Mathematical Analysis of Lengyel-Epstein Chemical Reaction Model by Fractional-Order Differential Equation’s System with Multi-Orders

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Abstract-The proposed model in this study is the fractional differential equation’s system with multi-orders of the dimensionless Lengyel-Epstein model being the oscillating chemical reactions. It is founded the positive equilibrium point. Also, the stability of the positive equilibrium point obtained from this system is analysed. The results founded from this qualitative analysis are corroborated by numerical simulations drawn by various programs.

Keywords- Fractional-Order Differential Equation’s System, Lengyel-Epstein Chemical Reaction, Mathematical Modeling, Stability Analysis, Equilibrium Points

I. INTRODUCTION

The oscillating chemical reactions as the Belousov-Zhabotinsky reaction and the Briggs-Rauscher reaction are well known. The mathematical models of these reactions are analyzed mathematical; on the other hand, these models are complicated. The Lengyel-Epstein reaction involved chlorine dioxide (ClO₂), iodine (I₂) and malonic acid (MA) is simpler reaction according to these. The reactions [1] are:

\[ \text{MA} + I_2 \rightarrow I^A + H^+, \]
\[ \text{ClO}_2 + I^+ \rightarrow \text{ClO}_2^- + \frac{1}{2} I_2, \]
\[ \text{ClO}_2^- + 4I^- + 4H^+ \rightarrow \text{Cl}^- + 2I_2 + 2H_2O. \]  

It was negotiated a mathematical modeling for the variables x and y which related to the iodide concentration (I⁻) and the chlorite concentration (ClO₂⁻). This model is the system which occurred from two differential equations. The change rates of the concentrations of variables have to be adjusted via experiments and it is not easy that the reactions transform to the differential equations. Let X and Y is the concentrations of iodide and chlorite respectively. Therefore, the proposed rate equations are given by

\[ \frac{dx}{dt} = k_4 [\text{MA}] [I_2] - k_4 [\text{ClO}_2^-] X - 4 \left( k_5 [H^+] XY + k_6 [I_2] \frac{XY}{a + xy} \right), \]
\[ \frac{dy}{dt} = k_4 [\text{ClO}_2^-] X - \left( k_5 [H^+] XY + k_6 [I_2] \frac{XY}{a + xy} \right), \]  

(2)

where the k₄ for k₁,₂,₆ are rate constants and (mass/volume)² is a constant too. The rate equations have applied to all molecules and ions involved in the process. [2]. However, it can be specified throughout experiments that the iodide and chlorite concentrations must change more rapidly than other molecules. In this sense, it is feasible to presume for easiness which it remains constant the concentration of other molecules as long as reaction. Therefore, this assumption does not have to be applied. Nevertheless, We have to choose to approach real values in all mathematical modeling. After choosing the right direction for sustainability, the k₅ term will come to ignore too as in the Lengyel and Epstein [3] for no obvious reason except perhaps, since it is certain that the hydrogen concentration (H⁺), which is the lightest nucleus, is very small. The above-mentioned hypotheses causes to the differential equation’s system as the following:

\[ \frac{dx}{dt} = A - BX - 4C \frac{XY}{a + xy^2}, \]
\[ \frac{dy}{dt} = C \left( X - \frac{xy}{a + xy^2} \right), \]
\[ A, B, C > 0 \]  

(3)

For a better application in mathematical modeling, It is necessitated that mathematical models are to be made dimensionless. This situation is succeeded by changing the variables

\[ X = \sqrt{a} x, \quad Y = \frac{b \sqrt{a}}{c} y, \quad t = \frac{t}{b} \]  

(4)

and two lumped parameters which are dimensionless are

\[ a = \frac{A}{B}, \quad b = \frac{C}{b \sqrt{a}}, \quad a, b > 0. \]  

(5)

After all these operations, the Lengyel-Epstein model is as the following [2]:

\[ \frac{dx}{dt} = a - x - 4 \frac{xy}{1 + xy^2}, \]
\[ \frac{dy}{dt} = bx \left( 1 - \frac{y}{1 + xy^2} \right). \]  

(6)
Fractional-order differential equation have been the focus of many studies, since their very often appear in various applications in biomathematics, fluid mechanics, economic, viscoelasticity, biology, physics and engineering. Recently, a large quantity of literature has been developed concerning the application of fractional differential equations in nonlinear dynamics [4,5,6,7,8,9].

II. ASYMPTOTIC STABILITY OF THEIR EQUILIBRIUM POINTS IN THE FRACTIONAL-ORDER DIFFERENTIAL EQUATION’S SYSTEM

Definition 2.1 The fractional integral of order \( \beta \in R^+ \) of the function \( f(t), t > 0 \) is definable by

\[
I^\beta f(t) = \frac{1}{\Gamma(\beta)} \int_0^t (t-s)^{\beta-1} f(s)ds
\]  

(7)

and the fractional derivative of order \( \alpha \in (n-1, n) \) of \( f(t), t > 0 \) is defined by

\[
D^\alpha f(t) = I^{n-\alpha}D^n f(t), \quad D = \frac{d}{dt}
\]  

(8)

The following properties are some of the main properties of the fractional derivatives and integrals.

Let \( \beta, \gamma \in R^+ \) and \( \alpha \in (0,1) \). Then

i. \( I^{\beta+\gamma} f(t) = I^{\beta}I^{\gamma} f(t) \)

and if \( f(x) \in L^1 \), then \( I^{\beta+\gamma} f(x) = I^{\beta}I^{\gamma} f(x) \).

ii. \( \lim_{\alpha \to 0} I^{\beta} f(x) = I^\beta f(x) \) uniformly on \( [a, b] \).

iii. \( \lim_{\beta \to 0} I^{\beta} f(x) = f(x) \) weakly.

iv. If \( f(x) \) is absolutely continuous on \( [a, b] \), then

\[
\lim_{\alpha \to 0} D^{\alpha} f(x) = \frac{df(x)}{dx}
\]

v. If \( f(x) = k \neq 0 \), \( k \) is a constant, then \( D^\alpha k = 0 \).

Theorem 2.1 The fractional differential equation’s system with multi-order is as the following

\[
D^\beta \vec{x} = \vec{f}(t, \vec{x}), \quad \vec{x}(0) = \vec{x}_0
\]  

(9)

where \( \vec{x} = (x_1(t), x_2(t), ..., x_n(t))^T \), \( \vec{f} = (f_1, f_2, ..., f_n)^T \), \( \vec{x}(0) = (x_1(0), x_2(0), ..., x_n(0))^T \), \( \vec{\alpha} = (\alpha_1, \alpha_2, ..., \alpha_n) \) is the multi-order of system of (9) and \( D^\beta = \left[D^{\alpha_1}, D^{\alpha_2}, ..., D^{\alpha_n}\right]^T \), \( D^{\alpha_i} \) denotes \( \alpha_i \)-th order fractional derivative in the Caputo sense. In this sense, \( D^\beta \vec{x}(t) \) is the multi-order system in (10).

Theorem 2.2 It is assumed that \( \vec{f}(\vec{E}) \) is Jacobian matrix evaluated at equilibrium point \( E \). This point of the system (9) is asymptotically stable if all eigenvalues obtained from the polynomial

\[
\det(\text{diag}(\lambda^{\alpha_1}, \lambda^{\alpha_2}, ..., \lambda^{\alpha_n}) - J(\vec{E})) = 0.
\]

satisfies \( |\arg(\lambda)| > \frac{\alpha \pi}{2} \) [10].

Lemma 2.1 Consider definition 2.1. Also, let \( \alpha_1 = \alpha_2 = \alpha \in (0,1) \) and \( \beta \in (0,1) \) if \( f \in C[0, T] \), then \( I^\beta f(t)|_{t=0} = 0 \). In this respect, taking into consider the following system [11,9,12,13,5,6].

\[
D^\beta y_1(t) = f_1(y_1, y_2) \quad (10)
\]

\[
D^\beta y_2(t) = f_2(y_1, y_2)
\]

with the initial conditions

\[
y_1(0) = y_{10} \quad \text{and} \quad y_2(0) = y_{o2}
\]  

(11)

Figure 1. [4] Stability region of fractional-order system in (10).

For evaluate the equilibrium points, we have presumed that

\[
D^\beta y_i(t) = 0 = f_i(y_{i1}^{eq}, y_{i2}^{eq}) \quad \text{for } i = 1, 2.
\]

In this sense, we have the equilibrium point \( \left(y_{1}^{eq}, y_{2}^{eq}\right) \) of system (10).

Additionally, the Jacobian matrix is used as \( J = \left[\begin{array}{cc} \frac{\partial f_1}{\partial y_1} & \frac{\partial f_1}{\partial y_2} \\ \frac{\partial f_2}{\partial y_1} & \frac{\partial f_2}{\partial y_2} \end{array}\right] \)

used. If all of the eigenvalues \( \lambda_1 \) and \( \lambda_2 \) which obtained from the equation \( J(y_{11}, y_{21}) = y_{11}^{eq}, y_{21}^{eq} = 0 \) satisfies the conditions

\[
|\arg(\lambda)| > \frac{\alpha \pi}{2}, \quad |\arg(\lambda)| > \frac{\alpha \pi}{2},
\]  

(12)

then, the equilibrium point \( \left(y_{11}^{eq}, y_{21}^{eq}\right) \) is locally asymptotically stable point for system (10). The stability region of the fractional-order system by \( \alpha \)-order is showed in Figure 1 (in which \( \sigma, \omega \) refer to the real and imaginary parts of the eigenvalues, respectively, and \( j = \sqrt{-1} \)). From here, it is frankly seen that the stability region of the fractional-order case is broader than the stability region of the integer-order case [4,14,15].

The characteristic equation obtained from

\[
J(y_{11}, y_{21}) = y_{11}^{eq}, y_{21}^{eq} = 0
\]

is such as the following generalized polynomial:

\[
\det(\text{diag}(\lambda^{\alpha_1}, \lambda^{\alpha_2}, ..., \lambda^{\alpha_n}) - J(\vec{E})) = 0.
\]
Let us consider the conditions (12) and the polynomial (13). Therefore, the conditions for locally asymptotically stability of the equilibrium point \((x^*,y^*)\) are either Routh–Hurwitz conditions (16) or:

\[
|a_2 - \frac{\sqrt{a_2^2 - a_1 a_3}}{a_1}| > \frac{\alpha R}{2}.
\] (14)

**Theorem 2.3** (Routh-Hurwitz Criteria): The characteristic polynomial is

\[ P(\lambda) = \lambda^n + a_1 \lambda^{n-1} + \ldots + a_n, \]

where the \(a_i\) coefficients for \(i = 1, \ldots, n\) are real constants. The Hurwitz matrices by the coefficients \(a_i\) of upper polynomial are

\[
H_1 = \begin{pmatrix} a_1 & 1 & 0 & 0 & \cdots & 0 \\ a_2 & a_1 & 1 & \cdots & 0 \\ a_3 & a_2 & a_1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ a_n & a_{n-1} & a_{n-2} & \cdots & a_1 \end{pmatrix},
\]

and

\[ H_n = \begin{pmatrix} 0 & 0 & 0 & \cdots & a_n \end{pmatrix}. \]

The stability conditions of equilibrium point obtained from (12) and (13) are that

\[
(H_1)^T > 0, \quad (H_n)^T > 0.
\]

A. **Qualitative analysis of system (15)**

The existence and stability of equilibria of the system (15) are characterized in here.

**Proposition 3.1** (Equilibrium Points) The system (15) always has the equilibrium point \(E = \left(\frac{a}{5}, \frac{a^2}{5} + 1\right)\) namely positive equilibrium point.

**Proof.** We have assumed that the general term of equilibrium of the system (15) showed as \((x^eq, y^eq)\). For equilibrium solution of (15), we have

\[
D^{a_1}x(\tau) = 0, \\
D^{a_2}y(\tau) = 0
\]

and so,

\[
a - x - 4 \frac{xy}{1 + x^2} = 0, \\
bx \left(1 - \frac{y}{1 + x^2}\right) = 0.
\]

From second equation of (17), it is obtained \(bx^eq = 0\) or \((1 - \frac{y^eq}{1 + (x^eq)^2}) = 0\). In first equation of (17), these values are written, respectively. Firstly, let \(x^eq = 0\). We have contradicted due to \(a = 0\) (a > 0 in (5)). Lastly, let \((1 - \frac{y^eq}{1 + (x^eq)^2}) = 0\), that is, \(y = (x^eq)^2 + 1\). In this case, it is

\[
a - x^eq - 4 \frac{x^eq((x^eq)^2+1)}{1+(x^eq)^2} = 0.
\]

Therefore, we have the positive equilibrium point founded the following

\[ E = \left(\frac{a}{5}, \frac{a^2}{5} + 1\right). \]

**Proposition 3.2** (Stability Analysis) If \(|\arg(\lambda)| > \frac{\pi}{2}\) (when some conditions are met) for the eigenvalue \(\lambda\) (15), then this point is locally asymptotically stable (LAS) for system (15).

**Proof.** For the stability analysis, the functions of the right side of the system (15) are determined as follows:

\[
F(x,y) = a - x - 4 \frac{xy}{1 + x^2}, \\
G(x,y) = bx \left(1 - \frac{y}{1 + x^2}\right).
\]

That Jacobian matrix obtained from (19) is:

\[ J = \begin{pmatrix} F_x & F_y \\ G_x & G_y \end{pmatrix} = \begin{pmatrix} -1 - 4 \frac{y^2 x^2}{x^2 + 2 x^4 + 1} & -4 \frac{x}{x^2 + 1} \\ -\frac{y}{x^2 + 1} & 2 \frac{y x^2}{(x^2 + 1)^2} - \frac{b x}{x^2 + 1} \end{pmatrix} \] (20)
For ease of examination, the $\varepsilon$-th eigenvalue of equilibrium point $E = \left(\frac{a}{5}, \left(\frac{a}{5}\right)^2 + 1\right)$ was shown as $\lambda_\varepsilon$ for $\varepsilon = 1, 2$. Thus, the Jacobean matrix evaluated at this point is:

$$J \left(E = \left(\frac{a}{5}, \left(\frac{a}{5}\right)^2 + 1\right)\right) = \begin{pmatrix} -1 - 4 \left(\frac{a}{5}\right)^2 & -4 \left(\frac{a}{5}\right)^2 \\ \frac{2b(a/5)^2}{1 + (a/5)^2} & -b \left(\frac{a}{5}\right)^2 \end{pmatrix}$$

(21)

From $\text{det} \left(\operatorname{diag}(\lambda^m_{\alpha_1}, \lambda^m_{\alpha_2}) - J \left(E = \left(\frac{a}{5}, \left(\frac{a}{5}\right)^2 + 1\right)\right)\right) = 0$, it is found that:

$$\lambda^m_{\alpha_1} + \lambda^m_{\alpha_2} + \frac{ab}{\delta((a/5)^2 + 1)} + \lambda^m_{\alpha_2} \left(\frac{5 - 3(\alpha)^2}{(\alpha)^2 + 1}\right) + \frac{ab}{(a/5)^2 + 1} = 0 \quad (22)$$

Stability conditions of equilibrium point for system (15) are that the equation (22) satisfy $|\arg(\lambda)| > \frac{\pi}{2}$.

In case of special case $\alpha_1 = \alpha_2 = \frac{1}{m}$, we have $\text{Det}(J) = \frac{25ab}{a^2 + 25} \lambda^{20} + 5b \lambda^{15} + 1500 + 5b$ by (22). $\text{Det}(J)$ is positive due to parameters are positive and if $a < \frac{\sqrt{25}b^2 + 1500 + 5b}{6}$ or $a > -\frac{\sqrt{25}b^2 + 1500 + 5b}{6}$, then $\text{Tr}(J)$ is negative. Therefore the equilibrium point $E = \left(\frac{a}{5}, \left(\frac{a}{5}\right)^2 + 1\right)$ is LAS.

IV. NUMERICAL STUDY FOR SYSTEM (15)

In here, we have examined the behavior of the solutions of system (15) by valuing the parameters. We have used Matlab and pplane.jar. In this respect, it is obtained the following the results.

Let $\alpha_1 = \frac{1}{7}, \alpha_2 = \frac{1}{4}$ $(m = 4), a = 1, b = 12$ and $(x(0), y(0)) = (1, 1)$. In this case, we have

$$\lambda^3 + \lambda^2 \left(\frac{30}{13}\right) + \lambda \left(\frac{61}{13}\right) + \left(\frac{150}{13}\right) = 0$$

by (22), and so, Routh-Hurwitz stability conditions $(n = 3)$ are satisfied, because $a_1 = \frac{20}{13}, a_3 = \frac{150}{13} > 0$ and $a_1 a_2 = \frac{30}{13} \cdot \frac{61}{13} > a_3 = \frac{150}{13}$. Thus, $E = \left(\frac{1}{7}, \frac{26}{5}, \frac{20}{7}\right)$ is LAS as seen in figure 2.

Figure 2. For $\alpha_1 = \frac{1}{7}, \alpha_2 = \frac{1}{4}, a = 1, b = 12,(x(0), y(0)) = (1, 1)$. Temporary course of variables of system (15).

Let $\alpha_1 = \frac{1}{2}, \alpha_2 = \frac{1}{2}$ $(m = 4), a = 20, b = 8$ and $(x(0), y(0)) = (1, 1)$. In this case, we have

$$\lambda^2 + \left(\frac{91}{13}\right) + \left(\frac{150}{13}\right) = 0$$

by (22), and so, Routh-Hurwitz stability conditions $(n = 2)$ are satisfied, that is, $a_1 = \frac{91}{13}$ and $a_2 = \frac{150}{13}$ are positive. Thus, $E = (4, 17)$ is LAS as seen in figure 3.

Figure 3. For $\alpha_1 = \frac{1}{7}, \alpha_2 = \frac{1}{4}, a = 20, b = 8,(x(0), y(0)) = (1, 1)$. Temporary course of variables of system (15).
When $a = 5, b = 2, \alpha_1 = \frac{1}{4}$ and $\alpha_2 = \frac{1}{6}$, characteristic equation is $\lambda^2 + \lambda^2 + 2\lambda^2 + 5 = 0$. In this respect, the eigenvalues from characteristic equation $\lambda_1 \approx -1.43861$, $\lambda_2 \approx -0.184581 - 1.307451i$, $\lambda_3 \approx -0.184581 + 1.307451i$, $\lambda_4 \approx 0.903885 - 1.084641i$ and $\lambda_5 \approx 0.903885 + 1.084641i$.

Figure 4. When $a = 5, b = 2, \alpha_1 = \frac{1}{4}$ and $\alpha_1 = \frac{1}{6}$, the representation of eigenvalues in complex plane.

It is clear that $|Arg(\lambda_1, \lambda_2, \lambda_3)| > m_\pi = \frac{\pi}{2}$. On the other hand $|arg(\lambda_4, \lambda_5)| = \left|arctan\left(-\frac{0.184641}{0.903885} - \frac{1.084641}{0.903885}\right)\right| = 0.8760\pi > m_\pi = 0.04166\pi$.

Therefore $E = (1, 2)$ is LAS for system (15) as seen in figure 5.

When $a = 25, b = 1, \alpha_1 = \alpha_2 = 1$, characteristic equation is $\lambda^2 - \lambda_1^2 - \frac{25}{26} = 0$. In this respect, we have $\lambda_1 = -\frac{5\sqrt{5}}{52} + \frac{5}{4}$ or $\lambda_2 = -\frac{5\sqrt{5}}{52} + \frac{5}{4}$. It is clear that $\lambda_1 < 0$ and $\lambda_2 > 0$. Therefore, $E = (5, 26)$, namely nodal source, is unstable point.

Figure 6. For $\alpha_1 = \alpha_2 = 1, a = 25, b = 1$ and $(x(0), y(0)) = (1, 1)$, temporary course of variables of system (15) via pplane.jar.

V. APPENDIX

The Matlab codes used for the shapes drawn in this work are below:

Lengyel M-file

def function [T, Y]=lengyel(parameters, orders, TSim, Y0)
    h=.0001;
    % number of calculated mesh points:
    n=round(TSim/h);
    % orders of derivatives, respectively:
    q1=orders(1); q2=orders(2);
    % parameters of infection model:
    a_1=parameters(1);
    a_2=parameters(2);
    % binomial coefficients calculation:
    cp1=1; cp2=1;
    for j=1:n
        c1(j)=(1-(1+q1)/j)*cp1;
        c2(j)=(1-(1+q2)/j)*cp2;
        cp1=c1(j); cp2=c2(j);
    end
    % initial conditions setting:
    x(1)=Y0(1); y(1)=Y0(2);
    % calculation of phase portraits /numerical solution/:
    for i=1:n
        x(i)=(1-(1+q1)/j)*cp1;
        y(i)=(1-(1+q2)/j)*cp2;
    end
    % initial conditions setting:
    x(1)=Y0(1); y(1)=Y0(2);
    % calculation of phase portraits /numerical solution/:
    for i=1:n
        x(i)=(1-(1+q1)/j)*cp1;
        y(i)=(1-(1+q2)/j)*cp2;
    end
    T=0:h:TSim;

In case of $\alpha_1=1/4$ and $\alpha_2=1/6$, the dependent time concentrations of iodide and chloride

Figure 5. For $\alpha_1 = \frac{1}{4}, \alpha_2 = \frac{1}{6}, a = 5, b = 2, (x(0), y(0)) = (1, 1)$, temporary course of variables of system (15).
Run M-file

close all; clear all;
[t, y]=lengyel([5 2], [1/4 1/6], 70, [1 1]);
A=1:1:700000;
figure; plot(A, y(:,1));
figure; plot(A, y(:,2)); title('In case of alpha1=1/4 and alpha2=1/6, The dependent time concentrations of iodide and chlorite');
figure; plot(y(:,1),y(:,2)); title('In case of alpha1=1/4 and alpha2=1/6, The relative to each other concentrations of iodide and chlorite');

Memo M-file

function [yo] = memo(r, c, k)
temp = 0;
for j=1:k
    temp = temp + c(j)*r(k-j);
end
yo = temp;

VI. REFERENCES