COMPARISON OF NUMERICAL SOLUTIONS OF KINETICS OF PENTAERYTHRITOL PRODUCTION REACTIONS

***M. Basit, S. Riaz, M. Rafique[2], Q. A. Chaudhry, S Farid**
Department of Mathematics, University of Engineering and Technology Lahore, Pakistan
Faculty of Engineering, University of Central Punjab Lahore, Pakistan$_2$
*Corresponding Author: muhammadbasit.88@gmail.com

ABSTRACT: *For the preparation of explosive, dyes, paints and surface coatings pentaerythritol plays a very important role. Numerical solutions of the kinetics of pentaerythritol producing reactions have been important issue. The reacting system has been transformed into the system of ordinary differential equation. In this paper, the derived system of ordinary differential equations is unfolding the kinetics of pentaerythritol .Moreover, it has been solved numerically by using non-standard finite difference method and Runge-Kutta method of order 4.In daily life experimental data is not easily derive able. In that case we have expected solutions for reaction parameters using NSFD and RK-4. The approximated results of the attained system are same as experimental data. Derived results from these schemes have been compared with each other and also with the experimental data.*

KEYWORDS: Pentaerythritol, Polyfunctionalized, Runge-kutta method, Non standard finite difference method.

1. INTRODUCTION:

The solution of the system of differential equations has become the aim of many mathematicians. In our daily life, we have experienced that chemical reactions are time-consuming process for getting the experimental results, and error probability still exists. In this case, to achieve the experimental approximation we can convert chemical reactions to system of differential equations, and also construct numerical schemes, to reduce the error and time estimation. Real life problems can easily be converted into mathematical form using differential equations. The systems of differential equations, attained from the mathematical modeling of real world problem are sometime so composite and the attained system is so large that analytical methods are inflexible to apply. But we can move toward the solutions of these systems numerically. Improvement in technology makes it much easier to solve a huge system of differential equations numerically. In this paper, the constructed system of differential equations of kinetics of pentaerythritol will be solved by numerical schemes. Reaction kinetics of pentaerythritol is the study of chemical reactions of pentaerythritol [1]. Plastics, surface coatings, paints, dyes and explosives are made by using the pentaerythritol as an essential chemical. Confined publications are available on the reaction kinetics of pentaerythritol due to its complications [2,7-8]. Pentaerythritol s produced by aqueous alkaline mechanism of formaldehyde and acetaldehyde. Methanol formed by product of this reaction. By crystallization process we obtained pentaerythritol as a resulted compound. In the initial step of reactions, formaldehyde and acetaldehyde react with each other to form pentaerythrose. The most commonly used base in this reaction is sodium hydroxide or calcium hydroxide. These chemical reactions are called cannizarro type chemical reactions, in which combination of two aldehydes produce organic acid and alcohol. In the presence of base, when pentaerythrose reacts with formaldehyde, the least reaction of this process is pentaerythritol [2, 3]. The process of chemical reactions of pentaerythritol are mathematically modeled by using the resulted system of ODEs, which are produced under the conditions applied to the reactions [2]. This system of ODEs will solved numerically using non-standard finite difference (NSFD) method and Runge-Kutta method of order 4 in order to attain the numerical approximations for the concentration of C_x, C_y and C_z. A well-known technique in numerical analysis is non-standard finite difference method to attain numerical solutions. Numerical schemes gives the discrete model of differential equations [4, 5]. Runge–Kutta 4 method is an important iterative method, which is used to get the approximate solutions for ordinary differential equations [6]

2: MATERIALS AND METHODS

To solve ordinary differential equations (ODE) and partial differential equations (PDE), the most frequently known numerical schemes is a standard finite difference (SFD) method. In this method, finite difference scheme is applied to giving differential equations to get algebraic equations which are quite easy to solve [5]. Mickens [9] presented the idea of non-standard finite difference model by removing instabilities which were the deficiency of standard finite difference scheme. This scheme has been introduced, many authors in [5, 11-12] which presents the ideas of constructing numerically reliable schemes using the non- standard finite difference (NSFD) modeling. Non-standard finite difference scheme is the finite difference scheme with the specification of following rules [4]:

a. Discrete derivatives must be equal to the order of the derivatives in differential equation. .
b. Discrete representations of the derivatives should consist of non-trivial denominator functions.
c. In common, non-linear terms should be changed in non-local distinct representations.
d. Conditions that satisfy either or both the differential equations and their solutions should also comply with the difference equation model and its solutions.

Methanol is formed as a byproduct, aqueous alkaline medium of formaldehyde and acetaldehyde forms pentaerythritol. The required product is collected from mixture by the process of crystallization. The first step of the reacting system is formaldehyde reacts with acetaldehyde in the presence of base, to form

pantaerythrose. Mechanism of pentaerythritol reaction can be summarized in the following steps[2]:

$$HCHO + 3CH_3CHO \xrightarrow{OH^-} (HOCH_2)_3CCHO \quad (1)$$

$$HCHO + OH^- + (HOCH_2)_3CCHO \xrightarrow{K_1} (HOCH_2)_4 + HCOO^- \quad (2)$$

$$2HCHO + OH^- \xrightarrow{k_2} CH_3OH + HCOO^- \quad (3)$$

Equation (2) shows condensation reaction that is comparatively fast. First, pentaerythrose formed at low temperature by reaction of formaldehyde and acetaldehyde and then finally pentaerythritol is formed by the condensation reaction. Cannizarro reactions take place when we increase the temperature in the reactor. By running a batch process in these reaction steps, we can easily calculate approximately the kinetic parameters in equations (1)-(3). We labeled the concentration of HCHO,OH and $(HOCH_2)_3CCHO$ by C_x, C_y and C_z respectively. Resulted in the form of following set of ordinary differential equations by using the law of mass action [2, 3],

$$\frac{dC_x}{dt} = -k_1 C_x C_y C_z - 2k_2 C_x^2 C_y \quad (4)$$

$$\frac{dC_y}{dt} = -k_1 C_x C_y C_z - 2k_2 C_x^2 C_y \quad (5)$$

$$\frac{dC_z}{dt} = -k_1 C_x C_y C_z \quad (6)$$

We will be appropriate non-standard finite difference scheme to fairly accurate the solution of this system of ODEs.

$$C_x(n+1) = \frac{C_x(n)}{1 + hk_1 C_y(n) C_z(n) + 2hk_2 C_x(n) C_y(n)} \quad (7)$$

$$C_y(n+1) = \frac{C_x(n)}{1 + hk_1 C_y(n) C_z(n) + 2hk_2 C_x(n) C_y(n)} \quad (8)$$

$$C_z(n+1) = \frac{C_x(n)}{1 + hk_1 C_y(n) C_z(n)} \quad (9)$$

Solutions obtained for the concentration of formaldehyde, base and pentaerythrose. The rate constants k_1 and k_2 already given in literature [3].

Table-1 Showing numerical results of NSFD, RK-4 and experimental results

	[Experimental Data]			[Exact - NSFD]			[Exact - RK4]		
Time(s)	C_x	C_y	C_z	C_x	C_y	C_z	C_x	C_y	C_z
0	1540.2	932	301.8	1540.2	932	301.8	1540.2	932	301.8
50	1500.52	885.9	262.56	1494.82	888.05	262.26	1498.21	890.61	261.01
100	1454.46	856.11	232.28	1458.06	852.42	230.18	1463.99	856.93	227.87
150	1435.87	823.53	189.67	1427.64	822.92	203.61	1435.55	829	200.45
200	1402.37	807.21	177.64	1402.03	798.1	181.25	1411.57	805.49	177.41
250	1388.56	780.11	163.72	1380.19	776.93	162.19	1391.09	785.46	157.82
300	1368.05	771.26	152.73	1361.34	758.68	145.78	1373.43	768.21	141
350	1351.39	755.53	131.69	1344.93	742.81	131.51	1358.05	753.24	126.43
400	1340.76	729.96	115.52	1330.53	728.9	119.03	1344.56	740.14	113.73
450	1329.92	725.18	107.12	1317.79	716.62	108.03	1332.66	728.23	102.57
500	1314.32	711.83	112.64	1306.47	705.72	98.28	1322.1	718.42	92.74
550	1307.3	699.81	85.03	1296.35	696	89.61	1312.67	709.35	84.02
600	1287.82	697.17	73.89	1287.25	687.29	81.85	1304.23	701.24	76.26
650	1281.29	688.55	52.76	1279.05	679.45	74.89	1296.63	693.98	69.33
700	1282.37	678.31	60.78	1271.63	672.37	68.63	1289.76	687.44	63.12
750	1268.57	683.52	60.67	1264.88	665.96	62.98	1283.54	681.54	57.55
800	1263.14	672.27	65.68	1258.73	660.14	57.86	1277.88	676.21	52.53
850	1244.59	661.19	44.2	1253.11	656.83	53.21	1272.73	671.36	48
900	1245.99	661.19	44.68	1247.96	649.99	48.99	1268.01	666.96	43.9
950	1243.86	657.3	36.69	1243.23	645.56	45.15	1263.69	662.94	40.18
1000	1247.35	650.46	29.81	1238.87	641.5	41.64	1259.72	659.27	36.81

.

3: RESULT AND DISCUSSION

The aldol condensation reactions follow the production of pentaerythritose forming the pentaerythritol by reaction kinetics. Cannizarro reactions that produce pentaerythritose are relatively slow than condensation reactions [2, 3]. Rate constant expressions, k_1 and k_2, were used to express cannizarro reactions [3].The approximate solutions obtained by numerical techniques

such as NSFD and RK4 are compared with the experimental data in table-1.The results attained by applying NSFD on the system of ODEs, were compared with the experimental data. In order to study the results of NSFD with other numerical scheme, the obtained system of ODEs were treated with another numerical scheme using RK-4 method. Thus the relative results of two methods were made and represented in figure (1-3). Table 1 shows the estimated values of experimental results, NSFD and RK4 for the solution obtained for concentration of formaldehyde, base and pentaerythrose which is denoted by C_x, C_y and C_z respectively at same time step.

The table 1 shows the experimental results by experiments and NSFD and RK-4 results by numerical schemes. The above table shows that both numerical techniques which gives good approximation to experimental results. The first column shows the concentration of C_x, C_y and C_z experimental results, and the second column shows the NSFD approximated values. Similarly the third column shows the estimated numerical results by RK-4 of C_x, C_y and C_z. From these results we have prove that both numerical techniques give better results and both are closely to experimental results and little bit difference between NSFD and RK-4.The comparison results between experimental results and both numerical techniques clearly shown by graphs of figure(1-3).

Pentaerythritol is the major product of all cannizarro type reactions. These chemical reactions are converted into system of differential equations. NSFD and Rk-4 are the numerical techniques, which is used to convert the given system into numerical schemes for getting the approximate solutions. The numerical solution of system of ODEs, modeled for the concentration of formaldehyde (C_x), concentration of base (C_y) and concentration of pentaerythrose (C_z) by using numerical techniques, NSFD and RK4. The concentrations of C_x, C_y and C_z by using NSFD and RK-4, both numerical techniques give the approximate solutions, Our analysis by both NSFD and RK-4 gives better results. But overall NSFD gives better result than RK-4.The results gathered from experimental data, NSFD AND RK-4 have been compared and observed and found it better. This work shows the validity and great potential of numerical schemes which is better for solving system of differential equations. The solution of the given example with graphs and table shows that the results of the non standard finite difference method and RK-4 are closer to the experimental data. By this work we can easily calculate the concentration of chemical compounds prior by converting into the system of differential equation and then convert to numerical schemes and easily calculate reactions constants.

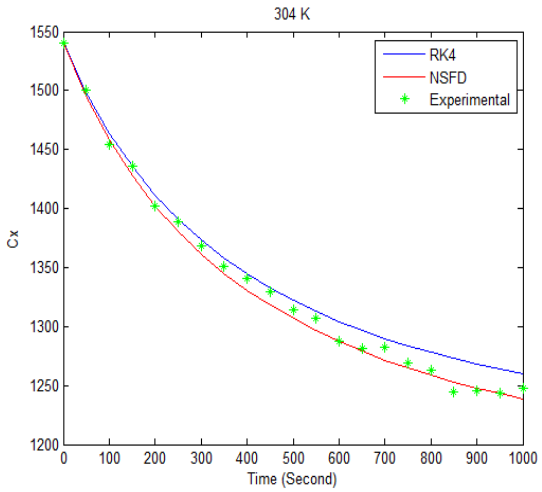

Figure 1: Comparison of NSFD, RK4 and experimental data for C_x

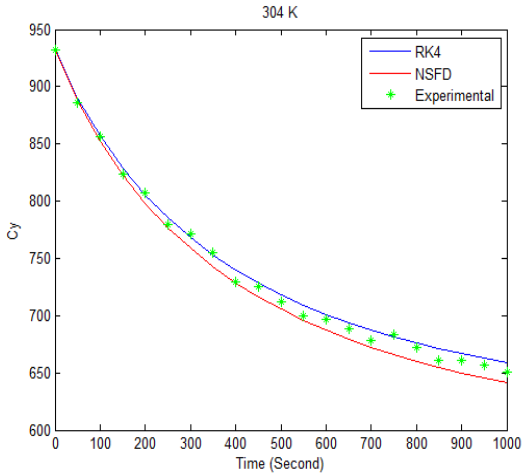

Figure 2: Comparison of NSFD, RK4 and experimental data for C_y

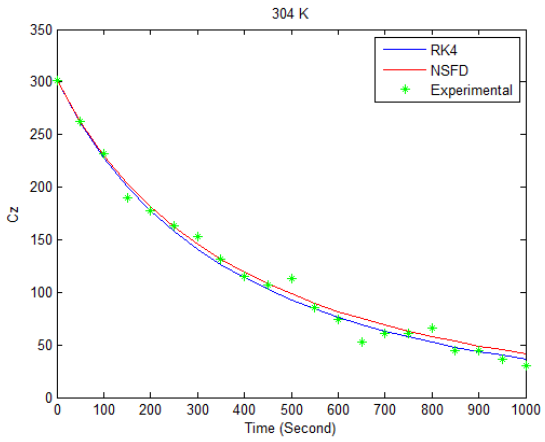

Figure 3: Comparison of NSFD, RK4 and experimental data for Cz*4: Conclusion*

:

REFRENCES:

[1]. Kenneth h A. Connors, Chemical Kinetics, The study of Reaction Rate In solution' VCH Publishers, Inc 1990.

[2]. Peters M.S, C.R. Cupits, Kinetics Of pentaerythritol-Production Reactions Chemical Engineering Division, University of Illinios, Urbana, Illinios U.S.A. no"5767", Received 11 July 1958, Available online 28 September 2001.

[3]. Comsol AB Stockholm (2010) Comsol Reaction Engineering lab Model Library, version 1.5, no's 246, (September 2008)

[4]. Peter M. Manning and Gray F.Margrave CREWES Research Report Volume 18(2006).

[5]. Ibijola, E.A and Obayomi, A.A. derivation of new non-standard finite difference schemes for non autonomous ordinary differential equation

[6]. J.C. Butcher; A history of Runge-Kutta methods Applied Numerical Mathematicains,vol.20 247(1996)

[7]. Barth R.H., J.E.snow., and E.H wood; Paper presented at amer. chem soc.,North Jersey Section Meeting-in-Miniature 8th January, 1951.

[8]. Wawzonek S. and D.A.J Rees; Amer. Chem.Soc.1948 70 2433.

[9]. Mickens R. E, "Exact solutions to a finite difference model of a reaction-advection equation: Implications of numerical analysis" Numerical methods for Partial Differenial Equations, nos 313-325, (1989).

[10]. Mickens R. E, Advances in the Applications of Non-Standard Finite Difference Schemes, Clark Atlanta University, nos 1-7, (2005)

[11]. Angeulov R,Lubma JMS(2003). Nonstandard Finite Difference method by nonlocal approximation, Mathematics and Computers in simulations6:465-475.

[12]. lbijola,E. A. and Sunday j.(2010).A comparative study of standard and exact Finite Difference Schemes for Numerical Solution of ODEs Emanating from the Radioactive decay of Substances. Australian Jornal of basic and Applied Science,4(4): 624-632.