A fractional order mathematical model for enzymatic biodiesel synthesis and its optimization

Fahad Al Basir, Priti Kmar Roy and Santanu Ray

Abstract— Biodiesel, the most possible alternative of diesel fuel, is produced through transesterification of vegetable oil using chemical or enzyme catalytic methods. In this study, a mathematical model for enzymatic transesterification is proposed using fractional order differential equation. Optimal control approach on the system dynamics is adopted to maximize biodiesel yield. Necessary conditions for the optimality of the system are derived using Hamiltonian. The optimal control problem is solved numerically by developing iterative schemes through Matlab. Results obtained from simulating the proposed model, are compared to the existing results and found to be satisfactory.

Keywords—Biodiesel, Mathematical modeling, Enzymatic transesterification, Fractional optimal control problem (FOCP).

I. Introduction

Biodiesel is gaining the most importance due to diminishing petroleum sources and the environmental consequences of exhaust gases from petroleum based engines. It is considered as the most appropriate alternative fuel for diesel engines. A number of pro- cesses have been developed for biodiesel production involving chemical [1] or enzyme catalysis [2] or supercritical methanol [3]. Enzymatic process for biodiesel production has gained a favourable attention because of its environmentally friendly nature, its mild reaction conditions, biodiesel recovery and high purity glycerol as by-product [4].

Mathematical modeling approach for the enzymatic production of biodiesel using different feedstock has been investigated by researchers [5, 6]. Cheirsilp et al. [7] established mathematical models for lipase- catalyzed biodiesel production in a batch system consisted of palm oil, enzyme, water and various ethanol concentrations.

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Liu et al. [8] have investigated the transesterification of waste cooking oil catalyzed by immobilized lipase establishing a mathematical model and determine the kinetic parameters used in the system. Basir et al. [6] established a mathematical model for biodiesel production from Jatropha oil using enzymatic process. Optimization of biodiesel production from vegetable oil has been studied using optimal control approach by some researchers using classical integer order differential equations [6, 9]. But there is no mathematical model of biodiesel synthesis available using fractional differential equations. In other fields also, the application of dynamic optimization or optimal control using fractional calculus is very few [13, 10].

Recently researchers have shown that fractional calculus is a powerful modeling tool to describe some biochemical, mechanical and electrical dynamic systems [11, 12]. In their work Toledo-Hernandez et al. [13] propose a fractional fermentation model which is based on experimental data and a non-linear fitting approach that includes fractional integration by which fractional orders is incorporated. They have established the feasibility and capabilities of fractional calculus as a tool for modeling dynamic systems in the area of process systems engineering.

Motivated by the above works, in this article, we have proposed a fractional order model of enzymatic transesterification. Enzyme catalyzed reaction suffers mass transfer limitation problems initially and enzyme inhibition by dead end complexes produced in the process. Stirring is applied to avoid these problems in the system [15]. System requires optimal control on stirring for optimum production in a cost-effective way. Thus we have applied mathematical control approach on mixing intensity in the formulated fractional ordered system to avoid mass transfer limitation problem. Thus, the fractional optimal control problem (FOCP) for the system is provided and Euler-Lagrange optimality conditions for the FOCP are derived. Numerical simulation using fractional order system and the FOCP have been provided to illustrate the main results using numerical iterative schemes through Matlab.

In the next section we provide the required definations and general formation of fractional optimal control problem.

II. FRACTIONAL CALCULUS AND FOCP

To model the dynamical system with fractional differential equation, it is necessary to use an appropriate definition of the fractional derivative. In fact, the definitions of the fractional order derivative are not unique and there exist several definitions such as Riemann-Liouville, Caputo etc [16]. Left-sided Caputo frac-tional derivative can be defined as:

$$ {}_a^C D_t^\alpha g(t) = \frac{1}{\Gamma(n-\alpha)} \int_a^t \frac{g^{(n)}(s)}{(t-s)^{\alpha-n+1}} ds \qquad (1) $$

and right-sided Caputo fractional derivative is defined as:

$$ {}_t^C D_b^\alpha g(t) = \frac{(-1)^n}{\Gamma(n-\alpha)} \int_t^b \frac{g^{(n)}(s)}{(t-s)^{\alpha-n+1}} ds, \qquad (2) $$

where α is the order of the derivative and $n-1 < \alpha < n$, Γ is the gamma function and n is considered as an integer.

The left-sided Riemann-Liouville fractional deriva-tive is defined as below:

$$ {}_a D_t^\alpha g(t) = \frac{1}{\Gamma(n-\alpha)} \frac{d^n}{dt^n} \int_a^t \frac{g(s)}{(t-s)^{\alpha-n+1}} ds \qquad (3) $$

and right-sided Riemann-Liouville fractional derivative is:

$$ {}_t D_b^\alpha g(t) = \frac{(-1)^n}{\Gamma(n-\alpha)} \frac{d^n}{dt^n} \int_t^b \frac{g(s)}{(t-s)^{\alpha-n+1}} ds, \qquad (4) $$

where α represents the order of the derivative and $n-1 < \alpha < n$, Γ is the gamma function and n is considered as an integer and $a > 0$, $b > 0$ are constants. We use the operator D_t^α for Left-Caputo derivative throughout the article.

An additional issue to consider is the fact that fractional derivatives are defined using integrals, so they are non-local operators. The fractional derivative in time contains information about the function at earlier points, so it possesses a memory. Therefore, fractional differential equation implies non-local dynamics and involves memory effects [18].

In [19], Agrawal presented a general formulation and the derivation of the optimality conditions for an FOCP. A short description is given below:

Consider the following control induced system with fractional order derivative:

$$ D_t^\alpha x = f(x,u,t),\ x(0) = C_0. \qquad (5) $$

Here, x is the state vector and t is the time. The objective function can be defined as

$$ J(u) = \int_0^t g(x,u,t) dt, $$

Now, the control problem can be described as:

$$ \text{Minimize } J(u) = \int_0^t g(x,u,t) dt, $$
$$ \text{subject to the system (5).} $$

The state system is given by

$$ D_t^\alpha x = f(x,u,t),\ x(0) = C_0, \qquad (6) $$

where, $u(t)$ is the control parameter and the costate system with $y(t)$ as the costate vector can given by

$$ D_{t_f}^\alpha y = \frac{\partial g}{\partial x} + y \frac{\partial f}{\partial x},\ y(t_f) = 0. \qquad (7) $$

The optimal control function u^* satisfies the following relation

$$ \frac{\partial g}{\partial u^*} + y \frac{\partial f}{\partial u^*} = 0. \qquad (8) $$

Equation (6), (7), and (8) represent the Euler-Lagrange optimality conditions for the FOCP with Caputo fractional derivatives. If the order of the fractional derivatives i.e. α becomes 1, the above system of equations reduces to the classical optimal control problem (OCP).

III. FRACTIONAL ORDER MODEL FOR BIODIESEL SYNTHESIS

To describe a simple mathematical model for enzyme catalytic transesterification reaction of Jatropha Curcas oil, the following assumptions have been taken:

Biocatlytic catalyzed transesterification (using Li-pase) of Jatropha Curcas oil with an alcohol (A) may be proposed to involve two-step mechanisms. The first step consists of hydrolysis of Jatropha Curcas oil or TG to produce acylated enzyme (AcE) and release of glycerol as only by product through a complex C_1

$(E.T)$. Here E stands for enzyme. The second step is the esterification of methanol (A) with AcE to form the desired product i.e. BD with the release of free enzyme (E) through a second complex C_2 $(AcE.A)$ [6, 20, 21].

$$E + T \underset{r_{-1}}{\overset{r_1}{\rightleftharpoons}} [E.T] \underset{r_{-2}}{\overset{r_2}{\rightleftharpoons}} AcE + G,$$
$$AcE + A \underset{r_{-3}}{\overset{r_3}{\rightleftharpoons}} [AcE.A] \underset{r_{-4}}{\overset{r_4}{\rightleftharpoons}} E + B,$$

To account for the inhibition of reaction by methanol in the system kinetics, here, a competitive inhibition is assumed when a AL molecule combines with the E to produce a dead-end complex, complex C3 (E.A)[8]. All the mechanistic steps for the biodiesel pro-duction can be represented by the following sequence of reactions:

$$E + A \underset{r_{-5}}{\overset{r_5}{\rightleftharpoons}} [E.A]. \tag{9}$$

Here, $r1$ and $r-1$, $r2$ and $r-2$ are the rate constants for the reversible formation of complex $C1$, acylated enzyme and by product glycerol respectively in the first step of biodiesel formation. $r3$ and $r-3$, $r4$ and $r-4$ are the rate constants for the reversible formation of complex $C2$ and biodiesel formation respectively in the final step. For the inhibition reaction, $r5$ and $r-5$ are the rate constants for the reversible formation of dead-end complex $C3$.

We denote the concentration of T, E, AcE, C1, C2, C3, A, B and G as CT , CE , CAcE, CC1, CC2, CC3, CA, CB and CG respectively. Now from the above assumptions, we can formulate the set of differential equations given below:

$$\begin{aligned}
\frac{dC_E}{dt} &= -k_1C_TC_E + k_{-1}C_{C1} + k_4C_{C2} \\
&\quad -k_{-4}C_EC_B - k_5C_EC_A + k_{-5}C_{C3} \\
&\quad +k_sC_AC_{C3}, \\
\frac{dC_T}{dt} &= -k_1C_TC_E + k_{-1}C_{C1}, \\
\frac{dC_{AcE}}{dt} &= k_2C_{C1} - k_{-2}C_{AcE}C_G - k_3C_FC_A \\
&\quad +k_{-3}C_{C2}, \\
\frac{dC_B}{dt} &= k_4C_{C2} - k_{-4}C_EC_B, \\
\frac{dC_A}{dt} &= -k_3C_{AcE}C_A + k_{-3}C_{C2} \\
&\quad -k_5C_EC_A + k_{-5}C_{C3},
\end{aligned}$$

$$\begin{aligned}
\frac{dC_{C1}}{dt} &= k_1C_TC_E - k_{-1}C_{C1} - k_2C_{C1} \\
&\quad +k_{-2}C_{AcE}C_G, \\
\frac{dC_{C2}}{dt} &= k_3C_{AcE}C_A - k_{-3}C_{C2} - k_4C_{C2} \\
&\quad +k_{-4}C_EC_B, \\
\frac{dC_{C3}}{dt} &= k_5C_EC_A - k_{-5}C_{C3} - k_sC_AC_{C3}, \\
\frac{dC_G}{dt} &= k_2C_{C1} - k_{-2}C_{AcE}C_G,
\end{aligned} \tag{10}$$

with the initial conditions

$$\begin{aligned}
C_E(0) &= C_{E_0},\ C_{C1}(0) = 0,\ C_{AcE}(0) = 0, \\
C_A(0) &= C_{A_0},\ C_T(0) = C_{T_0},\ C_{C2}(0) = 0, \\
C_B(0) &= 0,\ C_G(0) = 0\text{and } C_{C3}(0) = 0.
\end{aligned} \tag{11}$$

Mixing in the reaction system has significant effect on overall reaction rates. Here, we use k_s as the effect of stirring on reaction rate and the term can be defined as Boltzmann sigmoid form [22]:

$$k_s = \frac{a}{1 + e^{-b(F-c)}}, \tag{12}$$

where F is the speed of stirrer and a, b and c are constants. Thus, the effect of stirring on reaction rates can be expressed as [23, 24]:

$$k_i = k_s r_i. \tag{13}$$

i=1,2,...,9. r_i are given in Table 1.

Currently, in various research fields, numerous thoughts have been focused to the models of fractional-order equations [18, 26]. The significant of these model systems is the non-local features that do not appear in integer-order differential operators. Thus fractional differential equations involve a memory.

Generally, enzymes acts as catalyst and convert substrates into products. Microorganisms' activity forms the major source for enzymes. Microorganisms growth depends on the medium they situated. Thus, we can assume that the dynamic behaviour of a living microorganism does not depend only on their present conditions but also on their state at earlier points. Therefore, the dynamics of biological reactions can in general involve memory [14, 17]. On that basis here, we extend the above model with incorporation of the fractional-order differential equations into the mathematical model of integer-order system.

Now, the modified system of equations with the

concept of fractional-order is given below:

$$\begin{aligned}
D_t^\alpha C_E &= -k_1 C_T C_E + k_{-1} C_{C1} \\
&\quad + k_4 C_{C2} - k_{-4} C_E C_B - k_5 C_E C_A \\
&\quad + k_{-5} C_{C3} + k_s C_A C_{C3}, \\
D_t^\alpha C_T &= -k_1 C_T C_E + k_{-1} C_{C1}, \\
D_t^\alpha C_{AcE} &= k_2 C_{C1} - k_{-2} C_{AcE} C_G \\
&\quad - k_3 C_{AcE} C_A + k_{-3} C_{C2}, \\
D_t^\alpha C_B &= k_4 C_{C2} - k_{-4} C_E C_B, \\
D_t^\alpha C_A &= -k_3 C_{AcE} C_A + k_{-3} C_{C2} - k_5 C_E C_A \\
&\quad + k_{-5} C_{C3}, \\
D_t^\alpha C_{C1} &= k_1 C_T C_E - k_{-1} C_{C1} - k_2 C_{C1} \\
&\quad + k_{-2} C_{AcE} C_G, \\
D_t^\alpha C_{C2} &= k_3 C_{AcE} C_A - k_{-3} C_{C2} \\
&\quad - k_4 C_{C2} + k_{-4} C_E C_B, \\
D_t^\alpha C_{C3} &= k_5 C_E C_A - k_{-5} C_{C3} - k_s C_A C_{C3}, \\
D_t^\alpha C_G &= k_2 C_{C1} - k_{-2} C_{AcE} C_G, \qquad (14)
\end{aligned}$$

with the initial conditions given in 11.

A. Non-Negativity of Solutions

Here, we first prove the positivity of the solutions. Next, we will show the solution, with $x(0) > 0$, is always positive whenever the solution exists and the solutions will remain in $\Re^5_+$, where $\Re^9_+ = \{x \in \Re^9 : x \geq 0\}$ and $x(t) = (C_T, C_E, C_{AcE}, C_{C1}, C_{C2}, C_{C3}, C_A, C_B, C_G)$.

For the proof of the theorem about nonnegative solutions, we need the following Lemma:

Lemma 1 : (Generalized Mean Value Theorem): Let $f(x) \in C[a,b]$ and $D_t^\alpha \in C(a,b]$ for $0 < \alpha \leq 1$, then we have

$$f(x) = f(a) + \frac{1}{\Gamma(\alpha)} D_t^\alpha f(\xi)(x-a)^\alpha, \qquad (15)$$

with $0 \leq \xi \leq x$, for all $x \in (a,b]$.

Remark 1: $f(x) \in C[0,b]$ and $D^\alpha{}_t \in C(a,b]$ for $0 < \alpha \leq 1$ then it is clear from Lemma 1 that if $D_t^\alpha \geq 0$, for all $x \in (0,b)$ then the function f is non decreasing and if $D_t^\alpha \leq 0$ for all $x \in (0,b)$ then the function f is non increasing for all $x \in [0,b]$.

Theorem 1: There is a unique solution $x = [C_T, C_E, C_{AcE}, C_{C1}, C_{C2}, C_{C3}, C_A, C_B, C_G]$ for the initial value problem given by (14) and the solution remains in $\Re^9_+$.

Table 1: Values of parameters used for numerical calculations of for enzyme catalysed reactions at 40^oC [8, 20].

Parameters	Value (unit)
r_1	7.5128 $molL^{-1}\,hour^{-1}$
r_{-1}	0.1147 $hour^{-1}$
r_2	0.1032 $hour^{-1}$
r_{-2}	0.0988 $molL^{-1}\,hour^{-1}$
r_3	1.937 $molL^{-1}\,hour^{-1}$
r_{-3}	0.0323 $hour^{-1}$
r_4	1.9230 $hour^{-1}$
r_{-4}	0.0011 $molL^{-1}\,hour^{-1}$
r_5	0.1213 $molL^{-1}\,hour^{-1}$
r_{-5}	0.03887 $hour^{-1}$

Proof. The existence and uniqueness of the solution of (14) in (0, ∞) can be obtained from [17]. We need to show that the domain $\Re^9{}_+$ is positively invariant.

Since,

$$\begin{aligned}
D_t^\alpha C_E|_{C_E=0} &= k_{-1} C_{C1} + k_4 C_{C2} \\
&\quad + k_{-5} C_{C3} + k_s C_A C_{C3} \geq 0, \\
D_t^\alpha C_T|_{C_T=0} &= k_{-1} C_{C1} \geq 0, \\
D_t^\alpha C_{AcE}|_{C_{AcE}=0} &= k_2 C_{C1} + k_{-3} C_{C2} \geq 0, \\
D_t^\alpha C_B|_{C_B=0} &= k_4 C_{C2} \geq 0, \\
D_t^\alpha C_A|_{C_A=0} &= k_{-3} C_{C2} + k_{-5} C_{C3} \geq 0, \\
D_t^\alpha C_{C1}|_{C_{C1}=0} &= k_1 C_T C_E + k_{-2} C_{AcE} C_G \geq 0, \\
D_t^\alpha C_{C2}|_{C_{C2}=0} &= k_3 C_{AcE} C_A + k_{-4} C_E C_B \geq 0, \\
D_t^\alpha C_{C3}|_{C_{C3}=0} &= k_5 C_E C_A - k_{-5} C_{C3} \geq 0, \\
D_t^\alpha C_G|_{C_G=0} &= k_2 C_{C1} \geq 0, \qquad (16)
\end{aligned}$$

by Remark 1, the solution will remain in $\Re^9_+$. So we can say that on each hyperplane bounding the non-negative hyperspace, the vector field points into $\Re^9_+$. Therefore the non-negative octant $\Re^9_+$ is a positively invariant region.

B. The Fractional Optimal Control Problem (FOCP)

Here, the main objective is to control the rate of stirrer, so that we can get maximum yield of biodiesel. Also, it is our object to minimize the cost function. We use a control variable $u(t)$, which represents the stirring activator input at time t satisfying $0 \leq u(t) \leq 1$. Also $u(t) = 1$ represents the maximal use of stirrer.

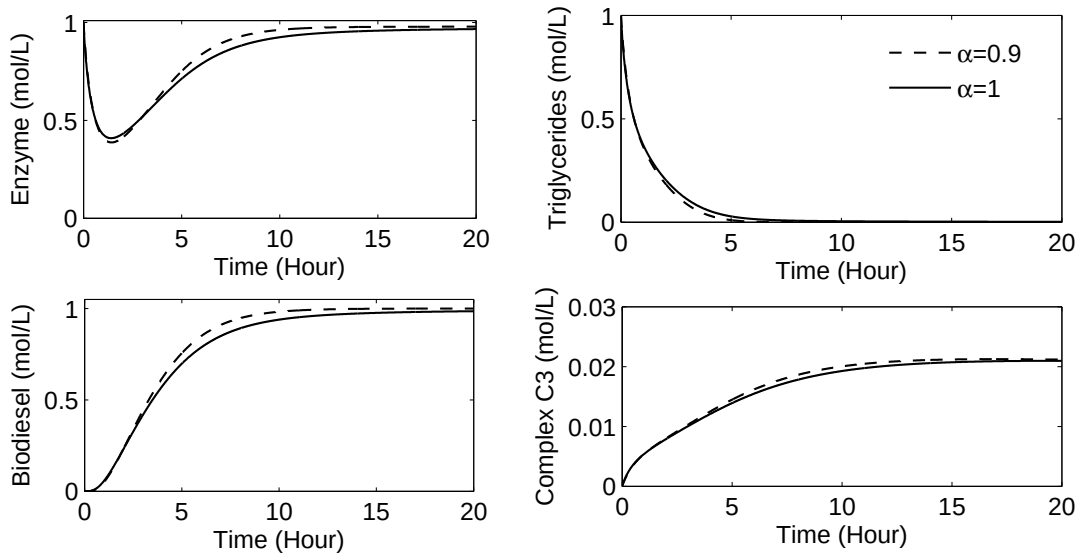

Figure 1: Numerical solution of fractional model system for different values of α and other parameters as given in table.

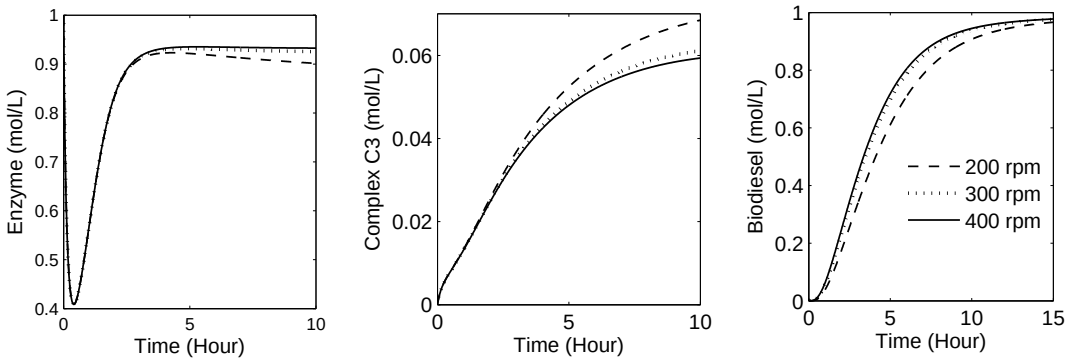

Figure 2: Numerical solution of fractional model system for different values of α and other parameters as given in table.

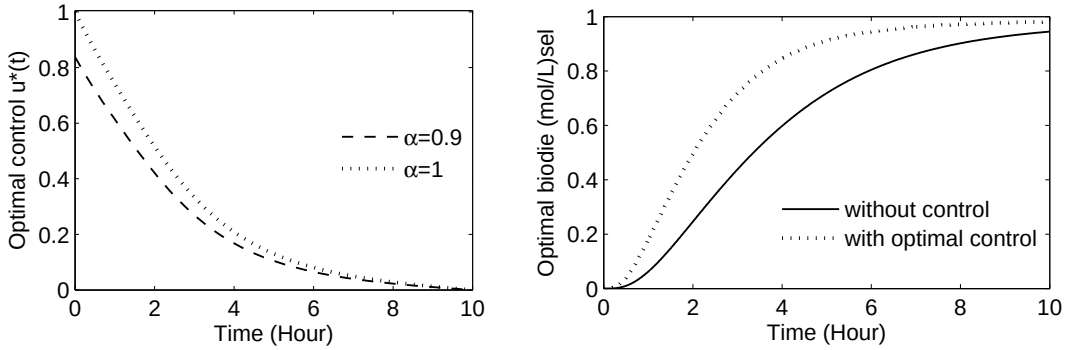

Figure 3: Numerical solution of the FOCP for $\alpha = 0.95$ and $\alpha = 1$ and other parameter values as in Table 1.

Introducing control into the system (14) we have,

$$\begin{aligned}
D_t^\alpha C_E &= -k_1 C_T C_E + k_{-1} C_{C1} + uk_4 C_{C2} \\
&\quad -uk_{-4} C_E C_B - uk_5 C_E C_A \\
&\quad +uk_{-5} C_{C3}, \\
D_t^\alpha C_T &= -uk_1 C_T C_E + uk_{-1} C_{C1}, \\
D_t^\alpha C_{AcE} &= uk_2 C_{C1} - uk_{-2} C_{AcE} C_G \\
&\quad -uk_3 C_F C_A + uk_{-3} C_{C2}, \\
D_t^\alpha C_B &= uk_4 C_{C2} - uk_{-4} C_E C_B, \\
D_t^\alpha C_A &= -uk_3 C_{AcE} C_A + uk_{-3} C_{C2} \\
&\quad -uk_5 C_E C_A + uk_{-5} C_{C3}, \\
D_t^\alpha C_{C1} &= uk_1 C_T C_E - uk_{-1} C_{C1} - uk_2 C_{C1} \\
&\quad +uk_{-2} C_{AcE} C_G, \\
D_t^\alpha C_{C2} &= uk_3 C_{AcE} C_A - uk_{-3} C_{C2} - uk_4 C_{C2} \\
&\quad +uk_{-4} C_E C_B, \\
D_t^\alpha C_{C3} &= uk_5 C_E C_A - uk_{-5} C_{C3}, \\
D_t^\alpha C_G &= uk_2 C_{C1} - uk_{-2} C_{AcE} C_G, \qquad (17)
\end{aligned}$$

where, D_t^α is symbolised as the Caputo fractional derivative. The above system can be written in the form as below:

$$D_t^\alpha x = f(x(t), u(t)), \qquad (18)$$

where,
$x = [C_T, C_E, C_{AcE}, C_{C1}, C_{C2}, C_{C3}, C_A, C_B, C_G]$. We need to minimize inhibition of enzyme which is measured through complex $C3$ and maximize biodiesel yield. So the objective function with $P > 0$, $Q > 0$ and $R > 0$ as weight constants is defined below:

$$\text{Minimize } J(u) = \int_{t_0}^{t_f} [Pu^2 - QC_B^2 + RC_{C3}^2]dt,$$
subject to the system (17). (19)

Here, the aim is to find the optimal control function $u^*(t)$ for the system (17) that minimizes the functional $J(u)$.

C. Optimal system for biodiesel synthesis

To find the optimal system we solve the equation (18). In case of our problem, the Hamiltonian function can be taken as:

$$H = g + yf, \qquad (20)$$

with

$$\begin{aligned}
g &= Pu^2(t) - QC_B^2(t) + RC_{C3}^2, \\
yf &= \sum y_i f_i
\end{aligned}$$

where, f_i, $i = 1 - 9$ are the right sides of system (17). Using the optimality conditions defined by equations (6), (7) and (8), the Euler-Lagrange optimality conditions that minimize the objective functional (19) can be obtained.

Now, the state system has already been given by (17). Using relations (7), the costate system is derived and given below as:

$$\begin{aligned}
D_{t_f}^\alpha y_1 &= -uk_1 C_T(y_2 + y_1) + uk_{-4} C_B(y_7 - y_1) \\
&\quad -uk_{-4} C_B y_4 - uk_5 C_A(y_1 + y_5 - y_8), \\
D_{t_f}^\alpha y_2 &= uk_1 C_E(y_6 - y_1 - y_2), \\
D_{t_f}^\alpha y_3 &= uk_3 C_A(y_7 - y_5) - uk_5 C_T(y_8) \\
&\quad -uk_{-2} C_G(y_6 - y_3 + y_9), \\
D_{t_f}^\alpha y_4 &= -2QC_B - y_4\{uk_{-4} C_E + y_7 uk_{-4} C_E, \\
D_{t_f}^\alpha y_5 &= uk_3 C_{AcE}(y_7 - y_5) + uk_5 C_E(y_8 - y_1), \\
D_{t_f}^\alpha y_6 &= uk_{-1}(y_2 - y_6) + uk_2(y_3 - y_6 + y_9), \\
D_{t_f}^\alpha y_7 &= uk_4 y_4 + uk_{-3} y_3 - uk_{-3} y_7, \\
D_{t_f}^\alpha y_8 &= 2RC_{C3} + uk_{-5}(y_2 - y_8 + y_3) \\
D_{t_f}^\alpha y_9 &= uk_{-2} C_{AcE}(y_6 - y_3 - y_9). \qquad (21)
\end{aligned}$$

with the boundary conditions: $y_i(t_f) = 0$, where i = 1,2,...,9.

From equation (8) and equation (20), we get the expression for optimal control function as:

$$u^*(t) = max\left(0,\ min\left(1,\ \frac{-\sum_{i=1}^{6} y_i f_i}{2P}\right)\right).$$

If $u(t)$ is replace by $u^*(t)$ then equation (17) together with equation (21) represent the optimality system which is a two-point boundary value problem includ-ing a system of fractional differential equations.

IV. NUMERICAL SIMULATION

In this section, we have applied iterative techniques in solving fractional-order mathematical model (14) to achieve approximate solutions. There are several analytical and numerical methods [12, 25] but we have

followed the method as provided in [26, 27] for solv-ing system of fractional-order differential equations. We have also solved the optimal control problem by numerical iterative procedure in Matlab.

The FOCP is a two point boundary value problem with state system and adjoint system. The state system is an initial value whereas adjoint system is a boundary value problem. We proceed through Matlab using the iterative scheme described below.

We perform forward integration of the state variables from t_0 to tf and similarly, using the final condition $y(tf) = 0$, we perform the back-ward integration of the adjoint variables y_i from tf to t_0. The states system (17) is solved by the following iterative scheme:

$$\begin{aligned}
C_E(i) &= [-k_1 C_T(i-1)C_E(i-1) + k_{-1}C_{C1}(i-1) \\
&\quad + uk_4 C_{C2}(i-1) - uk_{-4}C_E(i-1)C_B(i \\
&\quad -1) - uk_5 C_E(i-1)C_A(i-1) + \\
&\quad uk_{-5}C_{C3}(i-1)]h^\alpha - \sum_{j=1}^{i} m(j)c_1(i-j) \\
C_T(i) &= [-uk_1 C_T(i-1)C_E(i) + uk_{-1}C_{C1}(i \\
&\quad -1)]h^\alpha - \sum_{j=1}^{i} m(j)c_1(i-j), \\
C_{AcE}(i) &= [uk_2 C_{C1}(i-1) - uk_{-2}C_{AcE}(i- \\
&\quad 1)C_G(i-1) - uk_3 C_F(i-1)C_A(i-1) \\
&\quad + uk_{-3}C_{C2}(i-1)]h^\alpha \\
&\quad - \sum_{j=1}^{i} m(j)c_1(i-j), \\
C_B(i) &= uk_4 C_{C2}(i-1) - uk_{-4}C_E(i-1)C_B(i \\
&\quad -1)]h^\alpha - \sum^{i} m(j)c_1(i-j), \\
&\quad -1) - uk_5 C_E(i)C_A(i-1) + uk_{-5}C_{C3}(i \\
&\quad\quad\quad\quad j=1 \\
C_A(i-1) &= -uk_3 C_{AcE}(i)C_A(i-1) + uk_{-3}C_{C2}(i \\
&\quad -1)]h^\alpha - \sum_{j=1}^{i} m(j)c_1(i-j), \\
C_{C1}(i) &= uk_1 C_T(i)C_E(i) - uk_{-1}C_{C1}(i-1) - \\
&\quad uk_2 C_{C1}(i-1) + uk_{-2}C_{AcE}(i)C_G(i \\
&\quad -1)]h^\alpha - \sum_{j=1}^{i} m(j)c_1(i-j), \\
C_{C2}(i) &= uk_3 C_{AcE}(i)C_A(i) - uk_{-3}C_{C2}(i-1) - \\
&\quad uk_4 C_{C2}(i-1) + uk_{-4}C_E(i)C_B(i)]h^\alpha \\
&\quad - \sum_{j=1}^{i} m(j)c_1(i-j), \\
C_{C3}(i-1) &= uk_5 C_E(i)C_A(i) - uk_{-5}C_{C3}(i-1)]h^\alpha \\
&\quad - \sum_{j=1}^{i} m(j)c_1(i-j), \\
C_G(i) &= uk_2 C_{C1}(i) - uk_{-2}C_{AcE}(i)C_G(i-1)]h^\alpha \\
&\quad - \sum_{j=1}^{i} m(j)c_1(i-j), \qquad (22)
\end{aligned}$$

The last term of the above equations stands for memory. The parameter $m(j)$ is defined as C_{T0} = 1 mol/L, C_{A0} = 6 mol/L, C_{F0} = 0.15 mol/L, C_{E0} = 1 mol/L, a = 0.320 , b = 0.023 (rpm^{-1}) are the initial conditions and h is the time step length, and we take h=0.01.

Similarly, iterative scheme for solving the adjoint sys-tem (17) backward-in-time with terminal conditions $y_i(tf) = 0$ is developed.

The optimal control approach applied to fractional differential equation (FDS) and the effect of control is shown in Figures for different values of α. The figure reveals the changes in concentration by using two different values of the parameter α and other parameters as in Table 1.

Numerically we solved the system kinetics for better understanding of the dynamical behaviour of the transesterification reaction in the presence of enzyme for the production of biodiesel.

Figure 1 represents the time dependent concentration profiles of triglycerides, enzyme, dead end complex and biodiesel of transesterification reactions. Pa-rameters are taken from in Table 1.

It is seen that conversion of triglycerides is higher if we consider $\alpha = 0.9$ rather than 1. Though initially the rate of biodiesel production for $\alpha = 1$ is higher but at the end of the reaction the conversion of biodiesel is higher for $\alpha = 0.9$. This is due to the effect of memory and higher mass transfer can be observed for $\alpha = 0.9$ than $\alpha = 1$. Also, inhibition is higher in case of $\alpha = 0.9$ as expected.

Figure 2 shows the effect of stirring on the system taing $\alpha = 0.9$. It reveals that 300 rpm stirring is the best for biodiesel production using enzyme compare to 200 rpm stirring. Thus, stirrer has significant effect on biodiesel yield.

The optimal profile for the control variable is pre-sented in Figure 3. It shows the optimal profiles for the biodiesel, stirring. Here we observe the changes in concentration of the product by varying the value of α. Control profile of the system is also plotted for different value of α.

It is seen that more control on system is reduced if we consider the memory effect by taking fractional order model. Biodiesel concen-tration is optimized using the optimality system. We have compared the concentration of product obtained from integer order system and fractional system to see the combined effect of memory and optimal control on the system. For this we compare the concentration of biodiesel for two cases: case I: at optimum condition taking $\alpha = 0.9$ and case II: at $\alpha = 1$ when no con-trol is applied to the system. This figure shows that concentration highly depends on the parameter α i.e. the order of the system. Taking into account the mem-ory and control, it can be seen that rate of biodiesel production is also increased significantly.

V. DISCUSSION AND CONCLUSION

Fractional derivatives are defined by using integrals, so they possess non-local kernels. Thus, the fractional derivative of a function at a given point in time contains information about all of the values of the function at earlier points. Thus memory in a living can be described by fractional derivative. So, it is better to use fractional differential equation when modeling enzymatic transesterification than classical order derivative.

Our results show that biodiesel yield is significantly influenced by memory effect. The Fractional optimal control problem is solved numerically and it offers a better prediction about biodiesel optimization. Thus, our analytical and numerical analysis would be helpful to experimental researchers to predict the dynamics of a system for enzymatic biodiesel production. It can be expected that the proposed fractional order model and the control theoretic approach can be successfully applied to experimental findings.

In conclusion, the proposed model is functional and more accurate than integer order system. Our predictions will be helpful for experimental researchers for biodiesel production which may be a route for the alternative renewable energy sources.

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