



Optimal control of biodiesel production in a batch reactor Part I: Deterministic control

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ABSTRACT

The continuing depletion of fossil fuel reserves and the increasing environmental concerns has encouraged engineers and scientists to look for an alternative, clean, and renewable fuel that can reduce the negative environmental impact. Biodiesel has been considered as one of the best candidate of one of these renewable fuels. One of the pathways to biodiesel production is the transesterification reaction of triglycerides from vegetable oils and short-chain alcohols. A batch reactor is employed for the production of biodiesel. The flexibility of the batch process allows operating the reactor with different feed stocks and product specifications. This condition becomes challenging for the reactor modeling and control since uncertainty in the feed composition turns into time-dependent uncertainty and requires a batch-process based stochastic optimal control. In the first part of this work, the optimal control in this reactor involves optimization of the concentration of fatty acid methyl esters, well known as biodiesel, under the control of reactor temperature and the strategy applied to solve this problem is based on the maximum principle. The strategy increased the concentration by 8.46%. As far as the minimum time required to obtain the same base concentration, it reduced the reaction time by 69.5%.

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1. Introduction

Among the preoccupations that concern the world are the reduction of petroleum reserves due to the increased use of diesel fuel, and the environmental issues that caused by the climate change. This situation brings significant attention to new alternatives that secure the future energy supplies. For instance, researchers have focused their investigations to explore plant-based fuels, plant oils, and fats as promising bio-fuel sources. As a result, biodiesel derived from vegetable oils, can be an option to replace diesel. Biodiesel, consisting of methyl esters of fatty acids, is commonly obtained by transesterification of vegetable oils that compromise triglycerides with methanol in the presence of a catalyst. This clean renewable fuel is superior to diesel oil in terms of sulfur and aromatic content. Also, it is environmentally safe, non-toxic, and biodegradable [1]. Moreover, it can be used in any compression ignition engine without the need of any modifications [2]. Different raw materials can be used in order to produce biodiesel, such as rapeseed, palm and sunflower; however, one of the most common procedures is from soybean [3,4], which is used as a case study in this paper.

The transesterification reaction can be carried out in a batch reactor. Batch reactors are used for small-scale operations such as testing new processes, the manufacturing of expensive products, and for processes that are difficult to convert to continuous operations [5]. This type of reactor is appropriate for chemical, pharmaceutical, and biotechnological processes wherein the product quality and quantity play an important role in the process.

In the biodiesel reaction, the yield is affected by different parameters; however, researchers have considered four main factors: molar ratio between alcohol and triglycerides, reaction time, catalyst, and reaction temperature. For instance, an excess of alcohol can guarantee the complete conversion of fats or oils to esters in a short time. Usually, the molar ratio employed is 6:1 in a presence of alkali catalyst. On the other hand, the conversion rate of fatty acids esters increases with time and it has been found that the yield reaches a maximum at the reaction time of less than 90 min [6]. An excess of reaction time will decrease the yield due to the backward reactions and it will cause more fatty acids to form soap [6]. The catalyst also plays an important role since its concentration increases the conversion of triglyceride, which increases the yield of biodiesel. The most commonly used catalyst is sodium hydroxide. Finally, a higher reaction temperature can decrease the viscosities of oil resulting in an increased reaction rate and a shortened reaction time. Moreover, it is possible that the yield of biodiesel decreases when the reaction temperature rises beyond the

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Nomenclature

a_i	frequency factor	k_i	reaction constant of i reaction (L/mol min)
C_i	concentration of component i (mol/L)	R	universal gas constant (cal/mol K)
E	activation energy (cal/mol K)	T	temperature (K)
F_i	right hand side of equation i	t	time (min)
H	Hamiltonian	z_i	adjoint variables of component i

optimal level since it accelerates the saponification reaction of triglycerides [3].

The purpose of this paper is to find a control policy that can change with time using the dynamic optimization or optimal control in a batch reactor model. The control design of the biodiesel reaction is different from plant to plant and basically depends on the production technology adopted. Some of the most common control variables in chemical processes are temperature (e.g. temperatures of flow rates of cooling water in the coil or heating fluid in the jacket), pressure, flow, and level. For instances, in the Malaysia Palm Oil Board (MPOB) the reactant feed temperature and the reaction pressure is used as the manipulated variables. The pressure is operated at pressure higher than the atmospheric pressure and it is controlled in order to keep the methanol in the liquid phase. On the other hand, the ASAE (American Society of Agricultural Engineers) operates the transesterification reactor at atmospheric pressure and the reactor temperature is the control variable [7]. Paper [8,9] presents typical optimizing variables, control variables and performance index for optimal control problems in batch operations. As it can be seen, temperature is the most common variable used as a control variable. In addition, it provides a critical condition for different processes such as chemical reaction, and distillation. Therefore, the optimal control problem presented here is expressed in terms of reactor temperature.

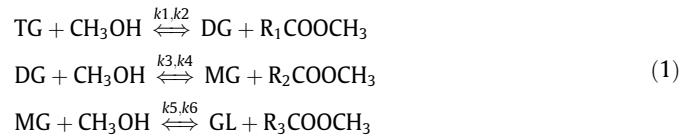
Most of the work in the area of batch reactors deal with a deterministic optimal control problem [10–14], but their applications are based on a general batch reactor and do not consider biodiesel kinetics. In contrast, research works such as [15–19] have highlighted the best operating conditions that can affect the yield of the transesterification reaction but their results depended upon the feedstock used. In [15,17,19], the response surface methodology was used to study the transesterification reaction and they present the factors that drive the conversion of triglycerides to biodiesel. However, these papers concentrate on static optimization and the uncertainties, which are inherent in biodiesel production, are neglected. The optimal control problem of a batch reactor becomes more challenging when variability in the feed composition, product specification, or model parameters is considered. In this two part paper, we address the problem of optimal control for biodiesel production by using the deterministic system of dynamic equation in part 1 to calculate the optimal temperature profile. This formulation is then extended in part II for uncertainty and variability consideration.

The present article is arranged in the following order. In Section 2, the batch reactor model is explained for the case of biodiesel production. Section 3 presents the optimal control problem for the deterministic scheme, including mathematical modeling of the process dynamic followed by the solution technique in Section 4. Finally, Section 5 shows the results and discussion based on the case study.

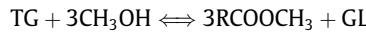
2. Batch reactor model for biodiesel

Biodiesel can be produced by the transesterification of triglycerides and methanol in the presence of an alkaline catalyst (e.g. sodium hydroxide). The reaction consists of three stepwise and reversible reactions where triglycerides (TG) are converted to

diglycerides (DG), diglycerides to monoglycerides (MG), and monoglycerides to glycerol. In each step an ester (R_iCOOCH_3) is produced resulting in three molecules of Ester from one molecule of triglycerides. The reaction steps are given by Eq. (1) where k_1 to k_6 are the rate constants; and the fourth equation represents the overall reaction. All reactions are carried out at atmospheric pressure [4].



Overall reaction:



The mathematical model for the production of biodiesel in a batch reactor is governed by the following Ordinary Differential Equations (ODEs) (2)–(7) derived from the mass balance of the batch reactor [4].

$$F_1 = \frac{dC_{TG}}{dt} = -k_1 C_{TG} C_A + k_2 C_{DG} C_E \quad (2)$$

$$F_2 = \frac{dC_{DG}}{dt} = k_1 C_{TG} C_A - k_2 C_{DG} C_E - k_3 C_{DG} C_A + k_4 C_{MG} C_E \quad (3)$$

$$F_3 = \frac{dC_{MG}}{dt} = k_3 C_{DG} C_A - k_4 C_{MG} C_E - k_5 C_{MG} C_A + k_6 C_{GL} C_E \quad (4)$$

$$\begin{aligned} F_4 &= \frac{dC_E}{dt} \\ &= k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A \\ &\quad - k_6 C_{GL} C_E \end{aligned} \quad (5)$$

$$F_5 = \frac{dC_A}{dt} = -\frac{dC_E}{dt} \quad (6)$$

$$F_6 = \frac{dC_{GL}}{dt} = k_5 C_{MG} C_A - k_6 C_{GL} C_E \quad (7)$$

where C_{TG} , C_{DG} , C_{MG} , C_E , C_A , C_{GL} are concentrations of triglycerides, diglycerides, monoglycerides, methyl ester, methanol, and glycerol respectively. The reaction constant, k_i , is expressed by the following equation:

$$k_i = a_i e^{-\frac{b_i}{T}} \quad (8)$$

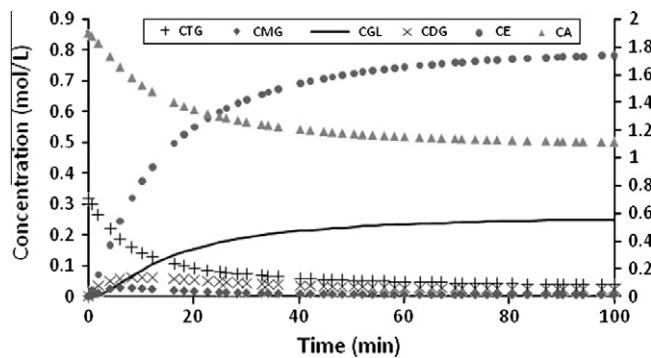
T is the reaction temperature, a_i is the frequency factor, and $b_i = Ea_i/R$ for which Ea_i is the activation energy for each component and R is the gas constant. The values of a_i 's and b_i 's are presented in Table 1.

It has been shown in the literature that the optimal temperatures for transesterification reaction are between 323 K and 333 K at atmospheric pressure [3], however, it can be found reaction temperatures from 241 K [20]. Therefore, two base cases are

Table 1Values of a and b^a .

a_1	a_2	a_3	a_4	a_5	a_6
3.92e7	5.77e5	5.88e12	098e10	5.35e3	2.15e4
b_1 6614.83	b_2 4997.98	b_3 9993.96	b_4 7366.64	b_5 3231.18	b_6 4824.87

^a The values of a_i and b_i are calculated from the Arrhenius equation (Eq. (8)) and the energy activation along with the values of k_i are reported in [4] at constant temperature (323 K).

**Fig. 1.** Concentration profile at constant temperature.

taken into account: constant temperature of 315 K and constant temperature of 323 K. Fig. 1 shows the concentration profile for the six components in the case of 323 K of reaction temperature, the set of ODEs are integrated using the explicit Runge–Kutta Fehlberg (RKF) method [21].

3. Optimal control problem

Optimal control has attracted interest in the industrial and academic field since it provides useful information for designing and controlling the reaction process. In general, a solution to these problems involves finding the time dependent profiles of the control variable so as to optimize a particular performance index [22]. For instance, one of the most common cases of optimal control problem is to find the best temperature profile, such that the performance index, yield or conversion, is optimized at a specific final time. Some of the alternatives used to solve these problems are the calculus of variations, dynamic programming, and maximum principle [23]. These techniques rely on appropriate mathematical representations that cannot be directly solved by simple mathematical models. Since the first two approaches are difficult to solve due to the presence of second order differential equations or partial differential equations [24], the maximum principle, which uses ODEs, can be employed. The maximum principle method adds adjoint variables and corresponding adjoint differential equations, and a Hamiltonian which needs to be optimized at each time step to obtain the control variable at each time step. The optimal control problem formulation for the case of biodiesel production in a batch reactor is presented in this section. Two different types of optimization problems are commonly encountered: the maximization of concentration and minimization of time. However, for the purpose of this paper, only the maximum concentration problem is solved. In this optimal control problem, the objective is to maximize the concentration of methyl ester (biodiesel) by finding the best temperature profile in a given reaction time (100 min). To solve this problem, the maximum principle formulation is used. In this method, the objective function is reformulated as a linear function in

terms of final values of state variables (C_i) and the constant values (A_i), thus, the objective function for this problem is shown in the following equation:

$$\text{maximize } J = \sum_{i=1}^n A_i C_i(t_f) = \bar{A}_i^T \cdot \bar{C}_i(t_f) = C_E(t_f) \quad (9)$$

Subject to:

State Eqs. (1)–(7) given in the generalized form below

$$\frac{dC_i}{dt} = f(C_i, T) \quad (10)$$

$$\text{For } C_i = [C_{TG}(t_0), C_{DG}(t_0), C_{MG}(t_0), C_E(t_0), C_A(t_0), C_{GL}(t_0)]$$

where C_i is the state variable that represents the concentration of each component: C_{TG} , C_{DG} , C_{MG} , C_E , C_A , and C_{GL} . T (temperature) is the control variable. A_i are constants values for the linear representation of the maximum principle. Initial conditions:

$$\text{Initial time } (t_0) = 0 \text{ min.}$$

$$\text{Final time } (t_f) = 100 \text{ min.}$$

$$C_i(t_0) = [0.3226; 0; 0; 0; 1.9356; 0] [\text{mol/L}].$$

$$A = [0; 0; 0; 1; 0; 0].$$

The maximum principle involves the addition of n adjoint variables (one adjoint variable per state variable), n adjoint equations, and a Hamiltonian which satisfies the following relations [23]:

$$H(\bar{z}_t, \bar{C}_t, T) = \bar{z}_t^T F(\bar{C}_t, T_t) = \sum_{i=1}^n z_i F_i(\bar{C}_t, T_t) \quad (11)$$

$$\frac{dz_i}{dt} = \sum_{j=1}^n z_j \left(\frac{\partial F_i}{\partial C_j} \right) \quad (12)$$

where n is the number of components (six components) and F_i is the right hand side of differential equation for each component i (Eqs. (2)–(7)). Eq. (13) shows the extended form of the Hamiltonian from Eq. (11):

$$H = z_1 F_1 + z_2 F_2 + z_3 F_3 + z_4 F_4 + z_5 F_5 + z_6 F_6 \quad (13)$$

The adjoint equations can be compute using Eq. (11), as it is shown next:

$$\frac{dz_1}{dt} = -z_1(-k_1 C_A) - z_2(k_1 C_A) - z_4(k_1 C_A) - z_5(-k_1 C_A) \quad (14)$$

$$\begin{aligned} \frac{dz_2}{dt} = & -z_1(k_2 C_A) - z_2(-k_2 C_E - k_3 C_A) - z_3(k_3 C_A) - z_4(-k_2 C_E \\ & + k_3 C_A) - z_5(k_2 C_E - k_3 C_A) \end{aligned} \quad (15)$$

$$\begin{aligned} \frac{dz_3}{dt} = & -z_2(k_4 C_E) - z_3(-k_4 C_E - k_5 C_A) - z_4(-k_4 C_E + k_5 C_A) \\ & - z_5(k_4 C_E - k_5 C_A) - z_6(k_5 C_A) \end{aligned} \quad (16)$$

$$\begin{aligned} \frac{dz_4}{dt} = & -z_1(k_2 C_{DG}) - z_2(-k_2 C_{DG} + k_4 C_{MG}) - z_3(-k_4 C_{MG} \\ & + k_6 C_{GL}) - z_4(-k_2 C_{DG} - k_4 C_{MG} - k_6 C_{GL}) - z_5(k_2 C_{DG} \\ & + k_4 C_{MG} + k_6 C_{GL}) + z_6 k_6 C_{GL} \end{aligned} \quad (17)$$

$$\begin{aligned} \frac{dz_5}{dt} = & z_1 k_1 C_{TG} - z_2(k_1 C_{TG} - k_3 C_{DG}) - z_3(k_3 C_{DG} - k_5 C_{MG}) \\ & - z_4(k_1 C_{TG} + k_3 C_{DG} + k_5 C_{MG}) - z_5(-k_1 C_{TG} - k_3 C_{DG} \\ & - k_5 C_{MG}) - z_6 k_5 C_{MG} \end{aligned} \quad (18)$$

$$\frac{dz_6}{dt} = -z_3(k_6 C_E) - z_4(k_6 C_E) - z_5 k_6 C_E + z_6 k_6 C_E \quad (19)$$

The boundary conditions for the adjoint variable are $z_i(t_f) = [0; 0; 0; 1; 0; 0]$, which correspond to the constant values of vector A. Using backward integration along with RKF method these equations can be solved. Finally, the optimal decision vector T(t) can be obtained by finding the extremum of the Hamiltonian at each time step, in other words, applying the optimality condition: $dH/dT|_t = 0$

As it was mentioned before, the optimal control problem can also be defined as the minimization of time problem. Here, the objective is to minimize the batch time given a final concentration. The objective function can be defined as shown in Eq. (20) and the differential equations (Eqs. (2)–(7)) can be transformed by multiple dt/dC_E , as shown in Eq. (21):

$$\text{minimum } J = \int_{C_E(t_0)}^{C_E(t_f)} \frac{dt}{dC_E} = t_f \quad (20)$$

$$\text{Subject to : } \frac{dC_i}{dC_E} = \frac{dC_i}{dt} / \frac{dC_E}{dt} \quad (21)$$

4. Solution technique: steepest ascent Hamiltonian method

The maximum principle formulation results in two point boundary value problem, where the initial conditions for the state variables C_i are known, but the conditions for the adjoint variables are only known at the final boundary. In order to obtain a solution, some iterative techniques including the shooting method and steepest ascent of the Hamiltonian method can be used [23]. To reduce the computational intensity, the optimal temperature trajectory for the system is achieved by using the approach proposed by Diwekar and co-workers [23–25], which uses the maximum principle. This algorithm starts with the initial estimate temperature $T(t)$. Subsequently, Eqs. (2)–(7) and (16)–(21) are solved by

employing the RKF method [21] with a step size equal to 0.01. Next, the values of dH/dT at each time are computed (see Appendix A) and then the convergence criterion ($dH/dT < \text{tolerance}$) is verified. If the convergence criterion is not satisfied, the temperature $T(t)$ is updated using this gradient, in such that the updated temperature profile improves the objective function, shown in Eq. (22). The value of M is a suitable constant that can be small enough so that no instability will result, or large enough for rapid convergence. Fig. 2 shows the flowchart for this algorithm. In order to obtain the derivative of the Hamiltonian, we used a novel approach by adding new differential equations whose solutions result in the derivative of the Hamiltonian. This is described in Appendix A.

$$T(t)^{\text{new}} = T(t)^{\text{old}} + M \left(\frac{dH}{dT}(t) \right) \quad (22)$$

5. Results and discussion

Figs. 3 and 4 present the profiles of Hamiltonian derivatives and Temperature per iteration. From these figures, it can be seen that as the profiles of the gradients (dH/dT) decrease (Fig. 3); the temperature profiles increase (Fig. 4) which improve the objective function (Eq. (9)). The solution technique presented in this paper proposes that the iterations proceed until the gradients reach a specific tolerance, thus, we decided a tolerance less than 2×10^{-3} . The value of tolerance was chosen based on the reaction temperature. This temperature cannot be exceed the boiling point of methanol (338 K at atmospheric pressure) due to the risk of leak out of alcohol through vaporization [3], therefore, twelve iterations were deemed to be sufficient. Besides, it can be seen from Fig. 4 in the last iterations that temperature profiles are not changing much.

Fig. 5 shows the initial guess of temperature $T(t) = 323$ K and the optimal temperature profile obtained after the stopping criteria

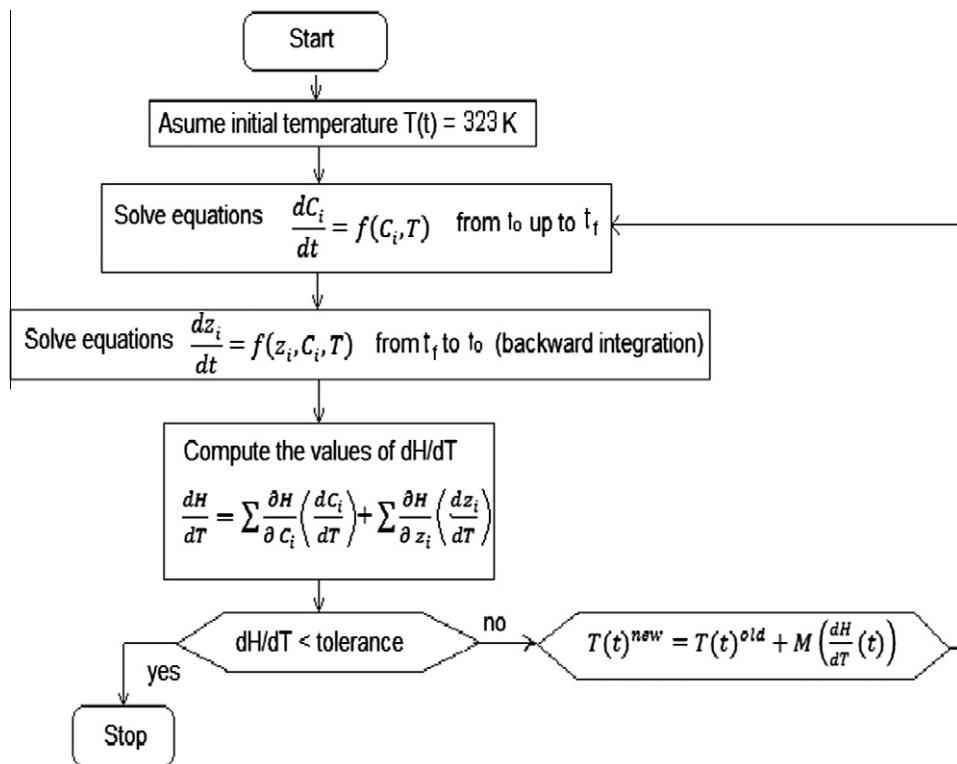


Fig. 2. Flowchart of solution technique.

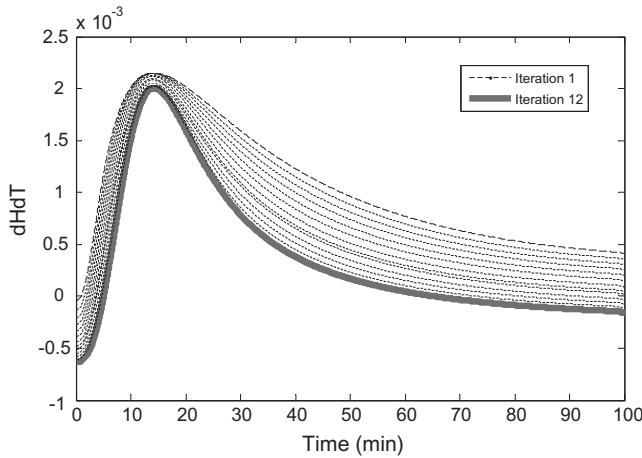
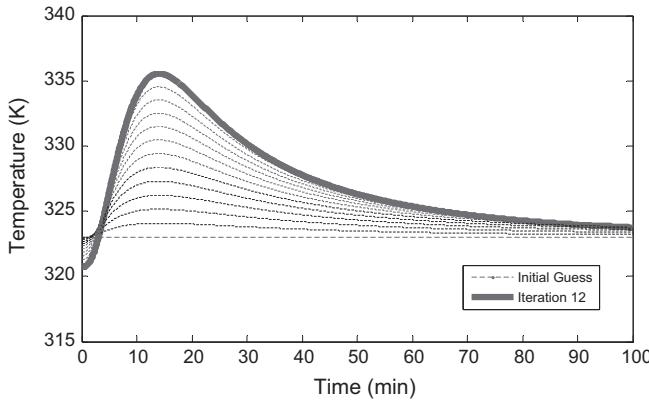
Fig. 3. Values of dH/dT for all iterations.

Fig. 4. Temperature profiles for all iterations.

were satisfied. This figure illustrates the significant variation of temperature with reaction time: at time zero the temperature value starts with 320.6 K, then, as the reaction proceeds between 10 to 20 min, the temperature increases to 335.5 K. According to [6,20,26], if the temperature goes beyond the optimal level, the yield of biodiesel product decreases because the saponification reaction of triglycerides accelerates. Finally, when the reaction time is 100 min the temperature drops to 323.7 K.

Fig. 6 presents concentration profiles for the six components. The purpose of this figure is to show that as the reaction precedes, the concentration of the desired product, methyl ester, increases; however, after 65 min there is no significant change in these values. This situation also happens with the rest of the components which no further change occurs after reaching this time.

Finally, Fig. 7 illustrates the concentration profile of methyl ester. Here we are comparing the concentration profiles at constant temperature from the two base cases with the values calculated at optimal temperature profile. From this figure, it is observed how the behavior of the temperature is reflected on the concentration of methyl ester, thus, when the temperature profile changes from constant values to the optimal profile, the concentration of methyl ester also changes. This situation is more significant when the optimal control is compared with constant temperature of base case 1. It can be seen that at 100 min of reaction time, the concentration of methyl ester at optimal control temperature reaches its maximum value, 0.7944 mol/L; while at constant temperature, the maximum concentration is 0.7324 mol/L. On the other hand,

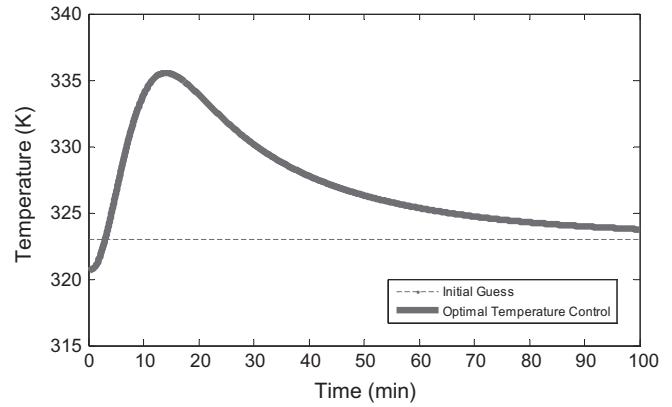


Fig. 5. Comparison between initial guess and optimal temperature profile.

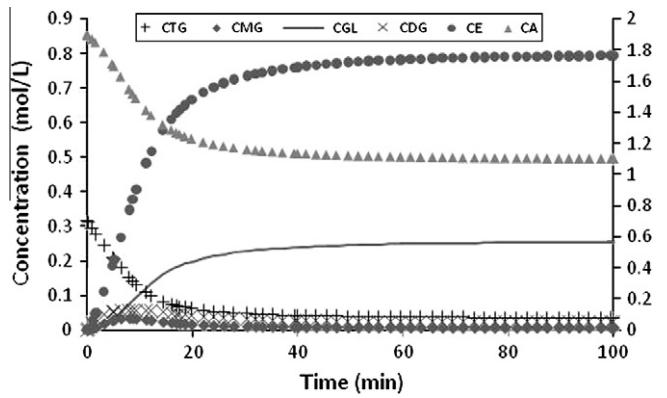


Fig. 6. Concentration profiles at the end of iterations.

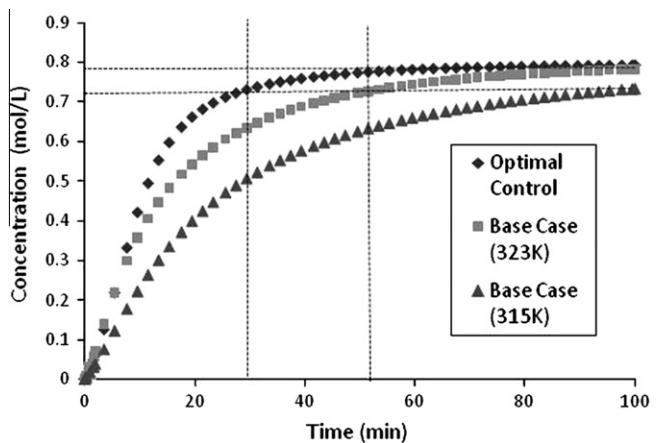


Fig. 7. Concentration profile of methyl ester.

for the base case 2 the maximum concentration value at 100 min is 0.7829 mol/L. Comparing these values, there is an increment of 8.46% with base case 1 and 1.47% with base case 2. For base case 2, the increment is not significant since the constant profile at 323 K belongs to the constant optimal profiles reported in the literature [3]. Alternatively, if we fix the concentration at 0.7324 mol/L, the reaction time needed would be 69.5% less than it was at the beginning. In the base case 2, the reduction on time represents 46% of the original reaction time if the concentration

is fixed to 0.7829 mol/L. This condition is the expected result from solving the minimum time problem. This improvement does not affect the other components because at the 50th minute of the reaction time, their concentration values are almost constant as shown in Fig. 6. It can be easily shown that the maximum concentration and minimum time problem results in similar equations for maximum principle and results in similar profiles.

6. Conclusion

In this article, the deterministic optimal temperature profile for biodiesel production in a batch reactor is determined. Under this framework, the feed composition remained constant. The maximum principle was used to solve the optimal control problem. The advantage of this method is that avoid the solution of second order differential and partial differential equations that are required in other techniques, such as calculus of variation and dynamic programming. Numerical results showed that twelve iterations were enough to reach the maximum concentration of methyl ester. The deterministic profile was compared with two base case methods: (1) constant temperature of 315 K and (2) optimal temperature of 323 K. As a result, it was presented that at 100 min of reaction time the concentration value of methyl ester increased 8.46% for base case 1 and 1.47% for base case 2 when the optimal temperature profile was employed. On the other hand, it was shown that the methyl ester profile obtained from the optimal temperature profile can reach the maximum concentration in less time; in other words, the profile with optimal control reached 0.7324 mol/L at 30.5 min for base case 1 and 0.7829 mol/L at 54 min for base case 2, which implied a reduction of 69.5% and 46% in batch time, respectively. For this reason, optimal control provides improvement to the effectiveness of batch processing. In the second part of this two paper series, we study the effect of uncertainties in feed composition uncertainties.

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Appendix A. Calculation of the derivative of the Hamiltonian

As it was mentioned before, the maximum principle is used in optimal control theory to find the best possible control of a dynamic system. This approach states that the Hamiltonian must be maximized over the control variable, in other words, it applies the optimality conduction $dH/dT < \text{tolerance}$. In the next part, the derivative of the Hamiltonian is calculated in order to determine the optimal temperature trajectory for this problem.

The Hamiltonian for the six components is presented as:

$$H = z_1F_1 + z_2F_2 + z_3F_3 + z_4F_4 + z_5F_5 + z_6F_6 \quad (\text{A.1})$$

This problem requires the use of the total derivative, which states that: if a continuous function $z = f(x, y)$ of several variables e.g. t, x, y , etc., is derived with respect to one of its input variables, e.g. t ; then the derivative can be expressed in terms of a series of partial derivatives.

As a result, the rate change of 'z' with respect to 't' can be calculated as:

$$\frac{dz}{dt} = \frac{\partial z}{\partial x} \left(\frac{dx}{dt} \right) + \frac{\partial z}{\partial y} \left(\frac{dy}{dt} \right) \quad (\text{A.2})$$

If we apply the total derivative concept to Eq. (A.1) shown in the previous paragraph, then the derivative of the Hamiltonian can be calculated by the following equation:

$$\frac{dH}{dT} = \sum_{i=1}^6 \frac{\partial H}{\partial C_i} \theta_i + \sum_{i=1}^6 \frac{\partial H}{\partial z_i} \emptyset_i \quad (\text{A.3})$$

where θ_i and \emptyset_i are represented by the following equations:

$$\theta_i = \frac{dC_i}{dT} \quad (\text{A.4})$$

$$\emptyset_i = \frac{dz_i}{dT} \quad (\text{A.5})$$

Then, to calculate the values of θ_i and \emptyset_i , we consider the following property, respectively:

$$\frac{d}{dT}(dC_i/dt) = \frac{d}{dt}(dC_i/dT) = \frac{d\theta_i}{dt} \quad (\text{A.6})$$

$$\frac{d}{dT}(dz_i/dt) = \frac{d}{dt}(dz_i/dT) = \frac{d\emptyset_i}{dt} \quad (\text{A.7})$$

where the differential equations for θ_i and \emptyset_i are given as:

$$\frac{d\theta_i}{dt} = f(C_i, \theta_i, T) \quad (\text{A.8})$$

$$\frac{d\emptyset_i}{dt} = f(C_i, \theta_i, z_i, \emptyset_i, T) \quad (\text{A.9})$$

As an example, the differential equation for θ_{TG} and \emptyset_{TG} (Triglycerides) are shown in the following equations:

$$\begin{aligned} \frac{d\theta_{TG}}{dt} = & - \frac{dk_1}{dT} C_{TG} C_A - k_1 \theta_{TG} C_A - k_1 C_{TG} \theta_A + \frac{dk_2}{dT} C_{DG} C_E \\ & + k_2 \theta_{DG} C_E + k_2 C_{DG} \theta_E \end{aligned} \quad (\text{A.10})$$

$$\begin{aligned} \frac{d\emptyset_{TG}}{dt} = & \emptyset_{TG} k_1 C_A + z_1 \frac{dk_1}{dT} C_A + z_1 k_1 \theta_A - \emptyset_{DG} k_1 C_A - z_2 \frac{dk_1}{dT} C_A \\ & - z_2 k_1 \theta_A - \emptyset_E k_1 C_A - z_4 \frac{dk_1}{dT} C_A - z_4 k_1 \theta_A + \emptyset_A k_1 C_A \\ & + z_5 \frac{dk_1}{dT} C_A + z_5 k_1 \theta_A \end{aligned} \quad (\text{A.11})$$

Finally, a numerical method such as RKF is used to integrate the system of equations represented by Eq. (A.8), with initial conditions: $\theta_i(t_0) = [0; 0; 0; 0; 0; 0]$. On the other hand, to compute \emptyset_i , backward integration and using again RKF method is also used to solve the system of equation represented by Eq. (A.9), but in this case, the boundary condition are expressed as: $\emptyset_i(t_f) = [0; 0; 0; 0; 0; 0]$.

Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fuel.2011.08.035.

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