Prediction of Runaway during the Nitration of DNT to TNT Mathematically-A Review

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Abstract- *In this paper a review on mathematical investigation of the reasons [1] causing the runaway reaction during the nitration of DNT to TNT has been made. A new numerical solution Picard Pade[3] technique, proposed by M.M.Khader[3] will be employed to solve the mathematical model and the results obtained will be substantiated by using results from G.D.Kozak's[1] experimental work on the nitration of DNT to TNT. The influence of mixture compositions on the Oxidation reaction can be explained clearly by analyzing the results obtained through solving the mathematical model. The way DNT dissociates in the presence of sulfuric acid has been discussed broadly in this paper. It is further can be analyzed mathematically using the concentration plots obtained through solving the mathematical model. The mathematical computation involved in this work will be executed using MATLAB programming.*

Keywords- Mathematical computation, MATLAB, Nitration, Oxidation, Picard Pade, Runaway.

I. INTRODUCTION

Tri Nitro Toluene known for its explosive properties [8] accounts for a large part of explosive contaminations in military operations. TNT has unique properties when compared to other explosives, even though it is an explosive it is chemically stable, low sensitiveness to impact and friction makes it safe to handle. TNT is manufactured from DNT through Nitration process [1]. It is considered safe process until the initiation of secondary reaction known as Oxidation reaction, which has unusual high activation energy and highly exothermic in nature. There were accidents in the history during the nitration of DNT to TNT and the main cause of these explosions is due to the high exothermal properties of Oxidation reaction resulting in the growth of temperature uncontrollably at a brisk pace leading to a runaway reaction.

The present work gives an outline about the Mathematical prediction of these conditions that leads to runaway reactions during the nitration of DNT to TNT. To predict the nature of a chemical reaction mathematically, we must create a mathematical model which represents the change in required parameter which may be Concentration or Temperature, with respect to time in the form of Differential equations. The number of Differential equations in a mathematical model depends up on the number of reactions and number of species those were considered. Now, these differential equations must be solved using a suitable numerical solution and must be compared with the experimental results.

II. IDENTIFY, RESEARCH AND COLLECT IDEA

Kozak[1] experimental work on the Nitration of DNT to TNT has taken as the basis for our work. All the experimental values involved in the chemical Kinetics were extracted from Kozak's[1] work. In his work Kozak[1] investigated the reasons for the hazard of runaway reaction during nitration of DNT to TNT and stated that the Concentration of Sulfuric acid, Reagent's content in the mixture and Inefficient cooling will result in the propagation of oxidation reaction leading to runaway reaction. Traditionally there were many methods existing in the literature like Adomian decomposition, Gillespie Algorithm, Euler's method, Runge Kutta 4th order method etc. for solving a chemical kinetics system. M.M.Khader[3] in his work has proposed a new technique Picard-Pade[3], which is a combination of Iteration and Approximation methods. In his work M.M.Khader[3] has considered a chemical kinetic system and solved it using Picard Pade[3] method. Then he compared his new method's result with the standard RK-4 method and was in good accordance.

III. METHODOLOGY

Kozak[1] in his work had clearly mentioned that runaway reaction is greatly possible at a temperature higher than 120^{o}C and he has given the behavior of temperature curve for different mixtures. So, the same procedure will be repeated in the mathematical computation also, the temperature variation for different mixtures will be found. This gives us an idea which mixture has more effect on oxidation reaction and leads to runaway reaction. The advantage in mathematical modeling is once the mathematical model is validated with experimental results, the temperature change for different mixtures can be found. The temperature at

which the oxidation reaction initiates is around 200°C and at temperature above 120°C the runaway reaction is greatly possible. This shows us that the oxidation reaction will enhance the chances of runaway reaction. The chemical reactions considered for the formation of mathematical model were taken from Kozak[1] experimental work and they are as follows,

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+HSO_4^- + H_3O^+HSO^-_4$$

Second and third step includes reaction of nitration and destructive oxidation of DNT

$$C_7H_6(NO_2)_2 + NO^+_2\,HSO^-_4 \longrightarrow C_7H_5(NO_2)_3 + H_2SO_4$$

$$C_7H_6(NO_2)_2 + aNO^+_2\,HSO^-_4 + 6H_2SO_4 \longrightarrow 4H_3O^+HSO^-_4 + (a+2)NO^+HSO^-_4 + bCO + (7-b)\,CO_2$$

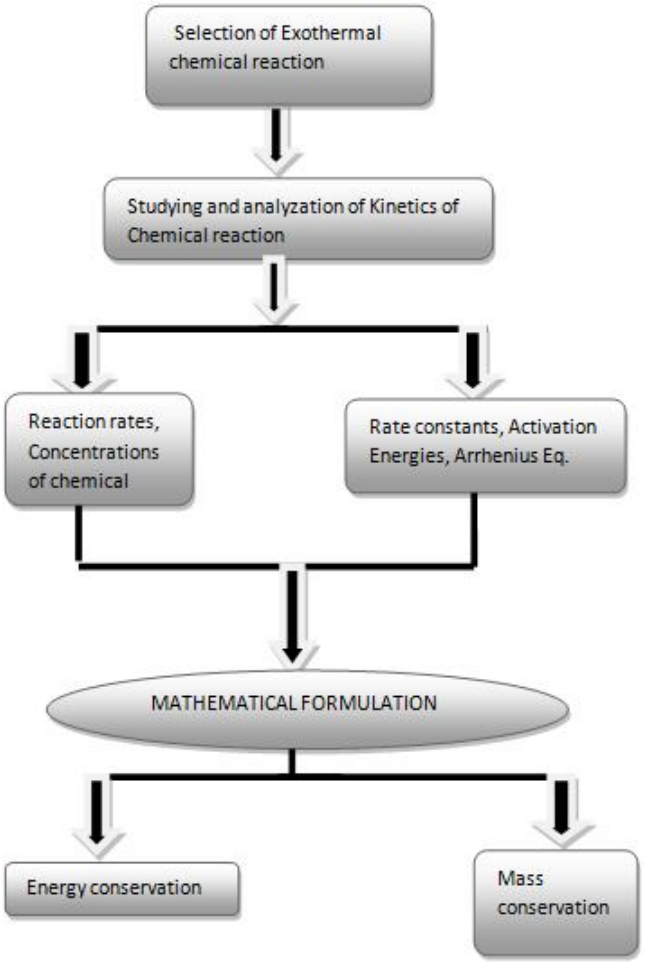

Fig 1 Methodology followed during mathematical formulation of chemical reaction

Nitration and Oxidation reactions are the important exothermic reactions that are considered for the formulation of Mathematical model. In the second step Chemical kinetics of these reactions must be determined. It is the important step as the values of Reaction rate and rate constants determine the nature of reaction. All the data required for chemical kinetics has to be considered from the experiment. Kozak in his experiments has determined some of the data required for solving the mathematical model.

The set of differential equations in a mathematical model can be broadly classified in to two types one is Mass Conservation and the other is Energy conservation. Mass conservation refers to the variation in concentration of species with respect to time. Energy here refers to heat energy, conservation of energy gives us an idea how the temperature is changing and the nature of that temperature curve at different points in the reaction period.

Now, the formulated mathematical model has to be solved using a suitable Numerical solution. The numerical solution we adopted in order to solve this chemical kinetic system is Picard-Pade technique.

PICARD-PADE Technique[3]:

M.M.Khader[3] in his work has adopted an algorithm in order to solve the mathematical model using Picard Pade technique.

Pade approximation can be denoted as follows

$P[N/M] = P_N(t)/Q_M(t)$……..1

$P_N(t) = p_0 + p_1 t^1 + p_2 t^2 + \ldots\ldots\ldots\ldots + p_N t^N$

$Q_M(t) = q_0 + q_1 t^1 + q_2 t^2 + \ldots\ldots\ldots\ldots + q_M t^M$

In the first step the mathematical model has to be solved by using Picard Iteration method. The solution obtained will be in the form of series and a function of time. Now, the solution should be truncated up to certain order depending up on the values of N and M. The obtained truncated series must be solved using equation 1.

The crucial step in Picard pade technique is choosing the values of N and M while solving in pade approximation. N and M are the degree of the numerator and denominator respectively. The total order of the equation is considered as N+M. The choice of the N and M leads to the approximation of the solution. M.M.Khader[3] states that the criterion in choosing the values of N and M should depend on the shape of the solution that is required. This means that no two solutions will have same N and M value. In case of M.M.Khader's[3] approximation the criterion N=M has worked well and fetched him satisfactory results. It should be noted that the truncation order also plays an important role, it must be chosen accordingly to the values of N and M.

IV. CONCLUSION

The reasons mentioned by Kozak[1] in his work will be investigated mathematically. A new method is going to be employed in order to solve this mathematical model, Picard Pade technique. As it has already been substantiated by comparing its results with RK-4 method it is a valid method for solving the chemical kinetics system. Growth in temperature is evaluated computationally with respect to time for different mixtures and evaluating different regions of the curve basing up on the slopes. The change in concentration also gives us an idea how the dissociation of one species can influence the reaction temperature. The same with the DNT dissociation in the presence of Sulfuric acid kozak[1], DNT dissociates so rapidly in the presence of Sulfuric acid which can be termed as substantial reason for the propagation of oxidation reaction. So finding the change in concentrations of DNT and Sulfuric acid with respect to time will provide us a lot of insight into the reaction mechanism involving in nitration of DNT to TNT.

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