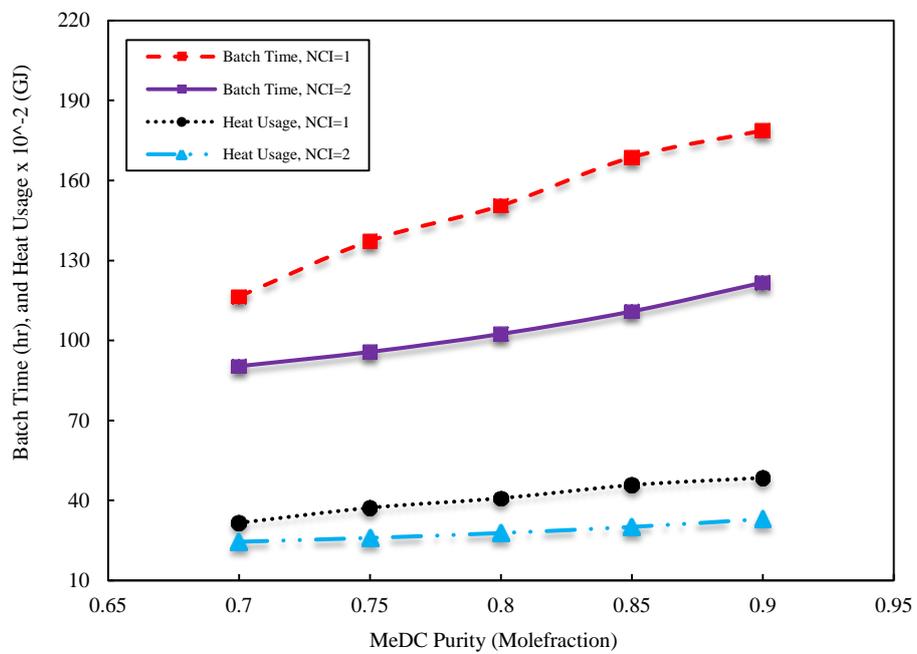


Figure 8

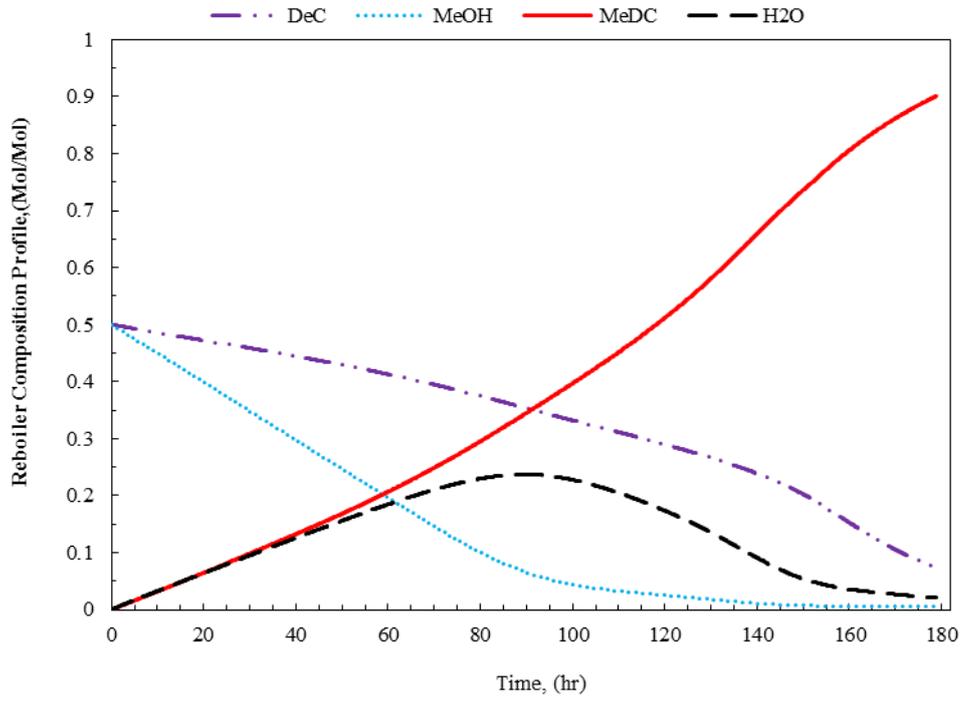


Figure 9

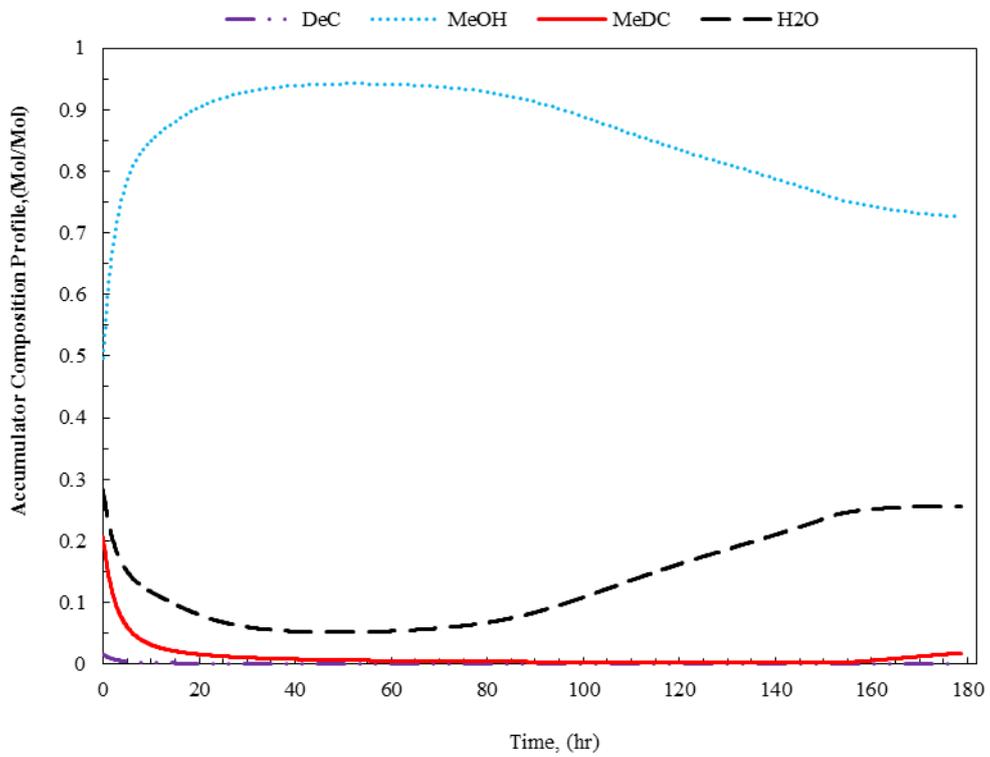


Figure 10

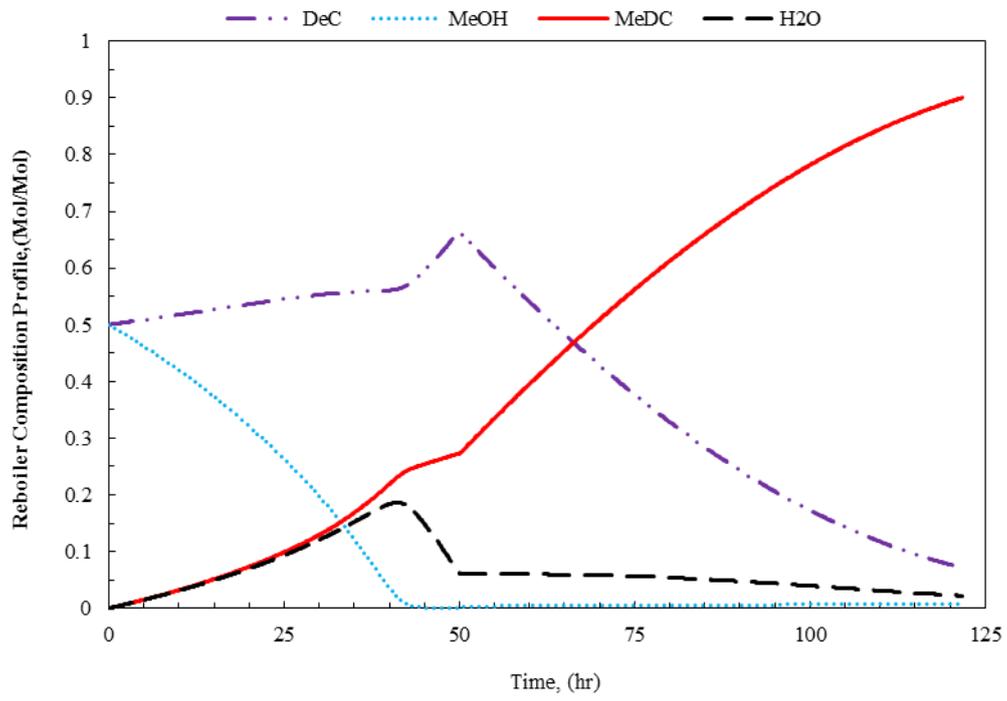


Figure 11

