Application of fractional derivative for the study of chemical reaction

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Abstract

The purpose of this research is to develop an application of fractional calculus for the study of chemical reactions. The rate of a chemical reaction is calculated from the rate of change of the substance per time change. The rate of chemical reaction at any time is calculated using the first derivative of the permutation function. The rate of chemical reactions from fractional order calculus was compared with integer order calculus. Calculating chemical reaction rates with fractional derivatives yielded significantly higher rates than the integer order calculus.

Keywords: Fractional derivative , Conformable fractional derivative , Fractional calculus, Chemical reactions

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Introduction

Data accuracy is an essential calculation in physics, engineering, hydrology, finance and economics. In the past two decades, many researchers have used fractional calculus for computational purposes and have achieved better results than integer order. [9] Chemical reactions are the calculation of the concentrations of reactant changes in chemical reactions while the concentration of the reactant decreases, resulting in a more concentrated product. Therefore, applying fractional calculus to the laws of chemical reactions will improve the accuracy of substrate concentration and yield. In addition, it will make the study of chemical reactions more convenient by developing applications.

Research Objective

1. Build knowledge using fractional calculus to study the rate of chemical reactions.

2. Develop applications for using fractional calculus to study chemical reactions.

Research Methodology

Scope of research

1. Fractional calculus applied to chemical reactions is a conformable fractional derivative of order.

2. Regression line of the chemical reaction was calculated by a second-degree polynomial.

3. The application is developed with the Android Studio program.

4. The application supports the Android operating system.

Research methods

1. Study of related research theories (fractional calculus, chemical reaction rate law and regression analysis)

The first concept of fractional calculus was conceived in 1965 when L'Hospital wrote to Gottfried Wilhelm Leibniz asking about the fractional order derivative. Which is not an integer; what will be the result? Leibniz described it would produce power valuable results in the future.[5]

Euler was a famous mathematician and defined fractional mathematics in 1730, Laplace defined it in 1812, and Lacroix was the first mathematician to refer to the term “fractional derivative”. The first application of fractional derivatives was made in 1823 by a mathematician named Abel to find solutions to integral equations in tautochronous problems. Many mathematicians define and assign symbols to fractional calculus. But there are some important and popular definitions in fractional calculus: the Riemann-Liouville definition, the Caputo definition and the R. Khalil definition.[11]

An important definition of fractional derivatives that many scientists have used in their research is the fractional derivative of Riemann-Leuville and Caputo's definition. However, both definitions do not correspond to the product rule, quotient rule and chain rule.[10]

Definition fractional derivatives of R. Khalil as follows

Let f be a function such that $f:[0,\infty)\to R$. The newly defined fractional derivative is called Conformable fractional derivative order α .[8]

$$T_\alpha(f)(t)=\lim_{\varepsilon\to 0}\frac{f\left(t+\varepsilon t^{1-\alpha}\right)-f(t)}{\varepsilon},t>0,\alpha\in(0,1]$$

The Conformable fractional conforms to the rules of conventional calculus. The theory of conformable fractional derivatives of order α where $\alpha\in(0,1]$.

The change in the reactants measures the speed of the reaction. The reaction between the initial substances A and B yields C and D while the responseaction is progressing. The starting substance is reduced while the production will occur.[6]

$$aA+bB\to cC+dD$$

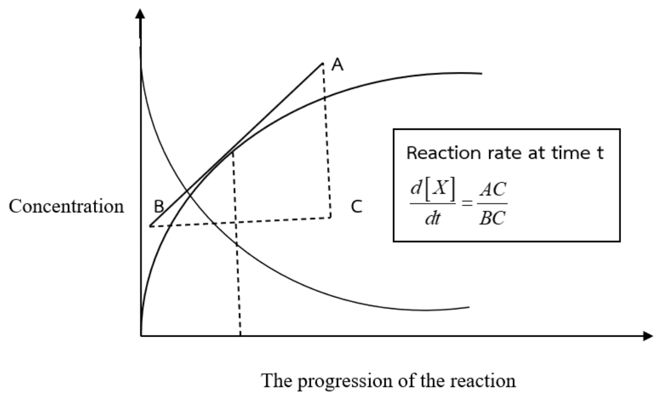

Figure 1 The relationship between Reactant concentration and product versus time

The speed of a reaction depends on the concentration of the reactants. The equation expressing the relationship between the speed and concentration of the reactants is called the rate law or rate equation.

The kinetics of chemical reactions determine the concentration of reactants or products at different times by various methods. One important method is the differential method by Vant Hoff, which measures the concentration of a substance at other times and uses the data to graph. The reaction rate at different times was calculated from the graph's slope at the desired time. [4]

The reaction rate can be written in differential form, known as the rate differential equation. (differential rate equation) or differential rate law (Differential rate law).[7]

$$v=\frac{d[A]}{dt}$$ where v be reaction rate.

Determining the relationship between mass concentrations and changing times gives the regression line equation in the research. Spline regression was used to construct the regression line equation. [2] The regression line equation is the equation

$$\hat{y} = b_0 + b_1 x + b_2 x^2 + \dots + b_m x^m .$$

The sum squares error values are as follows:

$$SSE = \sum_{i=1}^{n} \left(y_i - \left(b_0 + b_1 x_i + b_2 x_i^2 + \dots + b_m x_i^m \right) \right)^2 .$$

The partial derivative of SSE concerning $b_0, b_1, \dots, b_m$ set the value to zero.

$$\frac{\partial SSE}{\partial b_j} = 0, \quad j = 0,1,2,\dots,m$$

The partial derivative results of SSE compared with $b_0, b_1, \dots, b_m$

$$\sum_{i=1}^{n} \left(y_i - \left(b_0 + b_1 x_i + b_2 x_i^2 + \dots + b_m x_i^m \right) \right) = 0$$

$$\sum_{i=1}^{n} \left(y_i x_i - \left(b_0 + b_1 x_i + b_2 x_i^2 + \dots + b_m x_i^m \right) \right) = 0$$

$$\vdots \qquad\qquad \vdots$$

$$\sum_{i=1}^{n} \left(y_i x_i^m - \left(b_0 + b_1 x_i + b_2 x_i^2 + \dots + b_m x_i^m \right) \right) = 0 .$$

Arranging equations and writing them in matrix form yields the following results.

$$\sum_{i=1}^{n} b_0 + \sum_{i=1}^{n} b_1 x_i + \dots + \sum_{i=1}^{n} b_m x_i^m = \sum_{i=1}^{n} y_i$$

$$\sum_{i=1}^{n} b_0 x_i + \sum_{i=1}^{n} b_1 x_i^2 + \dots + \sum_{i=1}^{n} b_m x_i^m x_i = \sum_{i=1}^{n} x_i y_i$$

$$\vdots \qquad\qquad \vdots$$

$$\sum_{i=1}^{n} b_0 x_i^m + \sum_{i=1}^{n} b_1 x_i^{m+1} + \dots + \sum_{i=1}^{n} b_m \left(x_i^m \right)^2 = \sum_{i=1}^{n} x_i^m y_i$$

$$\begin{bmatrix} n & \sum x_i & \dots & \sum x_i^m \\ \sum x_i & \sum x_i^2 & \dots & \sum x_i^{m+1} \\ \vdots & \vdots & \vdots & \vdots \\ \sum x_i^m & \sum x_i^{m+1} & \dots & \sum x_i^{2m} \end{bmatrix} \begin{bmatrix} b_0 \\ b_1 \\ \vdots \\ b_m \end{bmatrix} = \begin{bmatrix} \sum y_i \\ \sum x_i y_i \\ \vdots \\ \sum x_i^m y_i \end{bmatrix}$$

Where $b_0, b_1, \dots, b_m$ be the regression coefficient.

2. System and data analysis, design programs for communicating with users in Graphic User Interface (GUI).

Chemical reaction values are calculated by considering the rate of change of reactant concentrations or products over time. The development of applications using fractional derivatives to study chemical reactions begins with the study of fractional calculus to be used in the computational process. Next, analyze and design the system user interface. Finally, we select the software used to develop the application, create an application and test the application.

2.1 system analysis and design

2.1.1) Define Data Flow Diagram

- Create the algorithm for calculating chemical reaction values.

- Create a Fit Curve algorithm

2.1.2) The procedure for calculating the chemical reaction

- Determine the concentration of reactant or product in each period.

- Create a graph showing the relationship between the concentration of reactants and time.

- Calculate the reaction rate with an integer order derivative.

- Take the concentration of the reactant (solvent) at each time to fit the curve with a quadratic equation.

- Take the quadratic equation that has been calculated for the reaction rate. Fractional Derivatives By using the definition of conformable fractional derivatives of order, consider comparing the calculation results between reaction rates from integer derivatives and fractional order derivatives at various levels.

2.1.3) User interface design

- The user interface for calculating chemical reactions

The start menu application is shown in figure 2. Users can study the data of the average reaction rate. Reaction rate at any time before the application calculates the speed of a chemical reaction with an integer derivative or fractional order derivatives by inserting the experimental results at different time points.

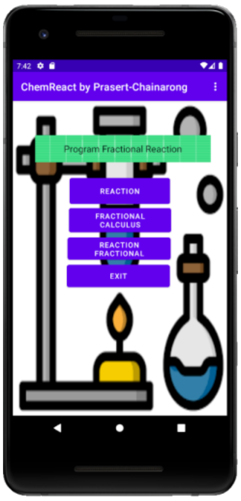

Figure 2 User Interface of the start menu application

The user can select the menu to study the reaction rate calculation; the user enters the screen explaining how to calculate the reaction rate, which is described on various pages (Figure 3).

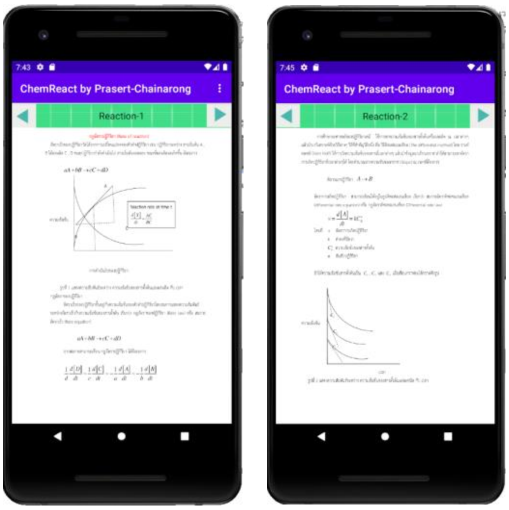

Figure **3** User Interface for explaining the reaction rate

The user can select the menu to study fractional calculus; the user enters the screen explaining the meaning of fractional calculus. (Figure 4).

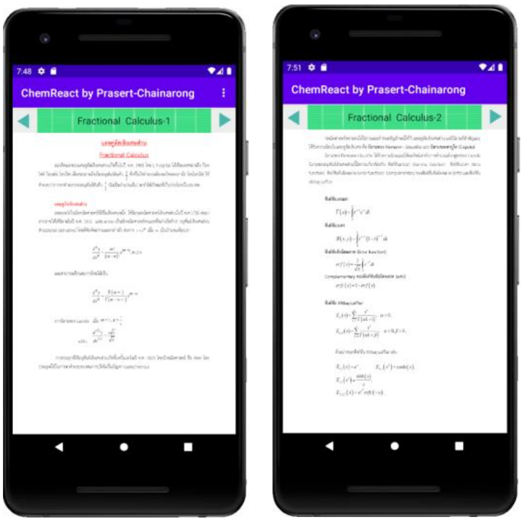

Figure **4** User Interface for explaining the fractional calculus

The user can select the chemical reaction rate calculation. The user enters the menu to choose the type of chemical reaction rate calculation (Figure 5), divided into two types: the rate of chemical reaction of the reactants and the rate of the chemical reaction of the products. In the case of calculating the reaction rate of the reactants, the information provided to the application is conditional that the amount of reactants decreases with increasing time. The calculation of the chemical reaction rate of the product is under the condition that the amount of the product increases with increasing time.

When the user selects the chemical reaction rate type, the user enters the screen to determine the reactant's concentration or product at various times. The least squares regression method was used. The reaction rate comparison results were obtained from the reaction rate calculation with integer order calculus and fractional order calculus at different ranks. The application defines fractional order derivatives as 0.1, 0.2, 0.3, …, 0.9, respectively.

Figure **5** User Interface for type of chemical reaction rate

Separating chemical reaction rate calculations is two types to prevent incorrect information from being provided to applications. The application protects incorrect data entry due to precursor concentration requirements, and the concentration of the product that changes over time is the opposite. The application generates a warning message box if the user provides incorrect information.

2.2 application development

2.2.1) Determine the operating system that supports the application. The applications can work under the Android version 6.0 (Marshmallow) operating system.[1]

2.2.2) Determine the software used for application development. The application is developed from Android Studio software version 3.1.4.

2.2.3) graph display module

The graph display uses library graphview to obtain time and precursor concentration information or the concentration of the product over time. The user provides data to the system in 5 time periods. Receiving data through an object textview stored in a 2 Dimension array variable is the nature of ordered pairs (time, reactant concentration or product) by the application.[3] The point of data the user enters every time interval shows via the scatterplot object.

2.2.4) Regression Equation Calculation Module

A spline regression equation was constructed from second-order polynomials. The data of time and concentration of reactant or product concentration that the user determines by using the data to calculate $b_0, b_1, ..., b_m$ the regression coefficient from solving the system of equations.

$$\begin{bmatrix} n & \sum x_i & \cdots & \sum x_i^{m} \\ \sum x_i & \sum x_i^{2} & \cdots & \sum x_i^{m+1} \\ \vdots & \vdots & \vdots & \vdots \\ \sum x_i^{m} & \sum x_i^{m+1} & \cdots & \sum x_i^{2m} \end{bmatrix} \begin{bmatrix} b_0 \\ b_1 \\ \vdots \\ b_m \end{bmatrix} = \begin{bmatrix} \sum y_i \\ \sum x_i y_i \\ \vdots \\ \sum x_i^{m} y_i \end{bmatrix}$$

and plot the regression line through an object graph.

2.2.5) Reaction Rate Calculation Module

Calculation of the chemical reaction rate at any time by transmission regression coefficient was calculated for the first derivative and the fractional derivative. User selects a choice (0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, …, 0.90) and displays a calculation of the rate of a chemical reaction at a user-specified time. The application will calculate the rate of a chemical reaction between first order derivatives and user-selected fractional order derivatives.

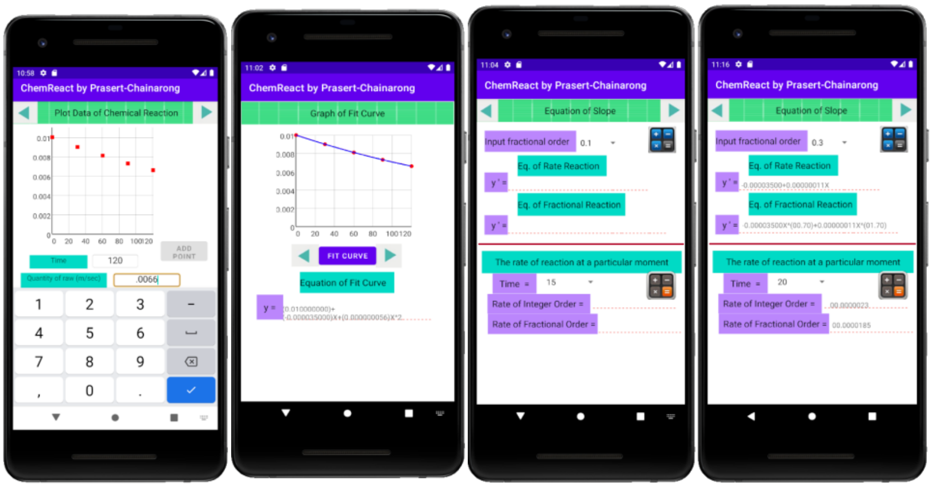

Figure 6 Diagram showing time entry and concentration of reactants and plot graphs

Chemical Reaction Rate Applications with fractional derivatives consist of the first part explaining the meaning of chemical reaction rate. The second part is the definition of fractional calculus. And the last part is calculating the reaction rate with fractional derivatives. In the first part, the user can choose to calculate the chemical reaction rate of the reactants or the rate of chemical reaction of the product by providing information on the time and amount of substances at different times to the application. The application will perform the fitting curve to obtain the regression line equation and use the regression equation to calculate the rate of a chemical reaction.

Calculating the chemical reaction rate of reactants or products will be determined by the user of the application and input dosage information at any time to the application. The application will generate the regression line equation. And the rate of chemical reaction was calculated using integer order calculus using the first order derivative formula. Part of calculating the rate of a chemical reaction with fractional derivatives. The application uses a formula for calculating fractional derivatives called the conformable fractional derivative. Users can choose to calculate the reaction rate of reactants or the product's chemical reaction rate with derivatives of 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80 or 0.90.

3. Experimental results

3.1 Data of reactants

Table 1. Data on time and concentration of reactants

Time (second)	Concentration (mol)
0	0.01
30	0.009
60	0.0081
90	0.0073
120	0.0066

The relationship between time and the amount of reactant concentration is the regression equation as follows $y = 0.01 - 0.000035x + 0.000000056x^2$.

The rate of chemical reaction of reactants for the experimental data set was calculated with integer order derivatives; fractional order 0.10 are as equations

$$y' = -0.000035 + 0.00000011x$$

$$y' = -0.000035x^{0.9} + 0.00000011x^{1.9} .$$

Comparison of the calculation results of chemical reaction rates of the reactants at 15 seconds by using fractional order derivatives and integer order derivatives as shown in Table 2.

Table 2. The Reaction rate of reactants

Order Derivative	Chemical reaction rate(mol/second)
0.10	-0.0003814
0.20	-0.0002909
0.30	-0.0002219
0.40	-0.0001693
0.50	-0.0001291
0.60	-0.0000985
0.70	-0.0000751
0.80	-0.0000573
0.90	-0.0000437
1	-0.0000333

The calculation of the chemical reaction rate of reactants with fractional order derivatives and first derivatives is negative because the amount of reactants decreases with chemical reaction. When calculating with the 0.10 order derivative, the result of the calculation of the chemical reaction rate had a significance level of 4. When increasing the order of the derivative, The significant value of the rate of a chemical reaction is reduced. Until calculating the rate of a chemical reaction with the first derivative, the significance level was 3.

3.2 Data of product

Table 3. Data on time and concentration of products

Time (second)	Concentration (mol)
0	0
100	0.0063
200	0.0115
300	0.0160
400	0.0197

The relationship between time and the amount of product concentration is the regression equation as follows $y = 0.000037143 + 0.000065957x - 0.000000042x^2$.

The rate of chemical reaction of products for the experimental data set was calculated with integer order derivatives; fractional order 0.10 are as equations

$$y' = 0.000065957 + 0.00000008\,x$$

$$y' = 0.000065957x^{0.9} + 0.00000008x^{1.9}.$$

Comparison of the calculation results of chemical reaction rates of the reactants at 15 seconds by using fractional order derivatives and integer order derivatives as shown in Table 4.

Table 4. The reaction rate of products

Order Derivative	Chemical reaction rate(mol/second)
0.10	0.0007402
0.20	0.0005646
0.30	0.0004306
0.40	0.0003285
0.50	0.0002506
0.60	0.0001911
0.70	0.0001458
0.80	0.0001112
0.90	0.0000848
1	0.0000647

The calculation of the chemical reaction rate of products with fractional derivatives and first derivatives are positive values because the amount of products increases with chemical reaction. When calculated with the order derivative of 0.10, the result of the calculation of the chemical reaction rate had a significance level of 4. When calculating with the order derivative increased up to the 0.80 order derivative, The significance level of the reaction rate remained constant at 4. Until figuring with the 0.90 derivative and the first derivative, The rate of chemical reaction decreased to a significance level of 3.

Conclusion

The application of fractional derivatives to the study of chemical reactions was developed by integrating the knowledge of fractional calculus chemical reaction rate and polynomial second-order spline regression analysis. As a result of the application, the rate of chemical reaction of reactants or products at the fractional differential level is compared with the rate of chemical reaction calculated with the integer derivative by experimental series. The performance of the application help to calculate the rate of chemical reaction of reactants or products at different ranks.

Discussion

Practical applications of fractional derivatives for chemical reactions have outputs at a higher significance level. In addition calculation of the reaction rate of the products have solutions at a higher significance level as well.

Therefore, using Conformable fractional derivatives to calculate the rate of chemical reaction rate of the reactants or products will be very suitable.

Recommendation

The development of applications for studying chemical reaction rates shows the benefits of applying fractional calculus. It makes learning easier to understand the rate of chemical reactions. In the future, the development of applications using fractional calculus can occur in other fields.

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