Non-Standard Finite Difference Scheme for the Kinetics of Pentaerythritol Production Reactions

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Abstract- Pentaerythritol plays very crucial role in the preparation of many polyfunctionalized compounds such as explosives, dyes, paints and surface coatings. Estimation of numerical solutions of kinetics of pentaerythritol production reactions has been an important issue. The kinetic model of this reacting system has been converted into system of ordinary differential equations. In this paper, the obtained system of ordinary differential equations describing the kinetics of pentaerythritol has been solved numerically by using non-standard finite difference method and semi analytical scheme 'differential transform method'. Sometime experimental data is not easily available, for such case we have estimated solutions for reaction parameters using NSFD and DTM. Obtained results are approximately same as experimental data. Results obtained from these techniques have been compared with each other and also with the experimental data.

Keywords-Pentaerythritol, Polyfunctionalized, Differential Transform Method, Non Standard Finite Difference Method.

I. INTRODUCTION

Study of the system of differential equations has been the center of focus of many mathematicians. We have observed that in our daily life chemical reactions are long time process and we require too much time to get experimental results, and still chances of error do exist. In this case, to reduce the time estimation and error, we can develop the system of differential equations of chemical reactions and also construct the numerical schemes for getting experimental approximation. Real life problems can easily be modeled in mathematical form using differential equations. The systems of differential equations, obtained from the mathematical modeling of real world problems are some time so complex or the obtained system are so large that analytical methods are hard to apply, but we can approach the solutions of these systems numerically. Advancement in technology has made it much easier to solve big systems of differential equations numerically. In this paper, we will study the numerical approach to the solution of the system of differential equations, which is modeled for the reaction kinetics of pentaerythritol. Reaction kinetics of pentaerythritol is the study of chemical reactions of pentaerythritol [i]. 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 complexity [ii-iv]. Aqueous alkaline mechanism of formaldehyde and acetaldehyde produces pentaerythritol, by-product of this reaction is methanol. Pentaerythritol is obtained from the resulted solution using crystallization process. In the first step of reactions, formaldehyde reacts with acetaldehyde to form pentaerythrose. Sodium hydroxide or calcium hydroxide is most commonly used base in this reaction. These chemical reactions are called cannizarro type chemical reactions, in which two aldehydes together give organic acid and alcohol. Pentaerythritol is achieved in the least reaction of the process when pentaerythrose reacts with formaldehyde in the presence of base [ii , iv].Chemical reactions to process pentaerythritol are modeled mathematically by using the corresponding system of ODEs, which are formed under the conditions applied to the reactions by using law of mass action [ii]. We will solve this system of ODEs numerically using non-standard finite difference (NSFD) method and semi analytic techniques differential transform method (DTM) in order to obtain the approximations for the concentration of Cm, Cn and Co. A most familiar method in numerical analysis is non-standard finite difference method to obtain numerical solutions, numerical schemes give the discrete model of differential equations [v-vi]. DTM is an important semi analytical scheme, to get the approximate solutions for ordinary differential equations [vii].

II. MATEIRAL AND METHODS

The most commonly known numerical method to solve ordinary differential equations (ODE) and partial differential equation (PDE), is standard finite difference (SFD) method. In this method finite difference scheme is applied on given differential equations to get algebraic equations which are rather easy to solve [v]. Mickens [viii], presented the idea of non-standard finite difference model by removing instabilities which were the shortcomings of standard finite difference scheme. Since this scheme has been introduced, many authors in [v,viii-ix] have presented 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 [v]:

a. Order of the derivatives in differential equation and discrete derivatives must be equal.
b. Discrete representations of the derivatives should consist of non-trivial denominator functions.
c. In general, non-linear terms should be replaced by non-local distinct representations.
d. Conditions that satisfy either or both the differential equaton and its solutions should also comply with the difference equation model and its solutions.

Aqueous alkaline medium of formaldehyde and acetaldehyde forms pentaerythritol, methanol is formed as a byproduct. The product is collected from mixture by the process of crystallization. In initial reaction, formaldehyde reacts with acetaldehyde in the presence of base, forming pantaerythrose. Mechanism of pentaerythritol reaction can be summarized in the following steps[x-xi]:

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

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

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

Equation "(2)" shows condensation reaction that is comparatively fast. Before the formation of pentaerythritol, condensation reaction carried out at low temperature to form pentaerythrose from acetaldehyde. When we increase the temperature in the reactor, only cannizarro reactions takes place. By running a batch process in these reaction steps, we can easily estimate the kinetic parameters in refer to "(1)-(3)".We represent the concentration of HCHO,OH and by and respectively, resulting in the form of following set of ordinary differential equations via law of mass action [iv,xi],

$$\frac{dC_m}{dt} = - k_1 C_m C_n^2 C_o - 2k_2 C_m^2 C_n \quad (4)$$

$$\frac{dC_n}{dt} = - k_1 C_m C_n C_o - 2k_2 C_m^2 C_n \quad (5)$$

$$\frac{dC_o}{dt} = - k_1 C_m C_n C_o \quad (6)$$

We will apply non-standard finite difference scheme to approximate the solution of this system of ODEs. After applying our proposed NSFD scheme, the above system of differential equations refer to "(4)", "(5)", "(6)" can be written as the following set of algebraic equations.

$$C_m(n+1) = \frac{C_m(n)}{1 + hk_1 C_n(n) C_o(n) + 2hk_2 C_m(n) C_n(n)} \quad (7)$$

$$C_n(n+1) = \frac{C_m(n)}{1 + hk_1 C_n(n) C_o(n) + 2hk_2 C_m(n) C_n(n)} \quad (8)$$

$$C_o(n+1) = \frac{C_m(n)}{1 + hk_1 C_n(n) C_o(n)} \quad (9)$$

Solutions obtained for the concentration of formaldehyde, base and pentaerythrose. The rate constant k_1 and k_2 for this system has been taken from the experimental data [iii].

III. Resuls and Discussions

The reaction kinetics in the making of pentaerythritol represents the aldol condensation reactions which follows the production of pentaerythritose. Condensation reactions are relatively fast, than cannizarro reactions that produce pentaerythritose [iv,xi]. Rate constant expressions, k_1 and k_2, were used to express cannizarro reactions [iv]. Numerical solution obtained using NSFD and analytic solution obtained by semi analytical scheme DTM are compared with the experimental data in Table I.The results obtained by applying NSFD on the system of ODEs, Thus the comparison of two methods was made and was represented in Fig. 1-3. Table I shows the estimated error between experimental results, NSFD and DTM of the solution obtained for concentration of formaldehyde, base and pentaerythrose which is denoted by Em, En and Eo respectively.

The Table I shows that the error between experimental results, NSFD and DTM results, the above table shows that numerical scheme NSFD gives good approximation to experimental results. The first absolute column shows errors estimations of Cm, Cn and Co between experimental results and the approximated values obtained from NSFD scheme. Similarly the second column shows the error estimations of Cm, Cn and Co between experimental results and DTM results. From these results we can see that the numerical technique NSFD gave better results and is closer to experimental results, whereas the DTM, which is a semi analytical scheme, first shows good agreements with the experimental data approximately up to 50 seconds, after that it started diverging. The comparison of the experimental results with both numerical and semi analytical techniques are shown by graphs in Fig. 1-3. The Fig. 4-6 shows the error between numerical scheme NSFD and semi analytic scheme DTM, from these graphs it is shown that NSFD a numerical scheme is much better than the semi analytic scheme DTM.

TABLE I
SHOWING ERROR BETWEEN EXPERIMENTAL RESULTS, SEMI ANALYTICAL SCHEME AND NUMERICAL SCHEME.

	|Experimental - NSFD|			**|Experimental - DTM|**		
Time(s)	**E_m**	**E_n**	**E_o**	**E_m**	**E_n**	**E_o**
0	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	0.0000E+00	9.0000E+00
50	5.7000E+00	2.1500E+00	3.0000E-01	1.7200E+00	5.3000E+00	9.6000E-01
100	3.6000E+00	3.6900E+00	2.1000E+00	1.5860E+01	2.4110E+01	2.8880E+01
150	8.2300E+00	6.1000E-01	1.3940E+01	3.9270E+01	3.4630E+01	2.8470E+01
200	3.4000E-01	9.1100E+00	3.6100E+00	7.6570E+01	8.5210E+01	6.7140E+01
250	8.3700E+00	3.1800E+00	1.5300E+00	1.0416E+02	9.7910E+01	9.1320E+01
300	6.7100E+00	1.2580E+01	6.9500E+00	1.1425E+02	1.1786E+02	1.0733E+02
350	6.4600E+00	1.2720E+01	1.8000E-01	1.1969E+02	1.2223E+02	1.0439E+02
400	1.0230E+01	1.0600E+00	3.5100E+00	1.2486E+02	1.1036E+02	9.9820E+01
450	1.2130E+01	8.5600E+00	9.1000E-01	1.2562E+02	1.1488E+02	9.8420E+01
500	7.8500E+00	6.1100E+00	1.4360E+01	1.1902E+02	1.0803E+02	1.0794E+02
550	1.0950E+01	3.8100E+00	4.5800E+00	1.1960E+02	1.0091E+02	8.2530E+01
600	5.7000E-01	9.8800E+00	7.9600E+00	1.0702E+02	1.0237E+02	7.2590E+01
650	2.2400E+00	9.1000E+00	2.2130E+01	1.0719E+02	9.7450E+01	5.2060E+01
700	1.0740E+01	5.9400E+00	7.8500E+00	1.1507E+02	9.0810E+01	6.0380E+01
750	3.6900E+00	1.7560E+01	2.3100E+00	1.0827E+02	9.9620E+01	6.0470E+01
800	4.4100E+00	1.2130E+01	7.8200E+00	1.1004E+02	9.1970E+01	6.5580E+01
850	8.5200E+00	4.3600E+00	9.0100E+00	9.8890E+01	8.4590E+01	4.4100E+01
900	1.9700E+00	1.1200E+01	4.3100E+00	1.0799E+02	8.8490E+01	4.4580E+01
950	6.3000E-01	1.1740E+01	8.4600E+00	1.1386E+02	8.8600E+01	3.6590E+01
1000	8.4800E+00	8.9600E+00	1.1830E+01	1.2555E+02	8.5860E+01	2.9710E+01
∑Error	1.22E+02	1.54E+02	1.34E+02	1.87E+03	1.75E+03	1.29E+03
Total Error	4.10E+02			4.91E+03		

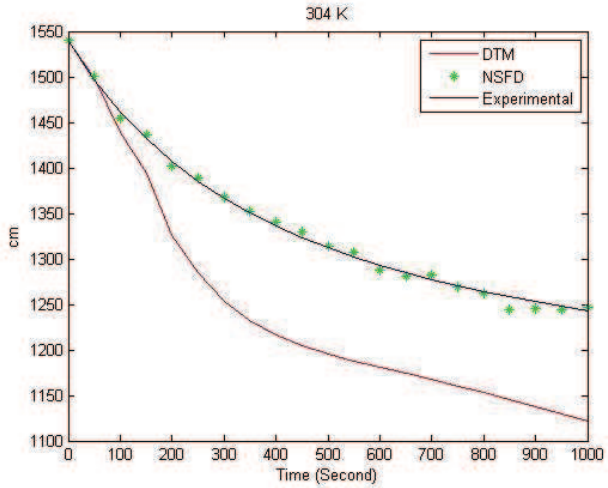

Fig. 1. Comparison between NSFD,RK4 and Experimental results for C_m.

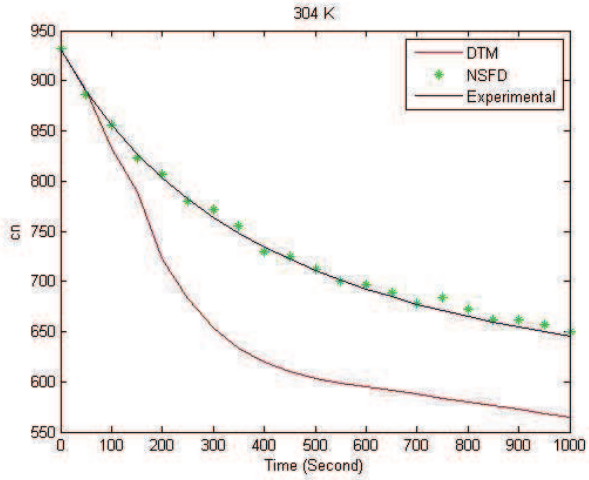

Fig. 2. Comparison between NSFD,RK4 and Experimental results for C_n.

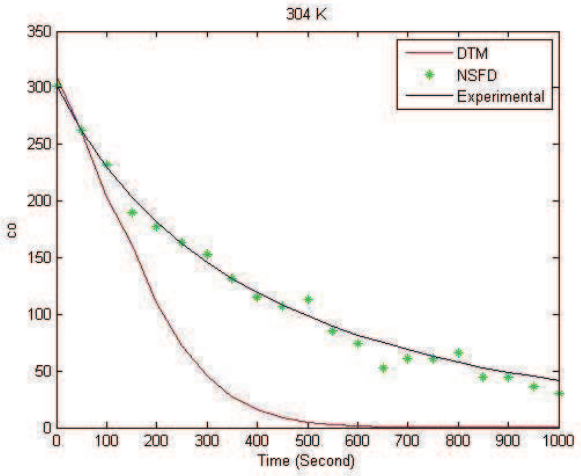

Fig. 3. Comparison between NSFD,RK4 and Experimental results for C_o.

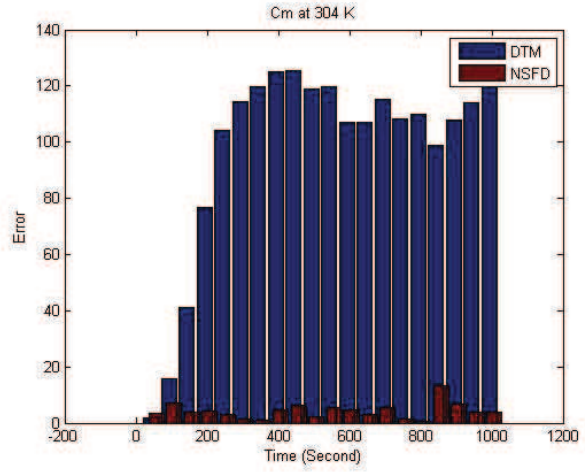

Fig. 4. Estimated error between NSFD and RK4

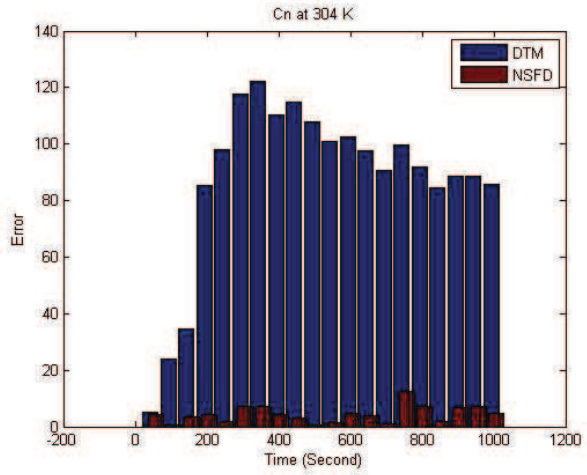

Fig. 5. Estimated error between NSFD and RK4

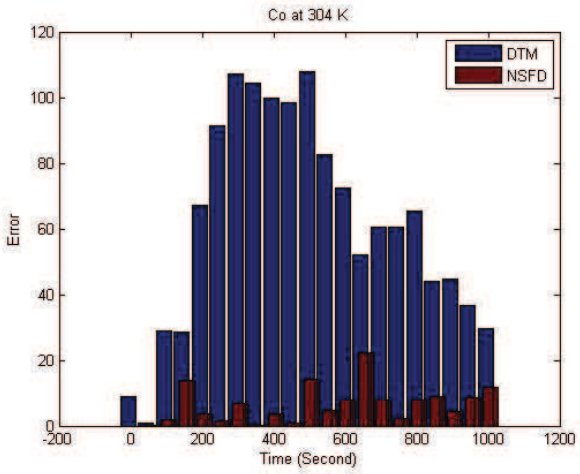

Fig. 6. Estimated error between NSFD and RK4.

IV. Conclusion

Pentaerythritol is the major product of all cannizarro type reactions. These chemical reactions are converted into system of differential equations of ODEs, modeled for the concentration of formaldehyde (Cm), concentration of base (Cn) and concentration of pentaerythrose (Co). We solved the obtained system of ODEs using NSFD, a numerical technique and DTM, a semi analytical technique to find out the rate of change of concentrations of Cm, Cn and Co with respect to time. We observed from the graphs and Table, that our proposed NSFD scheme is in good agreement to the experimental data. Whereas the DTM, which is a semi analytical technique converges for very short interval of time after that it started diverging. This work shows the validity and great potential of the non-standard finite difference method for solving the system of non-linear differential equations. We conclude that whenever a chemical process take a long time or it is not feasible to perform the experiments, we can approximate the rate of change of concentrations of the chemicals involved in the chemical reactions using our proposed scheme.

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