

**REACTION AND REACTOR MODELLING FOR  
SYNTHESIS OF INSENSITIVE HEMs**

A THESIS  
SUBMITTED TO THE  
**UNIVERSITY OF PUNE**  
FOR THE DEGREE OF  
**DOCTOR OF PHILOSOPHY**  
**(IN CHEMICAL ENGINEERING)**

**BY**

**ALOK KUMAR MANDAL**

**CHEMICAL ENGINEERING & PROCESS DEVELOPMENT DIVISION  
NATIONAL CHEMICAL LABORATORY  
PUNE – 411 008, INDIA**

**June 2010**

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*DEDICATED*

*TO*

*MY BELOVED PARENTS*

*SMT KALYANI & SHRI AMARENDRA NATH MANDAL*

## CERTIFICATE

This is to certify that the work incorporated in the thesis, "**REACTION AND REACTOR MODELLING FOR SYNTHESIS OF INSENSITIVE HEMs**" submitted by **SHRI ALOK KUMAR MANDAL**, for the Degree of **Doctor of Philosophy (Chemical Engineering)**, was carried out by the candidate under our supervision in the **Chemical Engineering & Process Development Division, National Chemical Laboratory, NCL Pune, INDIA**. Such materials as has been obtained from other sources has been duly acknowledged in the thesis.



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## DECLARATION

I declare that the thesis entitles 'Reaction and Reactor Modelling for Synthesis of Insensitive HEMs' submitted by me for the degree of Doctor of Philosophy is the record of work carried out by me during the period of study under the guidance of **Dr B.D.Kulkarni** Scientist 'H', & Director's Grade, NCL, Pune and Dr. S N Asthana, Associate Director, HEMRL, Pune has not formed the basis for award of any degree, diploma, associate-ship, fellowship, titles in this or any other University or other institutions of higher learning.

I further declare that the material obtained from other sources has duly been acknowledged in the thesis.

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# ABSTRACT

## ABSTRACT

This thesis is outlined broadly to investigate the process development, and reactor modelling for synthesis of 1,1-diamino-2,2-dinitroethene (FOX-7), a recent novel thermally stable insensitive high explosive material. The systematic studies and efforts have been made to combine the utilization of process selection followed by optimization studies, thermo-chemical studies in Reaction calorimeter, reaction kinetics studies, parametric sensitivity analysis of the process, modelling of reaction in micro reactor as well as batch reactor to select the best course of synthetic route for FOX-7 adhering to selectivity, quality, safety, process control etc. while scale-up. The efforts have also been made to prepare spherical particle of FOX-7 required for certain specific application in high explosives charges and propellant formulations. Besides, studies on polymorphic behavior of the FOX-7 have been studied to know the pattern of phase transition at different temperature while used in high explosive and propellant compositions.

Chapter 1 depicts the aim and outline of the thesis emphasising the significance of insensitive high energy materials (HEMs).

Chapter 2 brings out the process feasibility to prepare FOX-7 in most economical way. Feasibility studies on five different routes have been reported in the literature. Based on the feasibility fifth route have been selected for study at laboratory level. It's a batch nitration reaction of 2-methyl-4,6-dihydroxypyrimidine (MDP) (its keto form is 2-methyl-4,6-pyrimidine-dione, MPD) using concentrated nitric acid ( $\text{HNO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) to prepare 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione (NMDP) followed by hydrolysis to yield the FOX-7. Optimization of Nitration and hydrolysis process have been carried out and established at laboratory level. Parameters optimized are

temperature ( $^{\circ}\text{C}$ ) of Solubility of MDP in concentrated sulfuric acid, moles of sulfuric acid per mole of MDP, moles of nitric acid per mole of MDP, concentration (%) of nitric acid and sulfuric acid, nitration temperature ( $^{\circ}\text{C}$ ) domain for optimum yield, nitration time (minutes), mode of operation & type of reactor preferred, moles of water per mole of MDP, % sulfuric acid required for hydrolysis, temperature ( $^{\circ}\text{C}$ ) required for hydrolysis, hydrolysis time (hrs), runaway conditions, temperature ( $^{\circ}\text{C}$ ), tip-speed etc.

Chapter 3 presents details studies on evaluation of thermo-chemical parameters of the MDP nitration reaction which were evaluated by conducting experiments in Differential Scanning Calorimeter (DSC) followed by Reaction Calorimeter (RC) both in Mettler Toledo make and HEL(Hazard Evaluation Laboratory) make RC. Heat of reaction and associated hazards were evaluated by heat flow and power compensation method. Calorimetric data were analysed using DSC and RC software. Thermal Hazards for the process were assessed for design of safer process equipment while scaling up the process. Thermo-chemical parameters like heat of reaction, onset of decomposition of reaction mixture, adiabatic rise in temperature, overall heat transfer coefficients, equivalent heat transfer area required, mode of conducting the nitration reaction etc.

Chapter 4 illustrates the studies on reaction kinetics for nitration and hydrolysis process using differential method. As both nitration and hydrolysis were quite sensitive to temperature, reaction rates were studied at fixed temperature with the variation of time and maintained all other parameters constant. Activation energy of the nitration process have also been evaluated using Arrhenius's law. Nitration process heat generation were also measured while conducting the kinetics experiments. Suitable operating reaction

temperature, Reaction order, rate constants, reaction time, activation energy, frequency factor etc. were evaluated for the MDP nitration followed by hydrolysis of NMDP.

Parametric sensitivity describes the large changes in reactor trajectory induced by small changes in parameters across the threshold value. The critical behaviour of the reactor can also lead to runaway reaction as a result of unsafe reactor operation. Overall productivity, process control and safety of the MDP nitration in batch mode is highly restricted due to lower surface to volume ratio. In order to overcome such limitations of the batch reactor and also to understand the course of reaction, modelling followed by parametric sensitivity analysis has been carried out. In this work, the systems are modelled using the kinetic rate expression developed by conducting the experiments on nitration of MPD. The measured variables are the initial reactor composition (concentration), reactor temperature, coolant circulation temperature etc. Effect of initial reactor temperature, circulator temperature and concentration on reactor temperature are evaluated and discussed. These control parameters for nitration of MPD were used to find the reactor behaviour and parametric sensitivity of the system. Sensitivity analysis reveals that MPD reaction rate can increase drastically with increase in temperature by sharp reduction in time causing the system sensitive. For the temperature gradient (difference in reactor and jacket temperature) more than of  $10^0$  C and reaction temperature above  $20^0$ C, the reaction becomes more sensitive which needs proper temperature control mechanism. The study also guides reactor operation at various initial conditions.

Chapter 5 depicts the modelling of MDP nitration reaction in micro reactor and a batch reactor. Modelling of the nitration reaction is important as it is a

highly exothermic and hazardous reaction. Conducting such reaction in a batch reactor follow an unsteady state and its trajectory depends on various important parameters such as initial reactor temperature, initial composition of reaction mass, temperature of circulating coolant etc. As, overall productivity, process control and safety of the batch process is highly restricted due to lower surface to volume ratio, so, in the present work, deliberation has been made to overcome the limitations of batch reactor by using the novel micro reactor device. Micro reactor is having extremely high surface to volume ratio, which has been explored to carry out nitration of MDP both numerically as well as experimentally and the results were compared with conventional batch reactor.

The micro reaction system has been modelled using two dimensional (2-D) heat flow and mass transfer equations. The kinetic rate equation for nitration of MDP has evaluated experimentally by differential method which is used in modelling of the micro reactor. The numerical results from the 2-D model for conversion and temperature profile along the length and radius of micro reactor have been compared with corresponding results obtained in a batch reactor. In order to validate the model several experiments were conducted in micro reactor setup with the variation of flow rate, residence time, concentration, temperature etc. The experimental results from micro reactor revealed that the nitration of MDP takes place even at much lower concentration and lower residence time with better control of temperature profile. Also the reaction takes place in laminar region compared to turbulent region in corresponding batch reactor setup.

Chapter 6 deliberates the inevitability and preparation of spherical FOX-7 particles in order to meet certain special applications in high explosives and propellant formulation. Preparation of spherical FOX-7 particles have not been

reported in literature. In the present studies, a novel concept of micelle based nano reactor have been employed to study the feasibility on preparation of spherical FOX-7 particle and successfully prepared spherical particle. Spherical FOX-7 have been characterized using instrumentation methods like differential scanning calorimeter (DSC), high purity liquid chromatography (HPLC), Nuclear magnetic resonance (NMR), Infrared (IR) spectra, scanning electron microscope (SEM) etc. to confirm the product characteristics. Analysis of spherical FOX-7 confirms that properties are same as that of regular FOX-7.

Chapter 7 describes the polymorphic behaviour of insensitive high-energy material, FOX-7, a novel high explosive which combines two properties like high performance and low sensitivity. In order to understand such unique properties of FOX-7, the precise knowledge of both the atomic and molecular arrangements are essential. The single crystals structure investigations were carried out at various temperature along with hot-stage microscopy. The crystals were made in different solvent then the study is done by Single Crystal X-ray Diffraction method at different temperature to understand the polymorphic behaviour of FOX-7.

Finally, conclusions are made based on complete study of the thesis.

# Chapter 1 : Introduction

## **1. Introduction**

### **1.1 High Energy Materials**

The High Energy Materials (HEMs) are those which can detonate (explode) by supersonic disturbance (shock) rapidly in the form of explosion or undergo self sustained combustion with the release of large amount of energy to cause huge damage to the surroundings in the shortest span of time (mili sec to micro sec). HEMs are well known due to the significant potential for application in high performance and insensitive ammunition compliant explosive and propellant compositions. The performance of an explosive / propellant is dependent on the density (more energy per volume) and the oxygen balance, *i.e.* the energy content of the compound. The more the oxygen, the better is combustion since all carbon should be burned to carbon dioxide and all hydrogen to water. So, performance and sensitivity are the two main criteria for evaluating the suitability of high energy materials (HEMs) for a given explosive / propellant application. High performance is related to higher detonation pressure that results in higher velocity of heavy metal shrapnel, which increases the armour penetration capability. Lower sensitivity is not only of interest for safe handling, but also an important aspect of HEMs, as the survivability of platforms (ships, tanks and armoured vehicles) will increase.

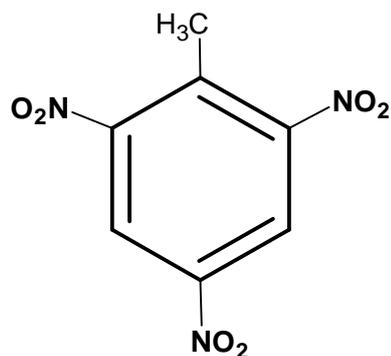
### **1.2 Insensitive high Energy Materials (IHEMs)**

Recently, research is in progress worldwide in search of HEMs for combination of properties like reliability, stability, cost effectiveness and eco-friendliness (1). HEMs also termed as High Explosives (HEs), belongs to the class of HEMs and are broadly classified as,

- Melt- castable explosives (MCE)
- High performance i.e. Explosives with high density (HD) and high Velocity of Detonation (VOD)
- Energetic binders for high explosives / propellant formulations
- Thermally stable i.e. Heat Resistant Explosives(HRE) / Heat Resistant Explosives Materials (HREMs)
- Insensitive High Explosives (IHE) / Insensitive High Energy Materials (IHEMs)

### **1.2.1 Melt- castable explosives (MCE)**

2,4,6-Trinitrotoluene (TNT), the nitro derivative of toluene, is the most commonly used high explosives in this field. It has been widely used as a military explosive since first world war and still acquires an important place in the explosive field. TNT derives its virtue from its relative insensitivity to shock, high chemical stability and low melting point (80 °C). As it can be melted with steam, it may be safely cast into shells as per convenient. TNT is usually used in conjugation with other high explosives such as cyclotrimethylenetrinitramine (RDX)/ cyclotetramethylene-tetranitramine (HMX) where TNT acts as energetic binder in addition to explosive. The basic properties of TNT are low melting point, high decomposition temperature ~300 °C and also it has the capability of binding explosive particles. So, it is termed as meltcastable explosive or explosive binder. New compounds in this directions reported very recently are 1,3,3-trinitroazetidine (TNAZ), 1-methyl-2,4,5-trinitroimidazole (MTNI) etc.

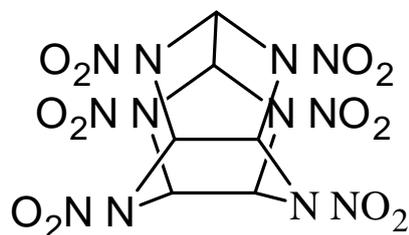


**TNT**

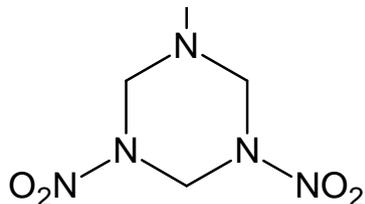
Melting Temp( <sup>0</sup> C)	: 80
Decomposition Temp( <sup>0</sup> C)	: 300
Velocity of detonation (m/s)	: 6900

### 1.2.2 High performance Explosives

Energetic materials of the strained-ring cage families constitute a promising new class of explosives for this purpose. This is based on the fact that such compounds have high strain energies locked in the molecules and this energy is released as extra energy on detonation. These molecules also possess rigid and highly compact structure resulting in compact density which helps to accommodate greater mass of poly-nitro poly-cyclic strained and cage compounds in a given volume which, along with their high molecular strain energies, results in a better performance on detonation over conventional high explosives like RDX, HMX. e.g. 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane, CL-20 (2), given below.

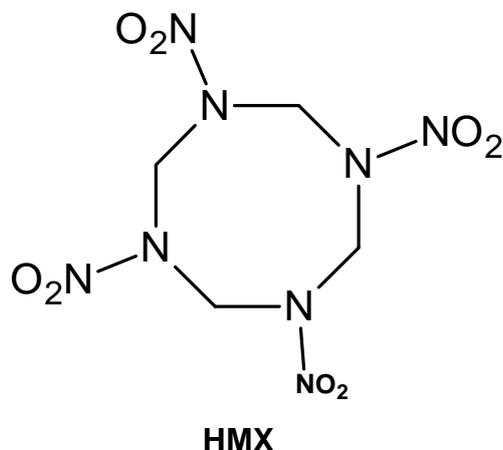


**CL-20**



**RDX**

DSC decomposition Temp( <sup>0</sup> C)	: 228
Impact sensitivity (h <sub>50</sub> , cm)	: 24
Friction sensitivity (kg)	: 14
Melting Temperature ( <sup>0</sup> C)	: 202
Impact sensitivity (h <sub>50</sub> , cm)	: 38
Friction sensitivity (kg)	: 12
Velocity of detonation (m/s)	: 8800



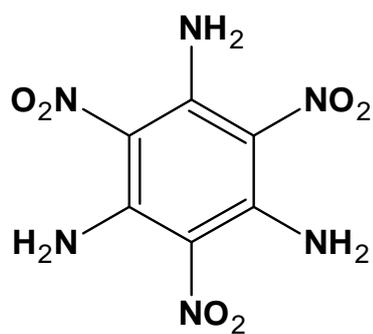
Melting Temperature ( $^{\circ}$ C)	: 272
Impact sensitivity ( $h_{50}$ , cm)	: 40
Friction sensitivity ( kg)	: 13
Velocity of detonation (m/s)	: 9100

### 1.2.3 Binders for High Energy Materials

A number of inert binders such as polyesters epoxies, poly-sulphides, polyurethanes are reported as binders for composite propellants and plastic bonded explosives (PBXs). However, hydroxyl-terminated poly-butadiene (HTPB) is regarded as a state-of-the art binder for such applications. Recent reports suggests to use of energetic binders such as Glycidyl-azide-polymers (GAP), nitrated HTPB, Poly (NIMO), Poly (GLYN) etc. for PBXs and composite propellants for better performance.

### 1.2.4 Thermally stable Heat Resistant Energetic Materials

Explosives with improved high temperature properties are usually termed as 'heat-resistant' or thermally stable explosives (3). The aim of use of such explosives or explosive formulations is to support the systems or applications which must be reliable and safe at high temperature. The development of space programmes, drilling of deep oil wells etc. has projected a need for thermally stable or heat resistant explosives e.g. 1,3,5-triamino-2,4,6-trinitro benzene (TATB) which is given below.



**TATB**

DSC decomposition Temp(<sup>0</sup> C) : 380

Impact sensitivity (h<sub>50</sub>, cm) : >175

Friction sensitivity (kg) : 36

### 1.2.5 Insensitive high explosives

In the recent past the major problems associated with the high explosives formulations / warhead compositions is the vulnerability (4). The solutions offered to this problem was the invention and use of Plastic-bonded Explosives (PBXs). PBXs mainly consist of polymer matrix encasing a conventional granular explosive, which gives resistance to unintended stimuli. However, subsequently it was observed that the PBX alone is not sufficient. In order to overcome this problem, an idea of using intrinsically less-sensitive explosives has gained importance in this area. This thought spawned another class of explosives (thermo-stable explosives molecule with low-impact sensitivity) termed as Insensitive High Explosives (IHEs). 1,3,5-triamino-2,4,6-trinitro benzene (TATB) was the first recognised candidate in this class of IHEs but it is inferior to cyclotrimethylenetrinitramine (RDX) / cyclotetramethylenetetranitramine (HMX). Hence, the research is indispensable to find the **IHEMs class of explosives** without compromising the performance equivalent to RDX and the present thesis is focused in this direction.

### 1.3 Significance of IHEMs

Among various HEMs, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20) is the most energetic compound known so far. CL-20 was first reported (5) in 1987. The nitramines like cyclotetramethylenetetranitramine (HMX) (6,7), cyclotrimethylenetrinitramine (RDX) (8, 9, 10) are the best commonly used ingredients in solid explosive compositions for various military applications. Research for more energetic compounds is approaching its limit with the strained ring nitro compounds and nitramines. Generally the more powerful compounds tend to be more sensitive to friction, shock and impact but the development of new energetic compounds is driven not by the requirement of increase in energy but also a superior sensitivity criterion. Thus, a new group of known or emerging energetic compounds will fill such requirement and preferably these will be called as insensitive high energy materials (IHEMs). So, there is a niche for such IHEMs which can be exploited in systems where good vulnerability properties are blended with maximum performance. IHEMs based munitions are those, which reliably fulfill the performance, readiness and operational requirements on demand, but the degree of violence of response to unintended stimuli is restricted to an acceptable level. Besides the performance and sensitivity, chemical and physical stability, compatibility, processability and cost are the other factors that determine the choice of energetic materials. This implies that the ingredient should not show any self-heating in normal temperature range of use. It should not be affected by humidity, sunlight and should have a high melting point and density for processing. It should not show polymorphism at the processing temperature and be compatible with common material of construction. Keeping these desirable properties in view, research is focused for

energetic compounds that have at least 75% or more of explosive performance of HMX / RDX but are definitely to be much less sensitive. The working capability of an explosive can be estimated theoretically from the various properties like heat of formation ( $\Delta H_f$ ), heat of explosion ( $Q_v$ ), density, velocity of detonation (VOD), impact sensitivity ( $h_{50}$ ), friction sensitivity (F) etc. Zeman and Krupka (11) have proposed a correlation between specific enthalpy, heat of formation and density for given composition. The heat of formation, heat of explosion, power index, velocity of detonation, impact and friction sensitivity value estimated / evaluated for commonly used / promising high explosives are given in Table 1.1 for comparison of properties of various explosives. It is seen from Table 1.1 that CL-20 is having highest explosive power but it is quite vulnerable to use in various formulations.

Table 1.1 Properties of High Explosives for Military Application

Name (Mol.wt.) / Year of report	$\Delta H_f$ (kJ/mol)	$Q_v$ (kJ/kg)	Power index (%)	Density(gcm <sup>-3</sup> ) / VOD (km/s)	$h_{50}$ ( cm ) / F (kg)
CL-20 (438) /1989	+420	6023	197	2 / 9.4	31/10.4
HMX (296) / 1952	+75	5010	168	1.91 / 9.1	40 / 13
RDX (222) / 1920	+62	5030	169	1.82/ 8.9	38 / 12
NQ (104) / 1901	-95	2471	99	1.77 / 7.6	>170 / 36
TATB (258) / (1978)*	-154	3496	117	1.93 / 7.7	>170 / 36
FOX-7 (148) / 1998**	-130	4920	164	1.89 / 8.9	50 / 36

\* Though TATB was first reported to be synthesised in 1884, however only in 1978 development and subsequent application trial was being explored.

*\*\* Diaminodinitroethene, the most recently developed promising high energy molecule.*

So, CL-20, RDX / HMX are having very high explosive power. 1,3,5-triamino-2,4,6-trinitro benzene (TATB) (12) is the most stable and have moderate explosive performance as compared to RDX / HMX. Nitro-guanidine (NQ) is one of the low vulnerable high explosive (13) but performance is even less than TATB. Besides, TATB is having strategic application due to its extreme insensitivity apart from its use in high explosives warheads and propellant composition. In present scenario, the most widely used high explosive all over the world for various military applications is the RDX / HMX based Composition (preferably composition B). Composition B is well known and has very good performance. It is easily processed and is made from relatively low-price raw materials like hexamethylenetetramine (Hexamine). Unfortunately RDX/HMX based composition suffers from lot of problems (14) in several applications due to its sensitivity. It may shrink during manufacturing, which results in cracks and voids. It is sensitive to impact / friction and reacts violently during cook-off. These drawbacks have resulted in a need to find low-vulnerability replacement to Composition B. Hence, scientists across the world are looking for insensitive powerful high explosives. Thus, it will be really interesting if a compound can be made available that is having equivalent performance like RDX / HMX based composition and can pass insensitive ammunition (IM) test. In view of the above, **1,1-diamino-2,2-dinitroethene (FOX-7)** the new energetic compound that reported first time by Swedish Defence Research Agency (FOI) in the year 1998(15), can fulfill the niche for insensitivity and exhibit equivalent performance like RDX and it can also be the

potential candidate to replace RDX. Along with insensitivity, it has also the features to be used in both military and commercial explosives application.

#### **1.4 Research on IHEMs**

The objectives of the present research on IHEMs is to produce and make available, more powerful, low vulnerable, safer and environment friendly high explosives for futuristic applications as well as replacement of sensitive energetic ingredients in existing formulations. The facts of IHEMs directs the research towards compositions with lower sensitivity, which improves the munitions safety and might find use in defence applications for domestic as well as international military operations. The approaches of this class of explosive formulations are generally met either by producing polymer bonded explosive (PBX) in which energetic material is incorporated in a flexible polymer matrix and other is to use less sensitive ingredients such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 1,1-diamino-2,2-dinitroethene (FOX-7) etc. The process of TATB is comprehensively reported long back by various advanced countries like USA, UK, Russia etc. on development, production and strategic formulation. The technology of TATB for production (16) and formulation in strategic programme is also well established in High Energy Materials Research Laboratory (HEMRL), Defence Research Development Organisation (DRDO), India, whereas the development of FOX-7 is the recent one and the process / product needs through investigation for the technology maturation as well as for production to meet the user's specification.

Report on preliminary studies on **FOX-7** by various researcher (17-25) suggest that, FOX-7 is a high energy material having velocity of detonation

(VOD) around 8.9 km/s, impact sensitivity ( $h_{50}$ ) around  $50\pm 5$  cm and friction sensitivity around 32-36 kg. It is insensitive to hazard stimuli compared to conventional cyclotrimethylenetrinitramine (RDX) and equivalent in performance. Owing to these special properties, FOX-7 is a promising candidate to consider as a replacement to RDX for enhancing safety without compromising performance.

Though the Information pertaining to application of FOX-7 based composition are reported (19-20), however, critical issues related to **process development, reaction kinetics, thermo-chemical data, parametric sensitivity, reaction & reactor modeling, scale-up methodology, product morphology, product characteristics etc. need to be investigated** thoroughly to understand the process and product insight. So, the development of FOX-7 is important in the field of Insensitive High energy materials (IHEMs) and the research in this direction would be of National interest.

### **1.5 Importance of FOX-7**

The main explosive component of artillery shells, high explosives warheads, gun propellant and other explosive devices for last five decades is the cyclotrimethylenetrinitramine (RDX, 1) shown in Table 1.2. RDX was one of the most energetic materials available during this period. Preparation of RDX was being carried out by nitration of hexamethylenetetramine (Hexamine) in presence of concentrated nitric acid and acetic anhydride as nitrating media. But unfortunately, RDX exhibits several unsatisfactory properties as high explosive. It is sensitive to impact, friction, heat, electrostatic discharge etc. and react violently during cook-off, bullet impact etc. Due to its sensitivity, many accidents took place due to unintended stimuli where weapons has either suffered direct impact by enemy fire or been subjected to heating in fire.

In order to overcome these drawbacks, there has been a search for replacement of explosive material that are at least equivalent energetic like RDX but at the same time it should exhibit low vulnerability. In this regard, one such potential replacement would be a simple molecule **1,1-diamino-2,2-dinitroethene (FOX-7, 2)** shown in Table 1.2. Only in late nineties (15) this material (FOX-7) was first reported to be synthesised at laboratory by the researchers at the Swedish Defence Research Agency (FOI, formerly known as FOA). The name FOX-7 derives from the acronym FOA, with X corresponding to explosive. In view of interesting properties of FOX-7 (2), a plethora of information on FOX-7 has been collected by A. J. Bellamy (26) which has been compiled in book edited by T. M. KalPotke for better understanding and comparison of FOX-7 with RDX and other potential high density molecules.

Unlike RDX, FOX-7 is structurally similar to several other known energetic molecule like 1,3,5-triamino-2,4,6-trinitrobenzene (TATB, 3), 2,6-diamino-3,5-dinitropyridine (DADNP, 4), 2,6-diamino-3,5-dinitropyrazine (DADNPN, 5), 2,5-diamino-3,6-dinitropyrazine (DADNPN, 6), 2,4,6-triamino-3,5-dinitropyridine (TADNB, 7) etc. shown in Table 1.2, possesses a similar combination of amino and nitro group in the juxtaposition. Between these two groups (nitro and amino), predominantly there exists hydrogen bonding which is believed to be responsible to reduce the sensitivity to external stimuli like impact, friction, thermal stability etc.

Main objective of designing such a new energetic molecule is to incorporate as much oxygen as possible to achieve complete conversion of carbon (C) to CO<sub>2</sub> (g) and nitrogen (N) to N-oxide. Various researcher have reported (27-32) such list of compounds which are structurally similar to FOX-7 and are

competitive to the potential and explosive power. Thus 2,6-diamino-3,5-dinitropyridine-1-oxide (DADNP-O, 8) rather than 2,6-diamino-3,5-dinitropyridine (DADNP, 4), 2,4,6-triamino-3,5-dinitropyridine-1-oxide (TADNP-O, 9), rather than 2,4,6-triamino-3,5-dinitropyridine (TADNP, 7), 2,6-diamino-3,5-dinitropyrazine-1-oxide (DADNP-O, 10) rather than 2,6-diamino-3,5-dinitropyrazine (DADNPN, 5), 2,5-diamino-3,6-dinitropyrazine-1,4-dioxide (DADNP-DO, 11) rather than 2,5-diamino-3,6-dinitropyrazine (DADNP, 6) were of great interest as explosives. Un-oxidized form of these compounds (8, 9, 10 and 11) is an intermediate in the synthesis of N-oxides. The compound (DADNP-O, 10) is also popularly known as LLM-105. The un-oxidized forms, compounds, (4), (5), (6), (7) are structurally more similar to FOX-7 (2). Compounds 8 and 9 were available since last decade but were not widely used as these are not much better than TATB in terms explosive properties and thermal stability. Explosive properties of compounds 10 and 11 are comparable to FOX-7, (2) but preparation involves multiple and complicated synthetic steps at least four steps compared to single step preparation for FOX-7. The other molecules (4 to 9) show inferior explosive performance, partly due to their poor oxygen balance and thus not attractive.

Compounds (12) and (13) are the *trans*- and *cis*- isomer of FOX-7 (2). Compound 1,3-dinitro-1,3-diazacyclobutane (14) is also an analogous to RDX (1).

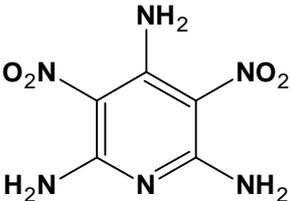
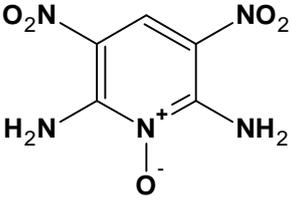
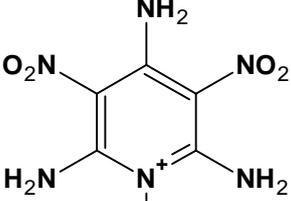
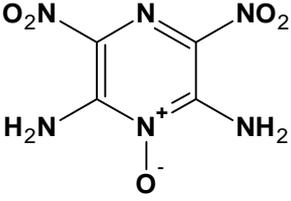
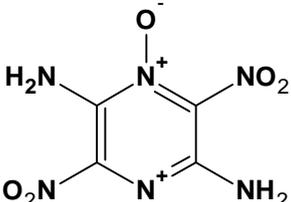
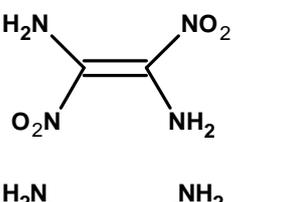
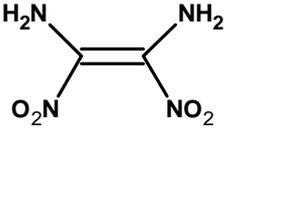
In spite of determined efforts by various researchers, the compounds 12, 13 and 14 have not yet been synthesized by the scientists and hence theoretically calculated properties were compared with FOX-7. Politzer et al. (33-34) computed the relative energies of above three isomeric diaminodinitroethenes (12,13 & 14) and concluded that the relative stabilities

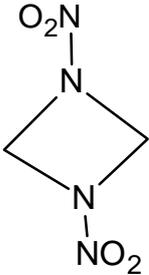
and molecular geometries of all three molecules are largely dictated by the available 'push-pull' electronic delocalization and intramolecular hydrogen bonds. The heat of formations of compounds (12, 13 & 14) at 25 °C were reportedly to be calculated by Politzer P et al. ( 35), Sorescu D C et al. ( 36) to be -80, -29 and 218 kJ mol<sup>-1</sup> respectively compared to -113 kJ mol<sup>-1</sup> for FOX-7 and +192 kJ mol<sup>-1</sup> for RDX . So the compound 1,3-dinitro-1,3-diazacyclobutane (14) contain considerably more energy than FOX-7. However as these compounds were not been able to be synthesised so far hence, not available for application trials and thus the **FOX-7 become the only focus as the replacement of RDX.**

Compound TATB (3) is extremely insensitive towards external stimuli which is not desirable always and has moderate performance compared to RDX / HMX. Performance of TATB (3) as insensitive munitions is widely tested and largely accepted only to meet special requirement in strategic weapon systems. Thus the compound, FOX-7 (2) is very attractive as replacement for RDX (1). FOX-7 (2) can easily be synthesised basically by single step reaction like RDX (1) and performance of (2) is equivalent to (1). Mostly strong hydrogen bonding (intra and inter molecular) and extended resonance exists in FOX-7 (2) which are responsible to exhibits such special behaviour. Swedish Defence Research Agency has first reported about the feasibility on synthesis of FOX-7 (2). However, detailed development, scale-up, formulation needs through investigation and hence it is of National interest to carryout research in such area like development of FOX-7 to prepare insensitive munitions for futuristic applications.

Table 1.2 Comparative data on physical and explosive properties of RDX, FOX-7, TATB and structurally similar compounds

Number	Compound	$\rho$ (g/cc)	MP or DP Temp (°C)	VOD (km s <sup>-1</sup> ) / $p_D$ (kbar)
1.		1.82	202	8.9 / 347
2.		1.89	278	8.87 / 366
3.		1.93	380	7.87 / 285
4.		1.75	345	7.4 / 242
5.		-	357	8.47 / 334
6.		1.88	288	8.46 / 334

7.		1.82	353	7.6 / 260
8.		1.84	340	7.8 / 276
9.		1.88	308	8.0 / 291
10.		1.91	343	8.7 / 358
11.		1.91	343	8.7 / 358
12.		-	-	-
13.		-	-	-

14.		-	163*	8.46*
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\* Predicted properties

### 1.6 Explosive Properties of FOX-7

The main international interest in FOX-7 is to consider it as the replacement for the secondary explosives (RDX). The detail explosive properties and performance (22) of FOX-7 is compared against that of RDX and given in Table 1.3 This properties demonstrates superiority of FOX-7 over RDX as an attractive. RDX is rather a vulnerable explosive material with relatively high sensitivity to both impact and friction. In contrast, FOX-7 is much less sensitive to impact and very insensitive to friction. The performance like detonation velocity and detonation pressures is comparable to that of RDX.

**Table 1.3 Comparison between RDX & FOX-7**

<b>Properties</b>	<b>FOX-7</b>	<b>RDX</b>
CRYSTAL DENSITY (g/cc)	1.88	1.81
VOD(m/s), cal.	9090	8940
Detonation press (G Pa)	36.6	34.7
Oxygen balance (%)	-21.6	-21.6
Heat of formation (kcal/mole)	-32	16
Impact sensitivity, h <sub>50</sub> (cm)	60	38
Friction sensitivity (kg)	36	12
Ignition Temp. (°C)	>215	>220
Activation Energy (kcal/mol)	56	40

## 1.7 Aim and outline

The present research work which has been carried out in close co-operation with research institutes and industry is outlined broadly to investigate the insight in 1,1-diamino-2,2-dinitroethene (FOX-7) process and product development in order to ascertain the better yield and quality. Detail Literature survey (37-47) has been carried out on the FOX-7. Information is mostly limited to synthetic route and its preparation at laboratory level, explosive hazards (like impact and friction sensitivity, detonation velocity, vacuum stability, thermal sensitivity, energy of formation, detonation pressure etc.) associated with the FOX-7, formulation based on FOX-7, applications in the military field, advantages of FOX-7 based composition over conventional high explosive like RDX etc. But the critical issues like preparation, process optimization, reaction kinetics, process thermal hazards, process heat transfer analysis, phenomena on batch and continuous mode of nitration reaction, parametric sensitivity and process safety for the batch reactor, reaction and reactor modeling for FOX-7 preparation, process scale-up and control strategy, spherical FOX-7, conformational structure of FOX-7 etc. are hardly ever reported. Hence, researches in the above directions were needed to understand the process as well as the product. Thus the present work was planned and carried out in the following order.

The synthesis process for FOX-7 has been established at laboratory level by batch nitration reaction of 2-methyl-4,6-dihydroxy-pyrimidine (MPD) using concentrated nitric acid ( $\text{HNO}_3$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) followed by hydrolysis to yield the product, FOX-7. Nitration and hydrolysis Process optimization were carried out by conducting the planned batch experiments to find the effect of reaction time, reaction temperature, mole ratio of raw materials, rate of addition, rate of agitation, order of addition of raw materials

etc. on the yield, purity, particle size distribution of the products. Trends were analysed by graphical techniques leading to give the optimal conditions. The work has been presented in International Seminar on High Energy Materials Conference and Exhibits (HEMCE), 2009 at Pune, India (48-49).

Thermo-chemical parameters of the nitration reaction were evaluated by conducting experiments in Differential Scanning Calorimeter (DSC) followed by Reaction Calorimeter (RC). Calorimetric data were analysed using DSC and RC software. The work (50) has been presented in International Seminar on High Energy Materials Conference and Exhibits (HEMCE), 2007 at Chennai, India. Thermochemical data for MDP nitration reaction have also been evaluated in RC under power compensation mode.

Reaction kinetics for nitration and hydrolysis process were find out by carrying out experiments to find the concentration profile and analyse the data by differential technique. The work has been presented in International Autumn Seminar on Propellants, Explosives and Pyrotechnic (IASPEP), 2007 at Xian, Chaina (51).

Modelling of the reaction and reactors primarily based on fundamental principles of reaction engineering and phenomenological explanations and validating the same using experimental results. In order to overcome the limitations of batch process, feasibility studies of nitration reaction carried out by continuous mode in micro-tubular reactor. The micro-tubular reaction system has been modelled using two dimensional (2-D) heat flow and mass transfer equations. Micro reactor is having extremely high surface to volume ratio, which has been explored to carry out nitration of MDP both numerically as well as experimentally and the results were compared with batch reactor.

These models were useful for analyzing, scaling up, designing and optimizing the reactor system (52-53).

Parametric sensitivity and stability of the MPD nitration reactor were studied on computer to visualize the reactor trajectory induced by small changes in parameters across threshold values. The system is modelled using the kinetic rate expression developed by conducting the experiments on nitration of MPD. The control parameters like initial reactor temperature, circulator temperature, concentration etc. for nitration of MPD were used to find the reactor behaviour and parametric sensitivity of the system. The work has been present in International Seminar on High Energy Materials Conference and Exhibits (HEMCE), 2007 at Pune, India (54).

In order to meet certain special application in high explosive / propellant formulation with spherical morphology of FOX-7 it was essential to prepare spherical particle of FOX-7. Spherical FOX-7 have no where been reported in literature. Morphology of as synthesised FOX-7 is rectangular layered type structure. Using the concept of miceller nano reactor spherical FOX-7 particle have been prepared at HEMRL and analyzed in association with National Chemical Laboratory (NCL), Pune. The research work is being published in Journal of Energetic materials (55).

Most of the properties of HEMs such as sensitivity, rate of deflagration to detonation, detonation velocity, detonation pressure, crystal density, thermal and shock stability and crystal morphology depends largely on their solid-state structure. In order to understand such unique properties of FOX-7, the precise knowledge of both the atomic and molecular arrangements are essential. Thus single crystals structure investigations were carried out at various temperature along with hot-stage microscopy. The crystals were made in different solvent at

HEMRL then the product X-ray diffraction at different temperature followed by analysis were done in association with National Chemical Laboratory (NCL), Pune. The research work is being published in Propellant Explosives and Pyrotechnics (56).

In order to analyse and characterize the FOX-7, chemical method was developed (57) for purity estimation as well as various instrumental techniques like differential scanning calorimeter (DSC), gas chromatography (GC), high purity liquid chromatography (HPLC), Nuclear magnetic resonance (NMR), Infrared (IR) spectra, scanning electron microscope (SEM) etc. were used for other properties. Explosive nature were characterized by impact, friction and spark sensitivity test.

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## Chapter 2

# Process selection and Optimization

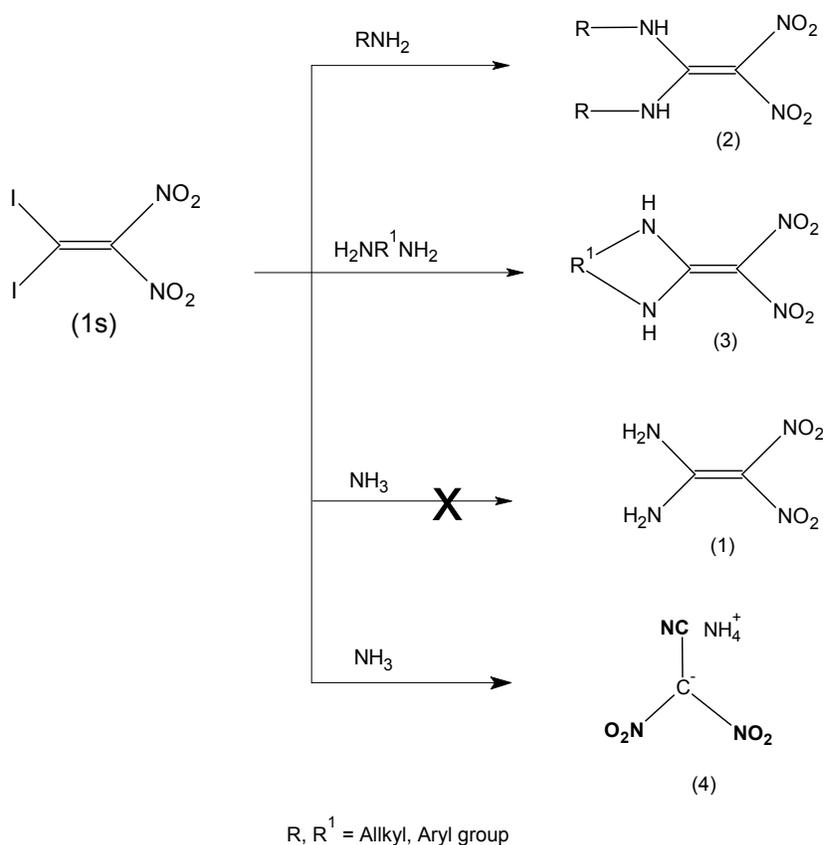
## 2.1 Introduction

1,1-Diamino-2,2-dinitroethene (FOX-7) has become widely known new insensitive high explosive with great potential for wide applications (1, 2) including the most important as the replacement of RDX. A few synthetic methods were reported to prepare FOX-7 at laboratory level, however these methods are tedious and multiple step procedure involving several unstable intermediates. Based on the initial feasibilities on synthesis by various researchers, the method suggested by Latypov et al. was the most promising which is published in 1998 (3). An alternative route suggested by Astra'ev et al. (4) by using commercially available 2-methyl-4,6-dihydroxy-pyrimidine and published in 2001. This method has been adopted (due to simplicity and better yield) for the present research work though the detail information about the course of reaction including various process parameters and its effect on the yield are not available. The process mentioned by Astra'ev et al. (4) and Chung et al. used excess quantity of the reactants (~18 equivalent moles of nitrating agent against 4 moles of stoichiometric requirement) leading to lesser yield as well as generation of excess effluent. Hence the research work presented in the thesis has been taken up for improvements not only for the process at the laboratory level but also to consider the important aspect regarding the scale-up issues as well as product development using the concept of micellar based nano reactor etc. In view of this, details about process selection as well as the optimization of all the process parameters have been carried out and discussed in the subsequent sections.

## 2.2 Synthetic route of FOX-7

### 2.2.1 Amination of 1,1-diiodo-2,2-dinitroethene

1,1-Diamino-2,2-dinitroethene (FOX-7) is a canary-yellow solid and may be re-crystallized from variety of solvents. It was first synthesised by Baum et. al. (6-8). The reaction of 1,1-diiodo-2,2-dinitroethene (1s) with various amines were examined critically during their study as shown in the Scheme 2.1 as below.



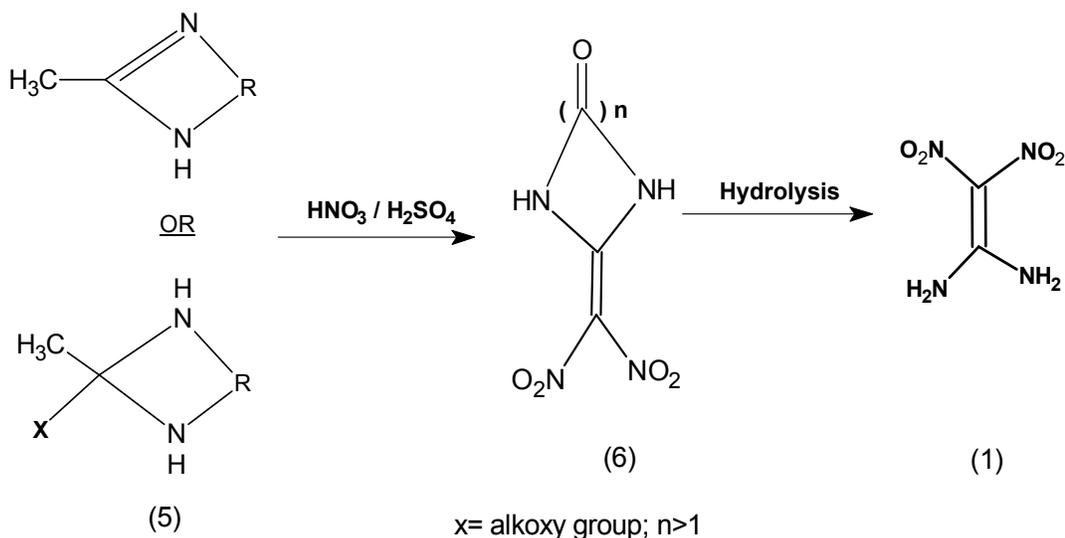
Scheme 2.1. Reaction of 1,1-di-iodo-2,2-dinitroethene to synthesis substituted di-nitroethene

In the Scheme 2.1 it was found that only a few types of amines were reported to react to give the replacement of both iodine by amine functions and forms the compounds corresponding to 1,1-bis-alkyl-amino-2,2-dinitroethene (2) and 1,1-bis-aryl-amino-2,2-dinitroethene (3). When it was

aimed to prepare the compound (1) by allowing 1,1-diiodo-2,2-dinitroethene to react with  $\text{NH}_3$ , the ammonium salt of cyanodinitromethane (4) is formed.

### 2.2.2 Reaction of Heterocyclic compound

The first feasibility of successful synthesis of FOX-7 was reported by Swedish researchers from the National Defence Research Establishment, FOA (present name Swedish Defence Research Agency, FOI) (3, 5, 6) about the synthesis of DADNE. The general approach involves the nitration of a heterocyclic compound (5) to get the nitrated compound (6) followed by hydrolysis to produce FOX-7 (1) shown in Scheme. 2.2.

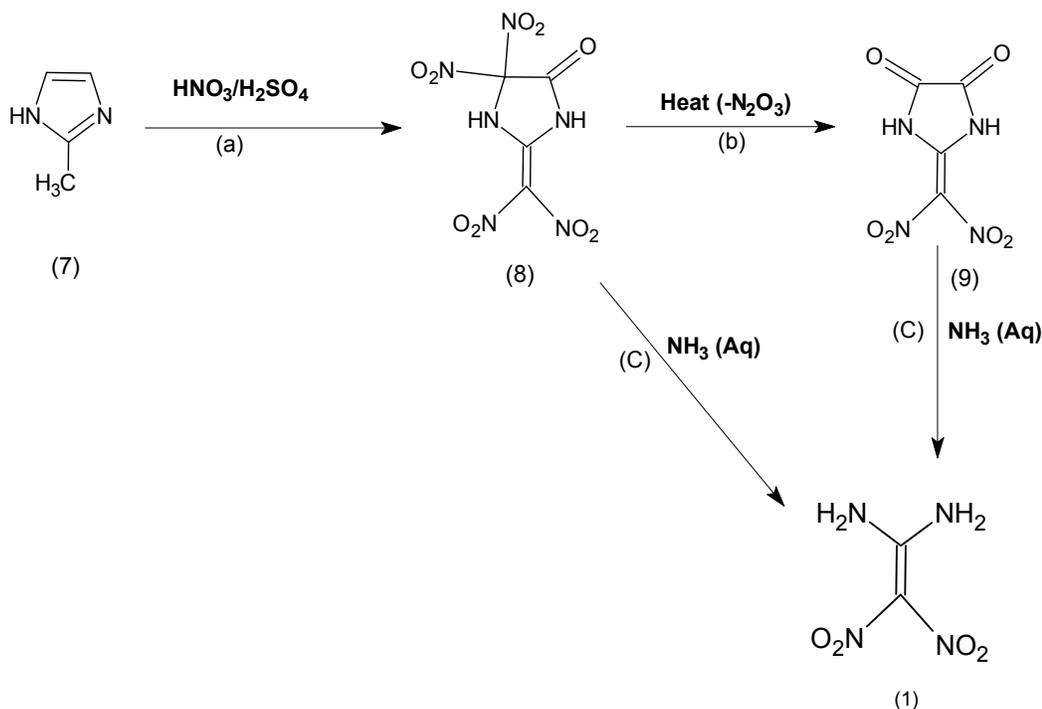


Scheme 2.2. Synthesis of 1,1-diamino-2,2-dinitroethene from hetero-cyclic compound

The nitration was carried out in low temperature ( $< 30^\circ \text{C}$ ) using mixed acid. Hydrolysis was described to be carried out by isolating nitrated intermediate either using aqueous ammonia or by adding acidic mixture of nitrated intermediate to water. Based on these, three different methods were suggested that looks to be promising which are discussed in subsequent sections.

### 2.2.3 Reaction of Methylimidazole

Nitration of 2-methylimidazole (7) using oleum and nitric acid as nitrating mixture produces a probable intermediate of tetra-nitro derivative, 2-dinitromethylene-4,4-dinitroimidazolidin-5-one (8) shown in Scheme 2.3.



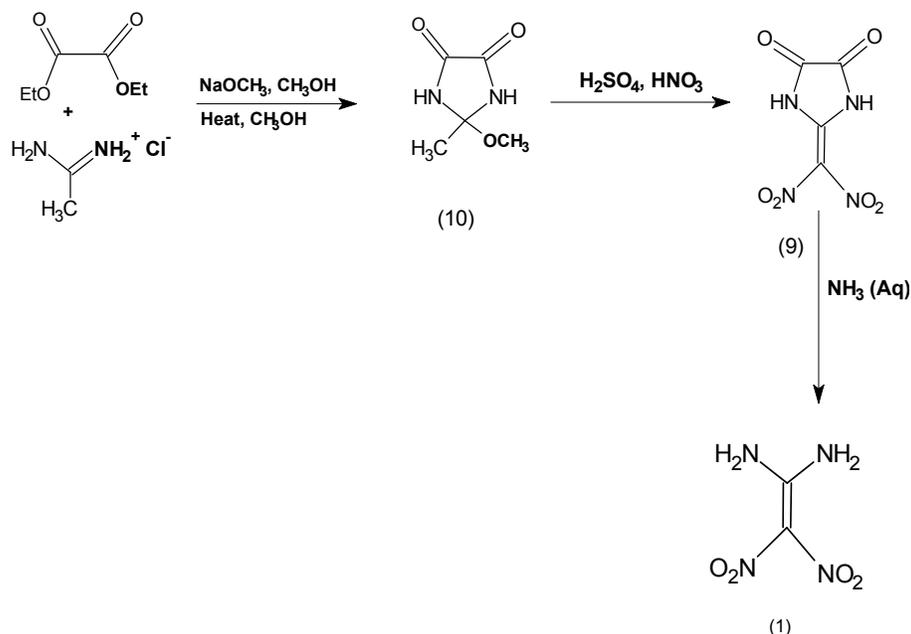
Scheme 2.3. Synthesis of FOX-7 by Nitration of 2 methylimidazole

This route was first suggested by Latypov. The nitration temperature was controlled at 15-20 °C. The compound (8) is thermally unstable which is easily decomposed to loss the elements equivalent to  $\text{N}_2\text{O}_3$  to form 2-dinitromethyleneimidazole-4,5-dione (9) at ambient temperature or in solution. The compound (9) was isolated as white precipitate. The dione (9) was subsequently hydrolysed with aqueous ammonia to give FOX-7 (1) as shown in Scheme 2.3. Factors disfavoring this approach is that, the intermediate, 2-dinitromethylene-4,4-dinitroimidazolidin-5-one (8) is highly sensitive energetic

material and the very inefficient nitration reaction results in an unacceptably low overall yield of <13%.

### 2.2.4 Reaction of Methoxy-Methylimidazoledione

Another route to the preparation of FOX-7 was also reported by Latypov et al.(3). This involves nitration of methanol adduct of 2-methoxy-2-methylimidazoledione-4,5-dione (10) shown in scheme 2.4.



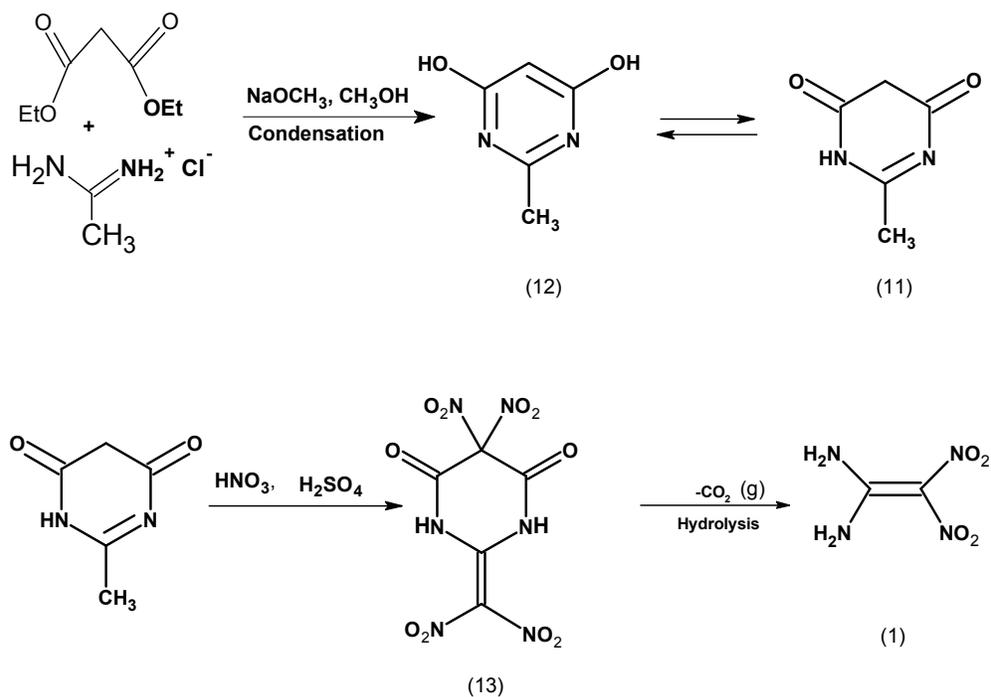
Scheme 2.4. Synthesis of FOX-7 from 2-methylimidazolidine-4,5-dione

The compound 2-methoxy-2-methylimidazoledione-4,5-dione was synthesised by Condensation of diethyl oxalate with acetamidine hydrochloride at high dilution in methanolic sodium methoxide, followed by recrystallisation from methanol .The reaction scheme is shown in the Scheme 2.4. The compound 2-methoxy-2-methylimidazoledione-4,5-dione (10) is then nitrated by using concentrated (98%) mixed acid to produce 2-dinitromethyleneimidazole-4,5-dione (9). The yield of the nitration step is about 65%. Hydrolysis of 2-dinitromethyleneimidazole-4,5-dione (9) with aqueous ammonia give 1,1-diamino-2,2-dinitroethene, FOX-7 (1). The yield of hydrolysis step is about 85% and overall yield from acetamidine hydrochloride is about 36%. Besides, the

other drawbacks of this process are high dilution is required in the first step which is inconvenient because large volume reaction vessels are required. An exotherm has been reported during the ammonolysis step, which also can result in the product out of the reaction vessel due to frothing which can not be controlled. The purity of FOX-7 in this route is above 95 % however some contamination of oxamide ( $\text{H}_2\text{NC(O)C(O)NH}_2$ ) present in the FOX-7. The chances of oxamide in the product is very less when the temperature of the ammonolysis process is maintained at about  $20^\circ\text{C}$  followed by recrystallisation of the product in dilute hydrochloric acid.

#### **2.2.5 Reaction of Methyl-Pyrimidine-Dione**

In order to overcome the above disadvantages, developmental work in this direction were continued in the various parts of the globe. Latypov et al. (9-11) have shown that nitration of the analogous 2-methyl-4,6-dihydroxypyrimidine (12) gives better yield of 1,1-diamino-2,2-dinitroethene, FOX-7 (1) than 2-methoxy-2-methylimidazoledione-4,5-dione (10) given in Scheme 2.5.



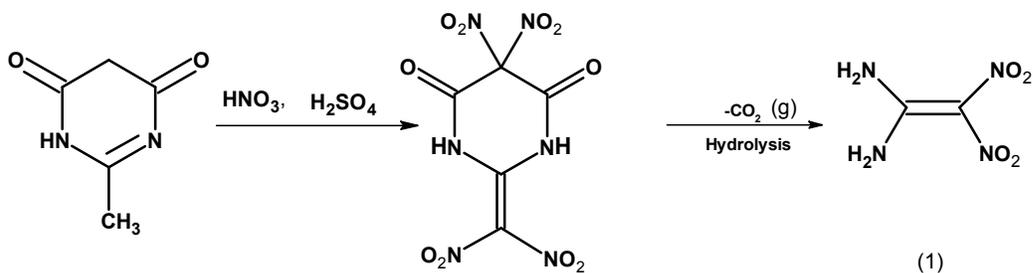
Scheme 2.5. Preparation & nitration of methyl-dihydroxypyrimidine (12)

After nitration, the nitrated intermediate, 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione(13) which can be separated from the spent mixed acid slurry followed by hydrolysis to get the product and the spent mixed acid can be recycled under modified nitrating conditions. However, the nitrated intermediate 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione (13) is unstable and easily absorbs moisture and gets liquefied. To overcome this problem, the unfiltered slurry was simply added to water and left for several hours under agitation to get the product 1,1-diamino-2,2-dinitroethene, FOX-7 (1). Yield of the process is more than 85%. The starting nitrating compound, 2-methyl-4,6-dihydroxy-pyrimidine (12) can be prepared by condensation of acetamidine-hydrochloride and diethylmalonate in presence of strong alcoholic base (e.g. Sodium methoxide / ethoxide) and corresponding alcohol (e.g. methanol / ethanol). The compound, 2-methyl-4,6-dihydroxy-pyrimidine (12), can exist in

2, methyl-pyrimidine-4,6-dione (11) through keto-enol tautomerism. This compound (12) is available commercially and gives a better overall yield.

### 2.3 Selection of FOX-7 Synthesis route

After the through study of all the routes described in the section 2.2 and also after analyzing the feasibilities of synthesis of these routes, the reaction scheme 5 has been selected for the present research work. Hence, the much effort on research has been made for the development of nitration and hydrolysis reaction which will be described in present research work. FOX-7 is prepared by nitration of commercially available MPD to get NMPD followed by acid catalyzed hydrolysis of NMPD. Both nitration of MPD and Hydrolysis of NMPD are critical because these reaction has the distinct tendency of runaway at temperature more than 25 °C for nitration and at temperature greater than 45 °C for hydrolysis. While nitration, this was clearly seen by generation of dense nitric oxide fumes in case of cooling failure and during hydrolysis it was also well seen to be generated by evolving a copious frothing of reaction mixture. In this regard, detail process information have not been reported in the literature. Besides, the key information like parameter optimization and hydrolysis mechanism under optimum hydrolysis conditions are not reported in the literature. Hence, to understand the synthesis process a thorough investigation was needed to generate the information for the same. The over all reaction is given below as Scheme 2.6.



Scheme 2.6: Overall reaction for preparation of FOX-7

## 2.4 Reaction mechanism

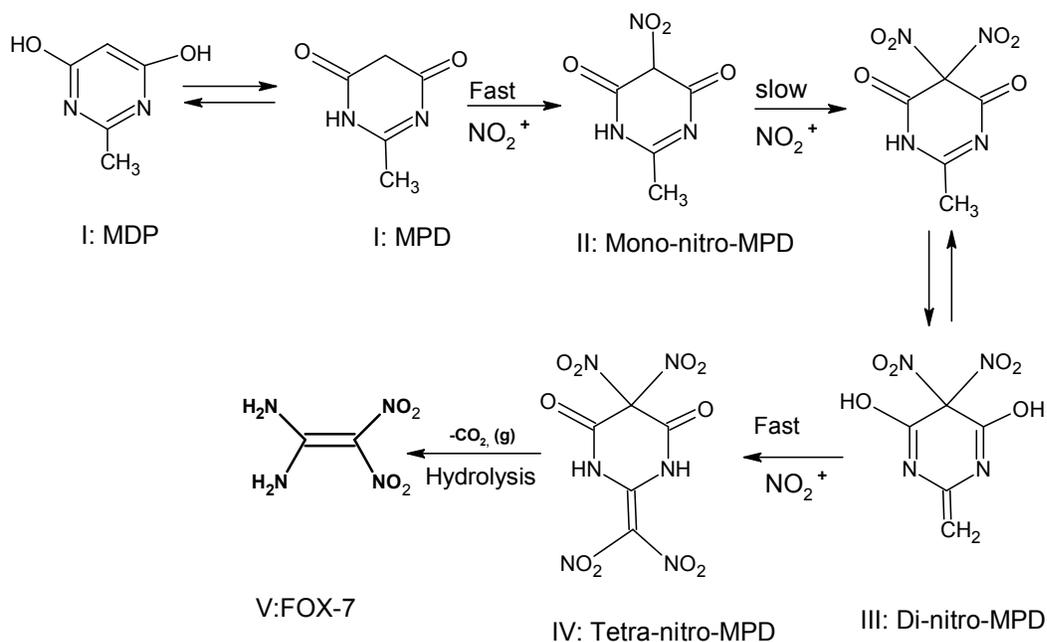
Nitration of MDP is a highly exothermic reaction where a mixture of concentrated sulphuric acid, H<sub>2</sub>SO<sub>4</sub> (98%) and nitric acid, HNO<sub>3</sub> (98%) are used as nitrating agent. MDP was first dissolved in the concentrated sulfuric acid followed by slow addition of concentrated nitric acid into it.

The probable mechanisms of formation of nitronium ion and progress of reaction are proposed in Scheme 2.7 and 2.8 respectively (8-9)



Scheme 2.7. Formation of nitronium ion in mixed acid

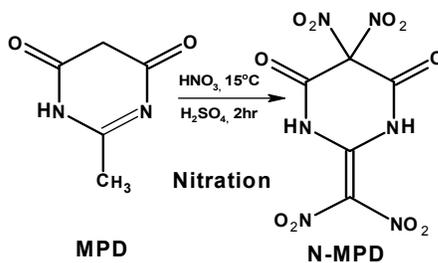
In the scheme 2.8 it is seen that, during Nitration the formation of mono-nitro derivative (compound II) is relatively fast while nitration to a di-nitro derivative (Compound III) is slow (allowing isolation of the mono-nitro derivative) and further nitration is fast (preventing the isolation of any other intermediate before the tetra-nitro derivative is formed). The relatively slow rate of the second nitration is probably a consequence of the destruction of the aromatic system when 5,5 di-nitro-derivative (compound III) is formed. This also probably facilitates enolisation on to the methyl group and further nitration at that position to form tetra-nitro-derivative (compound IV). Tetra-nitro-derivative is then hydrolyzed in presence of acid to form the desired product FOX-7. (V)



Scheme 2.8. Reaction Mechanism involve in nitration of MDP

## 2.5 Nitration Process Optimization

Nitration reaction studied is shown in Scheme 2.9.



Scheme 2.9 : Nitration of MPD (methyl-pyrimidine-dione)

During the nitration of MDP\* various process parameters like, nitration time, nitration temperature, quantity of acid, solubility of MDP in sulfuric acid, hydrolysis time, hydrolysis temperature, mode of addition (either addition of solid MDP in to the mixed acid or addition of concentrated nitric acid into the pre-dissolved solution of MDP in sulfuric acid) etc. were studied to optimize the process. The details study were described in the subsequent sections.

\* MDP, methyl-dihydroxy pyrimidine  $\equiv$  MPD, methylpyrimidinedione

### 2.5.1 Experimental and Discussion

In order to carry out the process development studies, a dedicated glass reaction unit was designed and installed at the laboratory. Experimental set-up (Fig.2.1) consists of cylindrical jacketed glass reactor (500 ml capacity) fitted with driving motor, agitator (pitch bladed turbine), condenser, temperature sensors / indicators, in the reactor as well as jacket inlet & outlet. The proportional-integral-differential (PID) controlled cryostat cum thermostat unit (5 lit capacity) for circulation of chilling/heating media through the jacket of the reactor is connected to maintain the reaction temperature. Photograph of actual experimental setup is shown in Fig. 2.2. Experiments were conducted at 10 g batch level. During experiments, predetermined quantity of MDP was dissolved in  $\text{H}_2\text{SO}_4$  at an optimized temperature. Metered quantity of  $\text{HNO}_3$  is then added at controlled rate to the  $\text{H}_2\text{SO}_4$  – MDP solution by maintaining the temperature at a desired level. Each experiment at a certain predefined process conditions was repeated at least three times to ensure the repeatability of the out-come. The products were subsequently analyzed / characterized using both chemical and instrumental methods before acceptance the quality of the product.

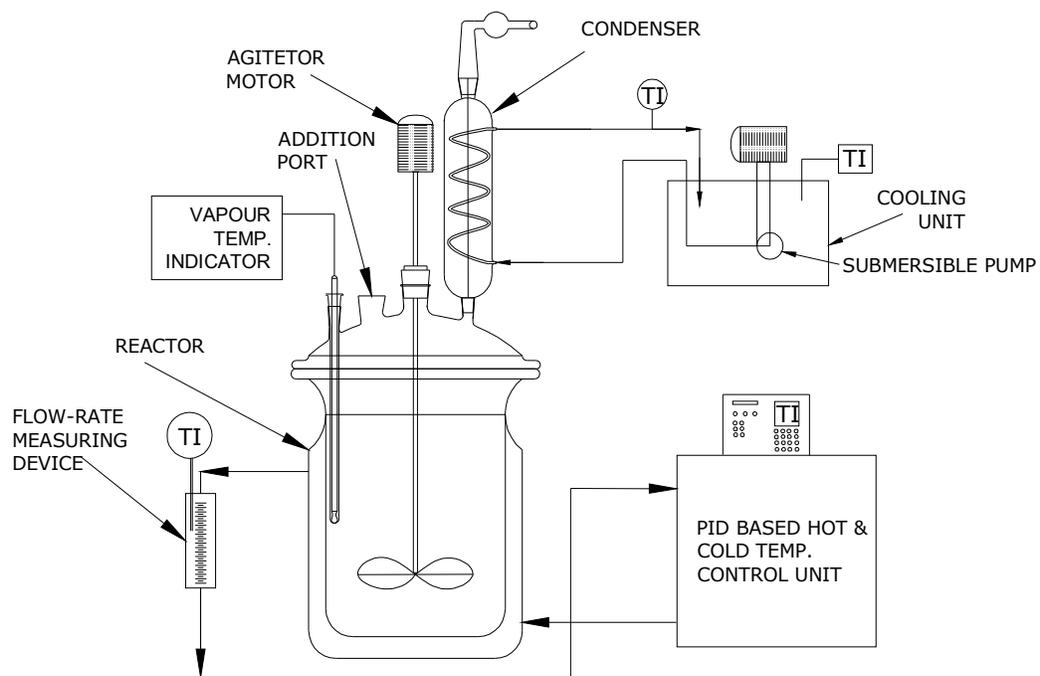


Fig.2.1. Experimental setup of Glass reactor to carry out the reaction



Fig.2.2. Photograph of Experimental set-up during hydrolysis

### 2.5.1.1 Effect of moles of sulfuric acid

During the course of nitration reaction it is observed that highly viscous (~7500 cp, calculated) nitrated reaction mass is formed. MDP is dissolved in Sulfuric acid (98%) followed by controlled addition of Nitric acid

(98%) is done to progress the reaction. Hence, it was essential to see that whether by increasing the amount of sulfuric acid, viscosity of the nitrated reaction mass can be reduced without compromising the yield of the process. In order to find out this, four sets of experiments were conducted with 10, 11, 12 and 14 moles of concentrated sulfuric acid keeping other parameters constants. Outcome of the experiments were plotted and shown in Fig. 2.3. It is observed though the viscosity of the reaction mass reduced but the yield of the process drops, hence it was decided to use 10 moles of  $H_2SO_4$  (98%) as optimum amount.

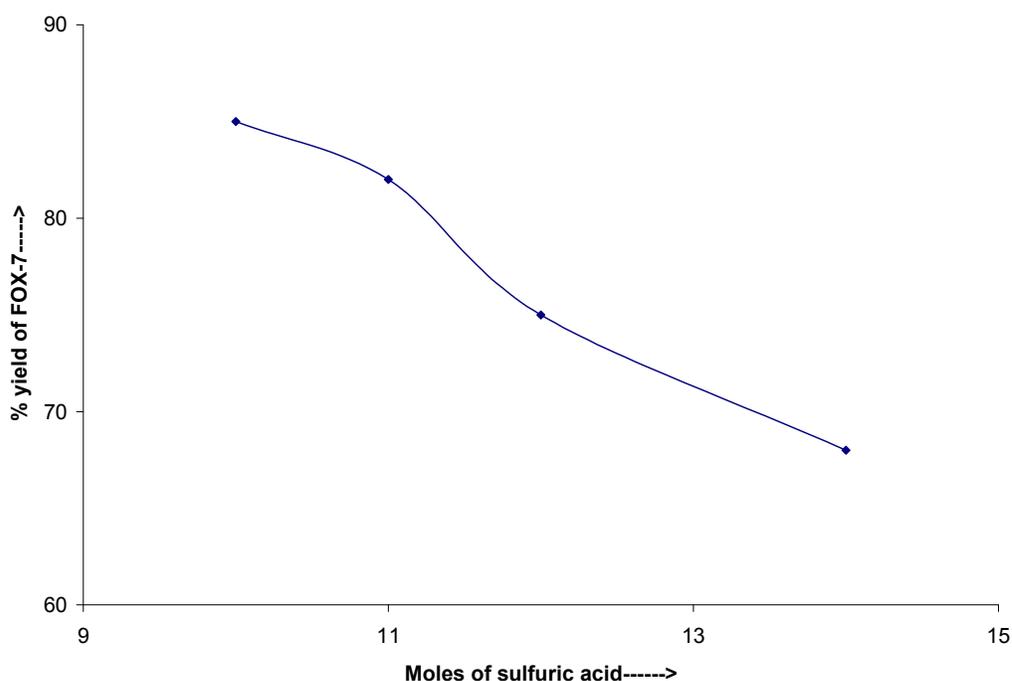


Fig. 2.3 Effect of Moles of Sulfuric acid on yield of FOX-7

### 2.5.1.2 Effect of moles of nitric acid

In order to optimize the moles of concentrated nitric acids (98%), for the fixed amount of concentrated sulfuric acid (98%) and MDP four sets of experiments were conducted. Stoichiometrically, 04 moles of nitric acids are required for the nitration reaction, so the experiments carried out starting with 04 moles and subsequently at 05, 06 and 07 moles of nitric acid. After each

experiment, product were analysed and characterized to ensure the quality. % Yield and corresponding moles of nitric acid were plotted and shown in Fig 2.4. It is observed that with 05 moles, yield of FOX-7 is maximum (~ 85%) and beyond 05 moles, yield declines.

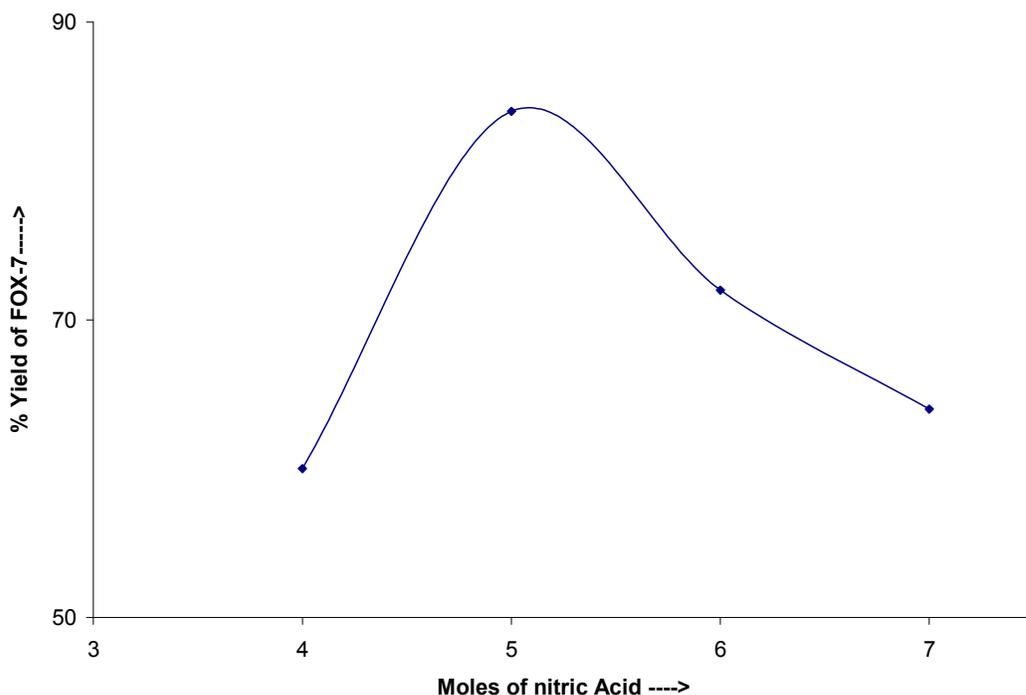


Fig.2.4 Effect of Moles of nitric acid on yield of FOX-7

### 2.5.1.3 Effect of temperature on solubility of MDP

In-order to optimize the dissolution time and temperature, measured quantity of MDP was added to the 98% concentrated sulfuric acid under continuous agitation. Six sets of experiments were conducted at different temperatures of 25, 40, 50, 60, 70 and 80 °C till the time of complete dissolve of the solid. Optimized amount (i.e. 10 moles per moles of MDP) of sulfuric acid was used in each set of experiment. Experimental results are shown in Fig.2.5. Dissolution of MDP in sulfuric acid is also an exothermic process. Details of the study on heat of dissolution of MDP in sulfuric acid is described

in Chapter 3. So, the dissolution of MDP at relatively higher temperature ( $> 50$  °C) is not preferable, while at lower temperature duration of dissolution extends longer. Hence, the temperature of  $50$  °C and dissolution time of  $\sim 40$  minutes are considered to be optimized for the process development.

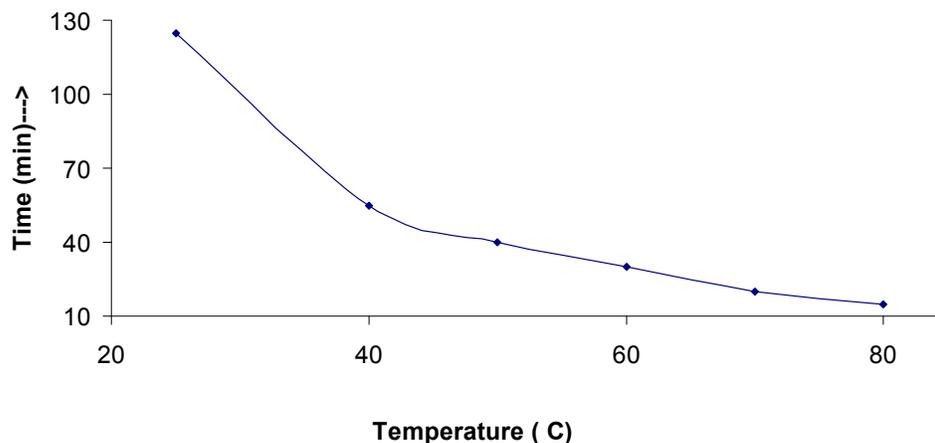


Fig. 2.5 Effect of Temperature on dissolution of MDP in sulfuric acid

#### 2.5.1.4 Nitration Temperature Domain

Nitration of MDP is highly exothermic reaction (heat of reaction evaluated during thermo-chemical studies discussed in chapter 3) with low decomposition temperature ( $\sim 100$  °C) for the reaction mass. Hence, it was essential to know the nitration reaction domain temperature. In order to determine the same, experiments were conducted in five different sets of temperature starting at  $5$  °C with an interval of  $10$  °C. Each set of experiment is carried out for a total reaction time of 2 hrs. Solid content produced in each set is plotted and shown in Fig.2.6. At higher temperature (both at  $25$  and  $35$  °C), nitration reaction proceeds faster, however side reaction increases to produce

undesired water soluble impurities (di/tri nitro methane) for longer duration (i.e. at 2 hrs) resulting in decline of overall yield of solid content.

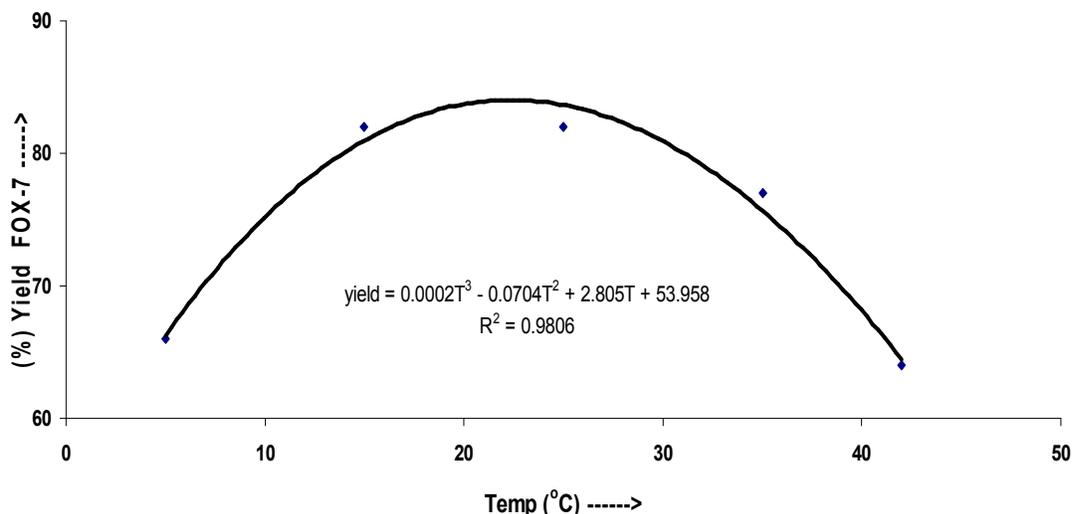


Fig. 2.6 Effect of Temperature on nitration reaction domain

At lower temperature (5 °C ) reaction is quite slow to produce desire quantities of solid content. However, at 15 °C, formation of solid content is consistent and progressively increased till formation desired quantities in 2 hrs. Hence, 15 °C is considered as optimum domain for the nitration.

#### 2.5.1.5 Effect of Temperature on the yield of FOX-7

In order to find the maximum yield of FOX-7, three sets of experiments at 5, 15 and 25 °C were conducted for different time interval. Product obtained after each experiment at different time interval was thoroughly washed and made acid free and then dry product is characterized by instrumental methods and product purity by chemical method. Based on the analytical results yield was calculated and plotted for different sets of temperature of 5, 15 and 25 °C as shown in Fig.2.7.

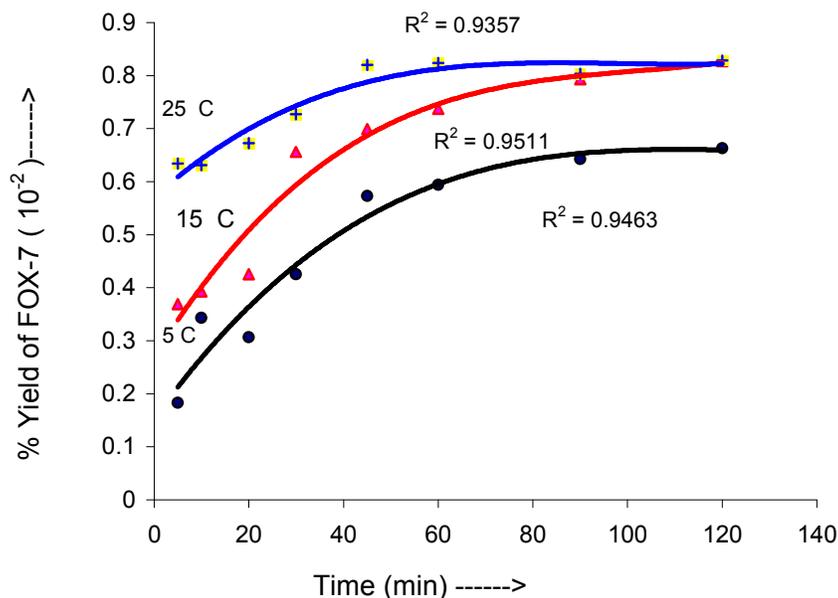


Fig. 2.7 Variation of yield of FOX-7 with time and temperature

yield of product at 35 °C and 45 °C are less and the purity of the product obtained at these temperature is also less than the desired mark (98% minimum) hence not taken in to consideration in this graph. It is seen from the Fig. 2.7 that though yield is nearly same at both 25 & 15 °C, the rate of formation of the product at 25 °C is much faster and also associated with higher rate of heat generation. However, at 15 °C the reaction progresses steadily with moderate rate of heat generation. Details of heat generation has been studied in reaction calorimeter and described in chapter 3. Hence, the temperature of 15 °C is seemed to be optimum from both process control and process performance point of view.

### 2.5.1.6 Effect of concentration of nitric acid

Generally, nitration of MDP is carried out with concentrated (98%) nitric acid. However, to reduce the process hazards, nitration reaction have been carried out at lower concentration up to 82 % for a period of 2 hrs. It is observed that even with less concentration of nitric acid, reaction takes place, but the yield is less. Experimental results are shown in Fig. 2.8.

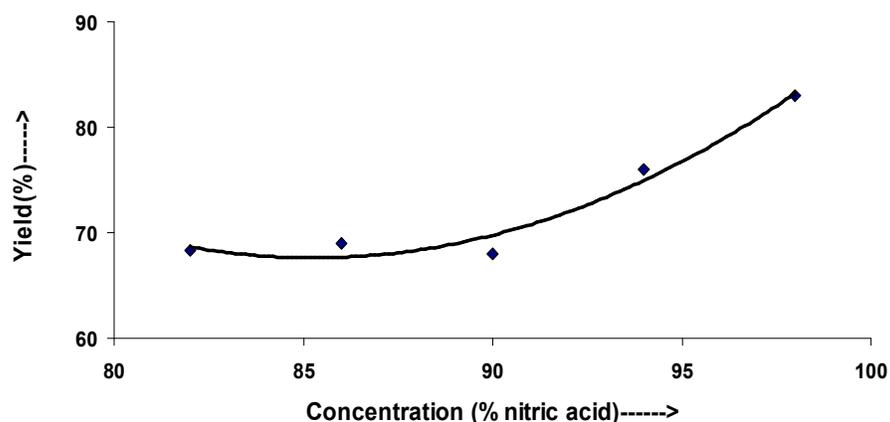
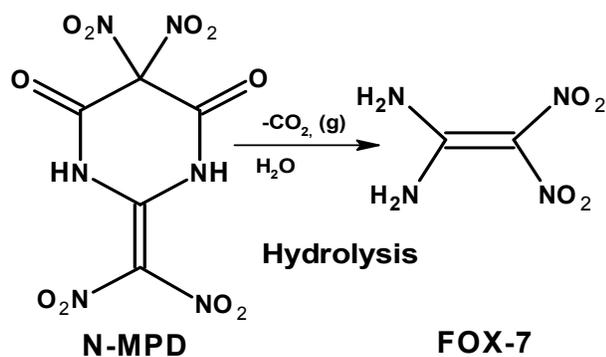


Fig. 2.8 Effect of Concentration of nitric acid on the yield of FOX-7

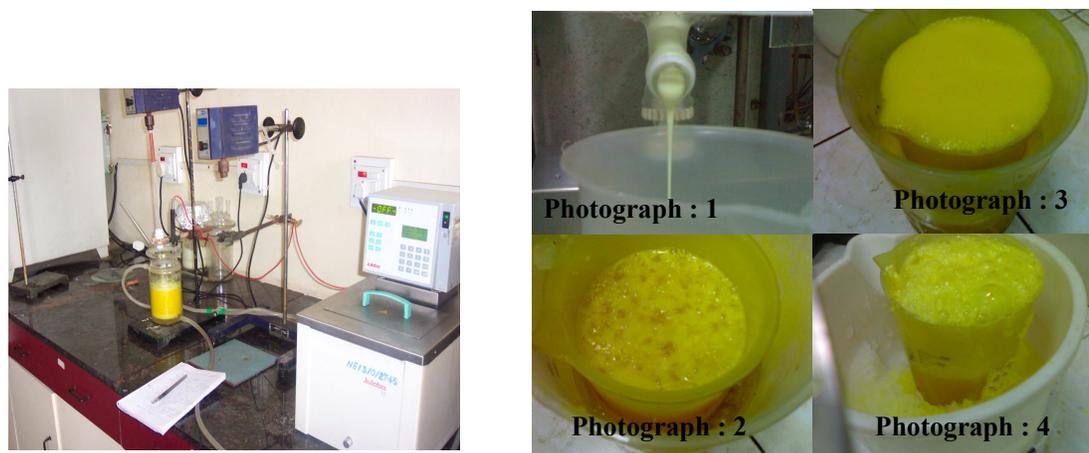
Hence, it is decided to conduct the nitration at 98 % concentration to maintain the process performance

### 2.6 Hydrolysis Process Optimization



Scheme 2.10 Hydrolysis step for NMPD

After nitration reaction, the reaction mass is quenched into the optimized quantity of water to carry out the acid catalyzed hydrolysis of Nitrated MPD under vigorous agitation. During acid catalyzed hydrolysis experiments, it was observed that the mixture is having a distinct tendency for runaway reaction at temperature  $\geq 45$  °C. This was clearly seen by copious frothing in the reaction mixtures and self-heating of the latter. Earlier preliminary experiments on hydrolysis by previous workers (10-16) have been reported however, a runaway phenomenon (Fig. 2.9) which is probably caused by  $\text{NO}_x/\text{HNO}_3$  catalyzed thermal decomposition of dinitromethane, a side product formed during nitration / hydrolysis. These problems were overcome, by carrying out designed experiments on hydrolysis and optimized the operating parameters like hydrolysis temperature, acid concentration (%), time and hydrolytic stability of NMPD.



a) Hydrolysis at 25 °C

b) Hydrolysis at  $\geq 45$  °C

**Fig.2. 9** Photograph of hydrolysis reaction at the temperature of 25 °C and at temperature  $\geq 45$  °C (runaway of hydrolysis reaction occurs )

### 2.6.1 Optimization of acid (%) for Hydrolysis

In order to optimize the quantity of water as well as acid % of aqueous solution for the hydrolysis process six sets of experiments were carried out at different acid concentration (%) of 11,13, 16, 20, 24, 28 and 44. After carrying out nitration reaction at predetermined optimized conditions as discussed in the previous section 2.5, nitrated reaction mass were put for acid catalyzed hydrolysis. All the hydrolysis experiments were conducted at a fixed temperature of 25 °C. and hydrolysis time of 6 hrs. After each experiments, product FOX-7 were isolated by filtration, washing followed by drying. % Yield of FOX-7 from the hydrolysis experiments were plotted against acid % in aqueous solutions for hydrolysis shown in Fig. 2.10. Maximum % of yield were observed at 20% of aqueous acidic solution and corresponding amount of water used ~300 ml for the batch size of 10 g MDP.

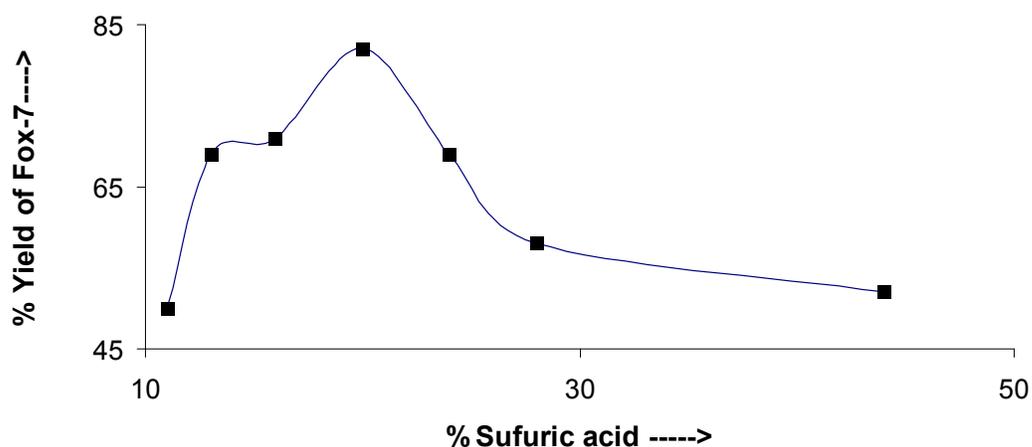


Fig. 2.10 Effect of % Sulphuric acid on hydrolysis of NMPD

### 2.6.2 Optimization of Hydrolysis Temperature & Time

In order to optimize other hydrolysis process parameters like temperature and time three sets of hydrolysis experiments were conducted at 15<sup>0</sup>C, 25<sup>0</sup>C

and 40°C. At each temperature, around 10 experiments were carried out under continuous agitation for different hydrolysis time ranging from 30 to 360 minutes at an interval of 30 minutes. After completion of each round, the solid product, FOX-7 is then filtered and washed with plenty of water for removal of acid present in it. The solid product after each run is then dried in the vacuum oven at 70°C for a period of 16 hrs. Maximum Moisture content allowed in the product FOX-7 was ~0.5%. The weight of the product was determined for each run after drying and decomposition temperature was determined by DSC. % Yield of FOX-7 from the hydrolysis experiments were plotted against time for all three sets of temperature is shown in Fig. 2.11. Experimental results suggest that the rate of hydrolysis becomes faster at higher temperature, besides the hydrolysis process is having a distinct tendency for runaway reaction at temperature  $\geq 45$  °C which was clearly seen by copious frothing in the reaction mixtures. Hence, 25 °C and the duration of 4 hrs are considered to be the optimum temperature for the hydrolysis process.

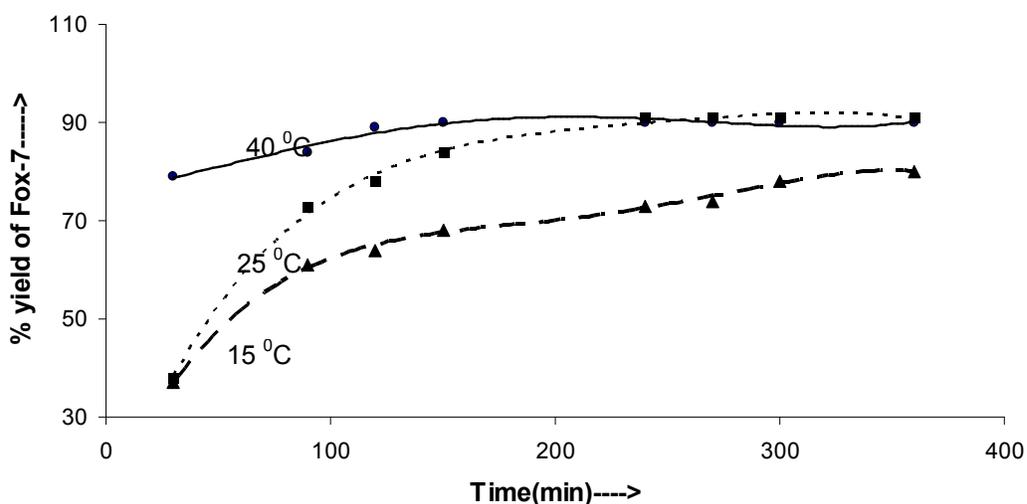


Fig. 2.11 Effect of Temperature on Hydrolysis with time

## 2.7 Conclusions

In this section of the thesis, process for synthesis of FOX-7 from the starting raw material of methyl-di-hydroxy-pyrimidine (MDP) also known as methyl-pyrimidine-dione (MPD) is selected and optimized the process parameters as well as operating conditions for maximum yield. During detail study of the process optimization which was carried out experimentally and results obtained were discussed in the above section. Detail study reveals, following optimized operating conditions which are selected for the process development given in Table 2.1 & 2.2

Table 2.1 Optimized operating conditions for nitration

Sr No.	Nitration Process parameters	Optimized Operating Conditions
1.	Moles of nitric acid per mole of MDP	5
2.	Moles of sulfuric acid per mole of MDP	10
3.	Temperature (°C) of Solubility of MDP in Concentrated Sulfuric acid	50
4.	Nitration Temperature (°C) Domain	5 - 35
5.	Temperature (°C) of nitration for optimum yield	15
6.	Nitration time (minutes)	120
7.	Concentration (%) of nitric acid and sulfuric acid	98
8.	Mode of operation & Type of reactor preferred	Batch process*

Feasibility of continuous process were also studied in details and discussed in the Chapter 5.

Table 2.2 Optimized operating conditions for nitration

Sr No.	Hydrolysis Process parameters <sup>@</sup>	Optimized Operating Conditions
1.	Moles of water per mole of MDP	210
2.	% Sulfuric acid required	20
3.	Temperature (°C) required for hydrolysis	25
4.	Hydrolysis Time (hrs)	4
5.	Run away conditions, Temperature (°C) & Tip-speed	≥45 & 0

The above optimum operating conditions have been used / authenticated in other developmental studies (like thermochemical studies, kinetics studies, feasibility on continuous MDP-nitration etc.) on the development of FOX-7 synthesis process.

<sup>@</sup> Characterization of the product, FOX-7 have been discussed separately in the Chapter 6.

## 2.8 References

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## Chapter 3

# Thermochemical studies of MDP Nitration process

### **3.1 Introduction**

#### **3.1.1 Calorimetry in Thermal hazard quantification**

Exothermic chemical reactions are generally accompanied by considerable amount of heat release. This needs a thorough investigation to quantify the magnitude before the reaction is taken up for scale-up at plant level. Amount of heat loss at laboratory level is relatively more which is essential to quantify the rate of heat release associated with the process chemistry. Uncontrolled and sudden release of thermal energy due to exothermic chemical decompositions often leads to serious fire and explosions in several chemical process plants. The explosion hazards are governed by the system thermodynamics and kinetics of the thermal process. But theoretical prediction of limiting temperature is difficult due to process complexities. Besides, the kinetic data generated through conventional methods at conditions far from runaway situation are often not valid for assessing the runaway behaviour of exothermic process.

Thermal hazard assessment basically relies on identification of dangerous process conditions, process deviations and thermal sensitivity of reaction mixtures and products. The main focus of this chapter is to discuss the causes and several contributing intrinsic safety parameters (Table-3.1) responsible for thermal runaway and instability conditions for MDP nitration process as well as quantitative assessment of such hazards by calorimetric methods. This will help in identification of various critical aspects of the MDP nitration reactions like,

- Assessing the sensitivity of critical operating parameters
- Avoiding the hazard course of reaction

- Assessing the temperature dependency of an undesired thermal event and its deviation from actual process operating conditions.

**Table 3.1 Intrinsic Safety Parameters Needed**

<b>Thermodynamic</b>	<b>Kinetic</b>	<b>Physical</b>
➤ Heat of Reaction / Reaction Energy	➤ Activation energy	➤ Heat Capacity
➤ Adiabatic Temperature rise	➤ Reaction Rate	➤ Thermal Conductivity
➤ Pressure rise and quantum of gas generated	➤ Rate of heat generation	
➤ On set temperature for decomposition of reaction mass	➤ Rate of rise in pressure in side the reaction vessel  ➤ Time to attain max. reaction rate  ➤ Apparent activation energy for on-set of decomposition	

For systematic assessment of thermal hazards experimentally, the important calorimetric techniques that have attained scientific importance due to their novelty in determining the reaction instability are

- Thermal analysis like Differential Scanning Calorimetry (DSC), Differential thermal analysis (DTA), Thermogravimetric analysis (TGA) etc.

- Accelerated rate Calorimetry (ARC)
- Reaction Calorimetry (RC)
- Reactive system screening tool (RSST)

DSC is regarded as a useful tool for the evaluation of thermal hazards and for evaluating the investigation of decomposition mechanism of reactive chemicals. The basic principle of DSC is to measure the heat flow as a function of temperature or time particularly at the temperature of phase transitions. This is achieved by measuring the difference in power required to maintain the temperatures of reference and test samples.

RC is also a very useful tool for evaluation of quantitative assessment of thermal hazards similar to the plant conditions. Data generated in the RC are useful in scale-up the process to plant level. The basic principle of the RC is heat flow measurement (temperature difference between jacket & reactor inside) and measurement of power compensation (flow power requirement to maintain reactor & jacket temperature constant).

In the present work, the evaluation of thermal hazards of the MDP nitration reaction has been carried out using Differential Scanning Calorimeter (DSC) followed by Reaction Calorimeter (RC) both.

### **3.1.2 Heat flow reaction Calorimetry**

The temperature of the reactor content ( $T_r$ ) is controlled by varying the temperature of the cooling liquid ( $T_j$ ). The heat flow rate from the reactor content through the wall into the cooling liquid ( $q_{Flow}$ ) is determined by measuring the temperature difference between reactor content and cooling liquid. In order to convert this temperature signal into a heat flow signal (e.g. Watt), a heat transfer coefficient is determined by using a

calibration heater. To allow a fast control of the ( $T_r$ ), the flow rate of the cooling liquid through the jacket should be high. Most of the commercially used reaction calorimeter is based on the heat flow principle. The phenomenon is represented in Fig. 3.1a

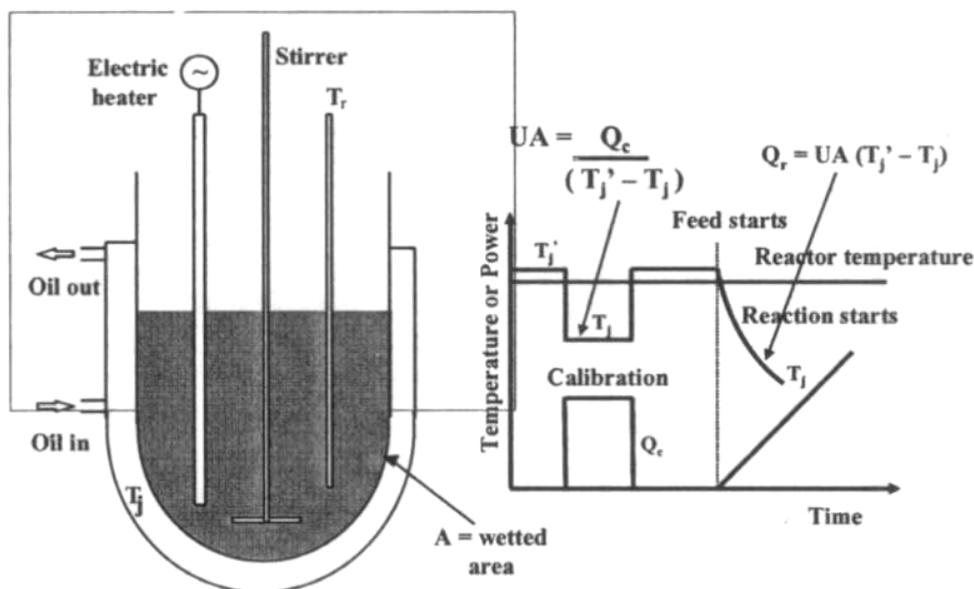


Fig.3.1a Reaction Calorimetry by heat flow method

### 3.1.3 Power compensation reaction Calorimetry

The temperature of the reactor content ( $T_r$ ) is controlled by varying the power of compensation heater inserted directly into the reactor content. As with an electrical heater cooling is not possible, the compensation heater always maintains a constant temperature differences between the reactor jacket and the reactor content. Thus cooling is achieved by reducing the power of the compensation heater. The heat flow rate from the reactor content through the wall into the cooling liquid ( $q_{Flow}$ ) is typically not determined because the reaction heat flow rate is directly visible in the power consumption of the compensation heater. The temperature of the cooling liquid ( $T_j$ ) is controlled at a constant temperature by an external cryostat. The phenomenon is represented in Fig. 3.1b

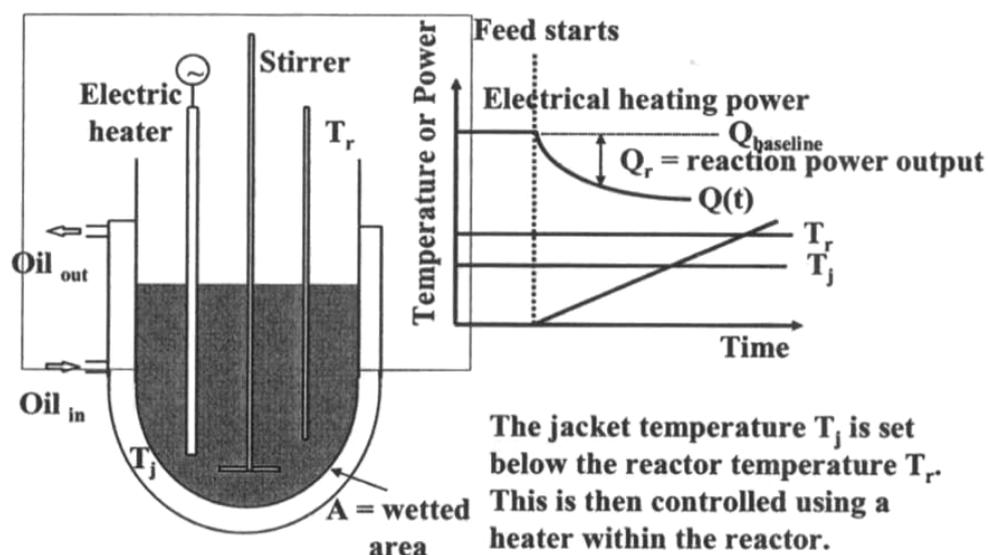


Fig.3.1b Reaction Calorimetry by power compensation method

### 3.2 Thermal Hazards in MDP Nitration

1,1-Diamino-2,2-dinitroethene (FOX-7), a thermally stable insensitive high explosive material which has gained (1) has gained significant interest due to its lower sensitivity and higher performance compared to RDX. Due to good thermal and chemical stability of FOX-7, it is envisaged as a futuristic insensitive high explosive and potential candidate to replace RDX. In the present research work, FOX-7 is selected to be synthesised by nitration of 2-Methyl-4,6-dihydroxy-pyrimidine (MDP) using concentrated nitric and sulphuric acid as nitrating mixture. Nitration of MDP is a low temperature and highly exothermic reaction. The evaluation of thermal hazards of this reaction has been carried out using differential scanning calorimeter (DSC) followed by reaction calorimeter (RC) both. Thermal hazards of the reaction have been determined with the change of various parameters such as (i) mole ratio, (ii) reaction time, (iii) change in

order of addition etc. Calorimetric experiments in RC also supports that the nitration of MDP is feasible either by addition of nitric acid in the pre-dissolved solution of MDP in sulphuric acid or by addition of solid MDP in mixed acid. The reaction is highly exothermic (2) and loss of thermal control can lead to decomposition of reaction masses followed by release of unwanted toxic gases. Sometimes the reaction exothermicity and auto accelerating behaviour can generate the occurrence of runaway reaction (3). Earlier, preliminary information on thermal behaviour of nitration reaction by RC was reported by Kyoo-Hyun et al (4). The only information available is the decomposition temperature of the reaction mixture, which is highly insufficient to use for safer design and scale up this process. The extent of thermal hazards is directly related to the rate of heat accumulation during the reaction. So, DSC followed by RC is used to quantify the measurement (5) of thermal hazards associated in the nitration reaction process. In the present study, the reaction was investigated in Mettler Toledo DSC and RC also in HEL(Hazard Evaluation Laboratory) make Simular-RC to assess the thermal hazards for design of safer process equipment for scaling up the process. Heat flow Calorimetry is used for evaluation of thermal Hazards of MDP nitration reaction in Mettler make RC. Power compensation and heat flow Calorimetry both are used for evaluation of the same in HEL make Simular-RC. In order to quantify the thermal hazards associated in the Nitration Reaction Process, it was first scanned in the Differential Scanning Calorimeter (DSC) followed by Reaction Calorimeter (RC) both Mettler as well as HEL make RC with the synthetic mixtures of raw materials in various proportions.

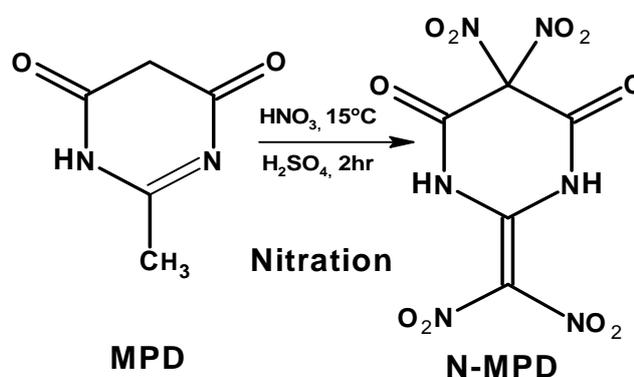
### 3.3 Experimental

#### 3.3.1 Chemicals and Sample

Chemicals required in the preparation of FOX-7 are sulphuric acid (98%), concentrated nitric acid (98%) & 2-methyl-4,6-dihydroxypyrimidine (MDP). The FOX-7 can be prepared in two ways, either by mixing concentrated sulphuric and nitric acid in desired mole ratio followed by addition of required quantity of solid MDP or by dissolving MDP in sulphuric acid followed by controlled addition of conc. nitric acid.

#### 3.3.2 Reaction

Nitration experiments were carried out in DSC & RC with standard mole ratio (MDP : HNO<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub> :: 1: 5.1 : 10.2). Overall reaction is shown in Scheme-3.1. Methyl-pyrimidine-dione (MPD) and methyl-dihydroxy-pyrimidine (MDP) are same as these are the keto-enol conjugate form.



Scheme 3.1: Nitration of MPD (methyl-pyrimidine-dione) / Methyl

The mechanism for nitration of MDP suggests that it is a consecutive reaction where nitrating acid mixture provides electrophilic nitronium ion as shown in Scheme-2.7 and steps of nitration proposed by Bellamy & et al (2) is shown in Scheme 2.8.

During nitration of MDP, formation of mono nitro derivative (II) is faster followed by dinitro derivative (III) at a relatively slower rate due to destruction of aromatic system. The formation of (III) probably facilitates enolization onto the methyl group and further nitration at that centre to get desired nitrated pdt (IV). Nitroform, dinitromethane,  $\text{NO}_x$  etc. are undesired product generated in the nitration reaction.

### 3.4 Methodology

#### 3.4.1 Differential Scanning Calorimetry

The Differential Scanning Calorimetry (DSC) (Fig. 3.1) facility consists of a furnace which is internally equipped with gold plated aluminum pans of diameter of about 3mm placed beneath two thermocouples.



Fig.3.1 Photograph of DSC-25

One of these pans is loaded, filled with typically 5 mg of sample while the other is empty. The pans are then sealed. An on-line PC is connected to control and monitor the DSC. The pans are kept in a chamber of approximately 250 ml capacity and purged with  $\text{N}_2$  gas. The DSC heats the pans at a constant heating rate. Here, the high-pressure gold plated aluminium crucible cell, DSC-25 and star software was used for Differential Scanning Calorimetric experiments. The DSC heats the pan at a constant heating rate by maintaining the isothermal heating at  $30\text{ }^\circ\text{C}$  as well as constant heating rate of  $4\text{ }^\circ\text{C}/\text{min}$  from  $30$  to  $360\text{ }^\circ\text{C}$ . Based on the thermal

responses generated during the experiments, the heats of evolution, onset of exothermicity or endothermicity etc. were evaluated. In the present study, the exotherm is detected based on the difference in constant heating rate & excess heat generation during the course of experiment. Various parameters like mole ratio, reaction time, order of addition etc. were studied during the DSC experiments. The rate of heat flow and potential of exotherm obtained were analysed from different thermo-grams, which reveal important characteristics of the reaction process. DSC thermo-gram are shown in Fig.3.2 to 3.5.

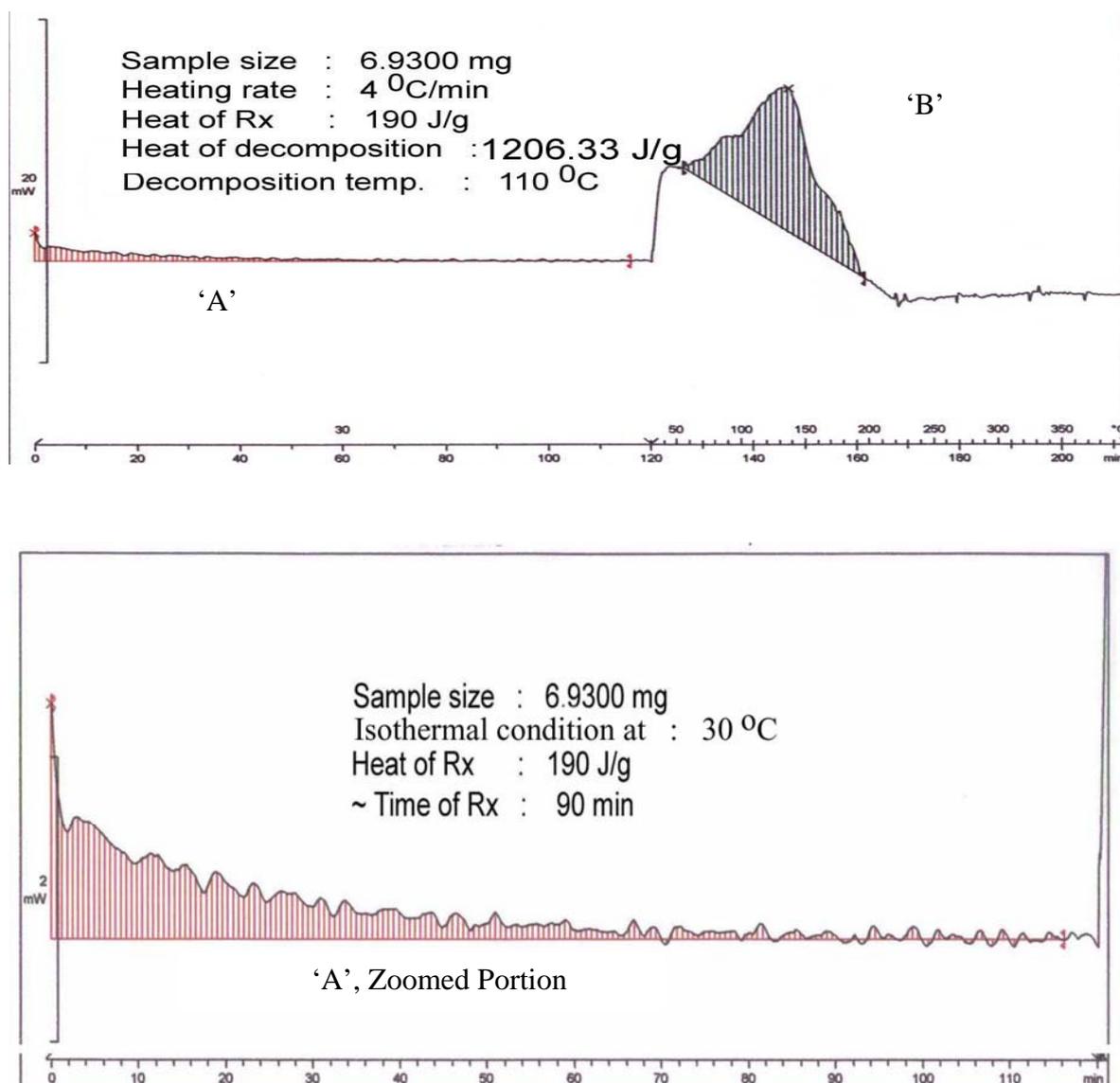


Fig.3.2 DSC experiments under isothermal condition

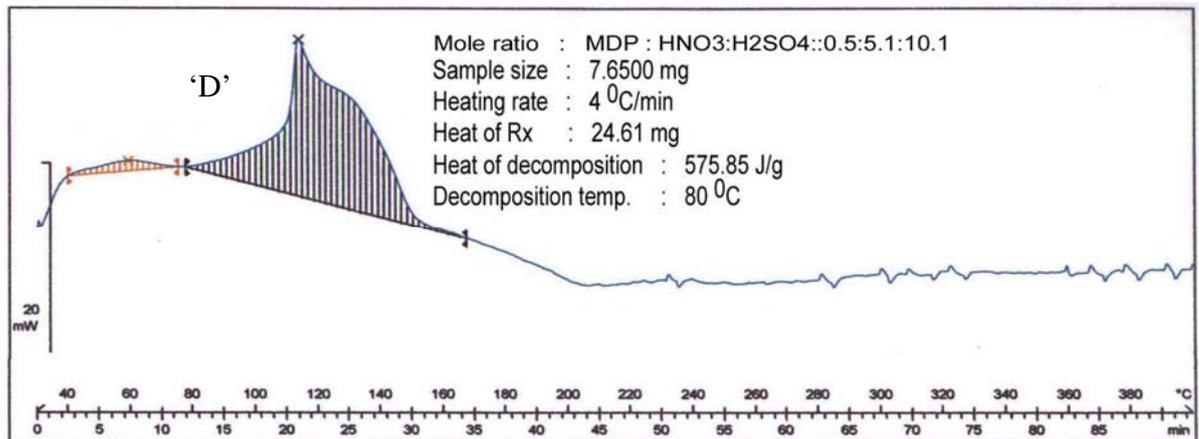
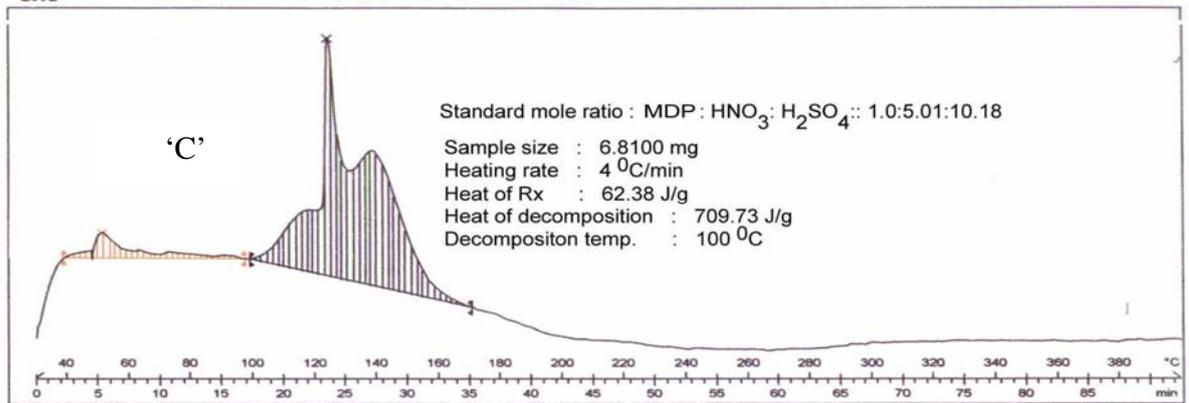


Fig.3.3 DSC thermogram comparing the effect of mole ratio

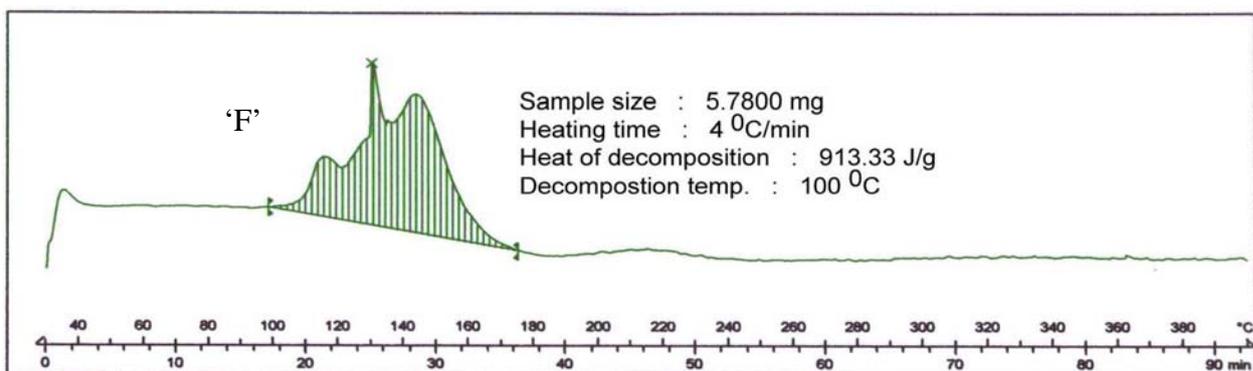
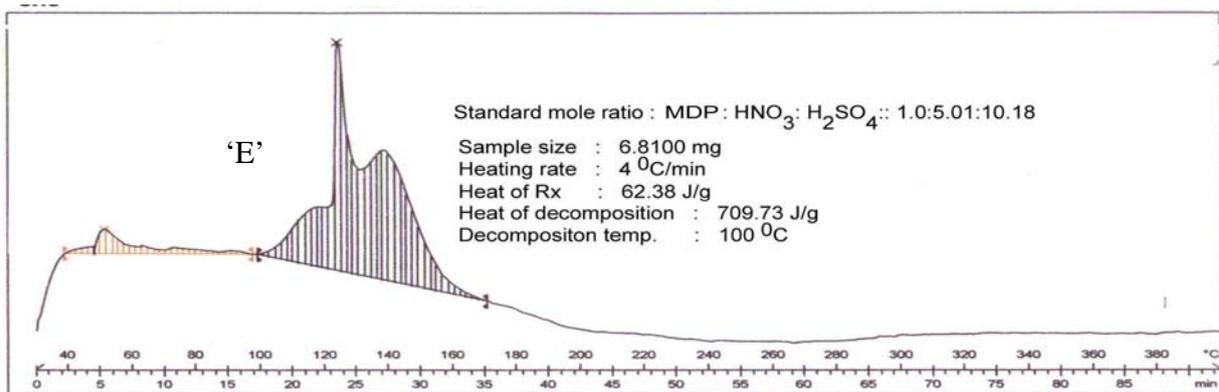


Fig.3.4 DSC thermogram comparing the effect of reaction time using reaction mass during nitration (E) and after nitration (F) reaction

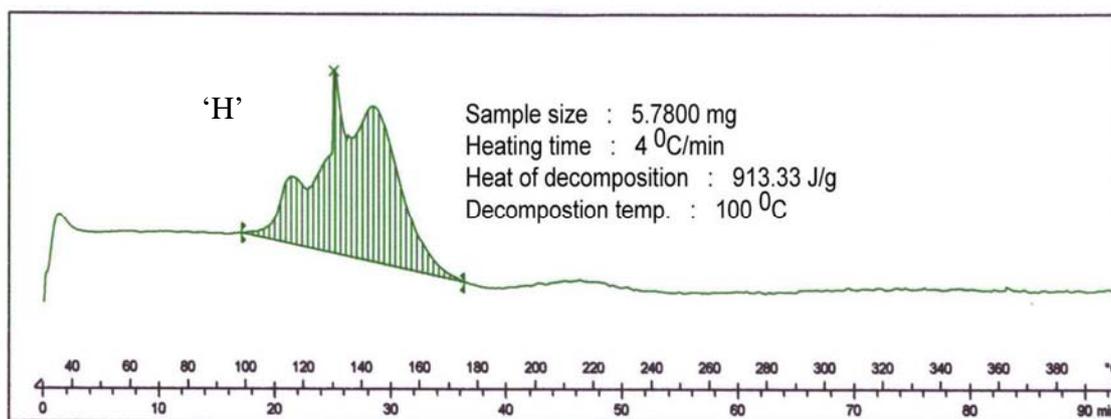
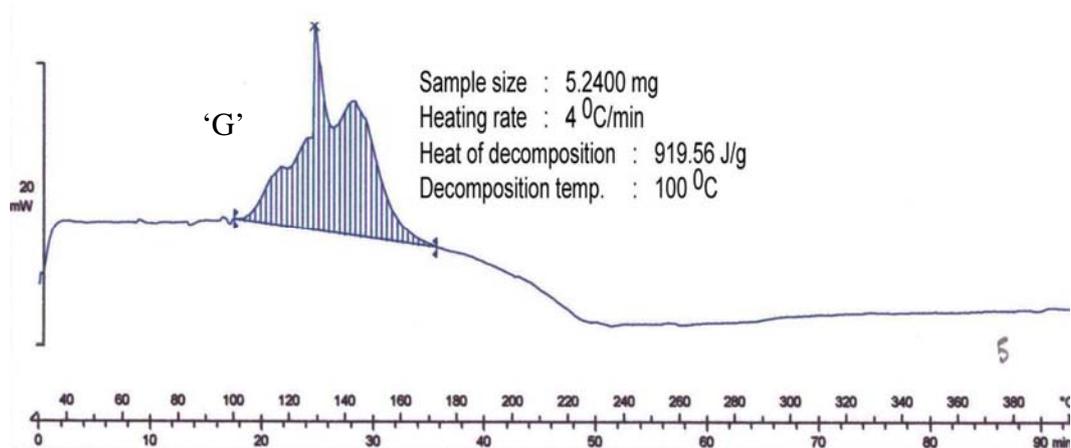


Fig.3.5 DSC thermogram comparing the effect of mode of addition of ingredient, liquid mode(G) and solid mode (H)

### 3.4.2 Experiments in Reaction Calorimeter

Reaction Calorimeter (RC) is a computer controlled stirred tank reactor which can be operated in batch or semi-batch mode under isothermal and adiabatic conditions. It is equipped with sophisticated instrumentation to measure and control reaction process parameters like temperature, pH, rpm, heat generation or heat absorption, flow rate of gas or liquid etc. Besides, the other information that can be obtained from

reaction calorimeter includes the heat of reaction, specific heat of reaction mixture, reactant accumulation as a function of process temperature and cooling load required to maintain the process temperature within the desired limits. Though the main limitation of the reaction calorimeter is to measure the rate of energy release in a reaction under runaway conditions, however the adiabatic rise in temperature can be measured on the basis of heat generation and specific heat.

#### **3.4.2.1 Nitration of MDP Experiments in RC ( Mettler )**

Mettler make SV-01 800 ml capacity jacketed glass reactor equipped with a propeller type up-flow agitator, automatically controlled hot oil circulator, addition funnel, condenser, temperature sensors, RC-win software etc. were used for reaction calorimetric experiments. The schematic diagram of the Mettler make RC is shown in Fig.3.5a.



Fig. 3.5a Photographs of Mettler Make RC1

Reaction was conducted in the automated jacketed glass reactor unit and software in the RC-system generated relevant thermo-grams using heat flow Calorimetry.

#### **Nitration reaction by solid mode addition**

554 g of concentrated sulphuric acid was charged into the reactor and cooled to  $12^{\circ}\text{C}$ . The measured quantity of concentrated nitric acid in the predefined molar ratio was added to the sulphuric acid and the temperature of the reaction mixture was maintained at  $15^{\circ}\text{C}$ . Then

around 70 g of MDP was added to the reaction mixture by maintaining the reaction temperature at 15 °C in about 2 hrs under continuous agitation. After addition of all the ingredients, the reaction was allowed to continue for another 2 hrs, and then the reaction mixture is quenched in the ice-cooled water.

#### **Nitration reaction by liquid mode addition**

554 g of concentrated sulphuric acid was charged into the reactor and cooled to 12 °C. The measured quantity of 70 g of MDP was added to this sulphuric acid and the temperature of the reaction mixture was maintained to 40 °C for complete dissolutions. The temperature of reaction mass is cooled to 15 °C under continuous agitation. Concentrated nitric acid in the predefined molar ratio is then added slowly by maintaining the temperature at 15 °C in about 2 hrs under continuous agitation. After addition of all the ingredients, the reaction was allowed to continue for another 2 hrs, and then the reaction mixture is quenched in the ice-cooled water

Inside reaction mass temperature ( $T_r$ ), mass of the reaction mixture ( $M_r$ ), heat flow of the reaction mass ( $Q_r$ ), specific heat ( $C_p$ ) of the reaction mixture, overall heat transfer co-efficient ( $U$ ) etc. were recorded during the run by heat flow calorimetry. Deviation from linearity (e.g. small rise) indicates calibration of the system by heat flow calorimetry whereas sharp rise indicates the 'onset' of an exotherm. The subsequent rise shows the severity of hazards which were recorded in the graphical form known as 'thermogram'. Analysis of various thermo-grams generated in both DSC and RC were done and the information like onset temperature of exotherm, potential of exotherm, adiabatic rise in temperature,

decomposition potential of reaction mass, overall heat transfer co-efficient etc were obtained.

Thermogram generated during the hazards estimation of MDP nitration using liquid mode addition (addition of concentrated  $\text{HNO}_3$  in pre-dissolved MDP in  $\text{H}_2\text{SO}_4$ ) in Mettler make RC is shown in Fig 3.6a and 3.6b. Thermogram generated using solid mode addition (direct addition of solid MDP in the nitrating mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ ) in Mettler make RC is shown in Fig 3.7.

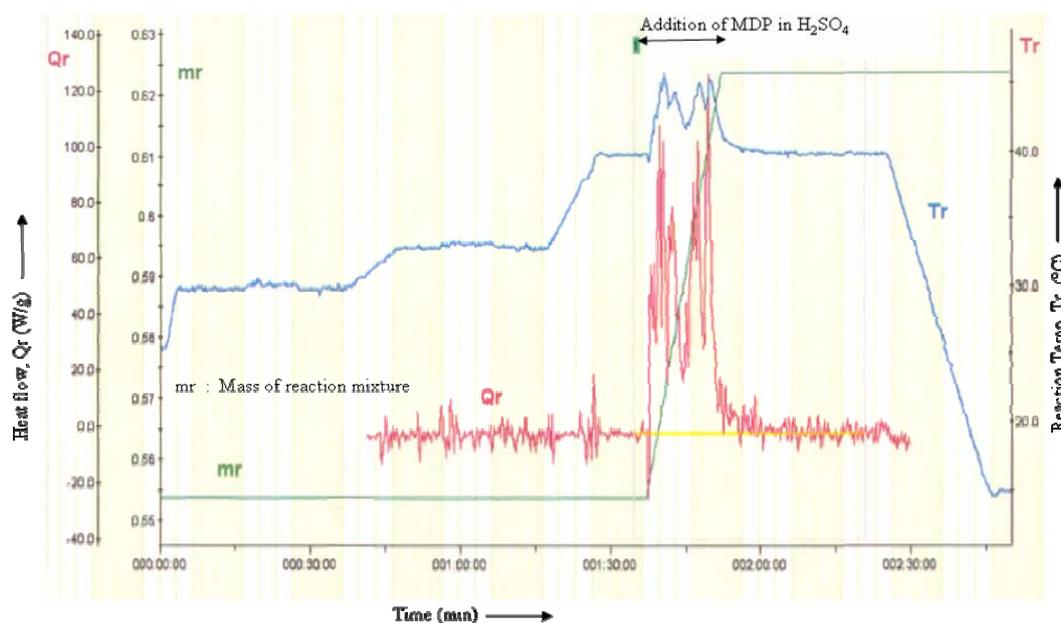


Fig .3.6a RC thermogram for heat of mixing of MDP in  $\text{H}_2\text{SO}_4$

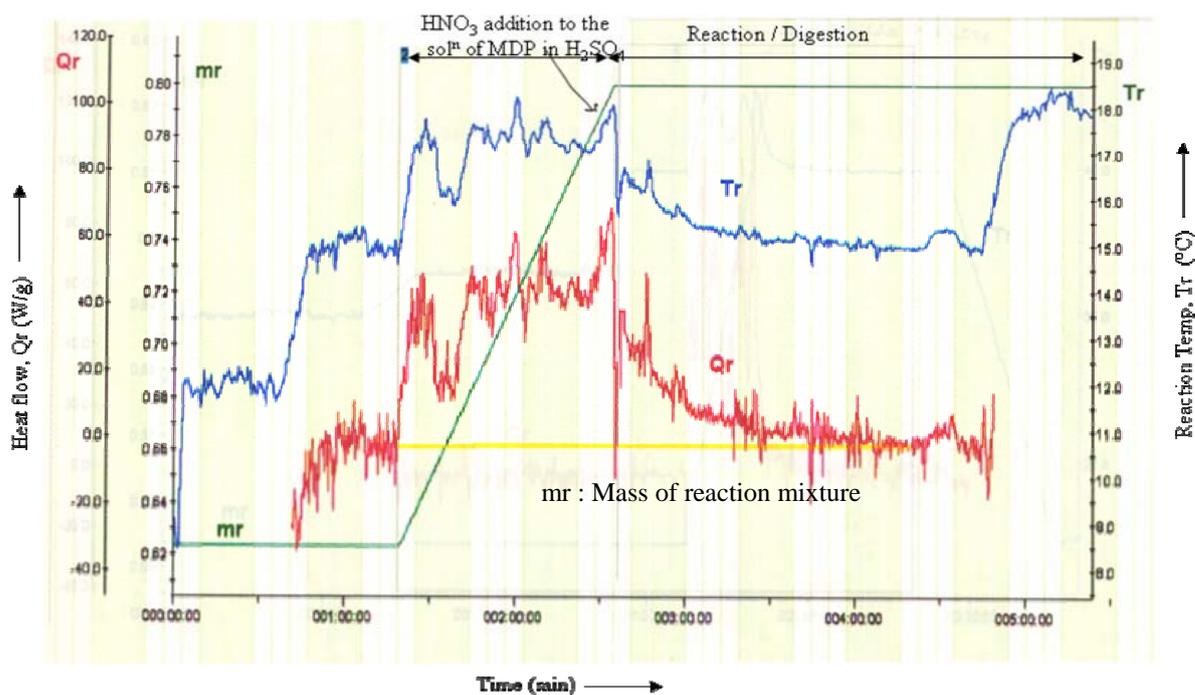


Fig. 3.6b RC Thermogram for addition of HNO<sub>3</sub> in the solution of MDP in H<sub>2</sub>SO<sub>4</sub>

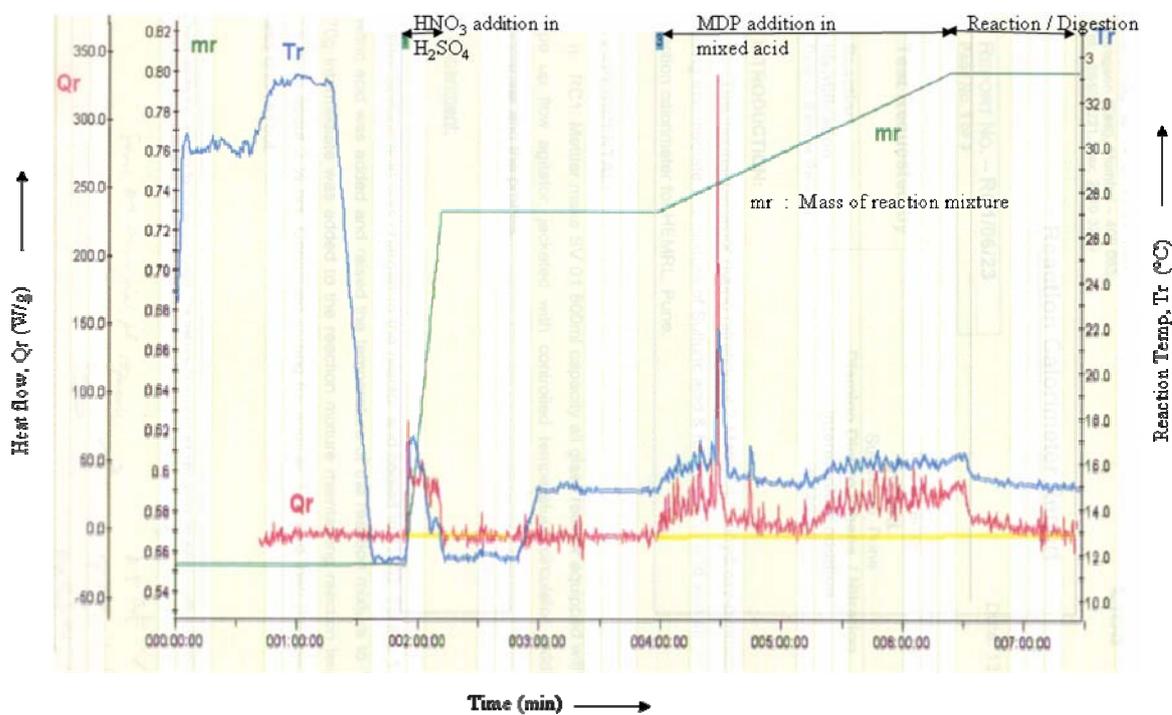


Fig.3.7 RC Thermogram for nitration by addition of MDP in mixed acid

### 3.4.2.2 Nitration of MDP Experiments in RC (HEL)

HEL (Hazard Evaluation Laboratory) make RC (E652 DUAL SIMULAR) unit is comprised of 2 lit capacity triple wall double jacketed glass reactor equipped with a pitch blade turbine agitator controlled through Variable frequency drive, automatically controlled hot/cold oil circulation unit using a thermostat cum cryostat unit, addition funnel, automatic chemical dosing pump through controller, condenser, temperature sensors cum controller etc. All the equipments/instruments are connected to a Computer through communication devices. The Computer is preloaded with WINISO software, used for planning and performing experiments on the system and WINIQ software, used for data analysis and interpretation after completion of calorimetric experiments. The schematic diagram of the HEL make RC is shown in Fig.3.8a. The SCADA (supervisory control and data acquisition) /Human machine interface is shown in Fig. 3.8b.



Fig. 3.8a Photograph Reaction Calorimeter ( HEL make)

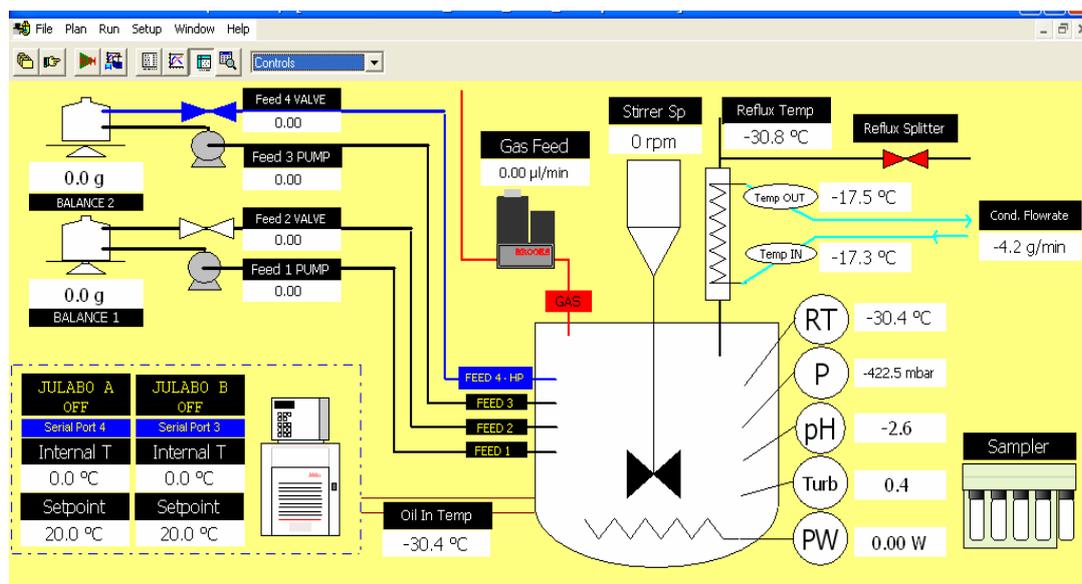


Fig. 3.8b Human Machine Interface for Reaction Calorimeter ( HEL make)

In the HEL make RC unit, Reaction was conducted both in heat flow Calorimetry as well as power compensation method as discussed in section 3.1.1 and 3.1.2. In both the methods, nitration batch size was 100 g of MDP. Quantity of nitric acid (98%) was 170 ml (~255 g) and sulfuric acid (98%) was 430ml (791g). In both the methods, reaction was conducted at 15 °C. Thermogram generated in heat flow Calorimetry are shown in Fig. 3.9a (heat generation during addition of MDP in H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>) and Fig. 3.9b (heat generation during nitration by addition of HNO<sub>3</sub> in MDP-H<sub>2</sub>SO<sub>4</sub> solution). Process details for liquid mode reaction are discussed in following steps which are involved in heat flow calorimetry,

Step-1: Base line creation at 15 °C for MDP-H<sub>2</sub>SO<sub>4</sub> solution

Step-2: Calibration of MDP-H<sub>2</sub>SO<sub>4</sub> solution at 15 °C by supplying known amount of heat ( 0.25% of heater) in to the reactor

Step-3: Base line creation at 15 °C for MDP-H<sub>2</sub>SO<sub>4</sub> solution for addition of HNO<sub>3</sub>

Step-4:  $\text{HNO}_3$  Addition in  $\text{H}_2\text{SO}_4$ -MDP solution and recording of heat generation.

Step-5 : Base line creation at  $15^\circ\text{C}$  for the nitration reaction mass  $\text{H}_2\text{SO}_4$ -MDP- $\text{HNO}_3$

Step 6: Calibration of nitration reaction mass  $\text{H}_2\text{SO}_4$ -MDP- $\text{HNO}_3$

Thermogram generated in power compensation is shown in Fig. 3.10

Following steps are involved during nitration by power compensation method,

Step-1: Base line creation at  $15^\circ\text{C}$  for MDP- $\text{H}_2\text{SO}_4$  solution for addition of  $\text{HNO}_3$

Step-2:  $\text{HNO}_3$  Addition in  $\text{H}_2\text{SO}_4$ -MDP solution and recording of heat generation in terms of decrease of power supply required to maintain isothermal condition of reaction mass.

Step-3 : Base line creation at  $15^\circ\text{C}$  after completion of  $\text{HNO}_3$  addition and calculation of heat of reaction by considering the power compensation during the reaction.

Thermodynamic design data generated for MDP nitration reaction in calorimetric experiments is tabulated and given in Table-3.1.

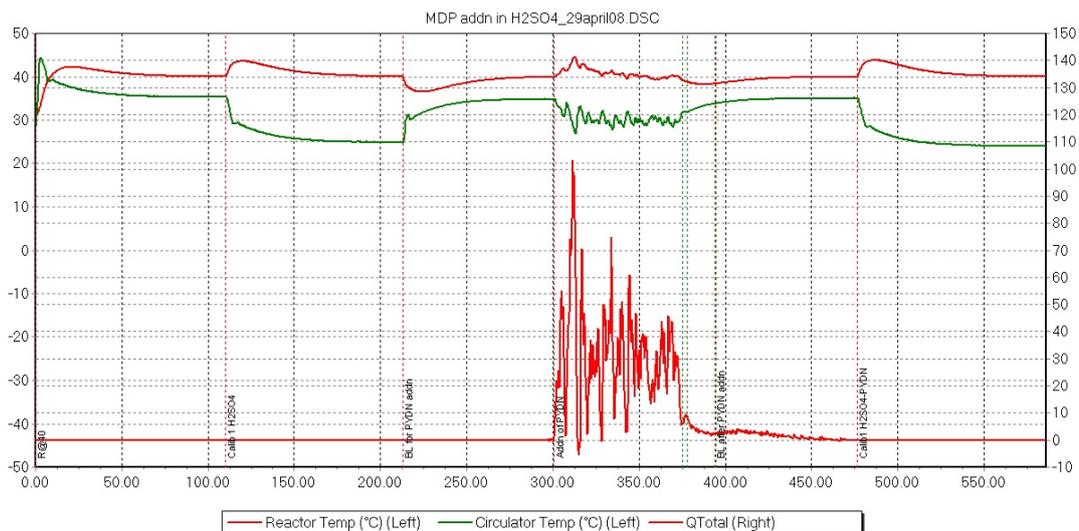


Fig .3.9a RC Thermogram for heat of mixing of MDP in H<sub>2</sub>SO<sub>4</sub>  
(Heat flow Calorimetry in HEL make RC)

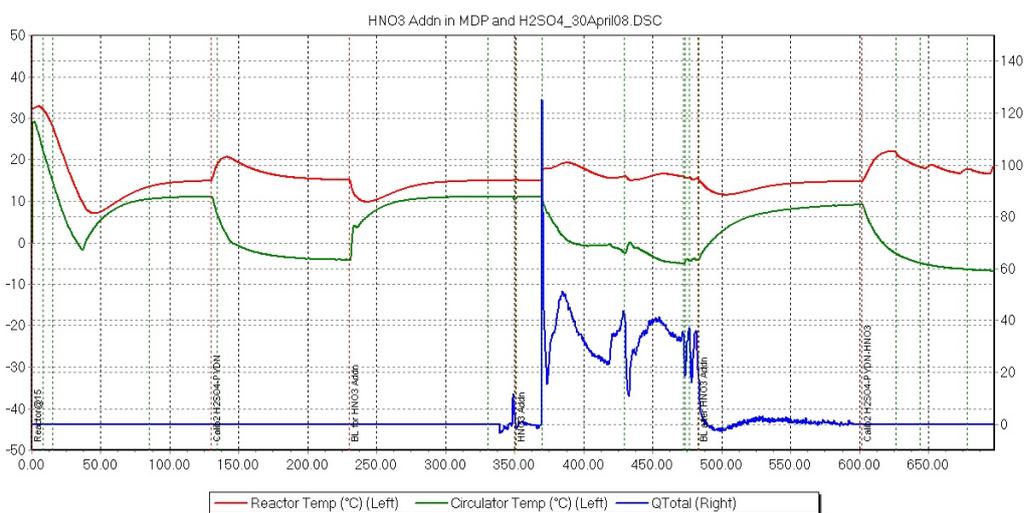


Fig. 3.9b RC Thermogram for addition of HNO<sub>3</sub> in the solution of  
MDP in H<sub>2</sub>SO<sub>4</sub> (Heat flow Calorimetry in HEL make RC)

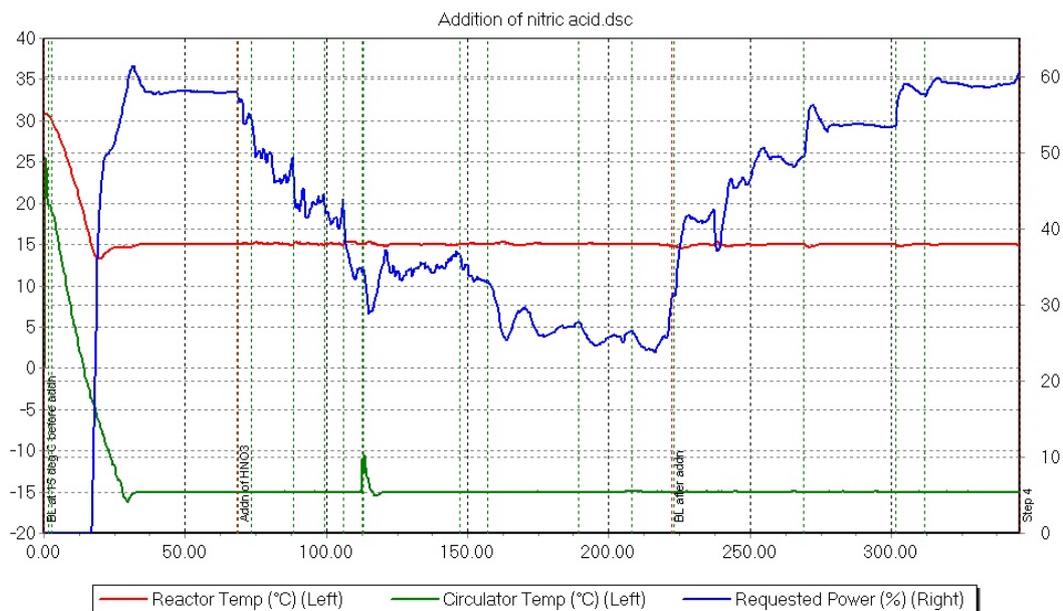


Fig. 3.10 RC Thermogram for addition of HNO<sub>3</sub> in the solution of MDP in H<sub>2</sub>SO<sub>4</sub> (Power Compensation Calorimetry in HEL make RC)

**Table 3.1: Thermodynamic design data for nitration reaction based on calorimetric experiments**

Process chemicals	Reaction temp (°C)/time (hr)	$\Delta H_R$ (kJ/mole of MDP)	$\Delta H_R$ mixing H <sub>2</sub> SO <sub>4</sub> & MDP (kJ/mole)	$\Delta H_R$ mixing H <sub>2</sub> SO <sub>4</sub> & HNO <sub>3</sub> (kJ/mole)	Cp of reaction mass (kJ/kg K)	U (W/m <sup>2</sup> K)	Decomposition potential (kJ/kg) / On set decomposition (°C)
MDP:HNO <sub>3</sub> :H <sub>2</sub> SO <sub>4</sub> :: 1 : 5.1 : 10.2	15/2	460	100	14.2	1.82	147	920/100

### 3.5 Results and Discussion

The outcome of the thermo-chemical study by both DSC and RC are described in Table 3.1 and Figs. 3.2 to 3.10. The first thermo-gram generated by DSC experiment, where the reaction was maintained at 30<sup>0</sup>C for 2 hr followed by heating at 4 <sup>0</sup>C/min up to 360 <sup>0</sup>C is shown in thermo-gram, Fig.3.2. The first exotherm, 'A' of Fig.3.2 is due to isothermal heat generation at 30<sup>0</sup>C during reaction followed by second exotherm, 'B' is due to decomposition of reaction mass at ~90 <sup>0</sup>C. Isothermal heat generation suggests that the exothermicity of the reaction continues at least up to 100 minutes. Fig.3.3 describes the effect of mole ratio on the reaction. It is seen that as moles of MDP are reduced to half, shown in exotherm 'D' of Fig.3.3 compared to standard mole, 'C', of Fig.3.3, both the heat of reaction and decomposition potential decrease. Onset of decomposition also reduces to 80 <sup>0</sup>C compared to standard at 100 <sup>0</sup>C. Fig.3.4 describes the effect of reaction time, Where exotherm, 'F' of Fig.3.4 is the reaction mass after 2 hrs of reaction compared to the reaction practiced as standard, exotherm 'E' of Fig. 3.4. No reaction exotherm is observed after 2 hours, but decomposition potential and onset of decomposition remains similar. Thermograms in Fig. 3.5 compares the effect of mode of addition of ingredients. Exotherm 'G' of Fig. 3.5 shows HNO<sub>3</sub> addition in the solution of MDP & H<sub>2</sub>SO<sub>4</sub> compared to MDP addition in mixed acid in exotherm 'H' of Fig. 3.5. Decomposition potential in both the cases is almost similar (919 & 913 J/g) with onset of decomposition at 100 <sup>0</sup>C.

Fig. 3.6a is the thermo-gram obtained in RC (Mettler) experiments which, describes the pattern of heat flow during mixing of MDP into the H<sub>2</sub>SO<sub>4</sub>. 70 g MDP is added to 554 g of H<sub>2</sub>SO<sub>4</sub> at 40 <sup>0</sup>C over a period of

15 minutes and the heat of mixing generated is 100 kJ/mole of MDP. At 40 °C it took around 45 minutes for complete dissolution of MDP in H<sub>2</sub>SO<sub>4</sub>, then the solution is cooled down to 15 °C and 180 g of nitric acid is added slowly into it by maintaining the temperature at 15 °C over the period of 75 minutes as shown in Fig. 3.6b. After addition, temperature is maintained at 15 °C for a period of another 2 hr. Overall heat evolved during nitration is 460 kJ/mole of MDP. This amount of heat generation can lead to adiabatic temperature rise of 223 °C. After the nitric acid addition, heat evolved is 355 kJ/mole which implies that about 77% of the reaction takes place at this stage, remaining 23% of the reaction takes place beyond nitric acid addition during digestion at 15 °C. After the reaction, the overall heat transfer co-efficient (U) and specific heat (Cp) of reaction mixture were evaluated by heat flow Calorimetry which were found to be 147 W/m<sup>2</sup> K and 1.82 kJ/kg K respectively. Fig. 3.7 is the RC thermogram for nitration where solid MDP is added in the mixed acid at 15 °C under continuous agitation. Heat evolved at this stage is 362 kJ/mole and heat of mixing of H<sub>2</sub>SO<sub>4</sub> with HNO<sub>3</sub> found to be 14.2 kJ/mole of HNO<sub>3</sub>, other parameters like heat of reaction, U, Cp are comparable to that of experiment described in thermo-gram Fig. 3.6a & 3.6b.

Fig. 3.9a is the thermo-gram obtained in RC (HEL) experiments which, describes the pattern of heat flow during mixing of MDP into the H<sub>2</sub>SO<sub>4</sub>. 100 g MDP is added to 791 g of concentrated (98%) H<sub>2</sub>SO<sub>4</sub> at 40 °C over a period of 75 minutes and the heat of mixing generated is 90 kJ/mole of MDP. At 40 °C it took around 45 minutes (similar to that of Mettler RC) for complete dissolution of MDP in H<sub>2</sub>SO<sub>4</sub>, then the solution is cooled down to 15 °C and 255 g of nitric acid is added slowly into it by

maintaining the temperature at 15<sup>0</sup>C over the period of 150 minutes as shown in Fig. 3.9b. After addition, temperature is maintained isothermally at ~15<sup>0</sup>C for a period of another ~2 hr to get the stable base line. Overall heat evolved during nitration is 410 kJ/mole of MDP. This amount of heat generation can lead to adiabatic temperature rise of 200<sup>0</sup>C. After the nitric acid addition, heat evolved is 370 kJ/mole which implies that about 90% of the reaction takes place at this stage, remaining 10% of the reaction takes place during the period of maintaining the reaction mass at 15<sup>0</sup>C.

Fig. 3.10 is the thermo-gram obtained in RC (HEL) experiments which, describes the pattern of heat flow during mixing of MDP into the H<sub>2</sub>SO<sub>4</sub> using power compensation method. 100 g MDP is added to 791g of concentrated (98%) H<sub>2</sub>SO<sub>4</sub> at 40<sup>0</sup>C over a period of 75 minutes and the heat of mixing generated is 90 kJ/mole of MDP. During stabilization the initial base line is found out, 25 W heater was used in the reaction media. The heat load was automatically compensated during the course of addition of nitric acid keeping the reactor temperature constant (15<sup>0</sup>C). After addition of MDP in H<sub>2</sub>SO<sub>4</sub>, the solution is cooled down to 15<sup>0</sup>C and 255 g of nitric acid is added slowly into it by maintaining the temperature at 15<sup>0</sup>C over the period of 200 minutes as shown in Fig. 3.10. After addition, temperature is maintained isothermally at ~15<sup>0</sup>C for a period of another ~2 hr and requested power is also reached to 25 W to get the stable base line. Overall heat evolved in power compensation method during nitration is 450 kJ/mole of MDP.

Thermodynamic design data generated for process scale up by calorimetric experiments are compiled in and given in Table 3.1. Based on

the data generated for heat of reaction, and overall heat transfer coefficient, required heat transfer area for 5 kg batch in a jacketed glass reactor would be 1.7 m<sup>2</sup>.

### 3.6 Conclusion

Nitration of MDP is highly exothermic and should be carried at lowest possible optimum temperature under continuous agitation. At standard and optimum mole ratio of MDP:HNO<sub>3</sub>: H<sub>2</sub>SO<sub>4</sub> = 1 : 5.1 : 10.1, heat of reaction ( $\Delta H_R$ ) is ~460 kJ/mole of MDP at 15 °C. Heat generated during preparation of mixed acid (addition of HNO<sub>3</sub> into the H<sub>2</sub>SO<sub>4</sub>) is recorded as 14.2 kJ/mole of HNO<sub>3</sub> compared to the heat of mixing of MDP in H<sub>2</sub>SO<sub>4</sub> is 100 kJ/mole of MDP. Onset temperature for decomposition of reaction mixture is 100 °C with the potential of ~1206 kJ/mole. If MDP is used half of the desired quantity compared to standard ratio used in nitration process the onset temperature of decomposition reduces to 80 °C which is not desirable. Adiabatic rise in temperature due to desired  $\Delta H_R$  is around 223 °C, which is very high and far from onset of decomposition. This indicates that for scale up of the process, efficient cooling system is required. Nitration of MDP is feasible either by addition of HNO<sub>3</sub> into the solution of MDP in H<sub>2</sub>SO<sub>4</sub> or addition of MDP in mixed acid. Hence, standard mole ratio at lowest optimum temperature under continuous agitation with efficient cooling system is not only important for optimum yield and purity of the product but also to prevent thermal runaway followed by decomposition due to highly exothermic nitration reaction.

Heat generation in Mettler-RC as well as HEL-RC are equivalent and variation is around 2%. It is experienced that, Nitration by solid mode

(adding solid powder, MDP in nitrating mixture) some times it forms lumps and generates higher heat unexpectedly which is undesirable. Hence, conducting nitration reaction by liquid mode of addition is preferred for ease of handling of raw materials and also better process control point of view.

### 3.7 References

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## Chapter 4

# Reaction Kinetics and Parametric Sensitivity for FOX-7 Synthesis Process

## 4.1 Introduction

1,1-Diamino-2,2-dinitroethene (FOX-7) is a thermally stable insensitive high explosive under UN (United Nation) classification of Hazard division (HD) 1.1 category. It is a futuristic insensitive high explosive and a potential candidate to replace cyclotrimethyltrinitramine (RDX). Due to its chemical and thermal stability, it has gained significant interest in recent past.

In the present research work, Fox-7 has been synthesised by nitration of 2-methyl-4,6-dihydroxy-pyrimidine (MDP) followed by hydrolysis of 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione (NMPD). Nitration of MDP is a low temperature and highly exothermic reaction. Since no literature is available on the nitration reaction kinetics, a study was undertaken in the present research work to determine the same for nitration of MDP and also for the hydrolysis of 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione (NMPD). Nitration kinetics is discussed in sections 4.2 and hydrolysis kinetics is discussed in section 4.3 of this chapter. Thermo chemical study of nitration reaction reveals that adiabatic rise in temperature of MDP nitration reaction is quite high ( $>220^{\circ}\text{C}$ ) which indicates that the conduct of reactions at lowest possible optimum temperature is safer and favourable. Kinetics of the overall reaction is basically the study of the slowest step (1, 2, 3). The study was carried out at fixed different possible temperatures keeping other parameters like vessel volume, agitator speed, feed rate etc. constant. During the study of nitration kinetics, predetermined quantities of MDP and mixed acid were allowed to react at a fixed temperature for different reaction period and generated a concentration profile of the reactant or product. Using this concentration profile, reaction order and

reaction rate constant was evaluated. Reaction temperature was maintained by circulating chilled water through the jacket. In order to optimise the reaction time without compromising yield, the nitration reaction kinetics have been studied at three different temperatures (5, 15 and 25<sup>0</sup>C) using differential method. Three sets of nitration experiments were conducted to optimise nitration reaction temperature and also to find the temperature dependent rate equation. The nitration of MDP is sensitive to temperature, rate of reaction was studied at fixed temperature with the variation of time and keeping all the other parameters constant. Activation energy of nitration is calculated, using reaction kinetic data based on temperature dependent rate equation derived from the Arrhenius's law. Process Heat generation rate is also studied during each experiment of nitration kinetics. In order to measure the exothermicity, process heat generation data was collected by measuring jacket inlet and outlet temperature of an insulated glass reactor. The hydrolysis kinetics have also been studied at three different temperatures viz. 15, 25 and 40 <sup>0</sup>C. Since, the hydrolysis of NMPD is sensitive to temperature, rate of hydrolysis was also studied at fixed temperature with the variation of time keeping all the other parameters constant. Study of hydrolysis reaction is discussed in section 4.3.

## **4.2 Nitration Kinetics**

### **4.2.1 Nitration Reaction**

Optimized quantity of moles of reactants (discussed in the chapter-2) were taken for the nitration kinetics study. Nitration of MDP is a highly exothermic reaction where a mixture of concentrated sulphuric acid, H<sub>2</sub>SO<sub>4</sub> (98%) and nitric acid, HNO<sub>3</sub> (98%) are used as nitrating agent.

MDP was added slowly into the mixed acid in the mole ratio of MDP : HNO<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub> :: 1 : 5.1 : 10.1 and the temperature is maintained at the desired level. The overall nitration reaction is shown in Scheme 2.9. The probable mechanisms of formation of nitronium ion and progress of reaction are proposed by the authors Bellamy et al. (4) and Ostmark et al. (5) are given in Scheme 2.7 and 2.8 respectively.

#### 4.2.2 Nitration Experiments

Experimental set-up (Fig.2.1, in chapter-2) was used to conduct the experiments at 10 g batch level. During experiments, nitrating mixture (H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub>) is prepared at pre-defined temperature, then MDP is added at controlled rate to the nitration mixture by maintaining the temperature at a desired level. In order to optimise the reaction temperature and temperature dependent rate constant, three sets of experiments were conducted at 5<sup>0</sup>C, 15<sup>0</sup>C and 25<sup>0</sup>C. At each temperature, around 10 experiments were carried out in different reaction times ranging from 5 to 120 minutes at an interval of 15 to 20 minutes. After completion of each run, the reaction mixture was quenched into the cold water followed by hydrolysis under high speed of agitation for 3 hrs to get the product, FOX-7 which is then filtered, washed with water (till removal of acid) to separate the solid product. The product weight was determined for each run after drying and decomposition temperature was noted. Conversions of MDP to FOX-7 at different temperatures are given in Table 4.1. Reaction rates & activation energy were calculated on the basis of these data. In order to estimate the heat generation during each experiment, flow rate of the cooling media through jacket is measured as well as corresponding jacket inlet /outlet temperature are noted keeping

inside reaction temperature constant. Based on flow rate, specific heat of cooling media and jacket inlet/outlet temperature, rate of heat generation during reaction have been calculated. Data are shown in Table-4.1.

Table 4.1. Reaction and heat generation data at different temperature

Batch size : 10 g of MDP, Nitric acid (98%) : 17 ml,

Sulphuric acid (98%) : 43 ml, Agitator rpm : 300

Sl. No.	Time (min)	Yield of FOX-7 (g) at different react-ion temp (°C)			Heat generation (W), during addition of MDP in mixed acid at different temp (°C)			Heat generation (W), after addition of MDP in mixed acid at different temp (°C)		
		5	15	25	5	15	25	5	15	25
1.	5	2.15	4.34	7.45	25	82	105	15	60	82
2.	10	4.03	4.62	7.42	30	83	110	18	58	79
3.	20	3.6	5.0	7.9	24	80	106	17	55	82
4.	30	5.0	7.71	8.54	32	81	110	16	56	81
5.	45	6.73	8.21	9.64	26	78	108	19	55	82
6.	60	6.98	8.66	9.68	28	78	109	14	54	83
7.	90	7.55	9.32	9.44	25	80	108	18	56	84
8.	120	7.79	9.72	9.73	26	74	109	19	55	85
Avg. value for heat generation					27	79	108	17	56	82

### 4.2.3 Analysis of kinetic data

#### 4.2.3.1 Reaction rate

Several methods are used for determining the order of the reaction and subsequently the rate law of the chemical reaction. These (1, 6) are mainly integral method, differential method, method of half-life period, isolation method, method of excess etc. As the nitration of MDP is

sensitive to temperature, rate of reaction was studied at fixed temperature with the variation of time keeping all the other parameters constant. In each method, it is essential to estimate the concentration of the reactant or the product at different reaction periods. In the present study, differential method was adopted to determine the rate law for this reaction. Hence, the reaction rate (r) can be expressed as,

$$-r = k \cdot (C_{MDP})^n \cdot (C_{HNO_3})^m \quad (4.1)$$

Where  $k$  is the reaction rate constant,  $m$  and  $n$  are order of reaction with respect to  $HNO_3$  and MDP. Concentration profile generated for MDP and  $HNO_3$  given in Figs. 4.1, 4.2 and 4.3, it is seen that change of nitric acid concentration is negligible as compared to MDP.

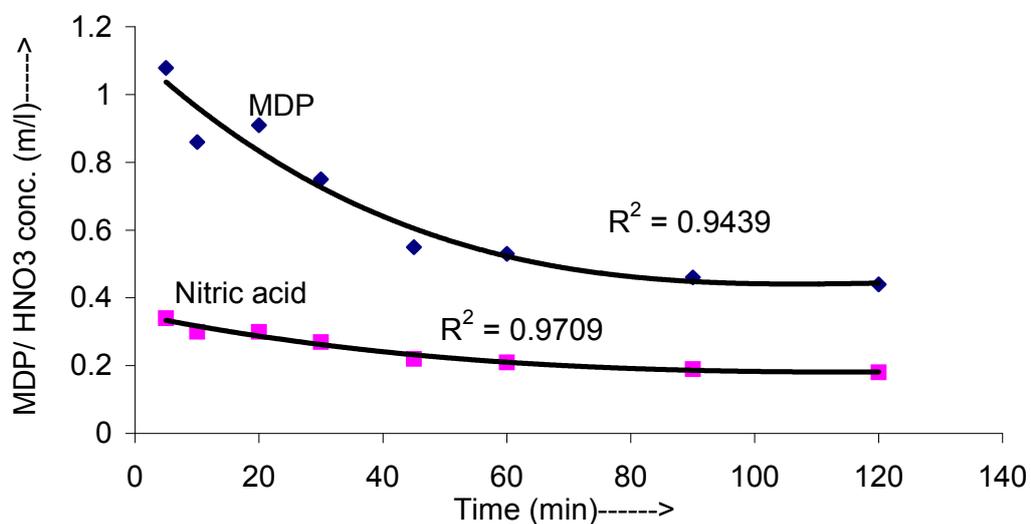


Fig. 4.1 Variation of MDP and nitric acid concentration at 5°C

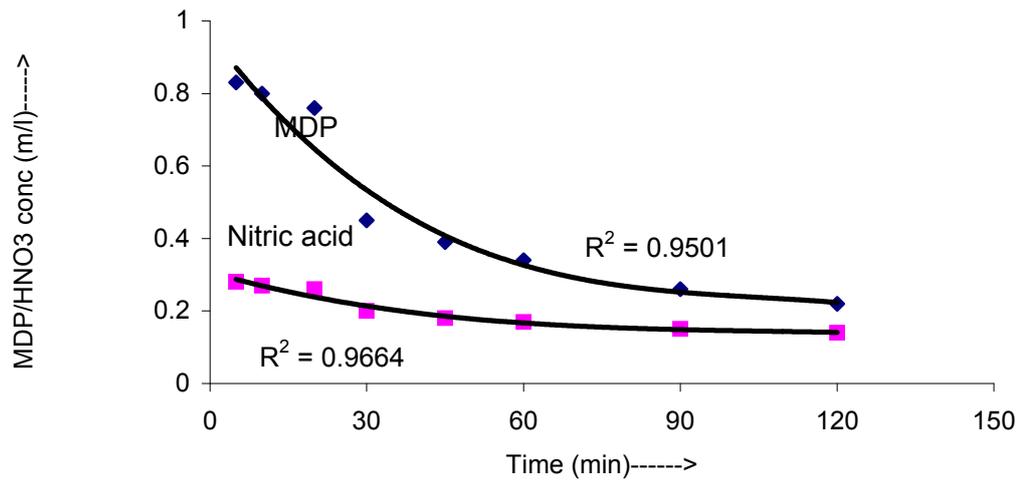
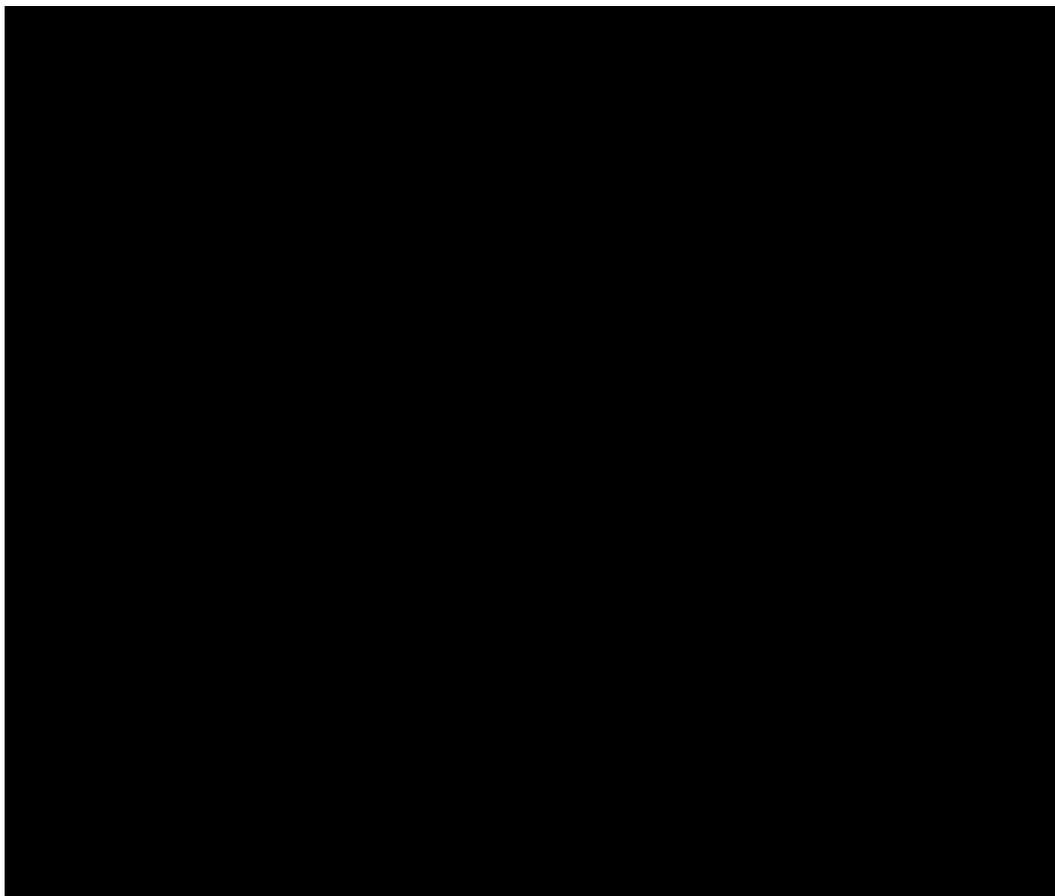


Fig.4.2 Variation of MDP and nitric acid conc. at 15°C



So the overall rate of the reaction can be written as,

$$-r_B = -\frac{dC_B}{dt} = k \cdot (C_B)^n \quad (4.2)$$

where, n is the order of the reaction,  $C_B$  is the concentration of MDP.

Taking natural logarithm (ln) of both sides, the equation (4.2) can be written as,

$$\ln \left( - \frac{dC_B}{dt} \right) = \ln (k) + n \ln (C_B) \quad (4.3)$$

From the experimental data, a plot of concentration ( $C_B$ ) Vs time (t) for depletion of MDP was obtained. The slopes of the curve are  $\left( \frac{dC_B}{dt} \right)$  in Figs. 4.2, 4.3 & 4.4. Thus, the order, n and the rate constant, k can be found out from a plot of  $\ln \left( - \frac{dC_B}{dt} \right)$  vs  $\ln(C_B)$ . By integrating the equation (4.2), reaction time for any amount of conversion can be calculated as below.

$$\text{Case-I : } \quad n \neq 1, \quad t = \left( \frac{1}{k} \right) \left[ \frac{C_B^{1-n}}{1-n} \right]_{C_{Bi}}^{C_{Bf}} \quad (4.4)$$

$$\text{Case-II: } \quad n = 1, \quad t = \left( \frac{1}{k} \right) \ln \left[ \frac{C_{Bf}}{C_{Bi}} \right] \quad (4.5)$$

Where t is reaction time,  $C_{Bi}$  and  $C_{Bf}$  are initial and final concentration of B.

#### 4.2.4 Temperature dependency rate equation

The kinetics of the above reaction have been carried out at 3 different temperatures  $5^{\circ}\text{C}$ ,  $15^{\circ}\text{C}$  and  $25^{\circ}\text{C}$ . As the temperature increases, rate constant (k) increases without altering the reaction order. With these values of k, the temperature dependency rate equation is derived using Arrhenious's Law.

$$k = k_o e^{-E/RT} \quad (4.6)$$

Where  $k_o$  is called frequency factor, E is the activation energy of the reaction and R is the universal rate constant. Taking natural logarithm of both sides of equation (4.6), it can be written as

$$\ln(k) = \ln(k_0) - \left(\frac{E}{R}\right) \cdot \frac{1}{T} \quad (4.7)$$

The reaction rate constants (k) are evaluated from the intercept of the plots given in Figs. 4.4, 4.5 and 4.6.

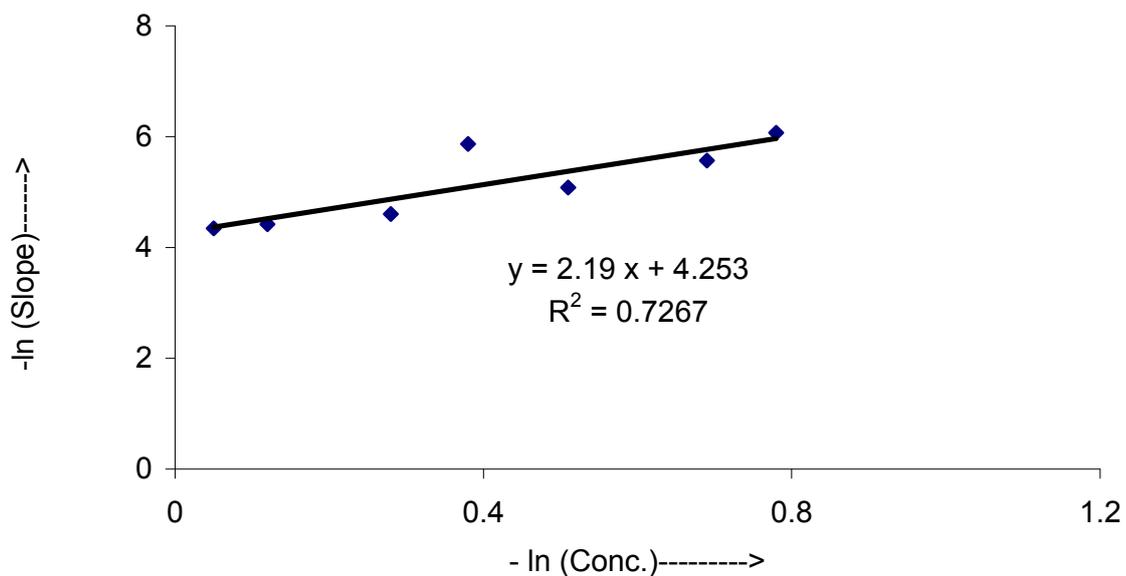


Fig. 4.4. Rate equation of nitration reaction at 5°C

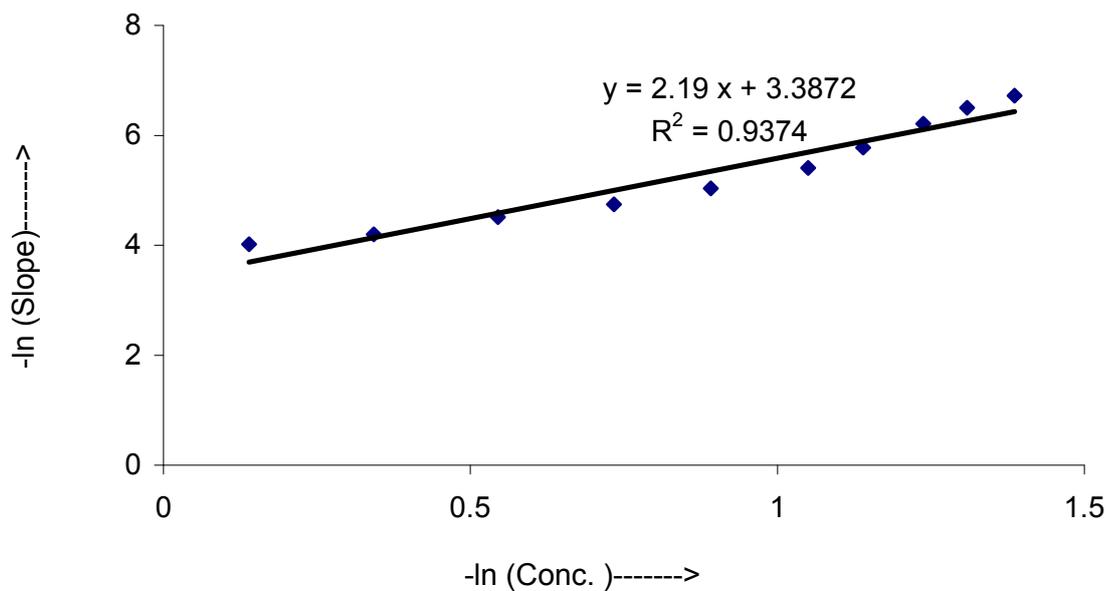


Fig. 4.5. Nitration rate equation at 15°C

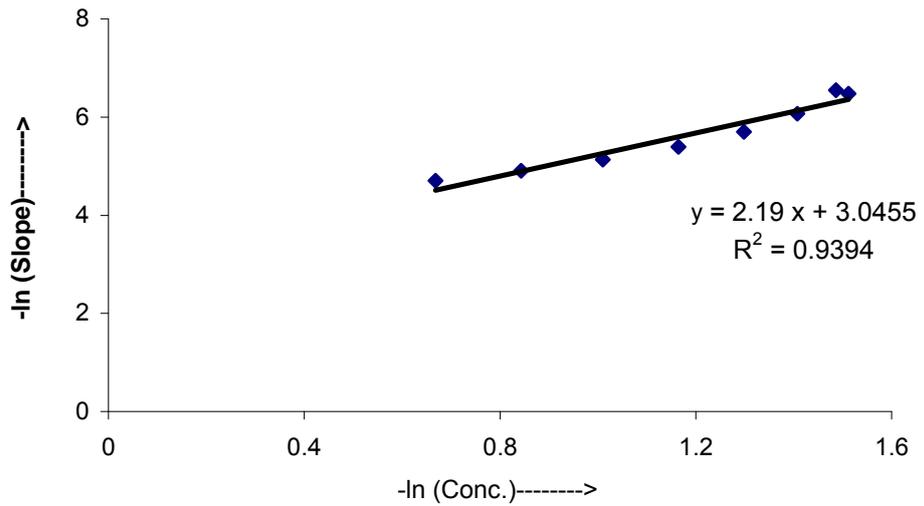


Fig.4.6. Nitration rate equation at 25°C

Temperature dependency rate equation i.e  $k$  as  $f(T)$  for nitration reaction is obtained from the plot of  $\ln(k)$  vs  $\left(\frac{1}{T}\right)$  is shown in Fig. 4.7.

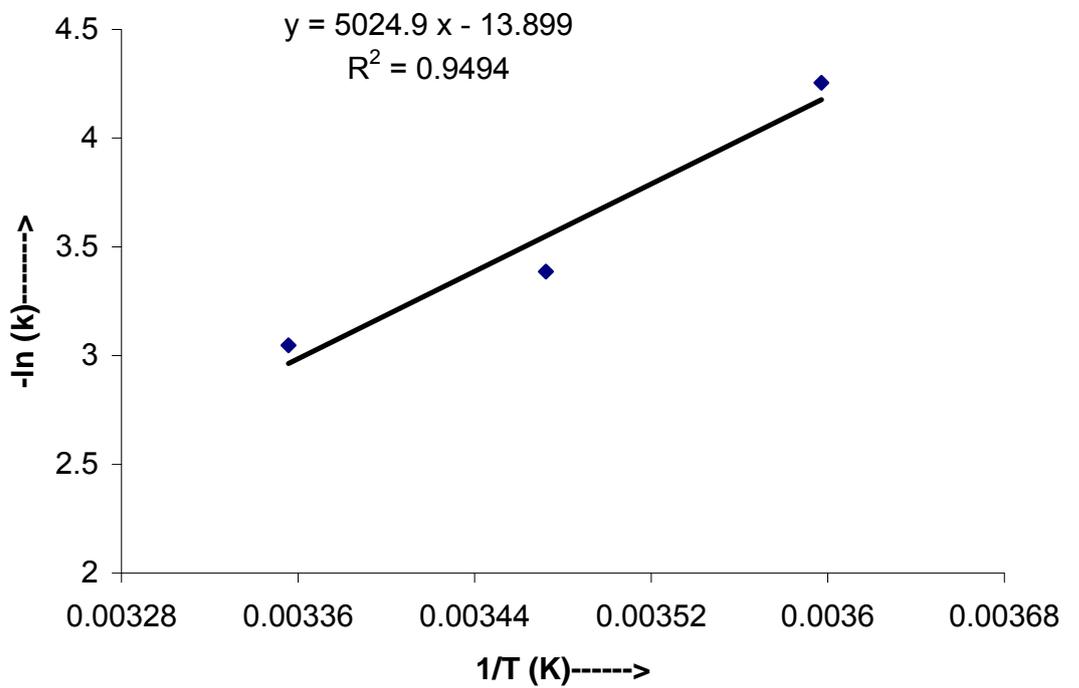


Fig. 4.7 Temperature dependency of reaction rate

#### 4.2.5 Estimation of heat generation during nitration

Nitration of MDP was conducted in a wide temperature domain ranging from 5 to 35°C where the reaction takes place at a reasonable rate. During the reaction, hazardous products like dinitromethene, nitroform etc are formed as side products and the decomposition of the reaction takes place at 100°C. Hence, it is essential to know the lowest possible operating temperature at which the reaction is having maximum yield and optimum heat generation rate during the process. Fig. 4.8 describes rate of heat generation (Q) as a function of temperature where Q increases with reaction temperature.

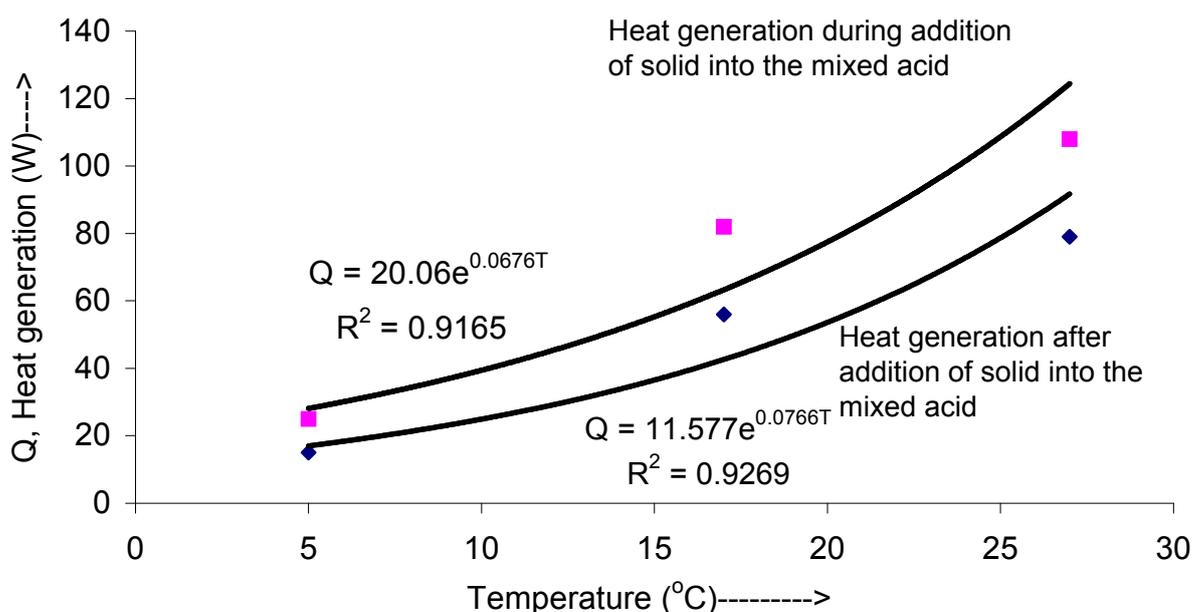


Fig. 4.8 Heat generation as function of Temperature

#### 4.2.6 Results and discussion : Nitration Kinetics

Experimental data in Table-4.1 is used for finding the concentration of MDP at different time with constant temperature. Variation of concentration with time at different temperatures 5°C, 15°C and 25°C are

shown in Figs. 4.1, 4.2 and 4.3 respectively. It is seen that change in HNO<sub>3</sub> concentration is almost negligible as compared to concentration of MDP. So the rate law is evaluated on the basis of MDP- concentration.

Natural logarithm (ln) of  $\left[-\frac{dC_B}{dt}\right]$  and ln (C<sub>B</sub>) values were calculated and plotted in Figs. 4.4, 4.5 and 4.6. Three equations for rate of reactions obtained from these figures are tabulated in Table 4.2. It is seen that the order, n of reaction is 2.19 ≈ 2 (pseudo 2<sup>nd</sup> order). Reaction rate constant, k (unit- (concentration<sup>-1</sup>) x (time<sup>-1</sup>)) increases with increase of temperature. The value of k is 0.014 at 5<sup>o</sup>C, 0.0338 at 15<sup>o</sup>C and 0.047 at 25<sup>o</sup>C. This implies that for increase of temperature by 10<sup>o</sup>C (from 5 to 15<sup>o</sup>C), rate constant increases by 2.4 times, whereas, k increases only by 1.4 times for increase of temperature from 15 to 25<sup>o</sup>C.

Table 4.2. Nitration rate equations by kinetic studies

Sl. No.	Temperature (°C)	Rate Equations	Pseudo Reaction Order, n	Pseudo reaction rate constant, k (Concentration <sup>-1</sup> ) (time <sup>-1</sup> )
1.	5	$\frac{dC_B}{dt} = -0.014 C_B^{2.19}$	~2	0.014
2.	15	$\frac{dC_B}{dt} = -0.0338 C_B^{2.19}$		0.0338
3.	25	$\frac{dC_B}{dt} = -0.047 C_B^{2.19}$		0.047

Using these rate equations, reaction times for different temperatures are calculated by common equations (4.4). It is found that for around 85% conversion of MDP to FOX-7, the required reaction time (minutes) would be 291, 112 and 64 at 5<sup>o</sup>C, 15<sup>o</sup>C and 25<sup>o</sup>C respectively.

The following temperature dependent rate equation, (4.8)

$$k = (44.24 \times 10^4) \cdot e^{\frac{-10}{RT}} \quad (4.8)$$

is obtained graphically by plotting  $\ln(k)$  vs  $1/T$ . Where activation energy (E) is  $\sim 10.048$  Kcal and frequency factor ( $k_0$ )  $\sim 44.24 \times 10^4$ . If exothermicity (460 kJ/mole, evaluated by RC experiments) of nitration reaction is compared with the activation energy (42.20 kJ/mole), it is seen that process is associated with high thermal hazards. This implies that to initiate the nitration reaction, small amount of energy is required but during reaction around 10 to 11 times more energy releases. So, lowest operating reaction temperature desirable without compromising yield and quality of product. Fig. 4.8 describes heat generation per mole of reactant with temperature. It is seen that as the temperature increases from  $5^\circ\text{C}$  to  $15^\circ\text{C}$  to  $25^\circ\text{C}$ , rate of heat generation, (Q) increases exponentially. Thus, the optimum reaction temperature is  $15^\circ\text{C}$  where yield (%) is maximum similar to that of  $25^\circ\text{C}$  but rate of heat generation is less compared to  $25^\circ\text{C}$ . Fig. 4.9a, compares the yield MDP nitration at different temperature.

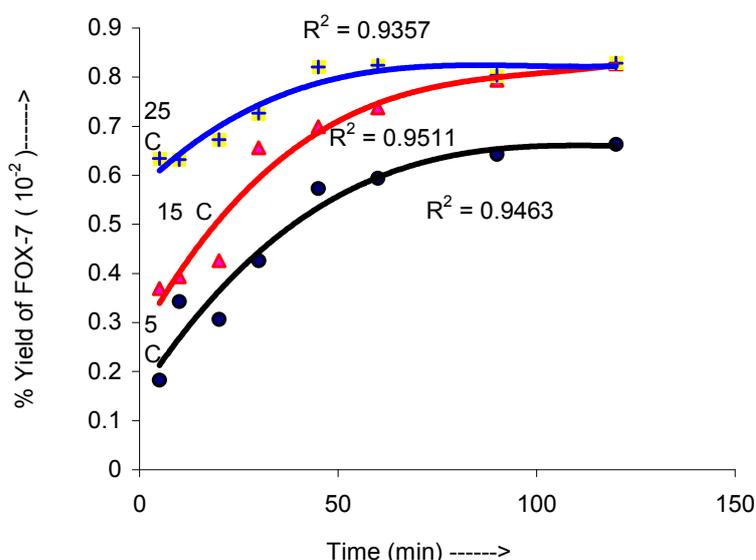


Fig. 4.9a. Variation of yield (%) of FOX-7 at different temperature

It is observed that at 5°C only 55 % conversion takes place in 2 hours, whereas, around 85% conversion takes place at 15°C in 2 hours and at 25°C reaction is still faster yet conversion is same as 15 °C in 2 hrs. But at 25°C, reaction takes place very vigorously and 80% of the reaction gets over by 40 minutes which is highly undesirable as nitroform and dinitromethane may form. Optimum reaction temperature, (15°C) is obtained by plotting of yield (%) Vs temperature shown in Fig. 4.9b. Details of the study (7) presented in IASPEP, 2007, Xian, China.

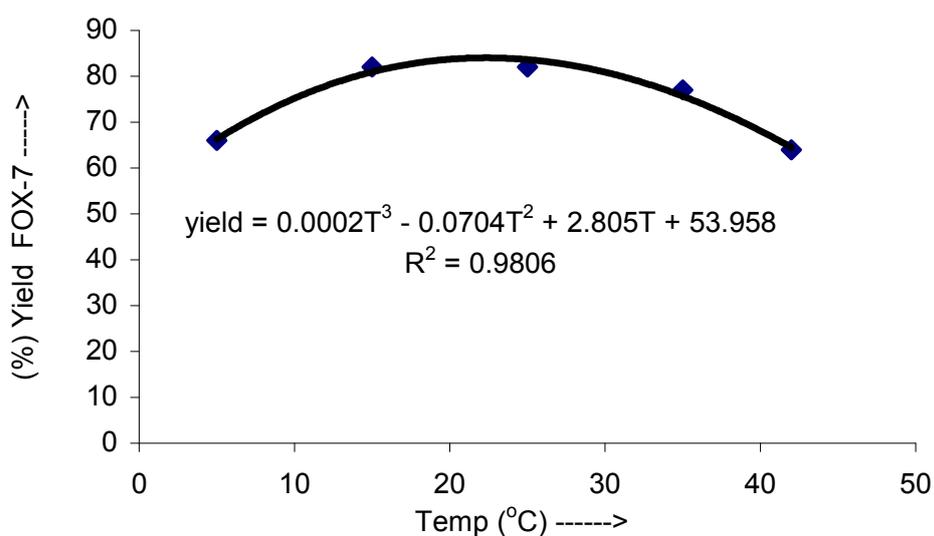


Fig. 4.9b. Effect of temperature on yield of FOX-7

#### 4.2.7 Conclusion : Nitration kinetics

Following few inferences are drawn from the above studies of kinetics:

- Nitration of MDP is a pseudo 2<sup>nd</sup> order reaction.
- Optimum reaction temperature for nitration is 15°C.
- Heat generation increases exponentially with temperature.

- Pseudo rate constant is  $0.0338 \text{ concentration}^{-1} \text{ time}^{-1}$  at  $15^{\circ}\text{C}$ .
- Using the rate equation, reaction time required is 110 min. at  $15^{\circ}\text{C}$ .
- Exothermicity (460 kJ/mole) of the reaction evaluated from temperature dependent rate equation is much higher compared to the activation energy (42 kJ/mole). This implies reaction to be carried at the lowest possible operating temperature without comprising the yield and quality of the product.
- Exponential rate of heat generation suggests efficient agitation and cooling system is important for scaling up of the process.
- With increase in temperature by  $10^{\circ}\text{C}$  (from 5 to  $15^{\circ}\text{C}$ ), reaction rate constant increases by 2.4 times. That is why at  $5^{\circ}\text{C}$  it requires 291 minutes to get 85% product compared to 112 minutes at  $15^{\circ}\text{C}$  for same conversion. Relatively higher activation energy suggests that the reaction is temperature sensitive.
- Frequency factor calculated for the reaction is  $44.24 \times 10^4$ .

### 4.3. Hydrolysis kinetics

#### 4.3.1 Hydrolysis Reaction

Synthesis of FOX-7 is being carried out by nitration of commercially available MPD (purity by HPLC >95%) using concentrated sulfuric acid,  $\text{H}_2\text{SO}_4$  (98%) and nitric acid  $\text{HNO}_3$  to produce tetranitro-MPD (NMPD) followed by acid catalyzed hydrolysis of this NMPD. After nitration of MPD, unreacted nitric acid as well sulfuric acid (~72% weight) contained NMPD produced which is added in the water under controlled condition to carry out the acid catalyzed hydrolysis to get the FOX-7. Overall reaction for hydrolysis is shown in the reaction scheme 2.10.

### **4.3.2 Hydrolysis Experiments**

Experimental set consists of cylindrical jacketed glass reactor (500 ml capacity) fitted with driving motor, agitator, temperature indicator-cum-controller for reaction in the jacket inlet and outlet. PID controlled cryostat/heating unit is connected to the reactor jacket to maintain the reaction as well as hydrolysis temperature. It is shown in Fig. 2.1 above. After nitration reaction, the reaction mass is quenched into the optimized quantity of water to carry out the acid catalyzed hydrolysis of NMPD under vigorous agitation. In order to optimize hydrolysis temperature and the temperature dependent hydrolysis constant, three sets of experiments were conducted at 15<sup>0</sup>C, 25<sup>0</sup>C and 40<sup>0</sup>C. At each temperature, around 10 experiments were carried out for different hydrolysis time ranging from 30 to 360 minutes at an interval of 30 minutes. After completion of each round, the solid product, FOX-7 is then filtered and washed with plenty of water for removal of acid present in it. The solid product after each run is then dried in the vacuum oven at 70<sup>0</sup>C for a period of 16 hrs. The weight of the product was determined for each run after drying and decomposition temperature was noted.

### **4.3.3 Hydrolysis Kinetics**

Several methods (4,6) available for determining the kinetic rate equation are mainly integral, differential, half-life period, method of excess etc. As the hydrolysis of NMDP is sensitive to temperature, rate of reaction was studied at fixed temperature with variation of time keeping all other parameters constant. In each method, it is essential to estimate the concentration of the reactant or the product at different reaction time. In

the present study, differential method was adopted to determine the rate law for hydrolysis reaction. Hence, the hydrolysis rate can be expressed as

$$r = k C_{FOX-7}^n C_{water}^m \dots \quad (9)$$

Where  $k$  is the hydrolysis rate constant,  $n$  and  $m$  are order of hydrolysis reaction with respect to FOX-7 concentration and water concentration. Amount of water being in excess than required (16 moles present as compared to 2 moles required), the rate equation is expressed as

$$r = \left( \frac{dC_A}{dt} \right) = k C_A^n \dots \quad (10)$$

Where  $n$  is the order of hydrolysis rate equation and  $C_A = C_{FOX-7}$ , taking natural logarithm ( $\ln$ ) in both sides, the equation (2) can be written as,

$$\ln \left[ \frac{dC_A}{dt} \right] = \ln k + n \ln [C_A] \dots \quad (11)$$

From the experimental data, a plot of concentration ( $C_A$ ) vs time for formation of FOX-7 was made. Using this concentration profile of FOX-7 at different temperatures, the slopes ( $\frac{dC_A}{dt}$ ) are evaluated.

Thus, the order  $n$  and rate constant  $k$  were found out from a plot of  $\ln \left( \frac{dC_A}{dt} \right)$  vs  $\ln(C_A)$  and the hydrolysis rate equation at 15 °C is

$$r = (2.02 \times 10^{-6}) C_{FOX-7}^{2.5} .$$

#### 4.3.4 Results and Discussion: Hydrolysis Kinetics

Variation of FOX-7 concentration with time at different temperature 15<sup>0</sup>C, 25<sup>0</sup>C and 40<sup>0</sup>C shown in Fig. 4.10, 4.11, 4.12. Pseudo order (n) of hydrolysis reaction is ~2.5. The rate constants at different temperatures are calculated from graphical Fig. 4.13, 4.14. Hydrolysis rate constants (k) and rate equations at different temperature are shown in Table-4.3. At 15<sup>0</sup>C hydrolysis is slow and takes more than six hours to complete. At 40<sup>0</sup>C hydrolysis is very fast within two hours it completes. Whereas at 25<sup>0</sup>C hydrolysis takes place at a moderate rate, which completes within 4 hours.

Besides, NMPD in unreacted nitrating acid mixture and dry NMPD (without mixed acid) were shown to have low hydrolytic stability and easily hydrolyzed in a humid atmosphere. The yield of FOX-7 at 15 <sup>0</sup>C is less compared to 25 & 40 <sup>0</sup>C. During experiments, it is observed that at 40 <sup>0</sup>C, rate of hydrolysis is very fast and rate of heat generation is also more compared to 15 & 25 <sup>0</sup>C. Dry NMPD, (after removing spent acid mixture) hydrolyzed in open moist air within 5 to 8 hours whereas; NMDP in 30-40% H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> is quite stable in open air for at least 2-3 days. Fig 4.15 shows that in 20% sulfuric acid as hydrolysis medium for a period of 4 hours at 25<sup>0</sup>C under high agitation yields around 90%. Details of the study (8) presented in International conference of HEMCE, 2009, Pune, India.

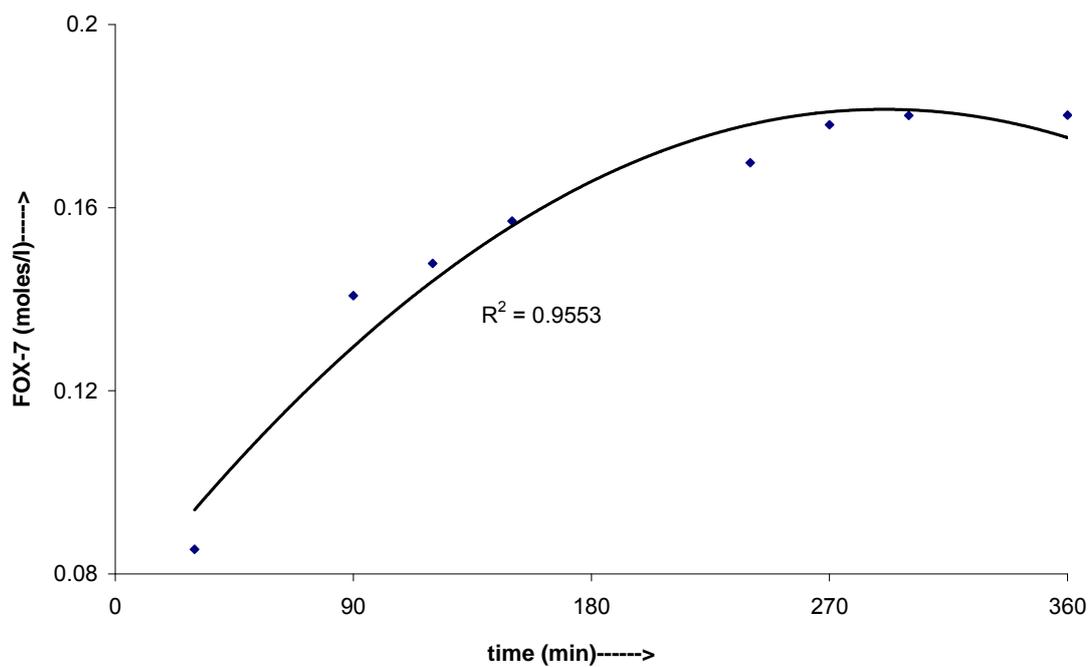


Fig.4.10. Concentration Profile of FOX-7 in hydrolysis at 15 °C

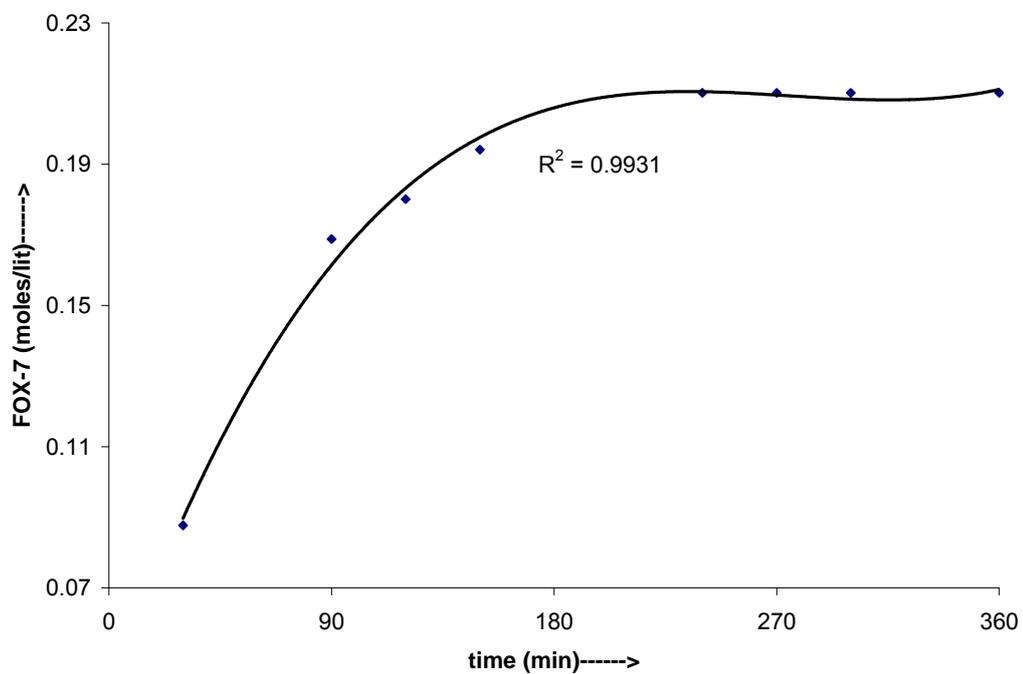


Fig.4.11. Concentration Profile of FOX-7 in hydrolysis at 25 °C

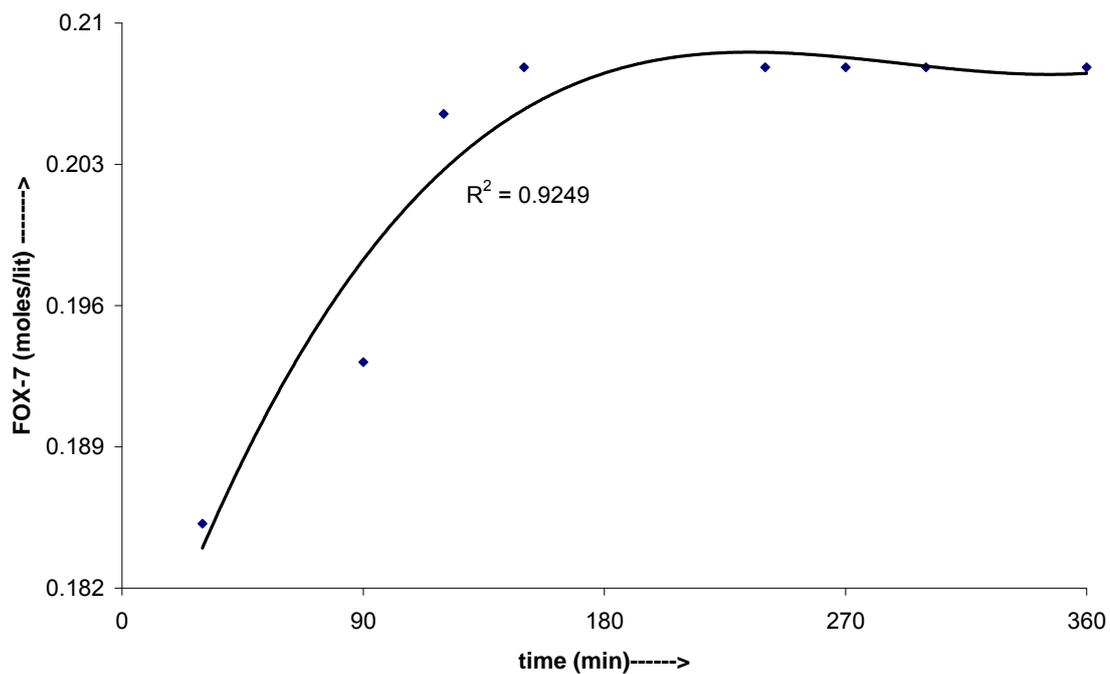


Fig.4.12. Concentration Profile of FOX-7 in hydrolysis at 40 °C

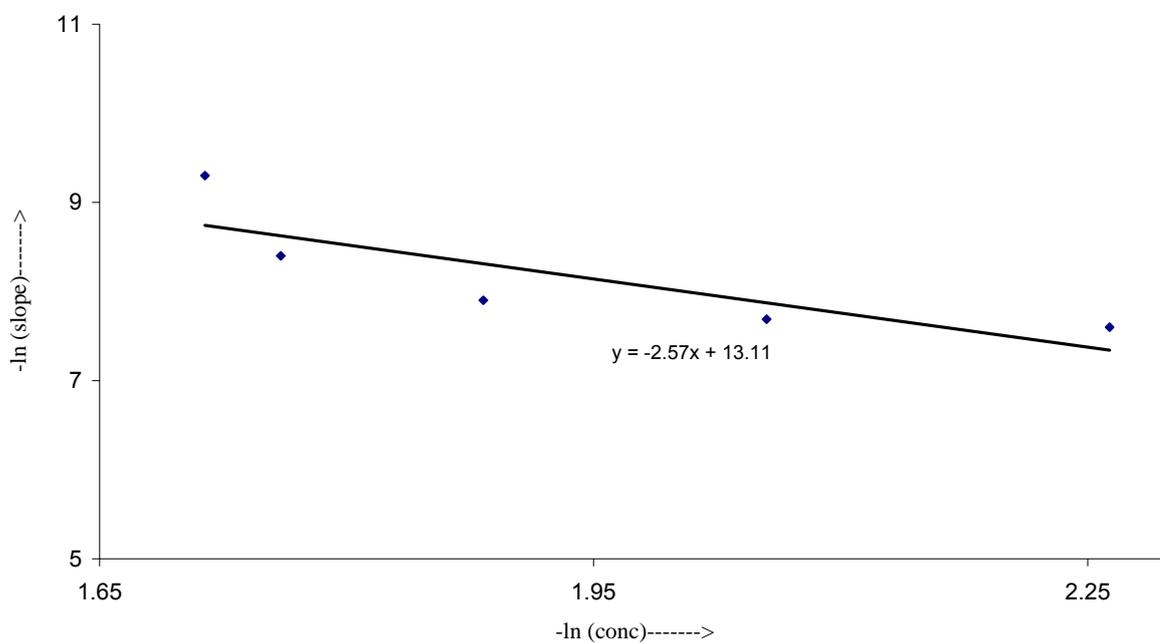


Fig.4.13. Hydrolysis rate equation at 15 °C

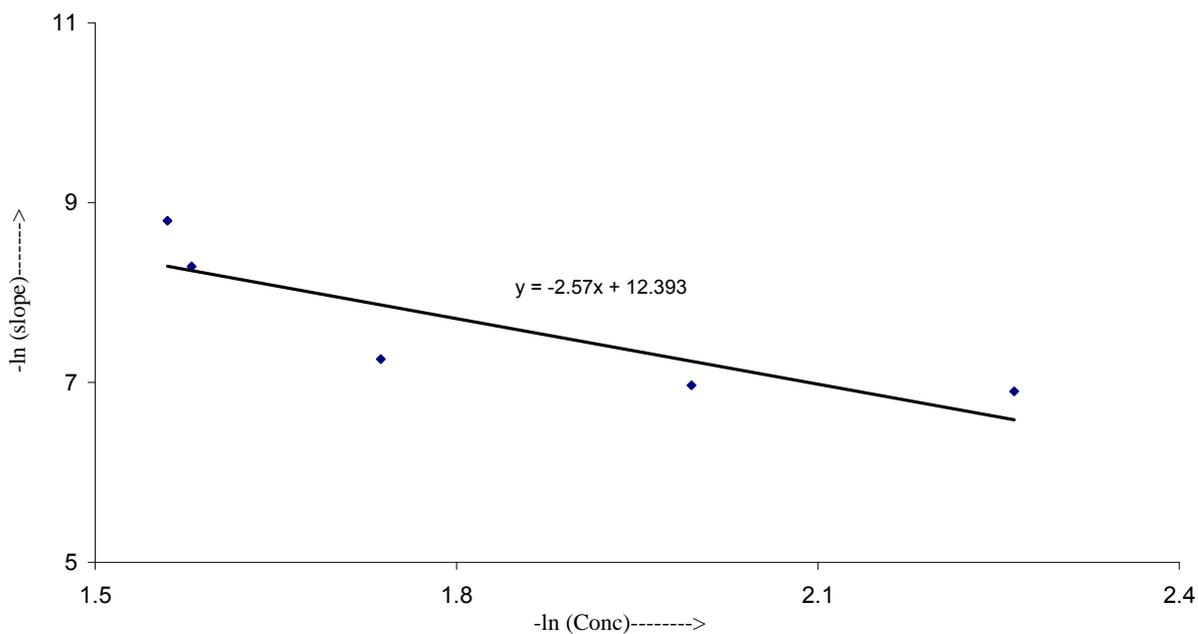


Fig.4.14. Hydrolysis rate equation at 25 °C

Table-4.3 Hydrolysis kinetic data at different temperature

Temperature ( °C)	Order of Reaction (n)	$-\ln(k)$	$k$ (mole <sup>-1.5</sup> lit <sup>-1</sup> min <sup>-1</sup> ) x 10 <sup>6</sup>
15	~ 2.5	13.11	2.01
25	~2.5	12.93	1.36
40	~2.5	8.8	1.50

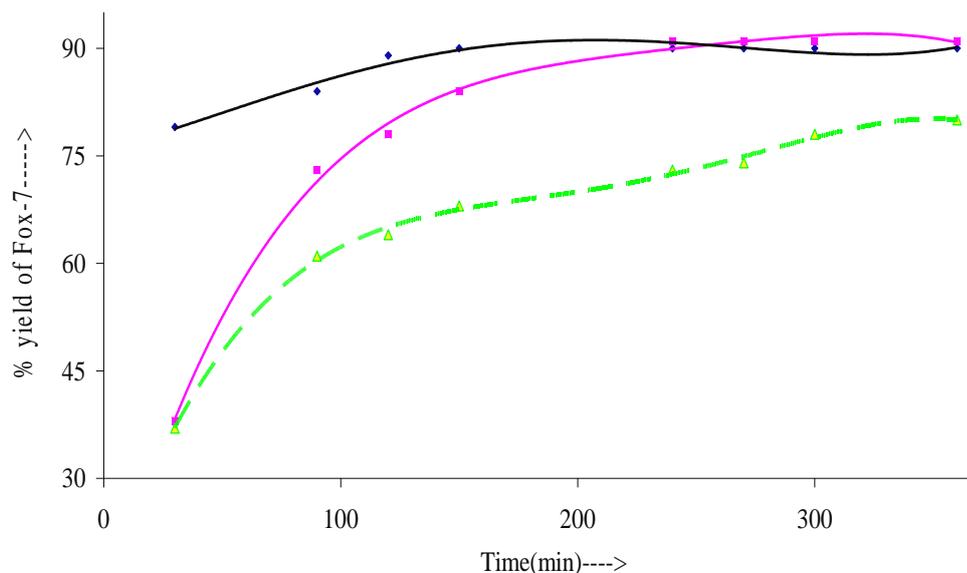


Fig.4.15. Effect of Temperature on hydrolysis with time

#### 4.3.5 Conclusion : Hydrolysis kinetics

The studies on hydrolysis of NMPD reveals following inferences like,

- Optimum hydrolysis temperature is  $\sim 25^{\circ}\text{C}$
- Rate of hydrolysis increases with temperature.
- Above  $45^{\circ}\text{C}$ , there is a distinct tendency for runaway reaction with copious frothing were noticed in hydrolysis mixtures.
- Hydrolysis of NMPD follows pseudo order of 2.5
- Hydrolysis rate constant is  $1.36 \times 10^{-4} \text{ moles lit}^{-1} \text{ min}^{-1}$  at  $25^{\circ}\text{C}$
- With increase in temperature by  $10^{\circ}\text{C}$  (from  $15^{\circ}\text{C}$  to  $25^{\circ}\text{C}$ ) hydrolysis rate increases by 1.3 times. That is why at low temperature rate is slow.
- Using the rate equation, the optimum hydrolysis time is 240 minutes at  $25^{\circ}\text{C}$ .

- Lower temperature ( $<30^{\circ}\text{C}$ ) is preferred to avoid frothing and runaway reaction which generally starts at higher temperature ( $>45^{\circ}\text{C}$ ).

#### **4.4 Studies on Parametric Sensitivity of MDP Nitration**

##### **4.4.1 Introduction:**

In order to operate a chemical system in a reliable and safe manner, it is often required to identify the sensitive regions in the system parameter space. The behaviour of such system is affected by many physicochemical parameters. Changing these parameters, characteristics of the system can be altered to realize desired behaviour or to avoid undesired behaviour. In case of batch processes which are inherently dynamical systems, are preferred when better control in quality of end product are desirable and volume processed are relatively small. Numerous investigation have been carried out in determining the optimal temperature profiles in the batch system. Westerholt et al. (9) and Lewin et al. (10) have estimated optimal temperature profile and safe start-up temperature in terms of design parameters for batch reactor. The trajectory of the system to reach terminal state depends on operating conditions or system parameters.

Eigenberger et al. (11) have predicted that an exothermic reaction proceeds slowly and smoothly. Under conditions of sufficiently low coolant temperature with all other variable keeping constant. There exist a threshold value of the coolant temperature above which exothermic reaction proceeds very fast untill sharp rise in temperature. At this high temperature, the reaction goes to completion quickly and under non-adiabatic condition the temperature decreases to the ambient value. This drastic change in system behaviour across a threshold value of a

parameter is called a run away or the system may be considered to be parametric sensitive. This behaviour is characterized by analyzing the dynamic temperature profile for nitration of MPD in a batch system. In general, most of the investigations of parametric sensitivity are happened to be theoretical or based on numerical simulation.

Frank-Kamentskii et al.(12) evaluated theoretically the critical temperature above which the temperature rise in the reactor is very fast for 0<sup>th</sup> order of the reaction system. Besides, the second derivative of the temperature profile can also be used to determine the parametric sensitivity. A positive second order derivative of the temperature profile implies that the system is parametrically sensitive and the conditions for parametric sensitivity are,  $\frac{d^2T}{dt^2} > 0, \frac{dT}{dt} > 0$

Morbidelli et al. (13) have determined a generalized criterion for parametric sensitivity for batch and tubular reactor. The variation in maximum temperature of non adiabatic reactor is determined by them. According to Morbidelli, the maximum temperature in a batch reactor is equivalent to the hotspot temperature of the tubular reactor. Eigenberger et al. (11) have described the concept of stability and safety in the context of batch and continuous system. According to Eigenberger, the continuous system may have multiple steady states where a system may go from a desirable steady state to undesirable steady state due to large amplitude perturbation. They emphasis that, the reaction in a batch system should be allowed to occur smoothly at a reasonable rate. The reaction occurring slowly is inherently unsafe as a local hotspot can trigger a runaway condition. In order to overcome this problem, it is suggested to carryout such reaction in semi batch mode. Villermaux et al. (14) discussed

runaway criteria in terms of time constants for reactions and cooling. Shukla P. K. et al.(15) have described the parametric sensitivity and the safety of the batch reactor for homogeneous and heterogeneous exothermic reaction system using the literature reported reaction kinetics. In this work the reactions chosen is shown in Scheme-2.9.

The reaction is exothermic and having varying degrees of complexity. Mandal A.K. et al. (7) have established the rate equation and kinetics of the reaction experimentally at laboratory level using differential method. The same kinetics were used to simulate the behaviour of the batch reactor. The simulations are compared with the experimental results. The system is then classified as being sensitive or other wise as per different criteria.

#### 4.4.2 Modelling

A homogeneous model is used to simulate the behaviour of the batch reactor for nitration of MPD. The reaction is assumed to occur in single phase and the pseudo reaction rate expression is, considering the presence excess nitric acid during nitration and water during hydrolysis. The mass and energy balance equations for the batch reactor can be written as follows,

$$v \frac{dC}{dt} = v r(C, T) \quad (12)$$

$$v \rho C_p \frac{dT}{dt} = v(-\Delta H_r) r(C, T) - UA(T - T_c) \quad (13)$$

$$r(C, T) = k_0 e^{-E/RT} C^n \quad (14)$$

Transforming the above equations in dimensionless form and replacing (14) in (12) & (13) yields the following,

$$\frac{dx}{dt} = k_0 C_i^{n-1} (1-x)^n e^{-\gamma/y} \quad (15)$$

$$\frac{dy}{dt} = B k_0 C_i^{n-1} (1-x)^n e^{-\gamma/y} - \beta(y - y_c) \quad (16)$$

Initial conditions are,  $t = 0, x = 0; y = y_{in}$

All the variables are defined in the nomenclature. Every term in the equation has unit of  $s^{-1}$ . Equations 15 & 16 are integrated subject to the above mentioned initial conditions using Euler method. The parameters  $k_0, B$  and  $\gamma$  are the characteristics of the nitration reaction system. The values of these parameters are not reported in any literature. The same has been estimated during kinetics experiment at laboratory and are used in simulation. Kinetic rate expression used for this work is

$$r = 1.87 * 10^6 e^{-10048/(RT)} * C_{MDP}^2 \quad (17)$$

The heat transfer coefficient parameter,  $\beta$  have been estimated experimentally during carrying out calorimetric experiment in reaction calorimeter (RC). Activation energy (E) as well as heat of reaction are also find out by kinetics studies and RC experiments. With these values parametric sensitivity have been predicted using the equation (15) and (16).

#### 4.4.3. Experiment

The experimental set-up (Fig.2.1) was used to generate basic data on concentration profile and subsequently reaction kinetics rate expression. Since the heat transfer coefficient ( $\beta$ ) in the equation (16) is the characteristic of the experimental setup, it is need to be determined experimentally. Heat loss / heat input to be measured in terms of an

overall heat transfer coefficient ( $U$ ). The work involves simulation of the reactor temperature profile and comparing with the experimental results. Heat of reaction and heat transfer coefficient are experimentally measured in the reaction calorimeter, Fig.3.6 and Fig. 3.8a. The reactor of the RC unit is a double jacketed, triple wall glass vessel of 2 lit capacity fitted with computer controlled agitation, liquid dosing, calibration heater, heating & chilling circulator through the jacket, temperature & pressure transmitter etc. The overall heat transfer coefficient for reaction mass is measured by two step calibration using heat flow calorimetry. The known amount of heat (37 W) is supplied for certain duration of the reaction mass (100 g nitration batch of MPD) at a constant reaction temperature ( $15^{\circ}\text{C}$ ) and the jacket temperature (circulator) is allowed to vary accordingly. This is done before and after the reaction to get initial and final value of heat transfer coefficient ( $U$ ). Linear interpolation method was used with initial and final value to evaluate overall ' $U$ '. Over all heat of reaction were evaluated based on this ' $UA$ ' using RC software.

#### **4.4.4 Simulation Results and Analysis**

Based on the experimental results, parameters  $\gamma, B, k_0$  for the nitration reaction have been evaluated and used for theoretical prediction of parametric sensitivity by modelling technique. Experimental results on the conversion of MDP to FOX-7 at different temperature 5, 15 &  $25^{\circ}\text{C}$  for fixed initial concentration of 1.31 gmoles/l of MPD are shown in Table-4.1. The model equations (15) & (16) are used to predict the conversion of FOX-7 and temperature profile using the kinetic rate expression (17) is shown in Fig.4.16. Comparing the Fig. 4.9a and Fig.4.16, it is seen that theoretical conversion is higher by 5 to 7 %. A temperature gradient of

10<sup>0</sup> C is maintained during the theoretical prediction. This may be due to the handling and operation loss during carrying out the actual batches.

In order to check that the parametric sensitivity of the system, the above

equations are solved to find out both  $\frac{dT}{dt}$  and  $\frac{d^2T}{dt^2}$ . It is seen that for a

temperature gradient (difference in reactor and jacket temperature) of 10<sup>0</sup>

C and reaction temperature above 20<sup>0</sup>C both  $\frac{dT}{dt}$  and  $\frac{d^2T}{dt^2}$  becomes

positive for a initial period of around 5 to 10 minutes, which indicates that

the system is sensitive in temperature rise. Fig.4.17 shows the effect of

circulator temperature on the reaction temperature. For fixed reaction

temperature (Tr) of 25<sup>0</sup>C (298 K), if we keep jacket / circulator temperature

(Tc) at 5<sup>0</sup> C and subsequently increase by 5<sup>0</sup> C till 20<sup>0</sup> C (293 K), it is seen

that the reaction temperature increases slowly up to Tc i.e. 288 K. Beyond

this Tc, Tr suddenly jumps by around 60<sup>0</sup> C which may take at least 10

minutes to get stabilize. Fig.4.18 shows the conversion at the same

temperature maintained at Fig.4.17. As the circulator temperature

increases, conversion, x also increases till 288 K, beyond that the

conversion is very fast , but it is highly unsafe due to large temperature

rise. The effect of initial concentration on yield is shown in Fig.4.20. In Fig.

4.20 it is seen that for fixed Tc at 278 K, up to 308 K the reactor stabilizes

quickly but beyond that, at 310 K a huge instability is generated. Fig.4.20

shows that how this instability can be stabilized if the generated heat is

removed from the system. This result suggests that the nitration of MDP

is parametrically sensitive specially with temperature. Fig. 4.21 suggest

that in the temperature band of 278 to 308 K can be used at fixed Tc of

278 K. The actual operating condition can be chosen as combination where yield is maximum and reactor becomes stable.

Barkelew(16) criteria have also been used to demarcate the sensitive region from insensitive region in parameter space. It involves two dimensionless parameters: N, the rate of heat removal and S, the rate of heat generation. In terms of parameters, N & S, N<S indicates sensitive process or vice versa. These are defined for an n<sup>th</sup> order reaction as,

$$N = \frac{UA}{\rho C_p V k_0 (e^{-E/RT_c}) C_{in}^{n-1}} \quad S = \frac{(-\Delta H_R) C_{in} E}{\rho C_p R T_c^2}$$

For fixed initial concentration of MDP, value of N & S has been calculated at fixed ambient temperature of 208 K and at different reaction temperature (310, 308 and 298 K) and jacket temperature (288, 283 and 278 K). Value of N (2.5) is less than that of S (11.8) suggest nitration of MDP is sensitive to temperature.

Villermax<sup>6</sup> criteria have also been used to identify the process sensitivity by evaluating characteristics time constants, t<sub>r</sub> (reaction time) and t<sub>c</sub> (heat removal time). If t<sub>r</sub> is greater than t<sub>c</sub>, then the reaction induction time is larger than the time scale for the reactor to lose heat. So, the reaction is very slow and heat loss is very fast (more heat transfer area is available). The sensitivity criteria used here is t<sub>r</sub> < t<sub>c</sub> for sensitive process and vice versa. These are defined for an n<sup>th</sup> order reaction as,

$$t_r = \frac{T_c^2 \rho C_p}{T(-\Delta H) C_{in} k_0 e^{-E/RT_c}} \quad t_c = \frac{\rho C_p V}{UA}$$

For fixed initial concentration of MDP, t<sub>r</sub> and t<sub>c</sub> have been calculated at fixed ambient temperature and different reactor and jacket temperature. The value of t<sub>r</sub> (0.3) is slightly lower than t<sub>c</sub> (0.6) suggest that the reaction is marginally sensitive.

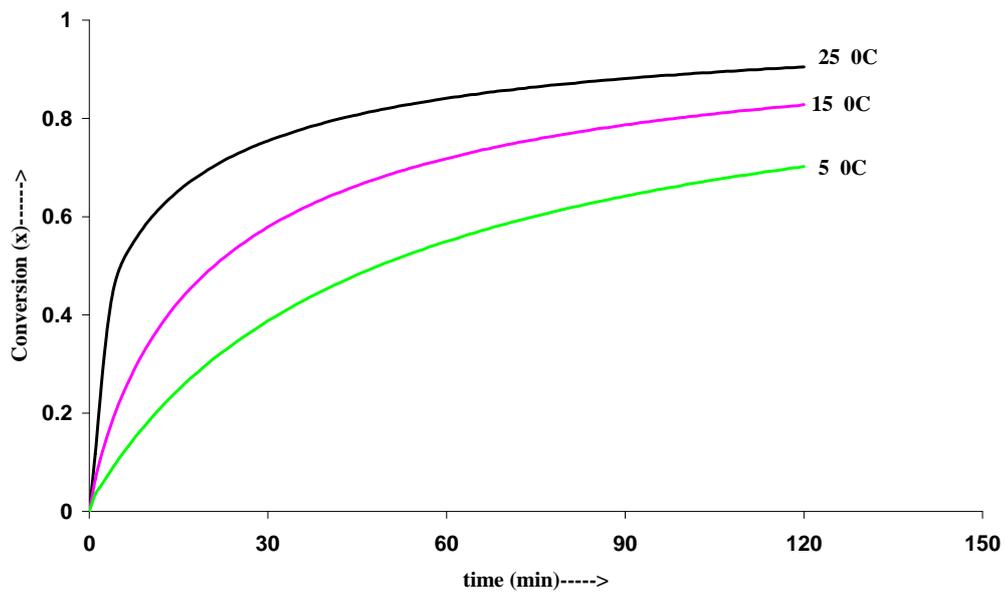


Fig.4.16 Concentration of FOX-7 with different Temp & time (simulated)

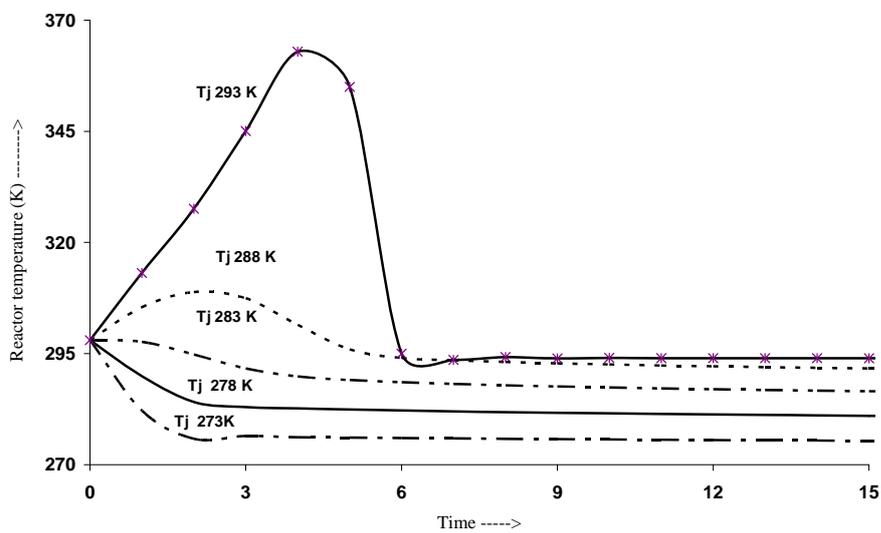


Fig.4.17 Effect of Temp on reaction at fixed reactor Temp, 298 K

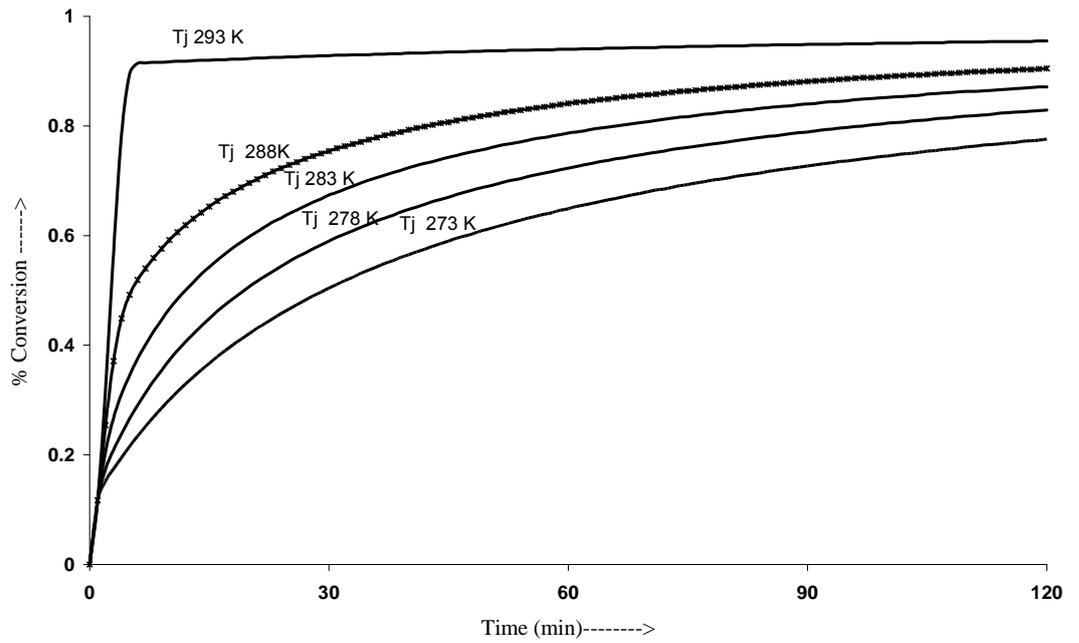


Fig.6 Effect of jacket temp for a fixed reaction temperature, 298 K

Fig. 4.18. Effect of jacket temperature for a fixed reaction temperature, 298 K

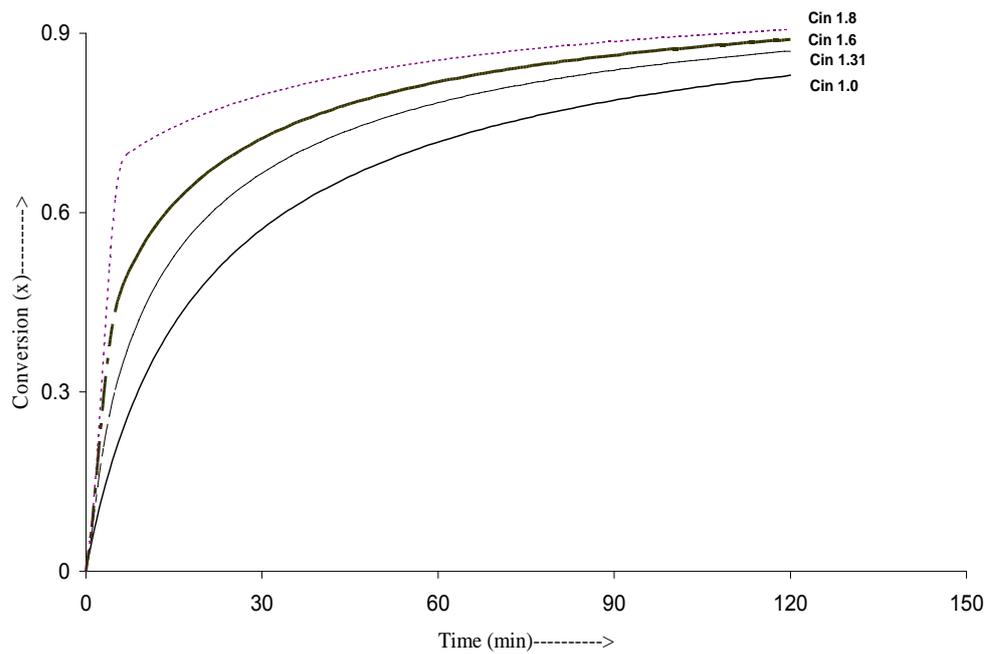


Fig. 4.19 Effect of initial concentration of MDP on yield at fixed reactor temp, 288 and jacket temperature, 288 K

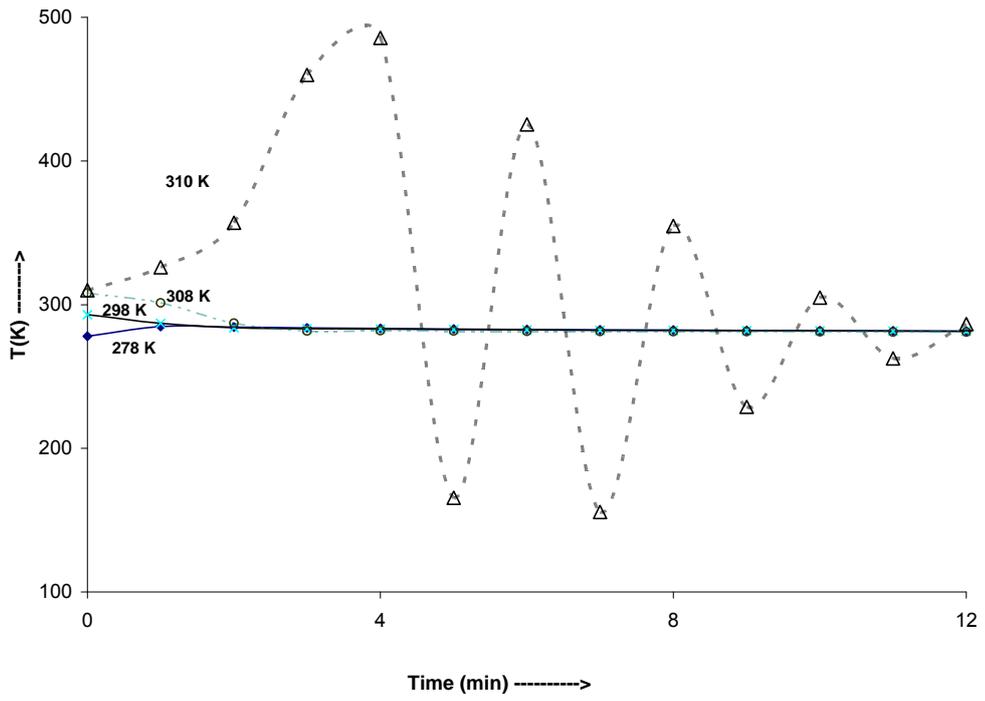


Fig. 4.20 Reactor stability at different reaction temperature and fixed jacket temperature, 278 K

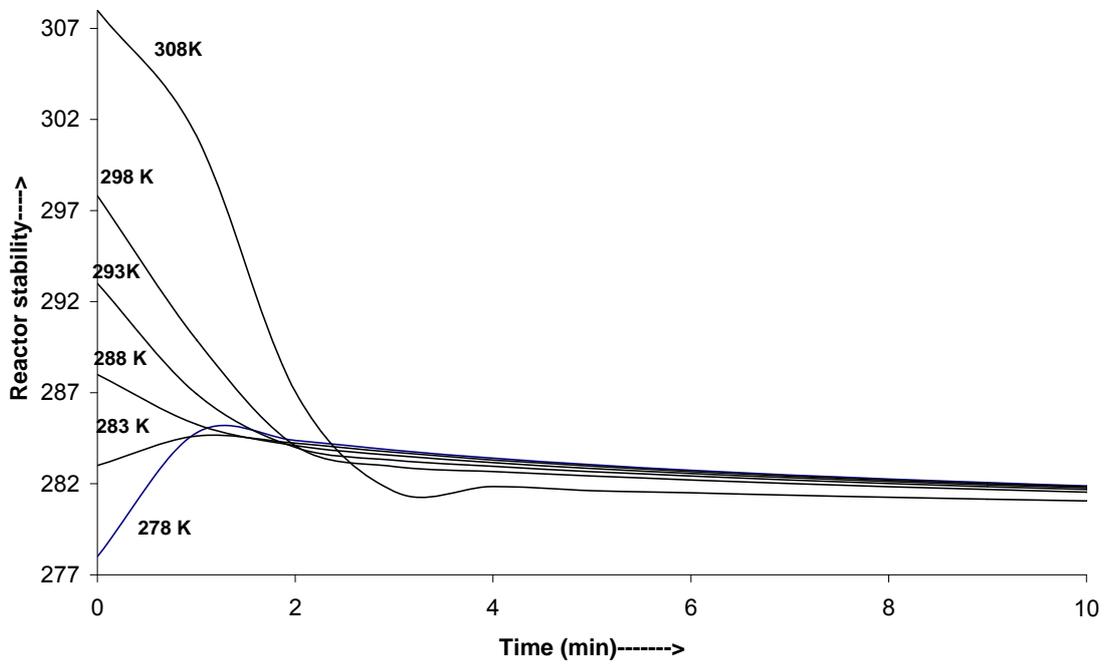


Fig 4.21 Temperature profile of reactor at a fixed jacket temperature, 278 K

#### 4.4.5 Conclusion

In this study, sensitivity is measured in terms of maximum rise in reaction temperature with the variation of other parameters. In several situations the maximum temperature rise is almost more than the decomposition temperature (100 C). Wide changes in operating conditions (other than the optimized conditions) for such reaction process is not recommended as both the reactor stability and yields get affected. However, the reaction rate can increase drastically with increase in temperature by sharp reduction in time causing the system sensitive. For the temperature gradient (difference in reactor and jacket temperature) more than of 10<sup>0</sup> C and reaction temperature above 20<sup>0</sup>C, the reaction becomes sensitive. This information is helpful during the plant operation. The existing criteria based on the literature appears to be conservative as they predict the system as sensitive under certain conditions, even at relatively low temperature 25 <sup>0</sup>C. So, there is a need for more rigorous criteria which can demarcate the boundary better.

## Nomenclature

A = Area of heat transfer, m<sup>2</sup>

B =  $(-\Delta H)C_{in} / \rho C_p T_{ref}$ , dimensionless heat of reaction

C = Reactant concentration, mole/cm<sup>3</sup>

C<sub>in</sub> = Initial reactant concentration, mol/cm<sup>3</sup>

C<sub>p</sub> = Specific heat, cal mole<sup>-1</sup> K<sup>-1</sup>

E = Activation energy, cal/mole

K<sub>0</sub> = rate constant, (mole/l)<sup>-1</sup> s<sup>-1</sup>

T = Reactor temperature, K

T<sub>C</sub> = Ambient temperature, K

T<sub>ref</sub> = Reference temperature, K

U = Overall heat transfer coefficient

v = Reactor volume, L

x = Dimension less conversion, (1-C/C<sub>0</sub>)

y = Dimensionless temperature, T/T<sub>ref</sub>

y<sub>C</sub> = Dimension less ambient temperature, T<sub>C</sub>/T<sub>ref</sub>

δ = Dimensionless activation energy, E/RT<sub>ref</sub>

β = Heat transfer coefficient parameter, (UA/V C<sub>p</sub>), s<sup>-1</sup>

ρ = Density of the reaction mixture, g/cm<sup>3</sup>

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# Chapter 5

## Micro Reactor Modelling & Simulation with MDP Nitration

### 5.1 Importance of Micro reactor

Nitration of 2-Methyl-4,6-dihydroxy-pyrimidine (MDP) is a highly exothermic and hazardous reaction. Conducting such reaction in a batch reactor follow an unsteady state and its trajectory depends on various important parameters such as temperature, reaction mass, circulating coolant etc. However, overall productivity, process control and safety of the batch process are highly restricted due to lower surface to volume ratio. In the present work, an effort has been made to overcome the limitations of batch reactor by using the micro reactor device. Micro reactor is having extremely high surface to volume ratio, which has been explored to carry out nitration of MDP both numerically as well as experimentally and the results were compared with conventional batch reactor.

Micro reaction system has been modelled using two dimensional (2-D) heat flow and mass transfer equations. The kinetic rate equation for nitration of MDP has evaluated experimentally by differential method which is used in modeling of the micro reactor. The numerical results from the 2-D model for conversion and temperature profile along the length and radius of micro reactor have been compared with corresponding results obtained for batch reactor.

In order to validate the model several experiments were conducted in micro reactor. The experimental results from micro reactor revealed that the nitration of MDP takes place even at much lower concentration and lower residence time with better control of temperature profile.

## **5.2 Introduction**

1,1-Diamino-2,2-dinitroethene (FOX-7) is a futuristic insensitive high explosive and a potential candidate to replace cyclotrimethyl trinitramine (RDX). Due to its chemical and thermal stability, it has created significant interest in the recent past. At High Energy Materials Research Laboratory (HEMRL), FOX-7 is prepared by adopting a two step batch process viz. nitration of 2-methyl-4,6-dihydroxy-pyrimidine (MDP) to get nitrated intermediate followed by acid catalyzed hydrolysis of nitrated MDP to get FOX-7. Nitration of MDP is highly exothermic and the heat of reaction evaluated by reaction calorimeter (RC) (1) is ~460 kJ/mole of FOX-7. Control of operating parameters like temperature, flow rate etc. is difficult in conventional stirrer tank reactor, therefore the higher productivity is difficult to realize mainly because of lower surface to volume ratio. Since the problem has not yet been addressed/reported in open literature by any researcher so far it is thought appropriate to overcome this problem with a novel approach by using micro-tubular reactor. It has high surface to volume ratio, efficient heat and mass transfer characteristics which vastly improved fluid mixing etc. in addition to provision of precision control of reaction with resulting in improved conversions, selectivity etc. The reaction time is less compared to conventional reactors with less degradation of side product. Also the optimization and scalability are significantly easier.

Modelling and simulation of micro tubular reactor for the above nitration reaction have been studied and subsequent validation to access the feasibility by conducting the experiments in micro tubular reactor have been presented in this work. The reaction kinetics for the nitration have been studied in detail and rate equation,  $\frac{dC_B}{dt} = -0.014C_B^{2.19}$  has already been developed (2) by differential method. The same rate equation has been utilized here for modeling and simulation.

In the present work, a tubular reactor surrounded by a cooling media/ambient atmosphere is considered for modeling and simulation. A few investigators/researchers (3-9) have described the analogous models of packed tubular reactor in which both radial and axial gradients of temperature and concentration were taken into account. Ahmed et al. (5-6) previously solved such two dimensional (2D) model by converting partial differential equations in to ordinary differential equations. However, in the present work the partial differential equations are solved step wise by converting it in to difference form. Besides, Information about advantages of micro reactors are also reported by various other authors (10-12).

### **5.3 Modelling**

#### **5.3.1 Reaction**

Nitration of MDP is a highly exothermic reaction, where a mixture of concentrated sulphuric acid,  $\text{H}_2\text{SO}_4$  (98%) and nitric acid,  $\text{HNO}_3$  (98%) are used as nitrating agent. MDP is first dissolved in sulfuric acid at desired concentration. Concentrated nitric acid and MDP is allowed to mix in a micro mixture and then allowed to flow through micro reactor at desired flow rate in the mole ratio of  $\text{MDP} : \text{HNO}_3 : \text{H}_2\text{SO}_4 :: 1 : 5.1 : 10.1$ . The temperature of the mixture is maintained at the desired level. The overall reaction is shown in Scheme 2.6.

#### **5.3.2 Micro Reactor**

Micro reactor implies a reaction chamber whose dimensions are typically in the range of micrometers ( $\mu\text{m}$ ) with volumetric capacity in the range of microlitres ( $\mu\text{l}$ ) and  $l/d$  ratio at least  $>2000$ . The possibility of reduction in dimensions with small volumes of reaction zone would allow application of high temperature or concentration with significant ease of process control and

thermal management. This would therefore, allow previously infeasible regimes of operation possible with improved performance. Richardson and Rase (1978) (11) reported a continuous stirred micro reactor for liquid-liquid reactions where by adjusting inputs and operating conditions it was possible to delineate the chemical steps from intervening transport efforts. In the present study the metallic reactor of about ~1mm diameter with  $L/D > 2000$  has chosen for the modeling and simulation.

### **5.3.3 Modeling of micro-tubular reactor**

The overall reaction rate equation used has been reported by Mandal et al (2) for a batch reactor. The rate equation reveals how much reaction has taken place at any time in the reactor provided the temperature and concentration are known. To evaluate the Temperature and Concentrations, energy and mass balances are formulated for a entering fluid flowing through the tubular reactor. These balances are in the form of differential equations, the solutions of which gives the temperature and concentrations at any location including the reactor exit. These concentration and temperatures are the solutions to the design problem. The analytical solutions of these differential equations are not possible due to prevailing temperature gradient and then the design process entails the numerical solution of a set of coupled differential equations. These differential equations are first converted to a difference form. The procedure adopted is described later.

The reactants are allowed to enter in the micro tubular reactor at a uniform temperature and composition, but as they pass through the reactor and the reaction occurs, the accompanying heat of reaction induces both longitudinal and radial variations in temperatures. In order to make the problem

simple, it is assumed that the entire reactor operates isothermally and the rate is a function of concentration. However, practically the rate will vary along the reactor because of concentration and temperature change in both radial and longitudinal directions. The integration of the mass balance requires the numerical solution technique. The calculation is done on the basis across the incremental diameter of the reactor tube for a small longitudinal increment and repetitions of the process for each successive longitudinal increment. The radial distribution of velocity would account for radial concentration and the temperature gradient by using Peclet numbers which themselves varied with radial position and would allow for axial dispersion if that were significant.

The following assumptions have been used for 2D model equations.

- The operation is considered to be at a steady state
- Longitudinal dispersion is neglected
- Both mass velocity and Peclet number for mass and heat transfer are constant across the reactor tube.
- Velocity is permitted to vary with radial position.
- External wall temperature is kept constant, however internal wall temperature is varying with axial direction
- Effective radial thermal conductivity and radial diffusivity are assumed to be constant.
- The temperature gradient at centre line is zero but at wall is determined by heat transfer characteristics. Considering standard equations for mass and heat balance of reactant in a tubular reactor, following model equations (10) used to represent concentration and temperature profile of micro reactor system as below,

$$\frac{\delta}{\delta r} \left( r E_r \frac{\delta C}{\delta r} \right) + r \frac{\delta}{\delta z} \left( -u_z C + E_z \frac{\delta C}{\delta z} \right) - r_c r = 0 \quad (5.1)$$

$$\frac{\delta}{\delta r} \left( r k_r \frac{\delta T}{\delta r} \right) + r \rho c_p \frac{\delta}{\delta z} \left( -u_z T + k_z \frac{\delta T}{\delta z} \right) - r_c r \Delta H = 0 \quad (5.2)$$

Considering that the diffusivities ( $E_r$ ) and thermal conductivities ( $k_r$ ) are not very sensitive to  $r$  or to  $z$  and the velocity ( $u$ ) is not the function of  $z$ , Eq.(5.1) and (5.2) may be written

$$E_r \left( \frac{1}{r} \frac{\delta C}{\delta r} + \frac{\delta^2 C}{\delta r^2} \right) - u_z \frac{\delta C}{\delta z} + E_z \frac{\delta^2 C}{\delta z^2} - r_c = 0 \quad (5.1a)$$

$$k_r \left( \frac{1}{r} \frac{\delta T}{\delta r} + \frac{\delta^2 T}{\delta r^2} \right) - u_z \rho c_p \frac{\delta T}{\delta z} + k_z \rho c_p \frac{\delta^2 T}{\delta z^2} - r_c \Delta H = 0 \quad (5.2a)$$

As the axial mixing in the bulk of the fluid is negligible i.e. the longitudinal diffusion is omitted, the flow is fully developed, density and specific heat are constant, the operation is at steady state, then the equation 5.1a & 5.2a describing heat and mass balance becomes,

$$u \frac{\delta C}{\delta z} - E \left( \frac{1}{r} \frac{\delta C}{\delta r} + \frac{\delta^2 C}{\delta r^2} \right) + r_c = 0 \quad (5.1b)$$

$$u \rho c_p \frac{\delta T}{\delta z} - k \left( \frac{1}{r} \frac{\delta T}{\delta r} + \frac{\delta^2 T}{\delta r^2} \right) - r_c \Delta H = 0 \quad (5.2b)$$

In the experimental reactor which is modelled in this work, the wall temperature is maintained by means of jacket of cold water circulation and drop across the wall could be assumed negligible. Therefore the wall temperature,  $T_w$  was taken as constant and equal to the coolant temperature,  $T_c$ , then the boundary conditions are,

$$r = 0, \quad \frac{\delta C}{\delta r} = 0, \quad \frac{\delta T}{\delta r} = 0 \quad (5.3)$$

$$r = r_w, \quad \frac{\delta C}{\delta r} = 0, \quad T = T_w \quad (5.4)$$

$$z = 0, \quad C = C_i, \quad T = T_i \quad (5.5)$$

### 5.3.4 Dimensionless Variables

Unlike radial position, the axial / longitudinal diffusion in the tubular reactor is neglected, the length of the reactor plays the same role as the axial position  $z$  and hence it is not required to be used as characteristic length. The tube radius,  $r_w$  is used as a characteristic length and The dimensionless reaction rate is defined as

$$r_c^* = r_c / r_{ci}$$

Where  $r_{ci}$  is the rate of reaction at starting feed condition ( $T=T_f$  and  $x=0$ ). In addition to the above, using  $T_f$ ,  $C_0$ ,  $\langle u \rangle$ ,  $\langle E_r \rangle$ ,  $\langle k_r \rangle$  as characteristic value, then Eq. 5.1(b) and 5.2(b) become,

$$u_z^* \frac{\delta x}{\delta z^*} - E_r^* \frac{1}{\alpha P_{em}} \left( \frac{1}{r^*} \frac{\delta x}{\delta r^*} + \frac{\delta^2 x}{\delta r^{*2}} \right) - r_c^* \frac{D_{am}}{\alpha P_{em}} = 0 \quad (5.1c)$$

$$u_z^* \frac{\delta T^*}{\delta z^*} - k_r^* \frac{1}{\alpha P_{em} L_e} \left( \frac{1}{r^*} \frac{\delta T^*}{\delta r^*} + \frac{\delta^2 T^*}{\delta r^{*2}} \right) - r_c^* \frac{H^* D_{am}}{\alpha P_{em}} = 0 \quad (5.2c)$$

Where,

$$H^* = \frac{\Delta H C_0}{\rho c_p T_f}, \quad L_e = \frac{\rho c_p \langle E_r \rangle}{\langle k_r \rangle}, \quad D_{am} = \frac{r_w^2 r_{ci}}{\langle E_r \rangle C_0}$$

are dimensionless adiabatic temperature rise , Lewis number and modified Damkohler number respectively.

Multiplying the equations 5.1c and 5.2c by  $\alpha P_{em} / D_{am}$  resulting in the dimensionless axial distance  $\zeta = z r_{ci} / \langle u_z \rangle C_0$  then the equations 5.1c and 5.2c becomes

$$u^* \frac{\delta x}{\delta \zeta} - E^* \frac{1}{D_{am}} \left( \frac{1}{r^*} \frac{\delta x}{\delta r^*} + \frac{\delta^2 x}{\delta r^{*2}} \right) - r_c^* = 0 \quad (5.1d)$$

$$u^* \frac{\delta T^*}{\delta \zeta} - k^* \frac{1}{D_{am} L_e} \left( \frac{1}{r^*} \frac{\delta T^*}{\delta r^*} + \frac{\delta^2 T^*}{\delta r^{*2}} \right) - r_c^* H^* = 0 \quad (5.2d)$$

The dimensionless boundary conditions become,

$$\begin{aligned} \text{at } r^* = 0, \quad \frac{\delta x}{\delta r^*} = 0, \quad \frac{\delta T^*}{\delta r^*} = 0 \\ \text{at } r^* = 1, \quad \frac{\delta x}{\delta r^*} = 0, \quad T^* = T_w^* \\ \text{at } \zeta = 0, \quad x = 0, \quad T^* = T_f^* \end{aligned}$$

### 5.3.5 Solution of PDE

Equation 5.1(d) and 5.2(d) are solved by a stepwise numerical procedure, starting at the entrance to the reactor. The equations are first written in difference form. Let n & L represent the number of increments in the radial and axial directions respectively, and  $\delta r^*$  and  $\delta \zeta$  be it's magnitude, so that

$$\begin{aligned} r^* &= n\Delta r^* \\ \zeta &= L\Delta \zeta \end{aligned}$$

The conversion and temperature at any point in the tubular reactor can be written using second difference form in r and z direction are,

$$x_{n,L+1} = x_{n,L} + \frac{E^* \Delta \zeta}{D_{am} u^* \Delta r^{*2}} \left[ \frac{1}{n} (x_{n+1,L} - x_{n,L}) + x_{n+1,L} - 2x_{n,L} + x_{n-1,L} \right] + \frac{r_c^* \Delta \zeta}{u^*} \quad (5.1e)$$

$$T_{n,L+1}^* = T_{n,L}^* + \frac{k^* \Delta \zeta}{L_e D_{am} u^* \Delta r^{*2}} \left[ \frac{1}{n} (T_{n+1,L}^* - T_{n,L}^*) + T_{n+1,L}^* - 2T_{n,L}^* + T_{n-1,L}^* \right] + \frac{H^* r_c^* \Delta \zeta}{u^*} \quad .. (5.2e)$$

The indeterminate form of the equations at n=0 can be avoided by using the special expressions

$$x_{0,L+1} = x_{0,L} + \frac{2E^* \Delta \zeta}{\Delta r^{*2} u^* D_{am}} (2x_{1,L} - 2x_{0,L}) - \frac{r_c^* \Delta \zeta}{u^*} \quad (5.1f)$$

$$T_{0,L+1}^* = T_{0,L}^* + \left( \frac{2k^* \Delta \zeta}{u^* L_e D_{am} \Delta r^{*2}} \right) (2T_{1,L}^* - 2T_{0,L}^*) - \frac{H^* r_c^* \Delta \zeta}{u^*} \quad (5.2f)$$

Equation 5.1e and 5.2e were solved stepwise to obtain the Conversion and Temperature profile during the course of reaction. The first step was to compute the value of  $\zeta$  (zeta) and  $x$  across the diameter.

For the first step  $\zeta = 1 * \nabla \zeta$ , therefore  $L=1$ . Which is to be calculated from the previous value of  $L=0$  (initial condition). Then continue to the next step in longitudinal direction at  $L=2$ . The indeterminate form of equation at  $n=0$  can be avoided by using the special expression (derived from the 'L hospital rule';  $\lim_{X \rightarrow \pi/2} \cos x / (x - \pi/2)^3$ )

$$X \rightarrow \pi/2$$

### 5.3.6 Simulation

The conversion and temperature profile during the exothermic nitration of MDP in micro tubular reactor at any point (except at  $n=0$ ) were obtained by solving the equation 5.1e and 5.2e. The equation 5.1f and 5.2f were solved to get the temperature and conversion profile at the entrance where  $n = 0$ . The reaction term in the equation 5.1e and 5.2e affects both temperature and conversion; since the rate depends upon these terms. The average value for the increment  $L$  to  $L+1$  is known only after the equation 5.1e and 5.2e are solved by trial and error procedure. During the simulation of MDP nitration reaction, the problem is considered and computed with the radial variation taken into account for a fixed position/increment along the axial position.. The rate equation used in simulation, was earlier generated experimentally during the kinetic study<sup>2</sup> of the same.

Simulation Steps mostly followed are,

For 2-D problem  $T^*$ ,  $x$  and  $r_c^*$  are represented as  $T_{r^*,\zeta}^*$ ,  $x_{r^*,\zeta}$  and  $r_{c,r^*,\zeta}^*$

The conversion at the entrance will be zero at all radial position and also the temperature at the entrance is considered as feed temperature. Now,

initial value of  $r_{c(1,0)}$  is obtained from the initial feed temperature and initial feed conversions (i.e.  $x=0$ ).

The steps followed for simulation are as follows,

1. Assume a value of  $r_{c1,1}$  after obtaining  $r_{c1,0}$ .
2. Compute  $T_{1,1}$  and  $x_{1,1}$  from equation 1(e) and 2(e)
3. Evaluate rate  $r_{c1,1}^*$  at the end of the increment
4. Average  $r_{c1,1}^*$  &  $r_{c1,0}^*$  and compare the result with assume  $r_{c1,1}$ .
5. If agreement is not obtained repeat the sequence with revised  $r_{c1,1}$ .

Thus the computation have been first made across the radius of the micro-tubular reactor at  $L=1$  and  $\Delta z=0.5$ . The successive calculation with increments  $L=2$  to 10 have been made across the radius to get the temperature and concentration profile.

### 5.3.7 Simulation Result

The code for the above equations were developed in MATLAB and the 2D model for micro tubular reactor derived for nitration of MDP has been solved across radius & length of reactor using the parameters selected as shown in Table 5.1. The conversion of reaction in tubular reactor along the radius of reactor is shown in Fig.5.1. Fig. 5.2 is the 2D profile of conversion along the length and radius of reactor. The simulated temperature profile in micro tubular reactor along radius is shown in Fig.5.3. It is seen that temperature varies along radius; it finally reaches to wall temperature. Fig. 5.4 is the 2D profile of Temperature along the length and radius of micro-reactor. The product conversion variation with temperature is shown in Fig. 5.5. Simulated conversion along the dimensionless length of micro reactor is shown in Fig.5.6. Comparisons of the experimental and simulated variation of conversion at

different reaction temperature of 5, 15, 25 °C is made and shown in Fig. 5.7, 5.8 and 5.9 respectively.

Table-5.1 Parameters used for simulation of the micro tubular Reactor for nitration of MDP

Physical parameters	Parameters Value
Feed temperature, $T_f$	15 °C
Wall Temperature, $T_w$	10 °C
Heat of reaction, $\Delta H_R$	460 kJ/molle
Activation energy, E	10000 cal
Universal gas constant, R	2 cal
Arrhenius constant, $k_0$ at 15 °C	$1.49 \cdot 10^6$
Reaction feed rate, $r_{ci}$	0.042 moles/l.sec
Initial feed concentration, $C_0$	1.84 moles/lit
Radius of the tube, $r_w$	$1.5 \cdot 10^{-3}$ m
Velocity along tube length, $u_z$	0.007 m/sec
Cross sectional avg velocity along lenth	$5 \cdot 10^{-6}$
Density without dilution, $\rho$	2.5 g/cc
Specific heat, $C_p$	1.5 J/g °C
Radial thermal conductivity, $k_r$	0.08 W/ m K
Lewis nos. Le	0.9
Cross sectional average $k_r$	0.2
Radial diffusivity, $E_r$	$1.1 \cdot 10^{-7}$
Cross sectional average radial diffusivity	$10^{-7}$

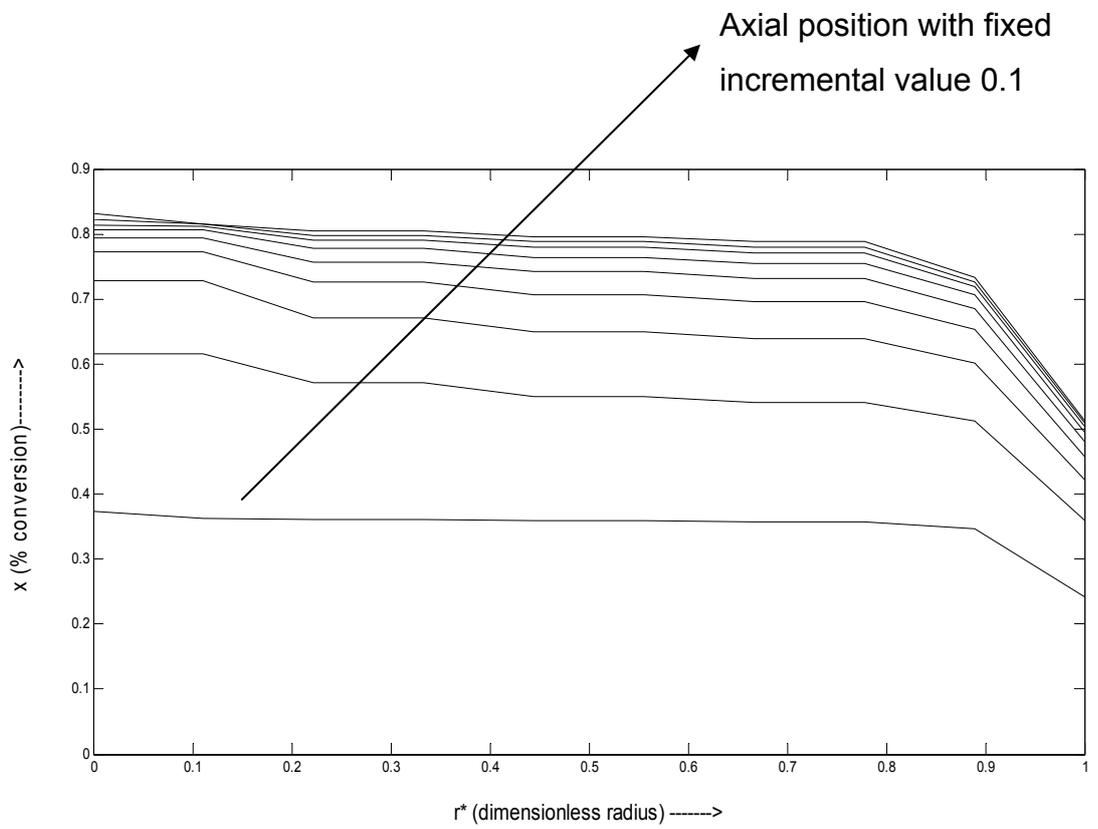


Fig.5.1. Simulated Conversion of Reaction in Micro Reactor along the Radius

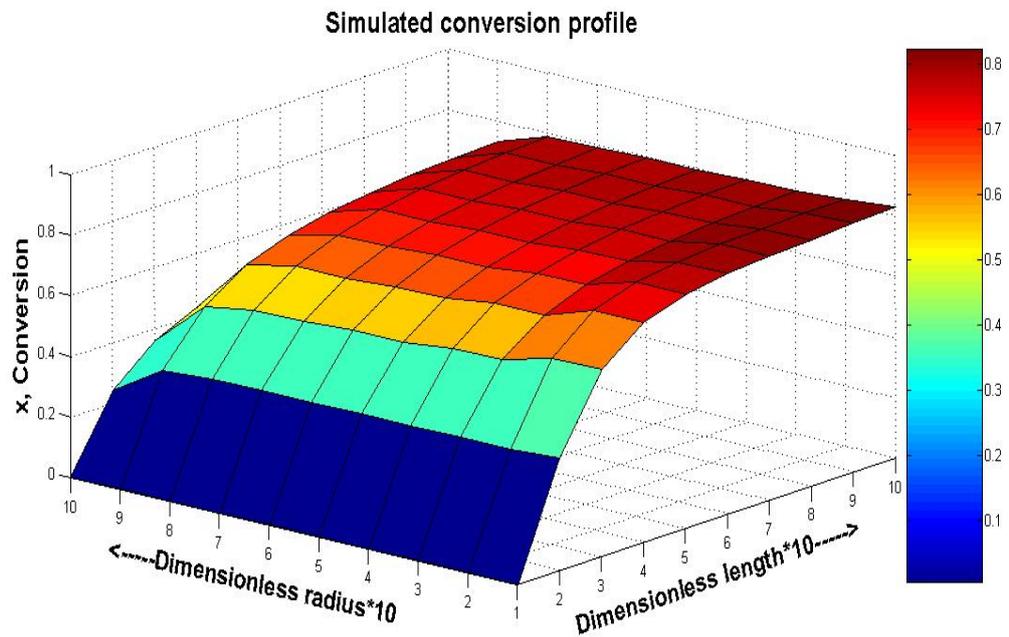


Fig.5.2. 2D Profile of Conversion along the Length and Radius of Reactor

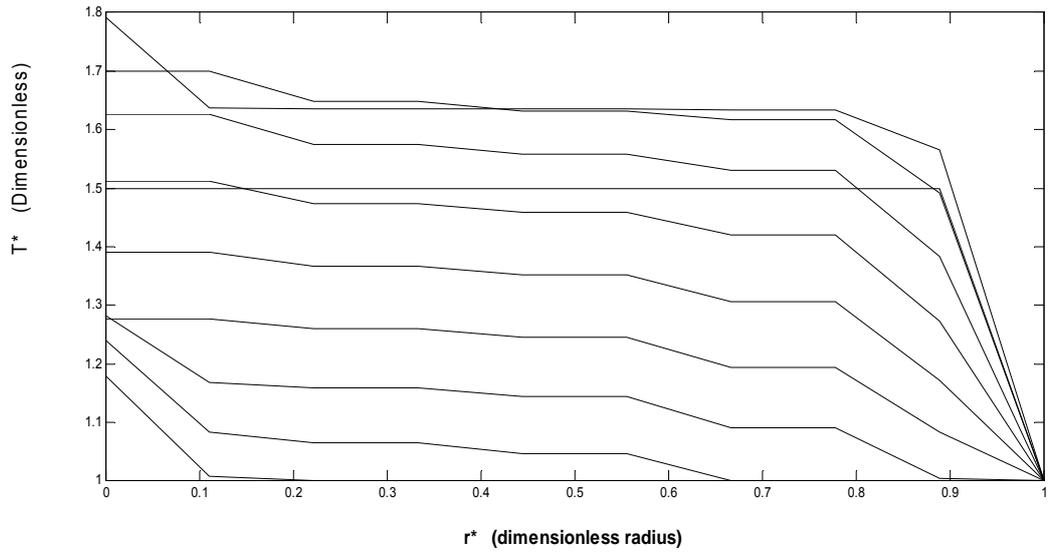


Fig.5.3. Simulated Temperature profile in Micro Reactor along the Radius

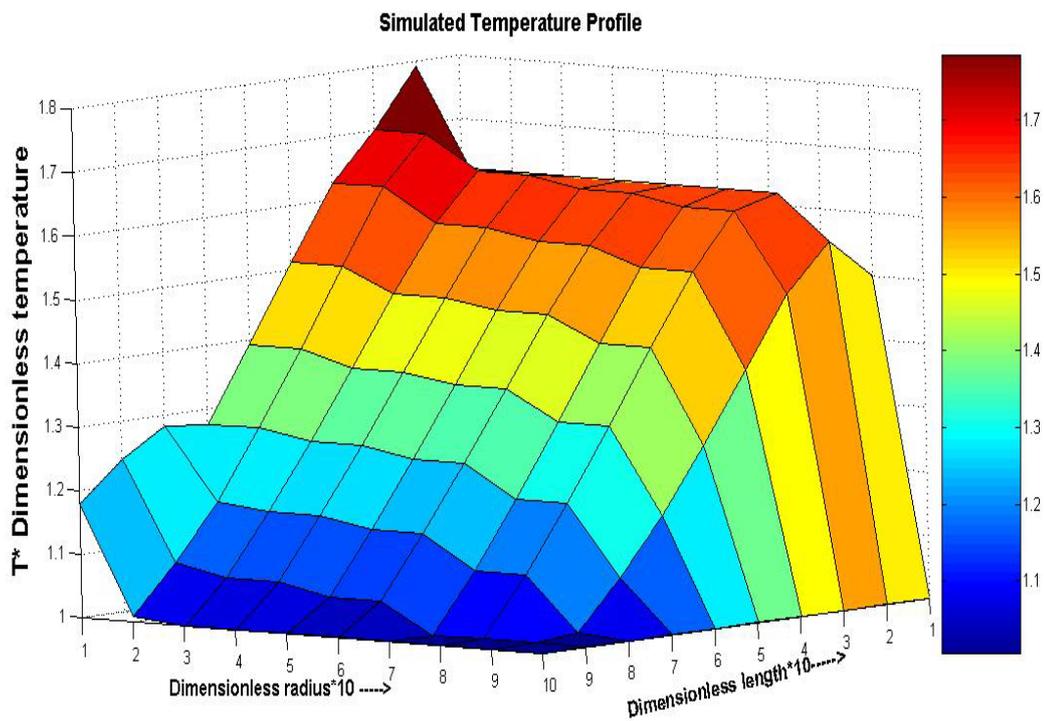


Fig.5.4. 2D Profile of Temperature along the Length and Radius of Reactor

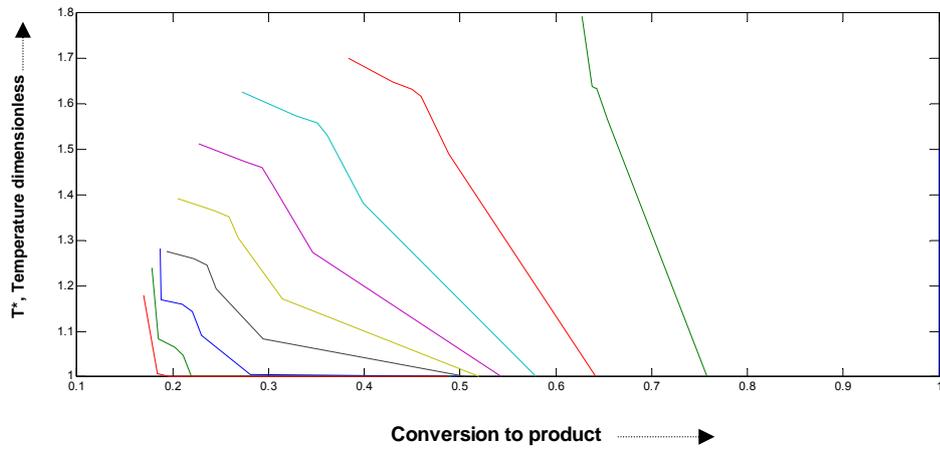


Fig.5.5. Simulated product conversion with different reaction temperature

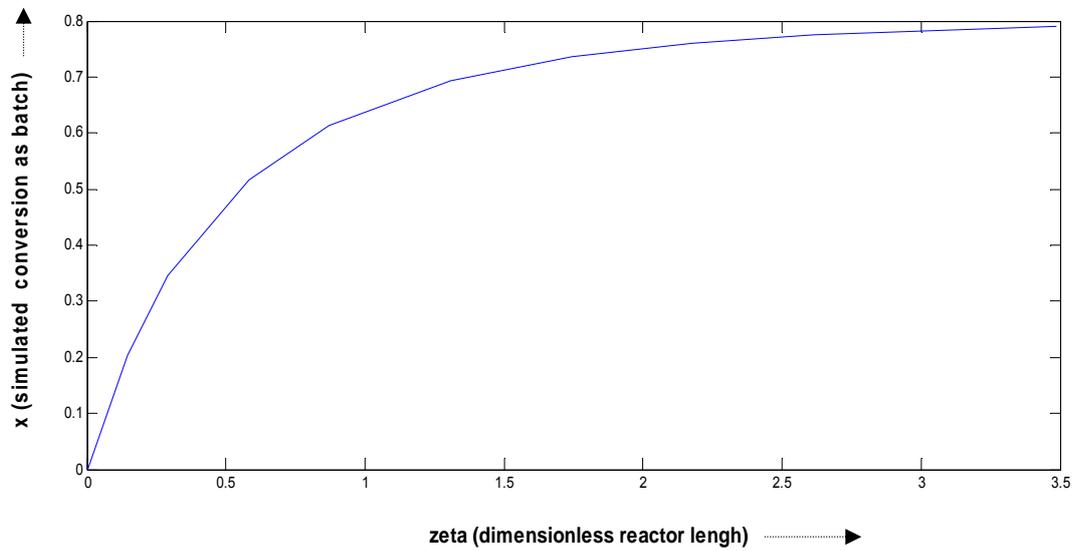


Fig.5.6. Simulated product Conversion along Dimensionless Reactor Length

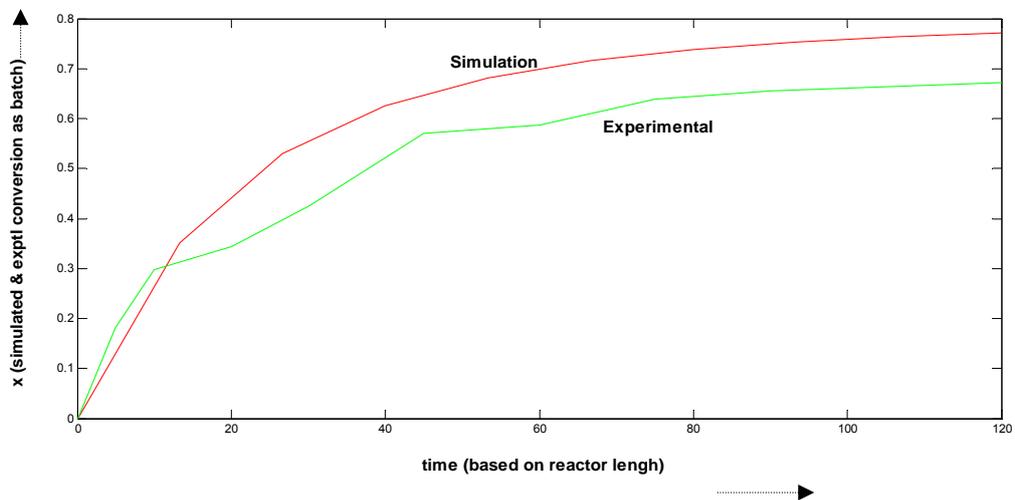


Fig. 5.7 Comparison of Experimental batch and simulated conversion at 5 °C

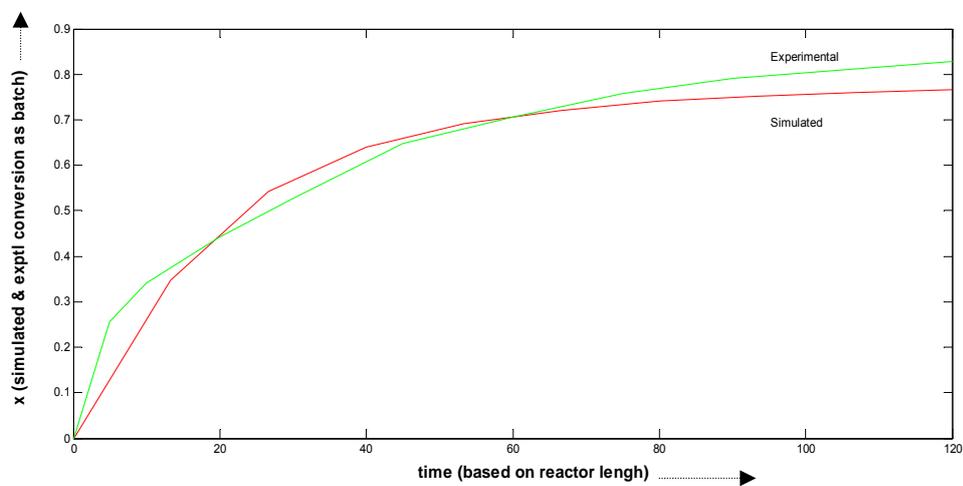


Fig. 5.8 Comparison of Experimental batch and simulated conversion at 15 °C

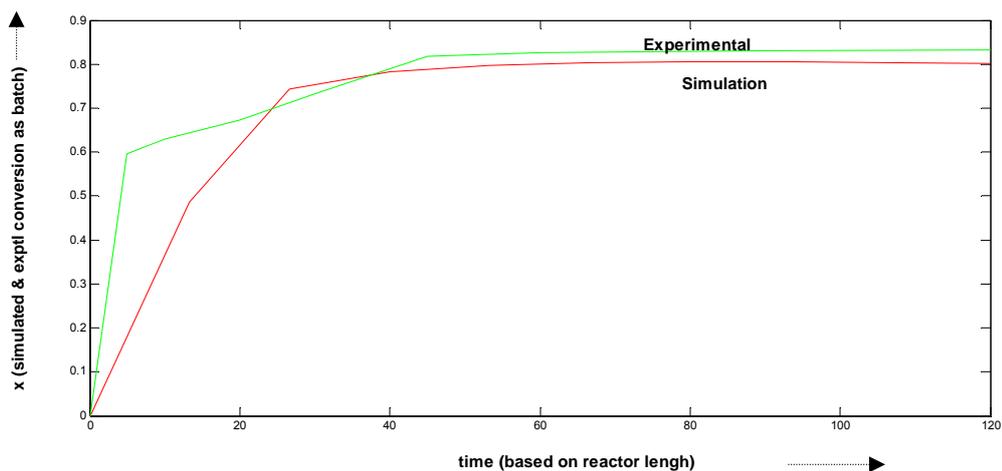


Fig. 5.9 Comparison of Experimental batch and simulated conversion at 25 °C

## 5.4 Model Validation

The model have been validated by conducting experiment on nitration of MDP in micro tubular reactor. The details of the experimental set up and procedure followed is described here along with analysis result.

### 5.4.1 Experimental

#### Micro-Reactor Setup for MDP Nitration

The typical experimental setup involves two fluid metering pump (make-FMI, USA) hooked-up with a 'T' to function as a micro mixer, which was subsequently connected to SS 316 micro tube. The micro tube (reactor) immersed in thermostat (make-JULABO, Germany) and nitrated reaction mass coming out of tube was collected in glass jacketed reactor fitted with electrically driven motor having agitator, temperature indicator etc. Experimental setup for nitration of MDP in micro tubular reactor is shown in Fig. 5.10 & 5.11.

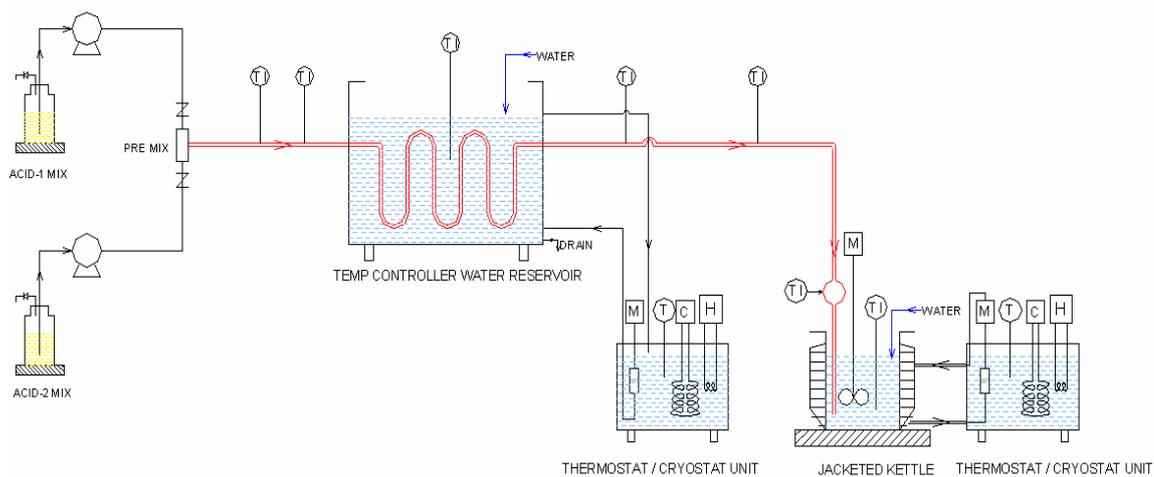


Fig. 5.10 Schematic of Experimental Setup for Nitration of MDP in Micro Reactor

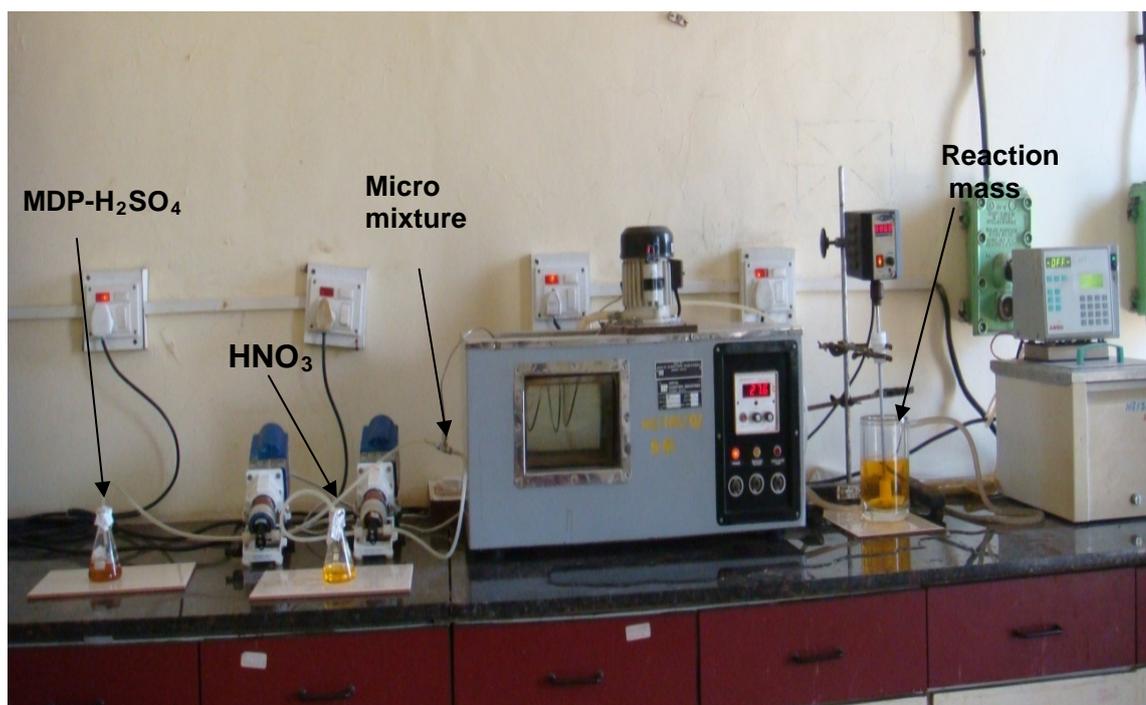


Fig. 5.11 Experimental setup for nitration of MDP in micro tubular reactor

## **FMI PUMP**

FMI pumps (Fig. 5.12) of low flow rate were selected for pumping reactant at low flow rate for nitration reaction. It consists of mainly two parts, pump drive module, and pump head module. The pump selected is a valve less pumping device and operates by synchronous rotation and reciprocation action. One complete piston revolution is required for each suction / discharge cycle. The pump has excellent chemical resistance to most acids, caustic, and solvents with some exceptions including acetone, methyl ethyl ketone (MEK), & methylene chloride. It is designed for flow rate of 0 to 5 ml/minute, infinitely adjustable through pump head rotation controller . Casing is made of PVDF and stroke cylinder is ceramic.



Fig. 512 Photograph of FMI Pump

## **Micro mixer**

T joint of SS 316 and I.D (~2 mm) was used as micro mixer for mixing MDP solution & Nitric acid is shown in Fig.5.13



Fig. 5.13 Photograph of Micro Mixture

#### 5.4.1.1 Experiment in Micro-tubular Reactor

Experiments were conducted in micro tubular reactor; initially MDP solution was prepared by using in sulfuric acid at desired concentration. The MDP solution & HNO<sub>3</sub> acid were allowed to mix in 'T' shaped micro mixer at desired flow rate. The reaction mixture comes out from end of tube was quenched into ice followed by hydrolysis under high speed agitation(400 r.p.m) for 2-3 hrs to get product FOX-7 which was then filtered, washed with water to get final product. The product weight was determined for each run after drying. The product formed was analyzed & characterizes by slandered analytical/Instrumental method.

No literature is available on Nitration of methyl-dihydroxy- pyrimidine (MDP) in micro tubular reactor. Hence, the experiments were planned systematically. Initially efforts were made to carry out the reaction with standard mole ratio of MDP: HNO<sub>3</sub> (concentrated nitric acid): H<sub>2</sub>SO<sub>4</sub> :: 1: 5.1: 10.1 reactant considered for experiment, no product was able to be isolated as tubular reactor get chocked due to formation of nitrated-methyl-pyrimidine-dione (NMPD) at required flow rate. So dilution of reactant at different concentration of MDP of 50%, 75% and 100 % in concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solution was used for experiment and the reaction was conducted in three different length of 1.2 m, 2.7 m and 3.7 m having L/D ratio 1000, 2250 and 3000 respectively. Such dilute solution prepared and used immediately. The reaction was carried out with this dilute solution in different length of micro tubular reactor mentioned earlier. During each run in micro Tubular reactor, variation of temperature was recorded at different zone along the length of reactor. Temperature variation with time is shown in Fig 5.14. It is seen that large heat released is compensated by large area available for heat transfer per

unit volume of fluid so very small variation in temperature were observed. Besides, other process parameters were noted and calculated such as rate of formation per minute, amount of product formed, yield etc. The rate of formation of product per minute at different concentration in reactor with various residence times is shown in Fig.5.15. It is seen that the rate of formation of product per minute at different concentration of MDP in reactor is inversely varies with concentration of MDP .The rate of formation of product per minute at different concentration of MDP in reactor with various length of reactor is shown in Fig. 5.10. The % yield of reaction in micro tubular reactor at different dilution & residence time is shown in Fig.5.16, Fig.5.17 and 5.18.

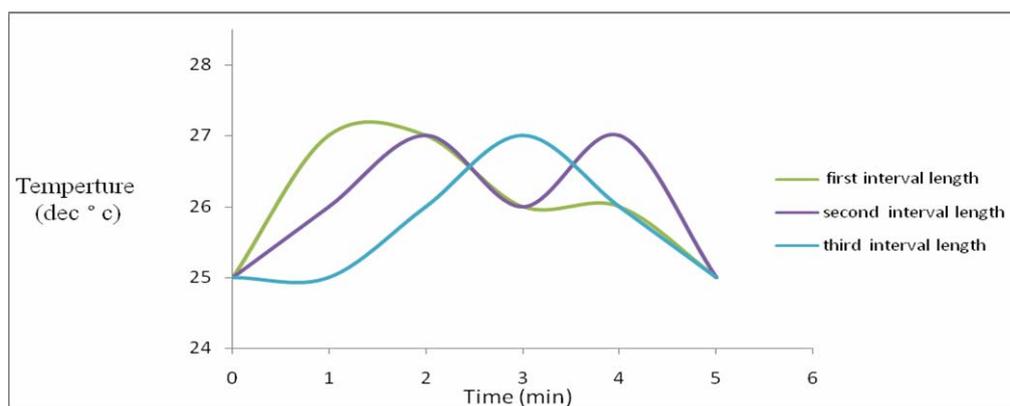


Fig.5.14 Variation of Temperature with time

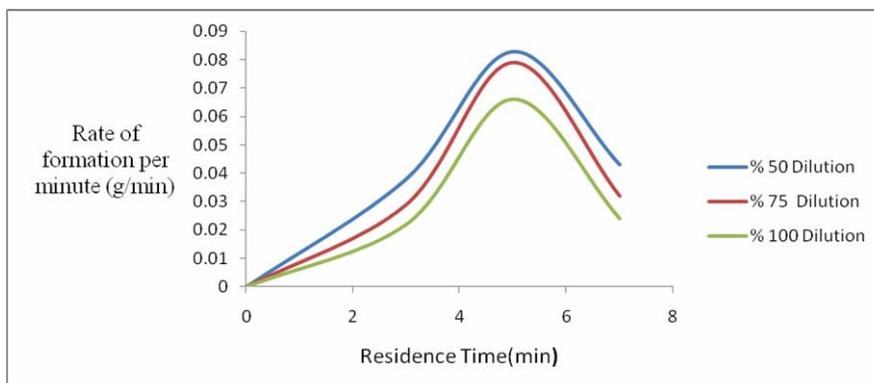


Fig 5.15 Variation of conc. Of MDP on rate of formation at different residence time

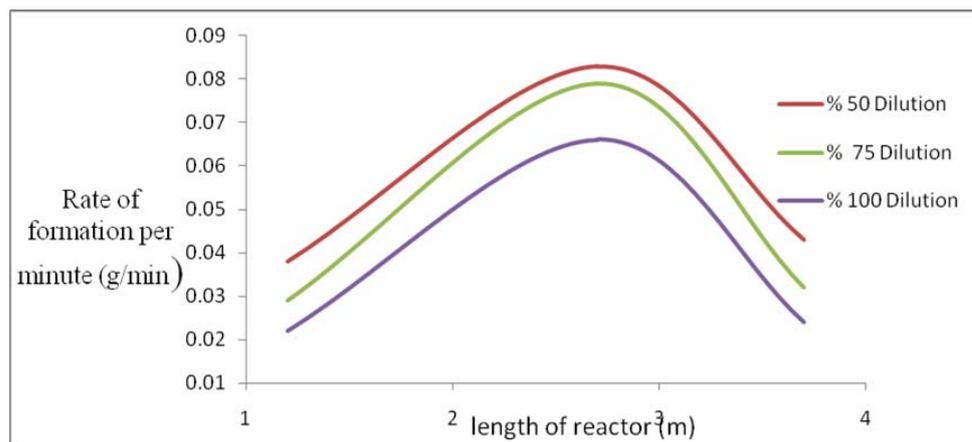


Fig. 5.16 Variation of conc of MDP on rate of formation at different reactor length

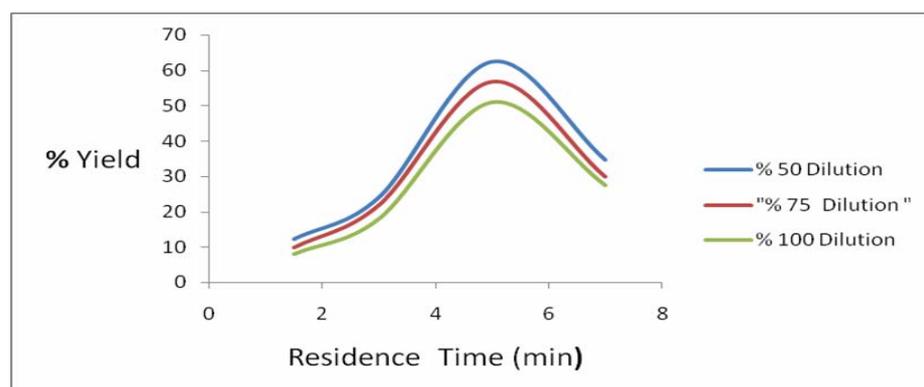


Fig.5.17 Variation of conc. Of MDP on yield at different residence time

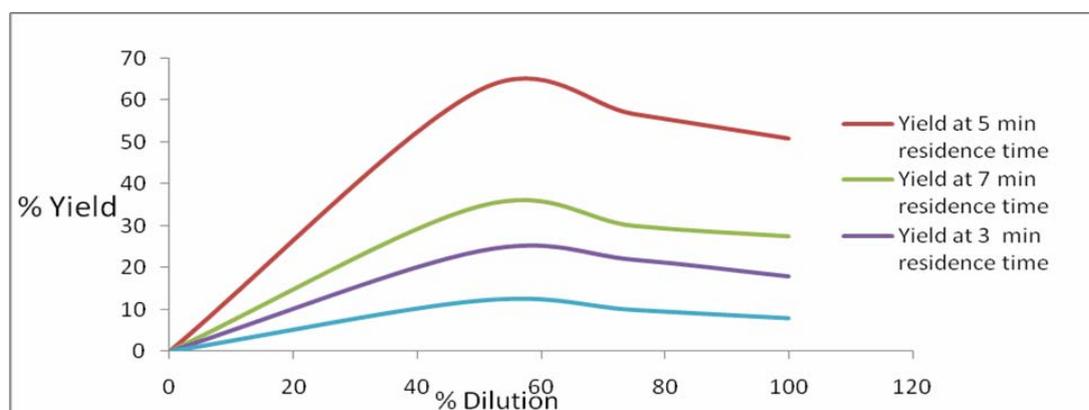


Fig. 5.18 concentration of MDP on yield at different length of reactor

#### 5.4.2 Comparison : Micro reactor vs Batch reactor

Experiment batches were carried out in cylindrical jacketed glass reactor (500ml capacity) fitted with driving motor, agitator, temperature indicator in the reactor as well in jacket inlet and outlet. The coolant outlet is at the top and inlet at the bottom of glass reactor. The inner diameter of the reactor was 300 mm. It was equipped with a motor driven agitator and heated and cooled by a thermostat and cryostat unit having PID controller (JULABO PT12). Heating medium was a mixture of glycol and water with a viscosity of 2.58 cp. During experiment MDP solution was prepared in sulfuric acid at predefined temperature then concentrated nitric acid was added at controlled rate to MDP solution by maintain the temperature at  $12\pm 2^{\circ}\text{C}$ . Addition of concentrated nitric acid in MDP solution is highly exothermic reaction which leads to runaway reaction. So, it was gradually added to the MDP solution. The reaction temperature was maintained at  $25\pm 2^{\circ}\text{C}$ . After reaction is over, the reaction mass was slowly quenched into ice followed by hydrolysis under high speed agitation (rpm~400) for 3 hrs to get product FOX-7 which was then filtered, washed with water to get product. The product weight was determined for each run after drying. The product formed was analyzed & characterizes by slandered technique. %Yield was compared with the corresponding value obtained in micro reactor are shown in Table-5.2 and 5.3.

Table-5.2 Comparison of yield in micro reactor & batch reactor

Dilution	Continuous reactor		Batch reactor	
	Residence Time(min)		Residence Time (min)	
	5	7	19	10
	% Yield			
50%	62.5	35	43	12
75%	57	30	38	9
100%	51	28	32	8

Table-5.3 Comparison of rate of formation in micro reactor & batch reactor

Dilution	Continuous reactor		Batch reactor	
	Residence Time(min)		Residence Time (min)	
	5	7	19	10
	rate formation of product (g / min)			
50%	0.163	0.075	0.022	0.0185
75%	0.113	0.043	0.020	0.017
100%	0.104	0.039	0.018	0.011

## 5.5 Result & Discussion

Experiments conducted with MDP and  $H_2SO_4$  ratio of 1:20.2, 1: 17.5, 1:15.05 gave satisfactory results. The Yield observed at 25 °C at different residence times for both continuous and batch types are shown in the Table 5.2 & 5.3. The results from the batch experiments were compared with continuous experiment at identical operating conditions. It can be seen that the % yield of FOX-7 in the continuous experiments in micro-reactor of ~1 mm I.D was as against % obtained in batch experiments. It is observed that, although in the batch as well as the continuous experiments the same mole ratio was maintained, in case of continuous flow experiments (micro reactor) yields higher amounts of product formation. It is also noted that the area available for heat transfer per unit volume of fluid is high in case of micro reactor which was sufficiently high to maintain the constant temperature in the entire length without circulating the cold fluid. Further, rate of formation of product irrespective of the different residence time was higher in case of micro reactor correspond to batch reactors given in Table-5.3. The yield of continuous experiment is having similar trend agreed with simulation result. The brief summary of nitration experiments in micro reactor is given in Table-5.4. The rate of formation of product at 50% concentration is highest and that of 100% dilution is least but, continuous flow of reaction mass is maximum in case of 100% diluted solution.

Besides, it is also found that during reaction with standard concentration of MDP in concentrated  $H_2SO_4$  (MDP:  $H_2SO_4$ : 1: 10.1.), micro reactor including 'T' mixture gets choked and also develops a very high pressure drop (more than 6  $kg/cm^2$ ) and practically no product was able to be collected form the micro-reactor . This kind of choking was observed even for different orientations (like

vertical, horizontal) of the micro-tube. In order to overcome such situations, lower concentration of MDP (like MDP : H<sub>2</sub>SO<sub>4</sub> :: 1: 20.2; 1:17.5; 1:15.05) were used and the experiments were carried out with minimum of choking problem.

Table-5.4 Summary of the Nitration Experiments Conducted in Micro Reactor

Micro reactor length: 2.7 m, ID: ~1 mm, T: 25 °C / room temperature, Pump MOC: Ceramic, Tube MOC: SS316

Sl no.	Date	% dilution of MDP soln with H <sub>2</sub> SO <sub>4</sub>	Residence time (min)/ continuous flow (min)	Amt of MDP + H <sub>2</sub> SO <sub>4</sub> (ml) / Wt of MDP (g) taken	Amt of HNO <sub>3</sub> (ml) taken	Flow rate HNO <sub>3</sub> / H <sub>2</sub> SO <sub>4</sub> (ml/min)	Density MDP solution (g/cc)	C <sub>MDP</sub> (moles/lit)	Amount of MDP soln (g) / MDP Passed (g)	Amt of HNO <sub>3</sub> passed (g)	Product formed (g)	Rate of formation per minute (g/min)
1.	06.01.09	50	5/8	15 / 2.3	20	0.5 / 0.5	1.82	1.2	14.8/1.26	15.3	0.69	0.086
2.	12.01.09	50	5/10	15/2.3	15	0.6/0.5	1.82	1.2	15.0/1.27	17.0	0.82	0.082
3.	13.01.09	50	5/10	15/2.3	15	0.6/0.5	1.82	1.2	15.5/1.27	15.8	0.84	0.084
4.	14.01.9	50	5/11	15/2.3	15	0.6/0.5	1.82	1.2	16.0/1.36	16.0	0.91	0.083
5.	15.01.09	75	5/17	17.5/2.3	20	0.6/0.5	1.82	1.0	17.7/1.29	18.0	0.88	0.052
6.	19.01.09	75	5/18	17.5/2.3	20	0.6/0.5	1.82	1.0	18.89/1.38	19.5	0.97	0.054
7.	20.01.09	75	5/20	17.5/2.3	20	0.6/0.5	1.82	1.0	21.09/1.54	20.5	1.1	0.055
8.	23.01.09	75	5/19	17.5/2.3	20	0.6/0.5	1.82	1.0	18.90/1.38	19.0	0.97	0.051
9.	22.01.09	100	5/24	23/2.3	25	0.6/0.5	1.82	0.9	20.5/1.31	20	0.91	0.038
10.	27.01.09	100	5/25	23/2.3	25	0.6/0.5	1.82	0.9	22.2/1.42	22	1.0	0.04
11.	29.01.09	100	5/24	23/2.3	25	0.6/0.5	1.82	0.9	19.72/1.26	20	0.86	0.036
12.	30.01.09	100	5/26	23/2.3	25	0.6/0.5	1.82	0.9	22.38/1.43	21	1.01	0.039

## 5.6 Conclusion

Application of micro reactor is a novel approach in the synthesis of key pharmaceutical intermediates and fine chemicals where either the reactions are highly exothermic or there are situations where the selectivity of the product is an issue. It is reported in the recent past that several reactions can show the better yield when carried out in micro reactors than in the conventional batch mode operation. The high heat transfer area helps to achieve a better control of temperature variation in the micro reactor. This further helps to maintain the rates of reaction in specific ranges and thus avoids byproduct formation. Besides, the small length scales also help to achieve faster mixing, thereby reducing the possibility of byproduct formation in fast reactions.

In the present work, the micro reaction system has been modeled for nitration of MDP by adopting two dimensional (2-D) heat flow and mass transfer equations. The numerical results from the 2-D model for conversion and temperature profile along the length and radius of micro reactor have been compared with corresponding value obtained for batch reactor. In order to validate the model several experiments on nitration of MDP were conducted in micro reactor setup with the variation of concentration, flow rate and residence time, temperature etc. The measurable findings of studies are,

- The experimental result from micro reactor revealed that nitration of MDP concentration takes place even at lower concentration of MDP and lesser reaction time with better control of temperature.
- The nitration of MDP reaction in micro reactor takes place in laminar region.

- The yield of final product i.e. FOX-7 is higher in continuous flow micro reactor than corresponding concentration in batch reactor irrespective of reactant concentration.
- The Rate of formation of FOX-7 (g /min) in continuous flow micro reactor is higher than correspond of batch reactor
- The nitration of MDP in micro reactor was found feasible at even room temperature at different flow rate & residence time and results in higher yield in comparison of batch mode.
- Nitration of MDP experiment carried out in the present study provides adequate information on design of micro reactor system.

#### **Future Scope**

- As future scope of work, the present studies can be considered as feasibility to investigate the economics of continuous process. Modeling and Simulation of the system will help in process optimization, finalizing operating condition and also the design parameter for a new system.
- It is recommended to carry out liquid–liquid reaction in micro reactor system to avoid chocking. Better control and productivity can be obtained in micro reactor even with lower concentration and residence time.

## NOTATIONS

$C$  = Concentration

$C_0$  = Initial concentration at the inlet of the reactor

$E_r$  = Effective radial diffusivity

$\langle E_r \rangle$  = Cross sectional average radial diffusivity

$D_{am}$  = Modified Damkohler number for mass,  $r_w^2 r_{ci} / (\langle E_r \rangle C_0)$

$H^*$  = Dimensionless temperature rise,  $(\Delta H)C_0 / (\rho c_p T_f)$

$k_r$  = Effective radial thermal conductivity

$\langle k_r \rangle$  = Cross sectional average radial thermal conductivity

$k_w$  = Thermal conductivity near the wall

$k_z$  = axial effective thermal conductivity

$k^*$  = Dimensionless radial thermal conductivity,  $k_r / \langle k_r \rangle$

$L_e$  = Lewis number,  $c_p \langle E_r \rangle / \langle k_r \rangle$

$P_{em}$  = Peclet number for mass  $\langle u \rangle d_p / \langle E_r \rangle$

$r_c$  = Rate of the reaction

$r_{ci}$  = Rate reaction at feed inlet

$r_c^*$  = Dimensionless reaction rate,  $r_c / r_{ci}$

$r^*$  = Dimensionless radial distance,  $r / r_w$

$r_w$  = Radius of the tube

$T$  = Temperature

$T_f$  = Temperature at the feed inlet

$T^*$  = Dimensionless temperature,  $T / T_f$

$u_z$  = Velocity at  $z$  direction

$\langle u \rangle$  = Cross sectional average velocity  
axial distance

$R$  = Universal gas constant

$E$  = Activation energy

$h$  = Heat transfer coefficient

$k_0$  = Arrhenius constant

$u^*$  = Dimensionless velocity,  $u_z / \langle u \rangle$

$x$  = Fractional conversion

$z$  = Axial distance

$z^*$  = Dimensionless axial position

$\zeta$  = Dimensionless axial position,  $z r_{ci} / \langle u \rangle C_0$

$\rho$  = Density

$c_p$  = Specific heat

$\alpha$  = Ratio of tube radius to particle diameter,  $r_w / d_p$

$\Delta H$  = Total heat of reaction

$\xi$  = Expression having the group  $\left( \frac{H^* \Delta \zeta}{u^*} \right)$

$\varphi$  = Expression having the group  $\left( \frac{E^* \Delta \zeta}{D_{am} u^* \Delta r^{*2}} \right)$

$\psi$  = Expression having the group  $\left( \frac{\Delta \zeta}{u_z^*} \right)$

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## Chapter 6

# STUDIES ON PREPARATION OF SPHERICAL PARTICLES OF FOX-7 USING MICELLAR NANO REACTOR

## 6.1 Abstract

The need and preparation of spherical 1,1-Diamino-2,2-dinitroethene (FOX-7) particles to meet certain special applications in high explosives and propellant formulation have been illustrated. Preparation of spherical FOX-7 particles by using micro emulsion technique have not been reported in the literature. In the present study, preparation of spherical FOX-7 particle has been described using the novel concept of micelle based nano-reactor. Micelle based nano reactors have been prepared using micro-emulsion of triton-X 100, Cyclohexane and water. Analysis of the experimental result revealed that, the particle size and shape of FOX-7 can be varied by changing water to surfactant molar ratio in micro-emulsion. Formation of spherical FOX-7 particles in the reverse micelle reactors have been described in the subsequent sections. It is observed that spherical particles of FOX-7 are formed within two hours in the micro-emulsion media. Spherical particles synthesised in this method are generally in the range of sub-micron to nano-range. Impact sensitivity ( $h_{50}$ ) of the spherical particles by fall hammer method obtained is around 45 cm compared to regular synthesised FOX-7 (i.e.  $50 \pm 5$  cm) without altering any change in friction sensitivity, i.e. 36 kg. Loadability of the explosive charges can be enhanced by using spherical particles of FOX-7.

## 6.2 Introduction

FOX-7 is a futuristic insensitive high explosive and a potential candidate to replace RDX. Due to its chemical and thermal stability, it has created significant interest in recent past. FOX-7 is a new explosive ingredient with significant potential for application in high performance, insensitive munition (IM)-compliant explosive compositions. FOX-7 is prepared by

adopting a batch process by nitration of 2-methyl-4,6-dihydroxypyrimidine (MDP) to get FOX-7. Morphology of this material shows a hexagonal layer type crystal structure. However, it was essential to know whether spherical morphology of FOX-7 can be synthesised for certain application as the sensitivity of solid explosive materials is closely related with particle size and shape. The requirement of higher value of impact sensitivity may be met with spherical particles with defined size. Particles tending to spherical shape in comparison to non-spherical (needles/plates) with the same mean particle size have the advantages like,

- Higher ratio of surface to volume
- Better free flowing properties
- Higher bulk density

This means the more spherical the outer shape of the particles, the higher weight proportion of solid energetic particles can be put in the formulation. Spherical particles, generally, can be formed via the dispersion of the liquid phase which then becomes droplets in continuous phase. Literature information revealed that various research activities are being carried out in order to produce spherical FOX-7 particles. Thomas Heintz et.al (1) prepared spherical ammoniumdinitramide (ADN) particles by emulsion crystallization using molten ADN (as disperse phase) and paraffin oil (as continuous phase). Waldemar et.al (2) attempted for spherodization of FOX-7 crystals by high degree of agitation of suspension of the non-spherical crystal in various solvents for six to seven hours at different temperature but the process produced crystals of similar shape where the sharp edges/corners become slightly rounded. Since, FOX-7 doesn't have sharp melting point it will be preferred to prepare such

spherical particle either at the stage of formation of nucleation while hydrolysis of nitrated- pyrimidinedione, NMPD or during recrystallisation in suitable organic solvent by using the micelles/micro-emulsions. Micelles are formed through a self assembling process which represents tiny template/nano-reactor which are generally used for preparing nano structured materials of desired size and shape with required functionalities and attributes. Using miceller nano reactor/micro emulsion, various experiments have been reported out (3) on nitration of phenol to synthesise ortho-nitrophenol with dilute nitric acid. However, there is no literature available to synthesise spherical FOX-7 particle/ nano particles of FOX-7 using any other concepts.

Hence, a feasibility study has been carried out to synthesise spherical particles of FOX-7 by using the concept of micelle based nano reactor. The basic aim was to design the experiments followed by conducting the same at laboratory level to prepare spherical particle of FOX-7 and analysis of data by various instrument techniques. As a outcome of this study, it is realized that spherical particles of FOX-7 can be synthesised using the concept of miceller based nano reactor. These spherical particle are generally in the range of submicron and nano range. Details of the study are described in the subsequent sections.

### **6.2.1 Design of Nano Reactor**

Nano reactors have been designed using the concept of micelles. Micelles are formed using the surfactants. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic tail as well as hydrophilic head as given in Fig. 6.1a.

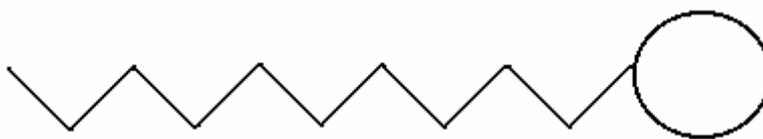


Fig 6.1a: Schematic diagram of surface active molecule

Surfactants are classified based on the nature of the hydrophilic group. Different types of surfactants considered during the design of micro reactor are given below.

- **Anionic Surfactants:** The hydrophile is a negatively charged group, e.g,  $\text{RC}_6\text{H}_4\text{SO}^{3-} \text{Na}^+$  (alkylbenzene sulfonate).
- **Cationic Surfactants:** The hydrophile bears a positive charge, e.g,  $\text{RNH}_3^+ \text{Cl}^-$  (salt of a long-chain amine).
- **Nonionic Surfactants:** The hydrophile has no charge, e.g,  $\text{R}(\text{OC}_2\text{H}_4)_x \text{OH}$  (polyoxyethylenated alcohol).
- **Amphoteric (Zwitterionic) Surfactants:** The molecule contains, both a negative charge and a positive charge group, e.g,  $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid).

A fundamental property of surfactants (surface-active agents) have been exploited is to form aggregates, known as micelles. The first-formed aggregates, just above the critical micelle concentration (CMC), are reported to be spherical in shape, and the concentration where they start to form is known as the critical micelle concentration. Besides, on the basis of arrangement of hydrophilic group i.e. towards centre and away from centre, two types of micelles, normal micelles and reverse micelles respectively were considered while designing the present experimental systems of nano reactors. These nano reactors provide a unique way for

development of special type of advance materials for wide variety of applications in electronics, photonics, biomedical and other areas also. Following are the type of nano-reactors.

- **Normal micelle Nano Reactor:** The oil-in-water micelle is called as normal micelle. Here oil acts as a dispersed phase and water acts as a continuous phase. The size of nano reactor by normal micelles can be varied from 100 nm to 20  $\mu\text{m}$ . Schematic of normal micelle is shown in Fig. 6.1b.

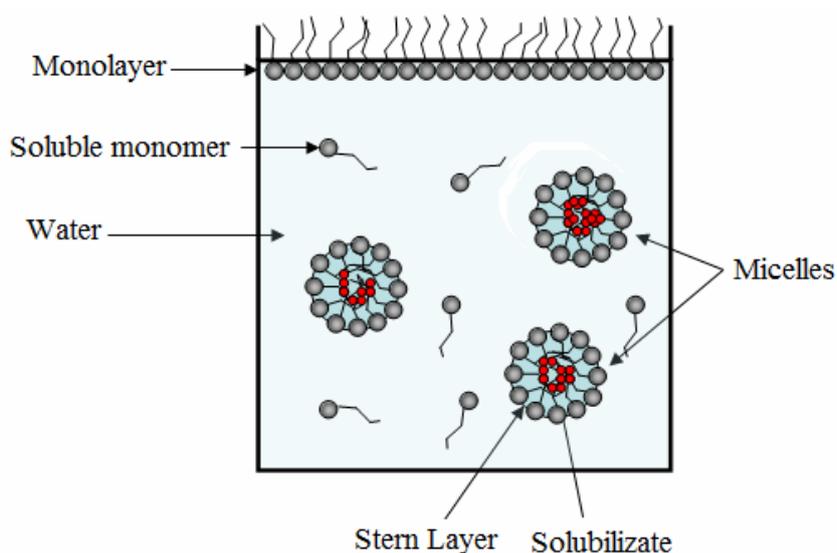


Fig. 6.1b Schematic of normal micelles

- **Reverse Micelle Nano Reactor:** Reverse micelles are fine dispersions of water in organic solvent stabilized by a surfactant molecule. Reverse micelles provide an example of organized self assemblies of surfactants in solution and are most widely used as reaction media or templates for biomimetic synthesis of various inorganic nano-particles. The hydrophilic head and hydrophobic tail of surfactants in a polar solvent self assemble to give reverse micelles where the polar core contains the hydrophilic heads and the a polar shell the hydrophobic chains. The size

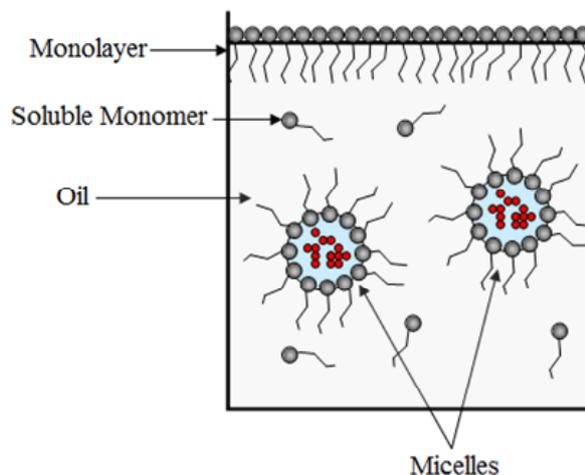


Fig. 6.1c Schematic of reverse micelles

These nano reactor can be solubilized in the core forming water-in-oil droplets (minimum 5 nm) which eventually become the water in oil microemulsion as the water content increases (5 to 100nm). So, the water to surfactant molar ratio has a decisive influence on the diameter of the reverse micelles. The aggregation number is typically in the range of 20 to 30, lower than in direct-micelles due to hydrophilic core. The shape can be spherical, rod-like or lamellar and it also depends on the concentration of surfactant, electrolyte, other additives, etc. The droplets undergo continuous collisions and exchange their contents. The shape of nanoparticles synthesized in reverse-micelles would normally be spherical unless some system specific special care is exercised. Microemulsions have been used to control the particle size of many inorganic and organic materials because they induce drastic changes in the reagent concentration and this can be particularly used for tuning the reaction rates (4-6). In a given composition (nature of oil and aqueous phase), the nature

of surfactant molecules determines the exchange rate through the elasticity (or rigidity) of the surfactant shell or interface. So, in order to prepare the spherical particles of FOX-7, design of spherical nano template have been produced by using selected surfactant and co-surfactant which is discussed in the experimental section.

## 6.3 Experimental

### 6.3.1 Chemicals

Following chemical composition is used in the present study,

- Surfactant (Triton X-100)
- Cyclohexane (oil media)
- Co-surfactant (n-hexanol)
- Water
- Target nitrated-MDP

#### Triton X-100 (C<sub>14</sub>H<sub>22</sub>O(C<sub>2</sub>H<sub>4</sub>O)<sub>n</sub>)

It is a nonionic surfactant which has a hydrophilic polyethylene oxide group (on an average it has 9.5 ethylene oxide units) and a hydrocarbon lipophilic or hydrophobic group. The hydrocarbon group is a 4-(1,1,3,3-tetramethylbutyl)-phenyl group. The critical micelle concentration is 0.22 – 0.24 m mole/lit. It is often used as a surfactant along with suitable co-surfactant for the preparation of reverse micro emulsion to generate the nano particle. It is also used in biochemical applications to solubilize proteins. The structure of triton X-100 is as shown in Fig. 6.1d.

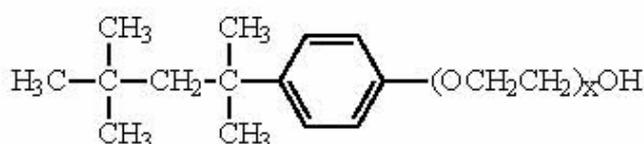


Fig. 6.1d. Chemical structure of Triton X-100

### **Cyclohexane (oil phase)**

Cyclohexane acts as oil phase (continuous phase) for the preparation of reverse micro-emulsion. It is reported that the chain length of continuous oil phase can influence the properties of an interface through a surfactant chain-oil interaction. The longer is the chain length of oil, more difficult is the penetration into surfactant tail and hence there is a tendency to align itself parallel to the surfactant tail. Such alignment increases the inter-micellar exchange rate and as a result size of particle decreases.

### **n-Hexanol (co-surfactant)**

n-Hexanol used as a co-surfactant (medium-chain alcohol) for the preparation of reverse micro-emulsion. The driving force for micro-emulsion formation is the low interfacial energy which is over compensated by the negative entropy of dispersion term. The low interfacial tension is produced by combination of two suitable molecules for example surfactant and co-surfactant. The addition of hydrophilic or lipophilic polar compounds (co-surfactants) can also change the hydrophilic or lipophilic character of the system, its solubility of water or oil, and the interfacial tension.

### **6.3.2 FOX-7 by Normal Synthesis method**

Synthesis of FOX-7 has been carried out by nitration of MDP followed by hydrolysis of nitrated derivative. Nitration of MDP is highly exothermic reaction where a mixture of concentrated sulphuric acid,  $H_2SO_4$  and nitric acid,  $HNO_3$  are used as nitrating agent. MDP was dissolved in  $H_2SO_4$  and  $HNO_3$  acid was added slowly into it at a mole ratio of  $MDP : HNO_3 : H_2SO_4 :: 1 : 5.1 : 10.1$  and the temperature was maintained at the desired level. After completion of each run, the reaction mixture was quenched into the cold water followed by

hydrolysis under high speed of agitation to get the product, FOX-7 which was then filtered, washed with water (till removal of acid) to separate the solid product. Scheme for synthesis of FOX-7 of regular particle size is given in Fig. 6.2.

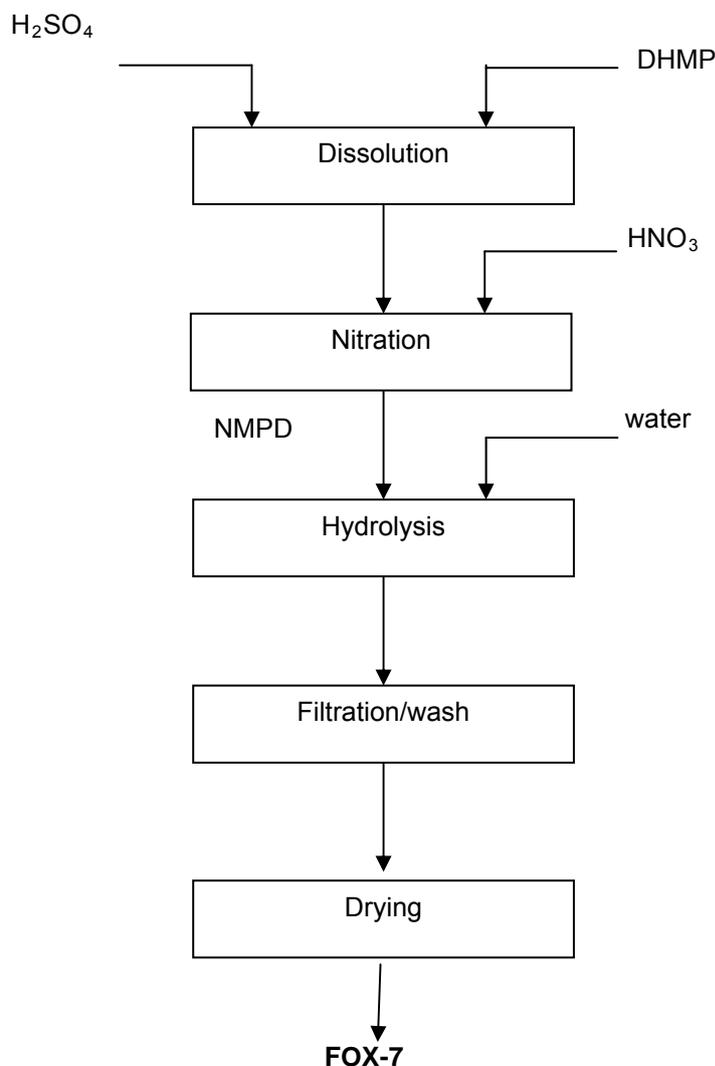


Fig. 6.2 Block diagram for preparation of FOX-7 of regular particles

### 6.3.3 Spherical FOX-7 Particles using Micro-emulsion method

Micro-emulsion solution was prepared by using 52 wt% of cyclohexane as oil phase, 22 wt% of Triton X-100 as surfactant, 11 wt% of *n*-hexanol as co-surfactant. Surfactant to co-surfactant ratio used was about 2:1 by weight along with 15 wt% aqueous phase. Surfactant with co-surfactant was added first to

cyclohexane as the oil phase followed by addition of aqueous phases and then stirred at room temperature till an optically clear and stable reverse micro-emulsion obtained. To this micro-emulsion, nitrated intermediate of MDP was added slowly under vigorous stirring maintaining the temperature of about 25 °C. The micro-emulsion containing nitrated MDP were kept for 2 hrs under vigorous agitation and then allowed to settled for 12 hrs. The precipitated powders were recovered / separated by centrifuge followed by washing with acetone and methanol. The separated FOX-7 material then dried in a vacuum oven at 70 °C for 16 hrs. The schematic diagram to prepare spherical FOX-7 particle using reverse micro-emulsion method is shown in Fig. 6.3.

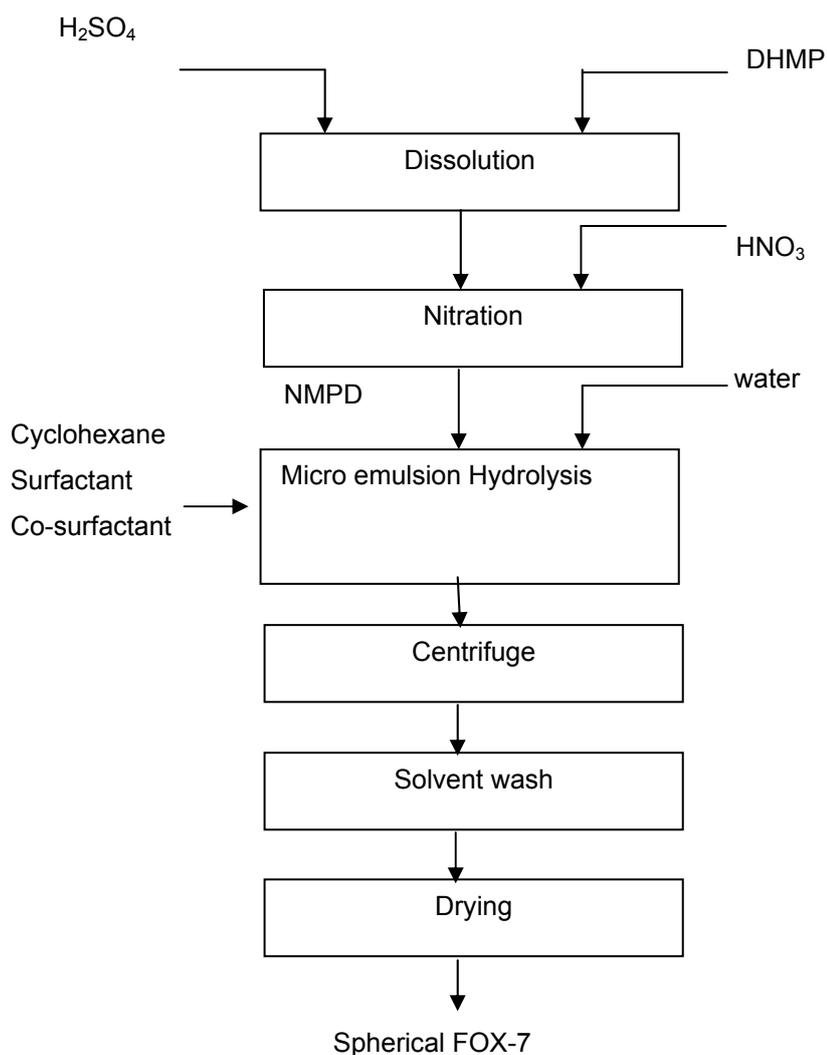


Fig. 6.3 Synthesis of Spherical FOX-7 particles using micro-emulsion.

## 6.4 Results and Discussion

Details of experiments using micro-emulsion is shown in Table- 6.1

Table 6.1 Details of batches carried out by reverse microemulsion

(Cyclohexane : 156g Triton X-100: 66 g, n-hexanol: 33g).

Batch No.	Wt of Intermediate (g)	Wt of water (g)	water/surfactant ratio	FOX-7 weight(g)
MCN-1	96	9.18	5	Product not formed
MCN-2	96	18.36	10	0.19
MCN-3	96	27.54	15	0.6
MCN-4	96	36.72	20	1.18
MCN-5	96	45	24.5	2
MCN-6	96	55.08	30	2.93
MCN-7	96	100	54.5	3.2
MCN-8	240	150	81.7	8

It is seen from the above table that as the water to surfactant ratio goes on increasing, the yield of spherical FOX-7 goes on increasing. Spherical FOX-7 is then characterized by various analytical / instrumental methods. A mechanism proposed for the hydrolysis reaction in micro-emulsion is shown in Fig. 6.4.

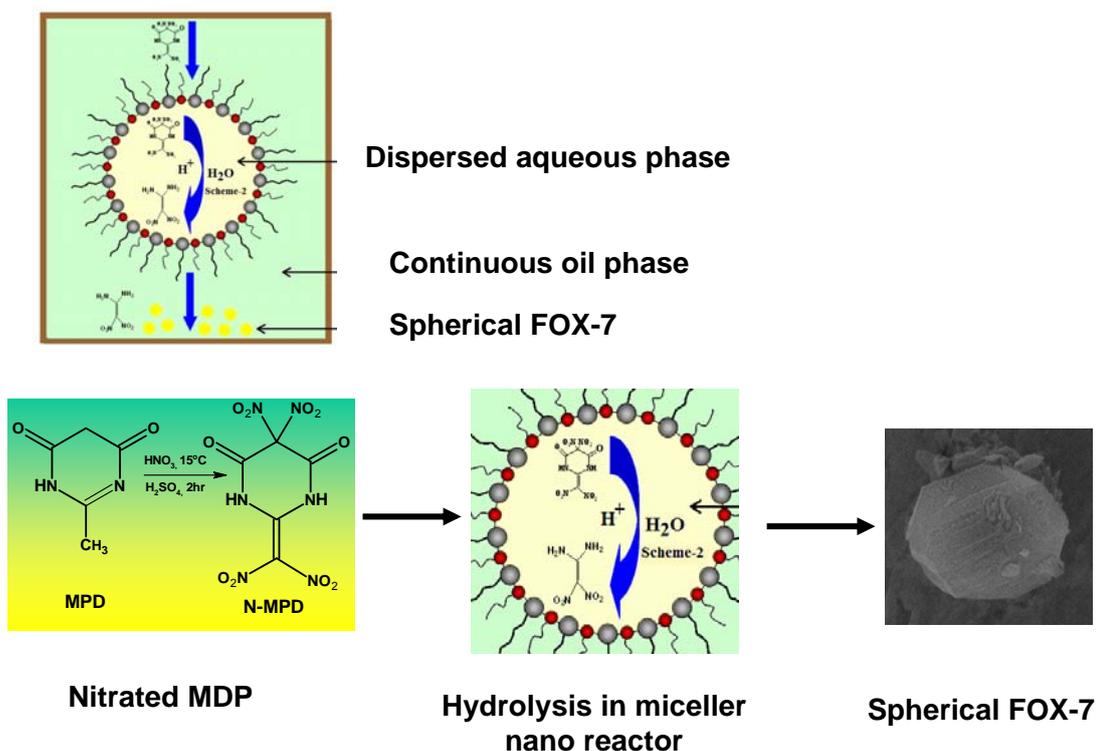


Fig. 6.4 Proposed mechanisms for the formation of spherical FOX-7

It can be seen that after mixing of 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione to reverse micro emulsion the hydrolysis of intermediate starts during the mixing process, Fig. 6.5.

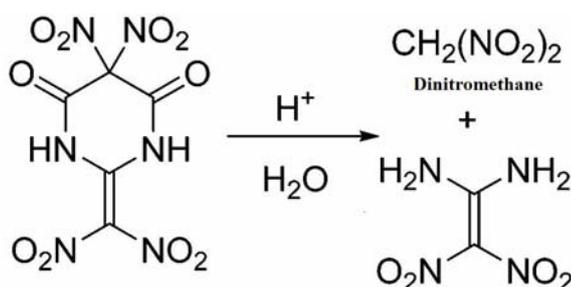


Fig. 6.5. Micro-emulsion assisted hydrolysis of 2-dinitromethylene-5,5-dinitropyrimidine-4,6-dione (NMPD) to FOX-7

The hydrolysis takes place inside the droplets (nucleation and growth) which control the final size of particles. This gives the homogeneous particle size distribution of FOX-7 nanoparticles. This is due to controlled hydrolysis in

reverse micro emulsion. The sizes of the micro emulsion droplets can be modified by varying the water to surfactant (R) ratio. The effect of water to surfactant molar ratio on the morphology of FOX-7 particles is seen to be one of the most important parameter, which determines the state of aggregation, size and morphology of the particles and nature of solubilized water molecules. The sample prepared in reverse micro-emulsion containing 15 wt.% aqueous phase (water/ surfactant molar ratio 25) shows nearly spherical particles with average particle size of 200 nm whereas the sample prepared in micro emulsion having water to surfactant molar ratio 30 shows spherical particle of FOX-7 with average particle size ~1 micron. The yield is around 30 %. This may be due to presence of less amount of water in reverse micro-emulsion. The characterization of **as synthesised** as well as **spherical** FOX-7 were confirmed by various analytical tools such as thermal analysis, **nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, differential scanning calorimetry (DSC), scanning electron microscope (SEM) etc.**

NMR spectroscopy reveals that FOX-7 is having two carbon atoms and four identical protons. In DMSO-D6 the single proton resonance for the amino protons occurs at approximately  $\delta$  8.8 ppm, shown in Fig. 6.6.

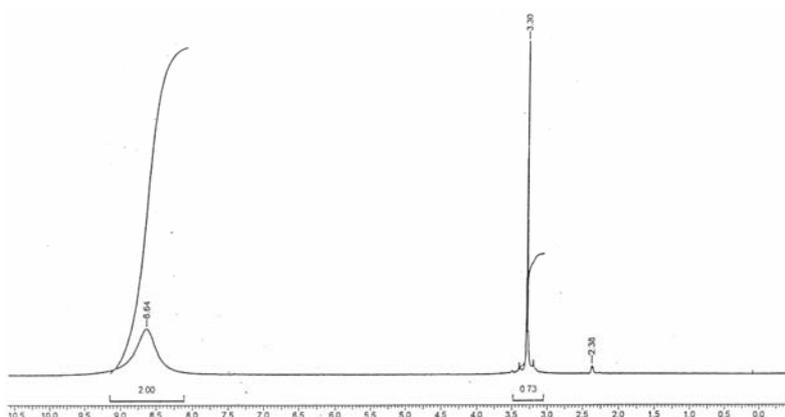


Fig. 6.6.  $^1\text{H}$  NMR of FOX-7 / Spherical FOX-7

$^1\text{H}$  NMR spectrum of the FOX-7 sample gives a singlet of four hydrogen atoms of two amino groups with the chemical shift  $\delta = 8.78$  ppm. Fig. 7 shows  $^{13}\text{C}$  NMR spectra to signals of carbon (C-1) with chemical shift  $\delta$  128.1 ppm and a singlet with chemical shift  $\delta$  158.2 ppm of carbon (C-2). The measured  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts as identical with the literature reported values.  $^{13}\text{C}$ ,  $^{15}\text{N}$ , spectra of FOX-7 were carried out with a Bruker AMX 360 spectrometer at 360.14, 90.57 and 36.50 MHz, respectively, at  $25^\circ\text{C}$ . For the measurement, the samples were dissolved in DMSO- $d_6$  and chemical shifts were referenced to the solvent signal ( $\delta$  ( $^1\text{H}$ ) = 2.55 ppm,  $\delta$  ( $^{13}\text{C}$ ) = 39.60, respectively).

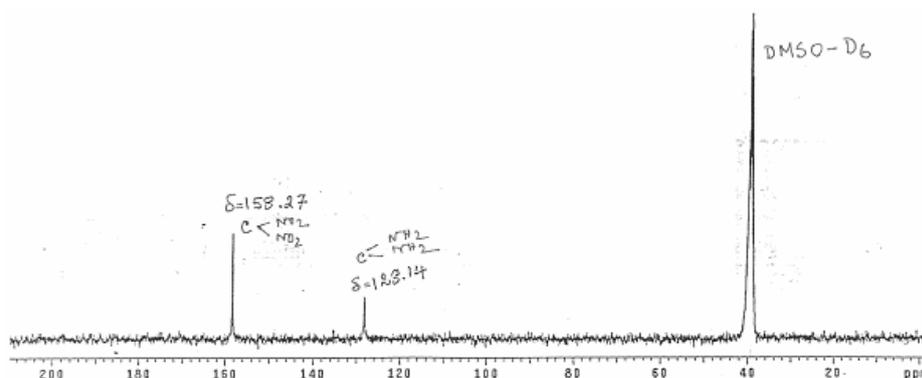


Fig. 6.7.  $^{13}\text{C}$  NMR of FOX-7 / Spherical FOX-7

The IR spectrum of DADNE was carried out on Shimadzu infrared spectroscopy (FTIR-8400) instrument. KBr was mixed with the sample. The powder was placed in the cup of diffused reflectance assembly and spectra were recorded. The infrared spectrum of FOX-7 shows absorbance in the  $\sim 3200$ - $3400$  and  $\sim 1350$ - $1650$  wave number range characteristic of the amino and nitro functionalities as well as numerous peaks in the fingerprint region (3), Fig. 6.8.

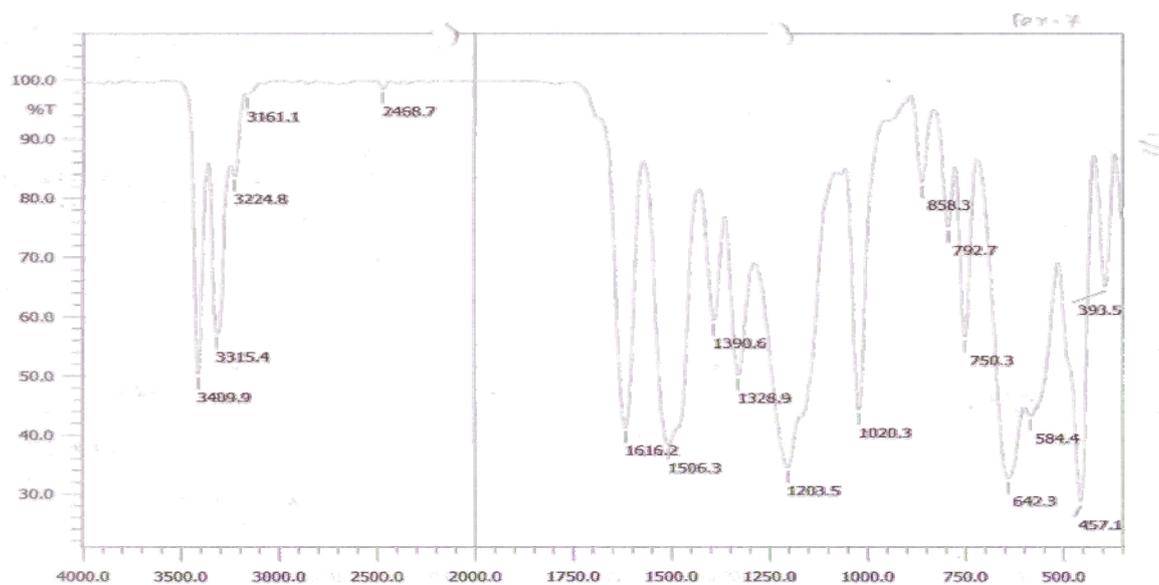


Fig. 6.8 IR Spectrum of FOX-7

Thermal analysis of spherical FOX-7 samples was carried out in DSC. The DSC thermogram, Fig. 6.9 recorded at a heating rate of 10°C per minute showed major exothermic peaks at 283°C (maximum peak) and almost merging into a single peak. This is consistent with a two stage thermal decomposition. Additional minor 'endothermic peaks' were observed at 112-115°C and 165-172°C suggesting to thermally induced phase transition. So, thermal analysis provides further evidences of a two step processes of phase transition. No melting point is observed. The value of decomposition of both as synthesised and spherical FOX-7 are similar to the results reported in the literature. Besides, small variations in DSC spectrum of values from different batches of FOX-7 have recently been partially explained by OSTMARK et al. (7) by proposing relationship between particles size and the decomposing temperature.

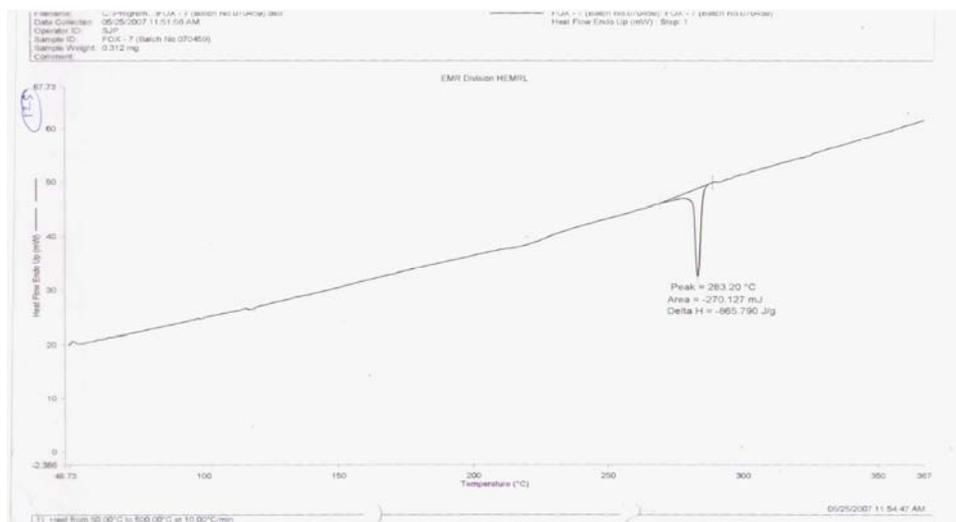


Fig. 6.9 DSC thermo-gram of FOX-7

SEM image of as synthesised FOX-7 shows layer structure of rectangular rod shape crystal structure shown in Fig. 6.10.

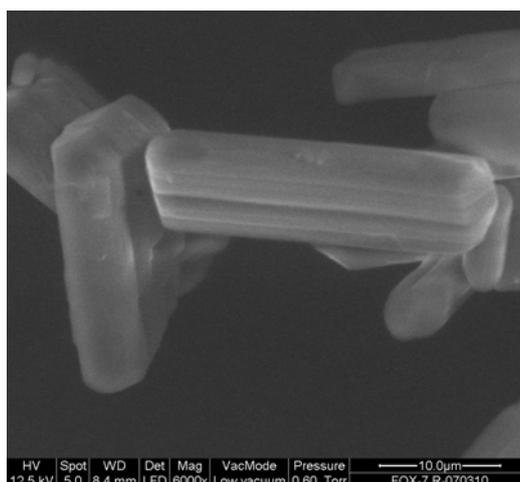


Fig. 6.10 SEM Image of as synthesised FOX-7

The particle size was measured by using scanning electron microscopy (SEM Leica 440). SEM images of dried powders prepared by microemulsion method (by varying water to surfactant ratio) are shown in Fig. 6.11.

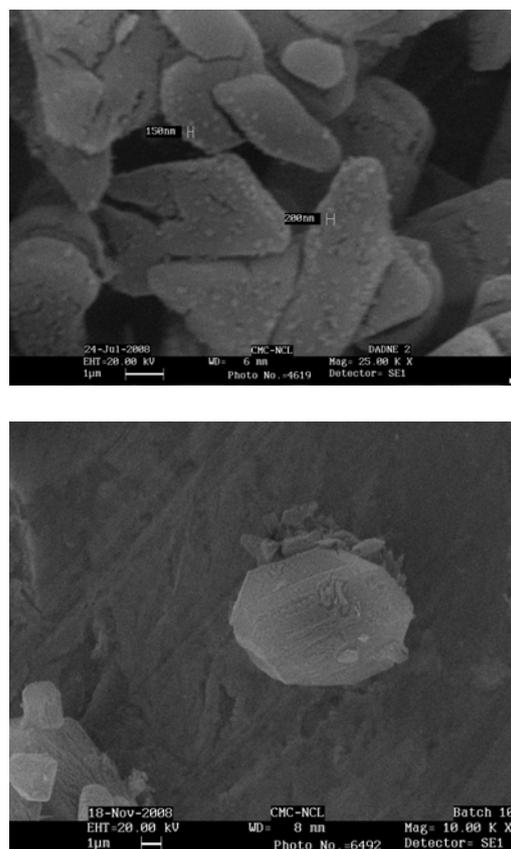


Fig. 6.11 SEM micrograph of spherical FOX-7 prepared by reverse micro-emulsion

## 6.5 Conclusions

Nearly spherical particles of 1,1-diamino-2,2-dinitroethene (FOX-7) have been successfully prepared in reverse micro-emulsion of Triton X 100/cyclohexane/ water. The particle size and shape of FOX-7 can be varied by changing water to surfactant molar ratio in microemulsion. The method gives formation of FOX-7 particles within two hours. Spherical particles synthesised in this method are generally in the range of sub-micron and nano-range. Impact sensitivity ( $h_{50}$ ) by fall hammer method is around 45 cm compared to regular synthesised FOX-7 (i.e.  $50 \pm 5$  cm) without altering any change in friction sensitivity i.e. 36 kg. This may be explained as the particle size is reduced, surface area is increased, which makes the particles more active towards impact. Since, the layer structure of the crystal remains unchanged friction

sensitivity remains unaffected. The data collected during the study is helpful for scale-up the process in preparation of spherical particles.

## 6.6 References

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## Chapter 7

### Investigation of Polymorphic Behaviour of FOX-7 Crystal

## 7.1 Abstract

Polymorphic screening of single crystal structure of insensitive high-energy material, FOX-7 was carried out to explore the polymorphic behaviour. It is important to know about the conformational change due to heating while it is being used in high explosive composition or propellant formulations. The study of FOX-7 by single crystal X-ray diffraction and hot stage microscopy techniques reveals the reversible thermal phase transition of  $\alpha$  form to  $\beta$  form occurs at 390 K and irreversible thermal phase transition of  $\beta$  form to  $\gamma$  form occurs at around 446 K. So, the  $\alpha$ - $\beta$  phase transformation in FOX-7 is reversible and first order. In both the forms the two-nitro groups are deviating from the molecular plane formed by the ethylene carbons and amino groups. The deviation is less in  $\alpha$  FOX-7 but in  $\beta$  FOX-7 both the nitro groups lie much more out of the plane. Also in both the forms the molecules form wavy layers by linking in head-to-tail fashion. Within the layer the molecules are associated via extensive intra and intermolecular H-bonds in both the forms, could be the reason for the unique properties of FOX-7, like high performance and low sensitivity. During  $\beta$  to  $\gamma$  transition, the crystals jumped and disintegrate into small crystallites. The almost similar unit cell parameters of the  $\gamma$  form compared to  $\alpha$  and  $\beta$  form suggest that the molecular arrangement in  $\gamma$  form is similar to  $\alpha$  and  $\beta$  form, although it has not been able to be solved its crystal structure.

## 7.2 Introduction

Polymorphism, the ability of a compound to exist in more than one crystal form or modifications, has gained paramount importance in pharmaceutical solids, dyes, pigments, explosives and specialty chemicals because of the required consistency in physical and chemical properties that can be achieved by restricting the formation of undesired solid form(1). Polymorphs have the same chemical composition but different physical properties due to their different molecular arrangements in the crystal lattice as a result of differences in non-bonded intermolecular interactions such as hydrogen bonding, Vander Waal's interactions, electrostatic and  $\pi \dots \dots \pi$  stacking interactions. Polymorphism can be broadly classified into three categories like packing polymorphism, conformational polymorphism and pseudo polymorphism or solvatomorphism (1-3). Packing polymorphism occurs in relatively rigid molecules, where the molecules are arranged differently in the crystal lattice resulting from different kinds of intermolecular interactions (4-7). Conformational polymorphism (8-11) generally occurs with flexible molecules, in which the molecules can adopt different orientations in the crystal lattice due to the involvement of intra-and intermolecular interactions. Pseudo-polymorphs (solvatomorphs) (1, 8, 9, 10) are different crystal forms of a compound that exhibits inclusion of solvents and have different molecular organization of molecules in their crystals.

The properties of high energy materials such as sensitivity, rate of deflagration to detonation, detonation velocity, detonation pressure, crystal density, thermal and shock stability and crystal morphology depends crucially on their solid-state structure and hence on the polymorphic modifications (11).

Thus, the aim of the present research was to explore the polymorphic behaviour of insensitive high-energy material, FOX-7 (1,1-diamino-2,2-dinitroethylene;  $C_2H_4N_4O_4$  (Fig. 7.1).

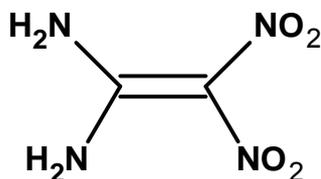


Fig. 7.1 Molecular Structure of 1,1-Diamino-2,2-dinitroethylene (FOX-7)

FOX-7 is a novel high explosive which combines two important properties like high performance and low sensitivity. This compound may be described as a push-pull ethylene with two electron donor amino groups ('head') and two electron withdrawing nitro groups ('tail') within its molecular framework (12).

The high activation energy for decomposition of FOX-7 molecule ( $E_a \sim 58$  kcal/mol) (13) compared to the RDX ( $E_a \sim 40$  KCal/mol) (14) and HMX ( $E_a \sim 35$  KCal/mol) (15, 16) is because of compact packing of molecules in FOX-7. In FOX 7, the hydrogen atoms are directly attached to the N-atoms and the nitro groups are bonded to carbon atoms whereas in RDX and HMX the bonding patterns are reverse. Therefore, molecules of FOX-7 formed strong intra and intermolecular hydrogen bonding between the hydrogen atom of amino group and oxygen atom of nitro group (N-H.....O). But in RDX and HMX molecules associate via weak C-H...O contacts. The extensive intra and intermolecular hydrogen-bonding pattern in molecular packing of FOX-7 makes it lower sensitive towards friction and impact.

Literature survey revealed FOX-7 occurs in three polymorphic modifications namely  $\alpha$ ,  $\beta$  and  $\gamma$  (17). The  $\alpha$  form exists at room temperature, which upon heating converts to  $\beta$  form (high temperature form) at 390 K and is reversible. On continuing heating the  $\beta$  form transforms to  $\gamma$  form at 446 K, however, in contrast to the  $\alpha - \beta$  phase transition, the phase transition  $\beta - \gamma$  is not reversible.

The key to understanding the unique properties of FOX-7 (e.g., its high activation energy for detonation) lies in obtaining precise knowledge of both the atomic and molecular arrangements. Therefore, its polymorphic screening, series of single crystals structure investigations were undertaken at various temperature from 298 K to 450 K along with hot-stage microscopy.

### 7.3 Experimental

Single crystal X-ray intensity data measurements were carried out on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized (Mo  $k_{\alpha}$  = 0.71073Å) radiation at different temperatures using OXFORD LN2 cryo-system. The X-ray generator was operated at 50 kV and 30 mA. Data were collected with  $\omega$  scan width of 0.3° at four different settings of  $\phi$  (0°, 90°, 180° and 270°) keeping the sample-to-detector distance fixed at 6.145 cm and the detector position ( $2\theta$ ) fixed at -28°. The X-ray data collection was monitored by SMART program (Bruker, 2003) (18-20). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2003). SHELX-97 was used for structure solution and full matrix least-squares refinement on  $F^2$  (21). Molecular and packing diagrams were generated using ORTEP-32 (Oak Ridge Thermal Ellipsoid Plot) (22) and Mercury-2.1 (23). Geometrical calculations were performed using SHELXTL (Bruker, 2003) (23) and PLATON (24).

The thermal studies of the FOX-7 crystals were carried out in differential scanning calorimeter (DSC).

## 7.4 Results and Discussions

### 7.4.1 Single Crystal X-ray diffraction of FOX-7

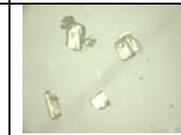
Different batches of FOX-7 crystals prepared at HEMRL were studied using single crystal X-ray technique at NCL, Pune. Preliminary scan suggest that, most of the crystals produced by cooling crystallisation method were found to be not suitable for single crystals XRD studies. However, by controlling the parameters of cooling crystallization batches, a few single crystals produced which chosen from each batch and unit cell measurements were carried out using single crystal X-ray diffractometer at room temperature. Crystals from all the batches were belonged to monoclinic system and their unit cell parameters were matched with  $\alpha$ -form of FOX-7 (Table 7.1).

Table 7.1 Unit cell parameters and morphology of FOX-7 crystals

Solvents	DMF	NMP	NMP-HCl	NMP-H <sub>2</sub> O	NMP-H <sub>2</sub> O-HCl
Crystal	Monoclinic	Monoclinic	Monoclinic	Poly-crystalline sample	No suitable Single crystals
$a$ (Å)	6.826(3)	6.921(1)	6.968(3)		
$b$ (Å)	6.774(3)	6.552(1)	6.612(3)		
$c$ (Å)	11.322(4)	11.274(2)	11.321(5)		
$\alpha$ (°)	90	90	90		
$\beta$ (°)	90.58(2)	90.06(1)	90.73(5)		
$\gamma$ (°)	90	90	90		
$V$ (Å <sup>3</sup> )	523.87(4)	519.19(2)	521.5(5)		

A few crystallization experiments of FOX-7 were also carried out at NCL and in most of the attempts good quality single crystals were obtained from different organic solvents (such as acetone, ethyl acetate, acetonitrile, nitromethane, and tetrahydrofuran). The unit cell measurements of all the crystals obtained revealed that all the crystals belong to monoclinic system and the unit cell parameters almost matched with the  $\alpha$ -form of FOX-7. A summary of the unit cell parameters and their morphologies of these crystals are summarized in Table 7.2.

Table 7.2 Unit cell parameters and morphology of FOX-7 crystals

Solvents used	Acetone	Acetonitrile	Ethyl-Acetate	Nitro-methane	Tetrahydro-furan
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
A (Å)	6.966(6)	6.864(3)	6.941(3)	6.952(6)	6.935(7)
B (Å)	6.649(6)	6.716(3)	6.628(3)	6.649(5)	6.664(7)
C (Å)	11.355(10)	11.278(4)	11.339(5)	11.348(9)	11.346(10)
$\alpha$ (°)	90	90	90	90	90
$\beta$ (°)	90.43(2)	90.89(2)	90.63(3)	90.63(2)	90.39(3)
$\gamma$ (°)	90	90	90	90	90
V (Å <sup>3</sup> )	526.0(8)	519.98(4)	521.73(4)	524.5(7)	524.38(6)
Morphology					

#### 7.4.2 Hot-stage Microscopy Studies

It was also explored the solid-state phase transitions of FOX-7 crystals using hot-stage microscopy study. Plates of FOX-7 crystals obtained from acetone were heated on a Leica polarizing microscope attached with heating stage. At  $\sim 117\text{ }^{\circ}\text{C}$ , some changes observed on the surface of the crystals with appearance of transverse lines across the plates. In fact, plate at the bottom segmented into three pieces (Fig. 7. 2A).

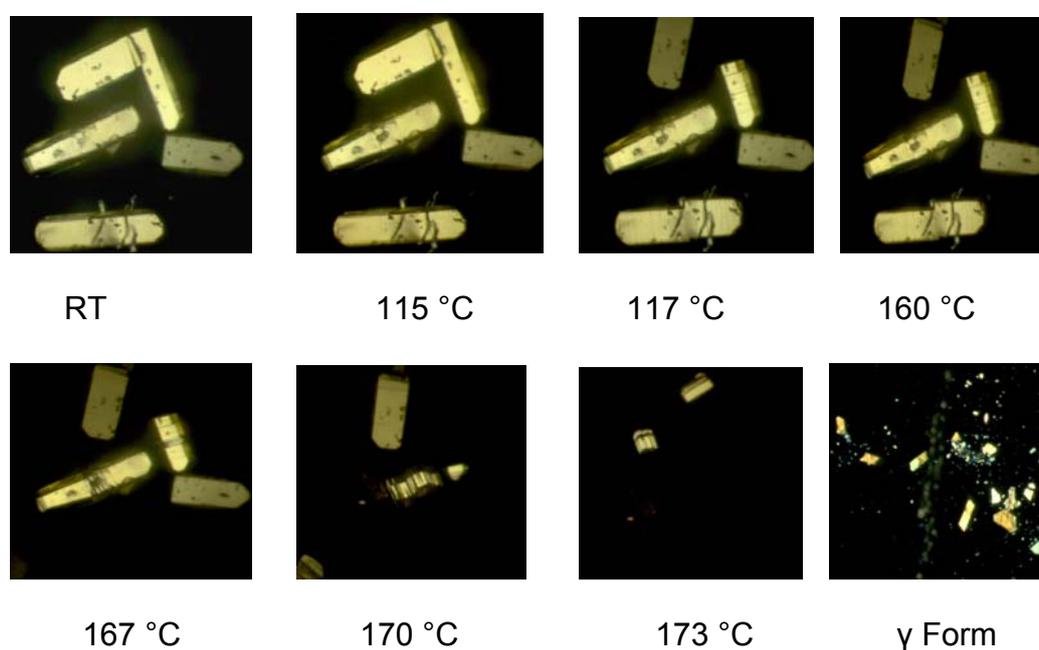


Fig 7. 2A Photo-micrograph of FOX-7 crystals (DMF) upon heating.

These changes attributed to  $\alpha$  to  $\beta$  phase transition of FOX-7. On continuing heating further at around  $170\text{ }^{\circ}\text{C}$  ( $\beta$  to  $\gamma$  phase. transition) some of the crystals showed jumping behaviour whereas some crystals contracted (bended) with more transverse lines on the surface. At this temperature heating is stopped. When touched with the needles, these crystals segmented into further small crystals each one showed crystalline nature but were too small for the data collections.

In the second heating experiment the single crystals of FOX-7 obtained from dimethyl-formamide were heated beyond 180 °C. Around 300 °C the crystals became glassy and opaque (Fig. 7.2B). No change is observed on the surface of the crystal above this temperature.

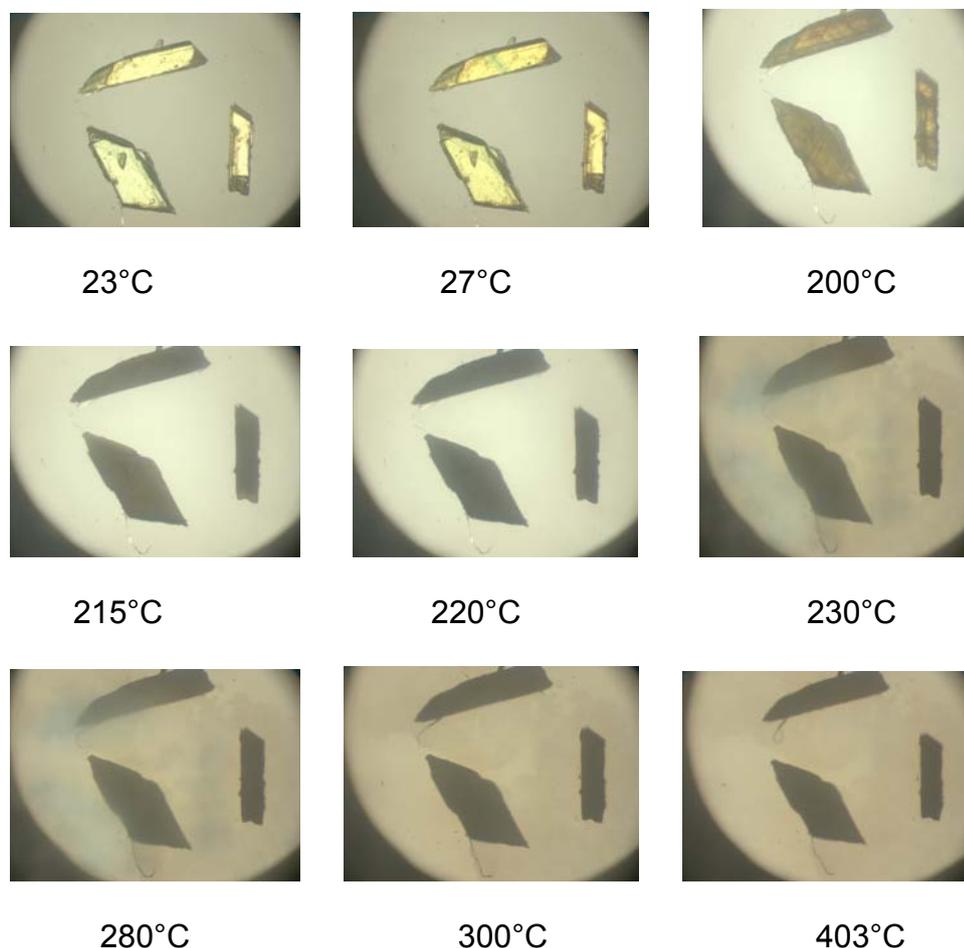


Fig. 7.2B Photo-micrograph of FOX-7 crystals (DMF) at higher temperature

#### 7.4.3 Thermal Phase Transformation Studies

The FOX-7 crystals were heated on the single crystal X-ray diffractometer equipped with OXFORD LN2 cryosystem to explore the probable polymorphic phase transformation. The unit cell determination indicate that the Form I ( $\alpha$ ) crystals converted to the Form II ( $\beta$ ) crystals upon heating at 400 K. The unit cell parameters of the crystals at various temperatures were tabulated in Table-7.3.

Table 7.3. Unit cell parameters of the crystals at various temperatures

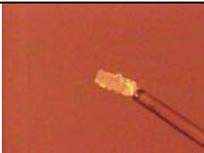
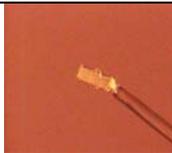
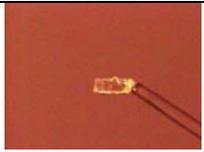
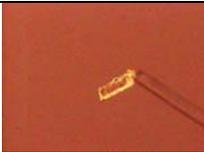
Temperature (K)	100(2)	200(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
a (Å)	6.5054	6.5655	6.6287
b (Å)	6.9027	6.9083	6.9562
c (Å)	11.2245	11.2487	11.3486
$\alpha$	90	90	90
$\beta$	89.859	89.871	90.682
$\gamma$ (°)	90	90	90
V (Å <sup>3</sup> )	504.03	510.20	523.25
Morphology			

Table 7.3 Continued.

Temperature (K)	350(2)	400(2)	450(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
a (Å)	7.0422	6.7011	6.9910
b (Å)	6.7447	6.9904	6.7224
c (Å)	11.5064	11.693	11.7028
$\alpha$	90	90	90
$\beta$	90.23	90	90
$\gamma$ (°)	90	90	90
V (Å <sup>3</sup> )	546.53	547.7	549.99
Morphology			

From the table it is seen that as the temperature increases the volume of the unit cell also increases indicates that the unit cell is expanding. Cooling the crystal to room temperature after heating to 425 K showed the decrease in volume suggesting that the phase transition is reversible. Heating the crystals beyond 450 K on the diffractometer revealed very weak and low angle diffraction.

#### 7.4.4 Crystal Structure Analysis of FOX-7

X-ray diffraction intensity data of the FOX-7 crystals (monoclinic,  $\alpha$ -form obtained from acetone) were collected at room temperature. At 390 K,  $\alpha$ -form is transformed into orthorhombic  $\beta$ -form. Therefore, the crystal data of  $\beta$ -phase was measured at 425 K, higher than the transition temperature. The summary of crystallographic data for the dimorphs ( $\alpha$  and  $\beta$ -forms) of FOX-7 is given in Table 7.4.

Table 7.4 Crystallographic data of FOX-7 dimorphs at different Temp.

Form	$\alpha$	$\beta$
Temperature (K)	298(2)	425(2)
Chemical Formula	C <sub>2</sub> H <sub>4</sub> N <sub>4</sub> O <sub>4</sub>	C <sub>2</sub> H <sub>4</sub> N <sub>5</sub> O <sub>4</sub>
Formula weight	148.09	148.09
Crystal Colour	Pale yellow	Pale yellow
Crystal morphology	Plate	Plate
Crystal size	0.32 × 0.15 × 0.05	0.20 × 0.12 × 0.04
Crystal system	Monoclinic	Orthorhombic

Space group	P21/n	P212121
a(Å)	6.966(6)	6.9904(14)
b(Å)	6.649(6)	6.7011(14)
c(Å)	11.355(10)	11.693(3)
$\alpha$ (°)	90	90
$\beta$ (°)	90.434(14)	90
$\gamma$ (°)	90	90
V (Å <sup>3</sup> )	526.0(8)	547.7(2)
Z, D <sub>cal</sub> (g/cm <sup>3</sup> ),	4, 1.870	4, 1.796
$\mu$ (mm <sup>-1</sup> )	0.178	0.171
Ab.correction	Multi-scan	Multi-scan
Transmission min/max	0.9453, 0.9912	0.9666 / 0.9932
F (000)	304	304
h, k, l (min, max)	(-8,8), (-7,7), (-13, 13)	(-7,7), (-5,8), (-12,13)
Reflections collected	3440 / 924	2732 / 949
Data / parameters	924 / 0 / 91	949 / 0 / 91
Observed reflns	862	871
R1[ $I > 2\sigma(I)$ ]	0.1178	0.0846
wR2[ $I > 2\sigma(I)$ ]	0.4218	0.2476
R1_all data	0.1206	0.0890
wR2_all data	0.4294	0.2551
GoF	2.159	1.084
$\Delta\rho$ max, $\Delta\rho$ min (eÅ <sup>-3</sup> )	1.207, -0.897	0.511, -0.418

The lattice parameters are only slightly changed for both the phases during transition (Table 4) suggesting the transition is displacive. An inspection of the R-values (Table 7.4) revealed that the structural refinement of the data for  $\beta$ -FOX-7 at 425 K leads to a very good R-value (0.0846). These values are substantially lower than those obtained with  $\alpha$ -FOX-7 at 298 K is 0.1178 suggest the structure of  $\alpha$ -FOX-7 thermally stressed due to high mobility of the atoms resulting in high R-value. The ORTEP view of both  $\alpha$  and  $\beta$  form given in Fig. 7.3.

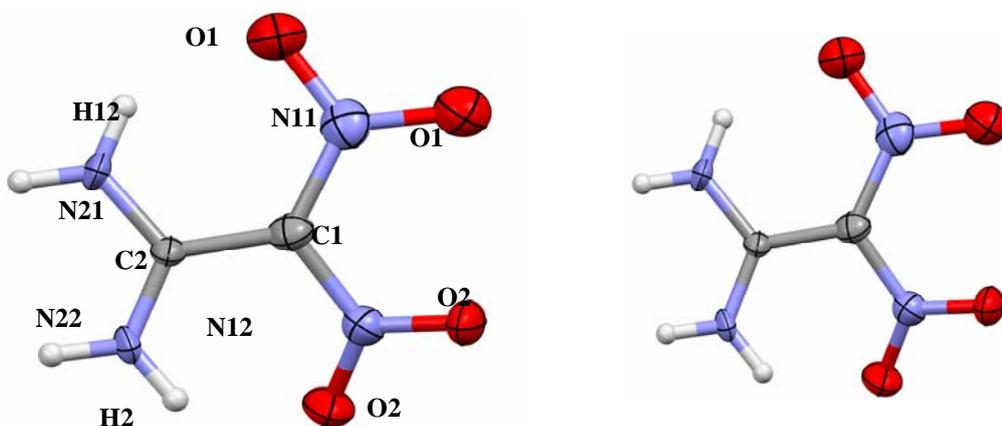
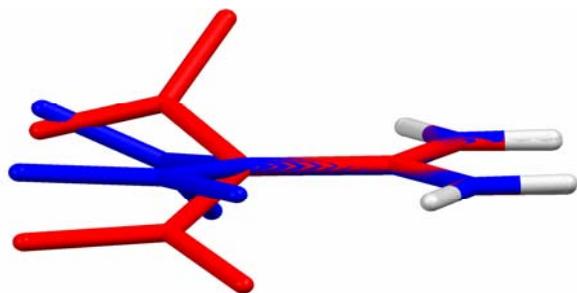


Fig. 7.3 ORTEP view of (i)  $\alpha$ -form (298 K) and (ii)  $\beta$ -form (425 K).

From the ORTEP view, it is noteworthy that the C-C, C-N, N-O and N-H bond lengths are almost similar in both the forms. However the difference were found in the orientation of nitro group, which deviates in  $\beta$ -form as shown in the molecular overlap plot (Fig. 7.4).



$\alpha$ -Fox 7,  $\beta$ -Fox 7

Fig 7.4 Molecular overlap plot of  $\alpha$ -form (blue) and  $\beta$ -form (red).

The two FOX-7 molecules were overlapped at the carbon-carbon bond of the ethylene molecule. The two nitro groups deviates strongly from the molecular plane formed by the carbon and two amino nitrogen atoms.

In  $\alpha$ -FOX-7 the nitro groups are twisted by  $7^\circ$  and  $39^\circ$  with respect to the carbon-carbon bond, but in  $\beta$ -FOX-7 at 425 K, these twist angles are changed to  $20^\circ$  and  $38^\circ$  (Fig. 7.5).

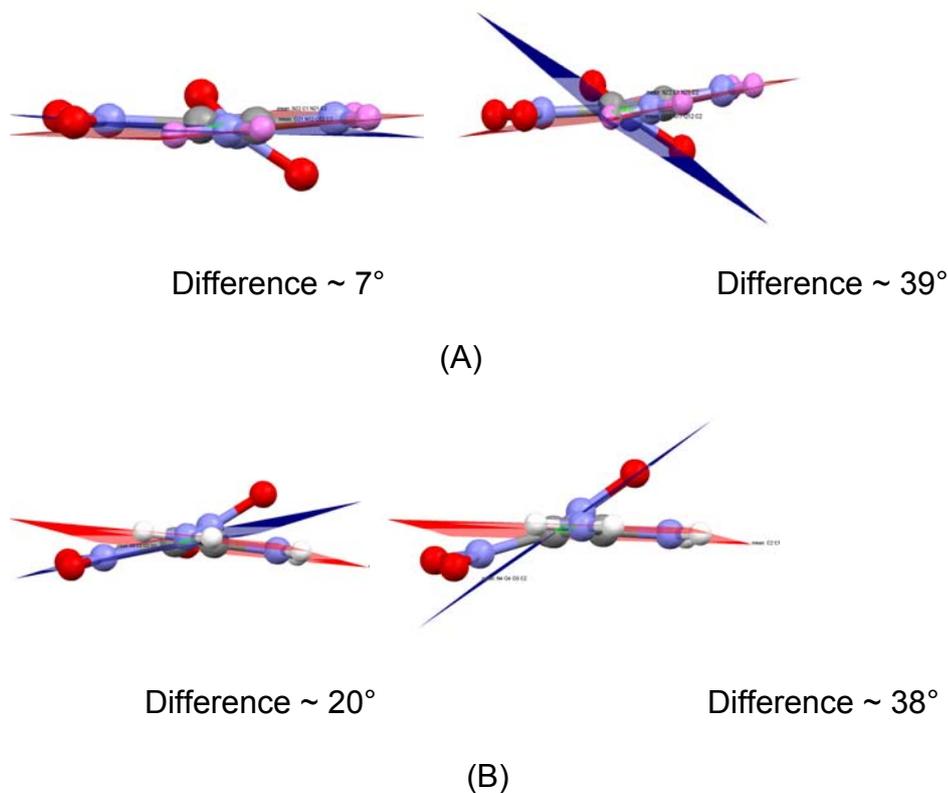


Fig. 7.5 Deviation of nitro group from the molecular plane formed by ethylene molecule and amino groups in (A)  $\alpha$ -FOX-7 and (B)

$\beta$  -FOX-7.

The structural studies of dimorph showed a difference in intramolecular hydrogen bonding interactions between the oxygen atoms of nitro group and the H-atoms of the amino group (Fig 7.6).

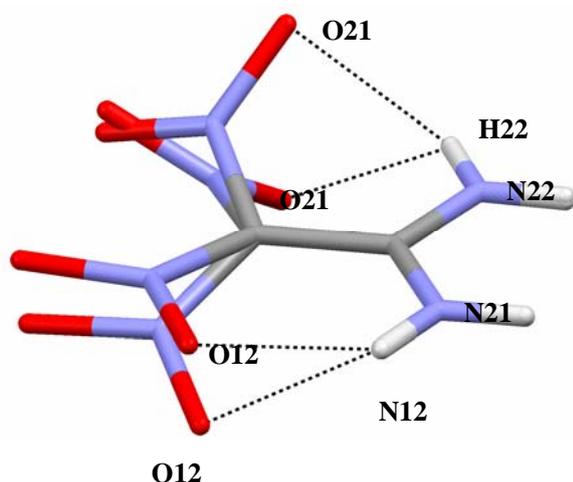


Fig 7.6 Molecular overlap of  $\alpha$ -form and  $\beta$ -form indicating the different intramolecular hydrogen bonding interactions.

Although there is significant change in the orientations of the nitro groups with respect to the ethylene plane the intramolecular H-bonding seems to be unaffected. The H-atoms of both the amino groups pointing towards nitro groups make intramolecular N–H $\cdots$ O interactions of comparable strengths (Table 7.5).

Table 7.5 Intramolecular H- bonding interactions in dimorphs of FOX-7

Form	D–H $\cdots$ A (°)	D $\cdots$ A (Å)	D $\cdots$ A (Å)	D–H $\cdots$ A (°)
$\alpha$	N21–H12 $\cdots$ O12	2.01	2.577(5)	122
	N22–H22 $\cdots$ O21	1.91	2.607(6)	137
$\beta$	N21–H12 $\cdots$ O12	1.97	2.596(5)	129
	N22–H22 $\cdots$ O21	2.03	2.531(5)	116

There is no significant change in the geometry of the H-bonding even after the phase transition.

Other than intramolecular H-bonding, the H-atoms and the oxygens of the nitro groups are engaged in extensive intermolecular hydrogen bonding pattern. There is slight change in the intermolecular H-bonding interaction made by the molecules in  $\alpha$  and  $\beta$ -forms as shown above in Fig. 7.6.

In both the forms each molecule is surrounded by six molecules within the layer. In  $\alpha$ -form, the other H-atoms (not involved in intramolecular H-bonding) H11 and H21 of the amino groups make bifurcated N-H...O interactions with the oxygen O21, O11 and O11, O22 respectively. While in  $\beta$ -form, only H21 is engaged in bifurcated N-H...O interactions but with different oxygen O12 and O22 and H21 makes N-H...O interactions with O11 alone. Additionally, H-atom H22 also takes part in N-H...O bonding with O12 and O11 in  $\alpha$  and  $\beta$ -forms respectively. The geometries of all these intermolecular H-bonds are comparable (Fig 7.7, Table 7.6).

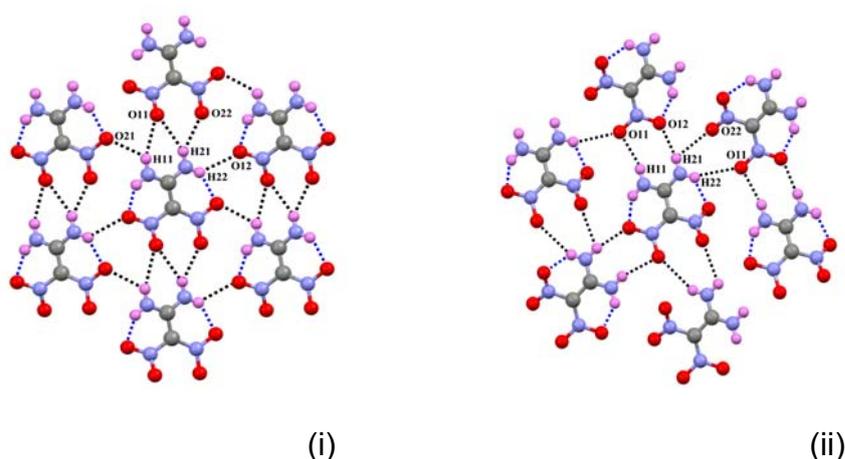


Fig 7.7 Molecular assemblies of FOX-7 molecules in (i)  $\alpha$ -form view down b-axis and (ii)  $\beta$ -form view down a-axis. Black and blue dotted lines indicate inter and intramolecular C-H...O interactions respectively.

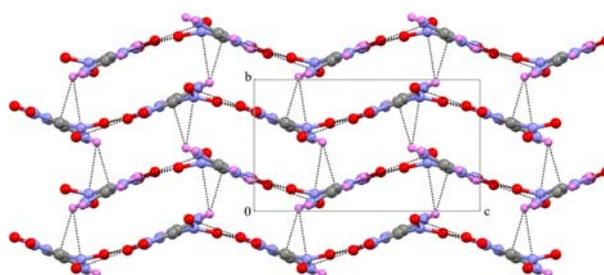
Table 7.6 Intermolecular H-bonding interactions in dimorphs of FOX-7

Form	D–H...A (°)	D...A (Å)	D...A (Å)	D–H...A (°)
$\alpha$	N21–H11...O11	2.43	3.233(5)	157
	N21–H11...O21	2.52	3.019(6)	118
	N22–H21...O11	2.51	3.296(6)	152
	N22–H21...O22	2.32	3.045(7)	142
	N22–H22...O12	2.39	3.028(6)	131
$\beta$	N21–H11...O11	2.42	3.180(2)	148
	N22–H21...O12	2.21	2.992(5)	152
	N22–H21...O22	2.59	3.000(2)	110
	N22–H22...O11	2.63	3.408(4)	151

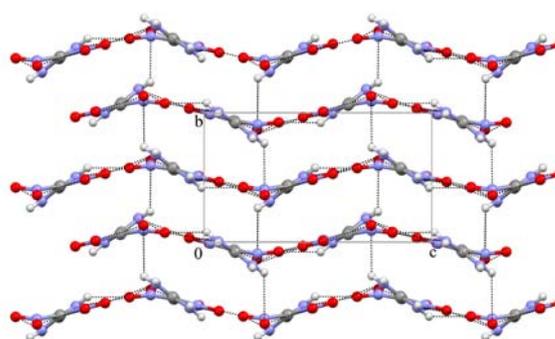
Thus in  $\alpha$ -form, molecules make two intramolecular and five intermolecular H-bonds and two intramolecular along with four intermolecular H-bonds in  $\beta$ -form. Therefore, the intermolecular H-bonding network in  $\beta$ -form is weakened as compared to  $\alpha$ -form. Molecular assemblies of FOX-7 molecules in (i)  $\alpha$ -form view down b-axis and (ii)  $\beta$ -form view down a-axis. Black and blue dotted lines indicate inter and intramolecular C–H...O interactions respectively.

In the third dimension, similar wave like molecular arrangements were observed in both the forms. The dipolar FOX-7 molecules are arranged by “head-to-tail” intermolecular hydrogen bonding, where the “heads” of the FOX-7 molecules are donating amino groups and the “tails” are the withdrawing nitro groups. In the wavy arrangement the head of the one molecule is hydrogen bonded with the tail of the next molecule. The head-to-tail-bonded FOX-7 molecules within the wave-shaped layers lie in the a-

c plane. Each wavy layer are stacked one over the other more closely with weak N-H... $\pi$  contacts in the direction of the b axis in  $\alpha$ -form whereas in the  $\beta$ -form the packing of layer is almost similar but via weak N-H...N and N-H...O contact (Fig . 7.8).



(A)



(B)

Fig. 7.8 Wavy layers of head-to-tail H-bonded FOX-7 molecules viewed down the a-axis; (A)  $\alpha$ -form and (B)  $\beta$ -form.

So the net effect of the temperature is the twisting of the nitro groups from the molecular plane formed by the ethylene moiety resulting in linking of layers via different weak contacts whereas it has minimum effect on molecular aggregation within the layer.

#### 7.4.5 Molecular organization upon phase Transformation

View of molecular packing down b-axis in  $\alpha$  form and down a-axis in  $\beta$  form is shown in Fig. 7.9.

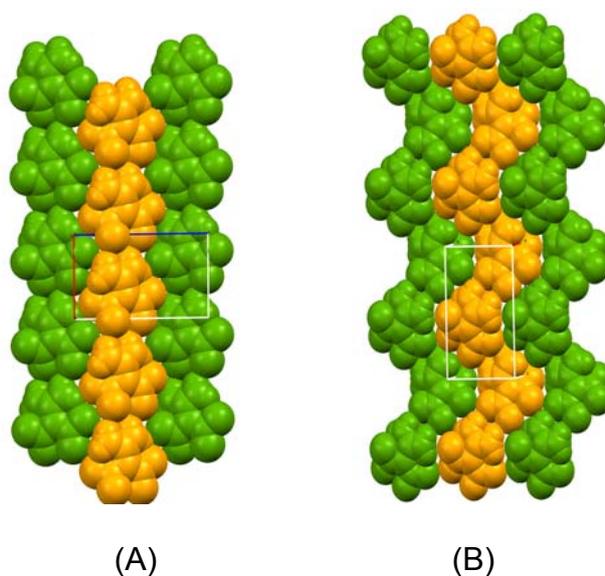


Fig.7. 9 Molecular organization of FOX-7 in (A)  $\alpha$  - form and (B)  $\beta$  form

Although there is not much change in the intra and intermolecular interactions after phase transition from  $\alpha$  to  $\beta$  form the organization of molecules has changed dramatically. The achiral crystals of FOX-7 ( $\alpha$  form) has been transformed to the chiral crystals ( $\beta$ -form). Therefore the molecules which were related by unit translation (one over the other, green or orange layer) in  $\alpha$  form are reorganized in the crystal lattice to produce  $\beta$  form in which molecules are assembled helically around the crystallographic  $2_1$ -screw axis (green or orange layer) .

#### 7.4.6 X-Ray Study of $\gamma$ form of FOX-7

The determination of the unit cell parameters of the crystal heated on the polarizing microscope till 175 °C revealed that the unit cell is almost similar to the  $\alpha$  and  $\beta$  form. It is observed that the unit cell volume slightly expanded in  $\gamma$  form. The unit cell parameters of  $\gamma$  Fox-7 are as

$$a = 7.163(15) \text{ \AA}, b = 6.859(16) \text{ \AA}, c = 11.709(24) \text{ \AA}, \beta = 90.74(5)^\circ, V = 543 (3) \text{ \AA}^3 .$$

### 7.4.7 Thermal studies

The thermal studies of the FOX-7 crystals were carried out in DSC. The DSC plot showed two exothermic peaks, one at ~ 230 °C and the second at ~ 278 °C corresponds to the decomposition (Fig. 7.10) of the compound.

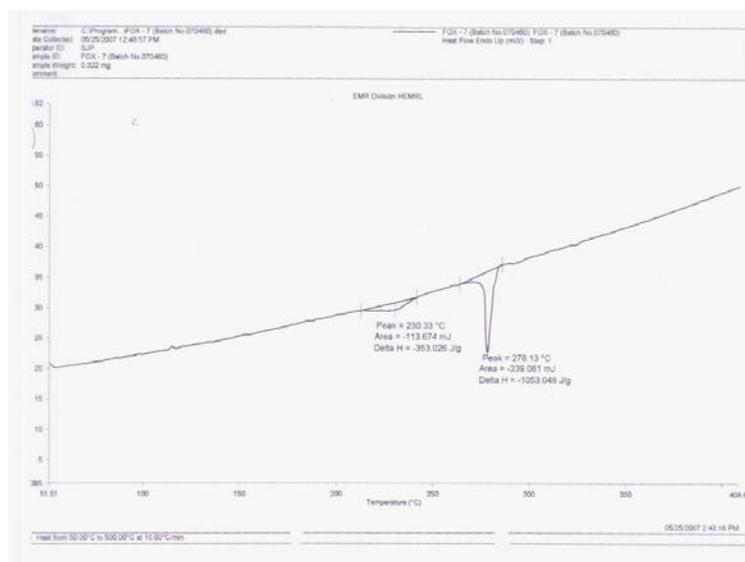


Fig 7.10. Thermo-gram of FOX-7 crystals by DSC

But the reversible  $\alpha$  to  $\beta$  transition and irreversible  $\beta$  to  $\gamma$ . transition had not been able to be captured by this DSC analysis.

However, the literature search (22-27) revealed that the first reversible phase transition ( $\alpha$  to  $\beta$ ) occurs at 116 °C and showed discontinuous increase of molar volume ( $\Delta V$ ) and entropy ( $\Delta S$ ) confirming it to be the first order. A second phase transition ( $\beta$  to  $\gamma$ ) takes place at 175 °C, however, in contrast to the  $\alpha$  to  $\beta$  phase transition, this phase transition ( $\beta$  to  $\gamma$ ) is not reversible.

### Computational Studies

Single point abinitio energy calculation on  $\alpha$  - Fox-7 and  $\beta$  - Fox-7 were performed using the 'Gaussian 03' suite of programs.(28) In each case, single point energies of isolated molecules were computed with the Hartree-Fock

theory at 6-31G level to correlate the relative energies of both the forms without taking into account of any intermolecular interactions. The single point energy calculation of  $\alpha$  - Fox-7 was found to be  $\sim 98.6$  kcal/mol lower than that of  $\beta$  - Fox-7.

## 7.5 Conclusion

The reversible thermal phase transition of  $\alpha$  form to  $\beta$  form at 390 K of FOX-7 and irreversible thermal phase transition of  $\beta$  form to  $\gamma$  form at around 446 K is studied by single crystal X-ray diffraction and hot stage microscopy techniques.

The  $\alpha - \beta$  phase transformation in FOX-7 is reversible and first order. In both the forms the two-nitro groups are deviating from the molecular plane formed by the ethylene carbons and amino groups. The deviation is less in  $\alpha$  FOX-7 but in  $\beta$  FOX-7 both the nitro groups lie much more out of the plane.

In both the forms the molecules form wavy layers by linking in head-to-tail fashion. Within the layer the molecules are associated via extensive intra and intermolecular H-bonds in both the forms could be the reason for the unique properties of FOX-7, namely, its high performance and low sensitivity.

During  $\beta$  to  $\gamma$  transition, the crystals jumped and disintegrate into small crystallites. The almost similar unit cell parameters of the  $\gamma$  form compared to  $\alpha$  and  $\beta$  form suggest that the molecular arrangement in  $\gamma$  form is similar to  $\alpha$  and  $\beta$  form, although it has not been able to be solved its crystal structure.

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# Chapter 8

## SUMMARY

## Summary

The thesis includes the survey and importance of high explosive materials (HEMs) as well as insensitive high explosive materials (IHEMs). The process of conventional HEMs like 2,4,6-Trinitrotoluene (TNT), Cyclotrimethyltrinitramine (RDX), Cyclotetramethyltetranitranine (HMX) etc. are well established and are being used regularly in military applications. Among the IHEMs, 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) and 1,1-Diamino-2,2-dinitro-ethene (FOX-7) are the most promising. Development, scale-up, characterization, formulations and military applications of TATB are well reported in the literature. However, FOX-7 is reported to be a very recent one and information on development, scale-up, characterization, formulations and applications etc are not available in details. Hence, FOX-7 has been selected for the present studies considering its futuristic potential in the military applications.

The research work in the thesis is outlined broadly to investigate the process development and reactor modelling for synthesis of a recent novel thermally stable insensitive high explosive material FOX-7. Preparation of FOX-7 involves two step processes viz. nitration followed by hydrolysis starting from the raw material of methylidyhydroxypyrimidine (MDP). Studies have been made on process selection for FOX-7 synthesis followed by optimization studies, evaluation of thermo-chemical parameters of nitration reaction in reaction calorimeter, reaction kinetics studies of nitration and hydrolysis process, parametric sensitivity analysis of the nitration process, modelling of reaction in micro reactor and comparison of micro reactor with batch reactor to select the best course of synthetic route for FOX-7 adhering to selectivity, quality, safety, process control etc. while scale-up. The studies have also been extended to

prepare spherical particle of FOX-7 required for improvement in the density of explosive charges which in turn exhibits superior performance of the same war head. Studies on polymorphic behavior of the FOX-7 have been studied to know the pattern of phase transition at different temperature while used in high explosive and propellant compositions.

The summary and conclusions of the studies carried out in the above area are given below:

### **8.1 Process selection and Optimization**

Process for synthesis of FOX-7 has been selected based on the feasibility of the processes reported in the literature. Both nitration & hydrolysis process parameters have been optimized by conducting large numbers of experimental batches with a aim to achieve maximum yield. Various parameters like moles of nitric acid per mole of MDP, moles of sulphuric acid per mole of MDP, temperature ( $^{\circ}\text{C}$ ) of solubility of MDP in concentrated sulphuric acid, nitration temperature ( $^{\circ}\text{C}$ ) domain, temperature ( $^{\circ}\text{C}$ ) of nitration for optimum yield, nitration time (minutes), concentration (%) of nitric acid and sulphuric acid have been optimized to 5,10, 50, 5-35, 15, 120 and 98 respectively. It found that that liquid mode of addition is preferred over the solid mode of addition during nitration. Batch type of reactor is preferred compared to continuous type of reactor to overcome the problem of chocking.

Various parameters of the hydrolysis process like moles of water per mole of MDP, % sulfuric acid required, temperature ( $^{\circ}\text{C}$ ) required for hydrolysis, reaction time (hrs) and run away temperature ( $^{\circ}\text{C}$ ) conditions have been optimized to 210, 20, 25, 4 and  $\geq 45$  respectively. Both the nitration and hydrolysis process have been optimized strictly adhering the safety norm. Optimized yield realized is ~85%. Thus using of optimum quantity of raw

materials makes the process more friendly in development and scale-up point of view.

## **8.2. Evaluation of thermo-chemical parameters for nitration process**

Heat of reaction ( $\Delta H_R$ ) evaluated at 15 °C with optimized mole ratio (MDP : HNO<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub> i.e. 1 : 5.1 : 10.1) for nitration is ~460 kJ/mole of MDP. Heat generated during preparation of mixed acid (addition of HNO<sub>3</sub> into the H<sub>2</sub>SO<sub>4</sub>) is recorded as 14.2 kJ/mole of HNO<sub>3</sub> compared to the heat of mixing of MDP in H<sub>2</sub>SO<sub>4</sub> is 100 kJ/mole of MDP. Onset temperature for decomposition of nitration reaction mixture is 100 °C with the potential of heat liberation in the order of ~1206 kJ/mole. If MDP is used half of the desired quantity compared to standard ratio used in nitration process the onset temperature of decomposition reduces to 80 °C. Adiabatic rise in temperature due to desired  $\Delta H_R$  is around 223 °C, which is considerably high and far from onset of decomposition. This indicates that for scale up of the process, efficient cooling system is required. Nitration of MDP is feasible either by addition of HNO<sub>3</sub> into the solution of MDP in H<sub>2</sub>SO<sub>4</sub> or addition of MDP in mixed acid. Hence, optimized mole ratio at lowest optimum temperature under continuous agitation with efficient cooling system is not only important for optimum yield and purity of the product but also to prevent thermal runaway followed by decomposition due to highly exothermic nitration reaction.

Thermal hazards associates with MDP-nitration process, calorimetric experiments have been conducted in two separate reaction calorimeter viz. Mettler make RC and HEL make RC. Both power compensation and heat flow Calorimetry methods were used for estimation of heat during experiments in HEL make RC. The quantum of heat generation in both Mettler-RC as well as HEL-RC is equivalent and variation is around 3 to 4 %.

### 8.3 Reaction kinetics for nitration and hydrolysis process

Kinetics studies have been carried out for both nitration and hydrolysis process using differential method. Studies on nitration kinetics reveals a few inferences like, nitration of MDP is a pseudo 2<sup>nd</sup> order reaction and pseudo reaction rate constant is 0.0338 concentration<sup>-1</sup> time<sup>-1</sup> at 15<sup>o</sup>C. Heat generation increases exponentially with temperature. Using the rate equation the reaction time evaluated is ~110 minute at 15<sup>o</sup>C. It is also observed that exo-thermicity (460 kJ/mole) of the reaction is much higher (about eleven times) compared to the activation energy (42 kJ/mole) evaluated from temperature dependent rate equation. This suggests that reaction is necessary to be carried at the lowest possible operating temperature without compromising the yield and quality of the product. Exponential rate of heat generation suggests efficient agitation and cooling system is important for scaling up of the process. With increase in temperature by 10<sup>o</sup>C (from 5 to 15<sup>o</sup>C), reaction rate constant increases by 2.4 times. That is why at 5<sup>o</sup>C, it requires 291 minutes to get 85% product compared to 110 minutes at 15<sup>o</sup>C for same conversion. Frequency factor calculated for the reaction is  $44.24 \times 10^4$  indicating interaction of the chemical species in the reaction media. Relatively lesser activation energy suggests that the reaction is temperature sensitive.

The studies on hydrolysis of tetranitro-MDP reveals that optimum hydrolysis temperature is ~25<sup>o</sup>C and rate of hydrolysis increases with temperature. Above 45<sup>o</sup>C there is a distinct tendency for runaway reaction of hydrolysis reaction mass by evolving copious frothing due to NO<sub>x</sub> catalyzed decomposition of di-nitromethane, hydrolysis reaction follows pseudo order of 2.5, hydrolysis rate constant is  $1.36 \times 10^{-4}$  moles lit<sup>-1</sup> min<sup>-1</sup> at 25<sup>o</sup>C. With the increase in temperature by 10<sup>o</sup>C (from 15<sup>o</sup>C to 25<sup>o</sup>C) hydrolysis rate increases

by 1.3 times. That implies that at low temperature hydrolysis rate is slow. Using the pseudo rate equation, the hydrolysis time is 240 minutes at 25<sup>0</sup>C. However, lower temperature (<30<sup>0</sup>C) is preferred to avoid frothing and runaway situation at higher temperature.

Studies on parametric sensitivity of MDP nitration reaction reveals that the reaction rate can increase drastically with increase in temperature by sharp reduction in time causing the system sensitive. For the temperature gradient (difference in reactor and jacket temperature) more than of 10<sup>0</sup> C and reaction temperature above 20<sup>0</sup>C, the reaction becomes sensitive. This is helpful during the plant operation. The information is helpful in safe process operation and plant design.

#### **8.4 Micro-Reactor Modelling and Simulation of MDP Nitration**

In this study, the micro reaction system has been modeled for nitration of MDP by adopting two dimensional (2-D) heat flow and mass transfer equations. The numerical results from the 2-D model for conversion and temperature profile along the length and radius of micro reactor have been compared with corresponding value obtained for batch reactor. In order to validate the model an experimental set was made using micro tubes as reactor, pumps with micro flow capacity, micro mixtures etc. and several experiments on nitration of MDP were conducted with the variation of concentration, flow rate, residence time and temperature etc. The measurable findings includes that the nitration of MDP concentration takes place even at lower concentration of MDP and lesser reaction time with better control of temperature. The nitration of MDP reaction in micro reactor takes place in laminar region. The yield of final product i.e. FOX-7 is higher in continuous flow micro reactor than corresponding concentration in batch reactor irrespective of reactant concentration. The Rate

of formation of FOX-7 (g /min) in continuous flow micro reactor is higher than correspond of batch reactor. The nitration of MDP in micro reactor was found feasible at even room temperature at different flow rate & residence time and results in higher yield in comparison of batch mode. Nitration of MDP experiment carried out in the present study provides adequate information on design of micro reactor system.

### **8.5 Studies on preparation of spherical FOX-7 particle**

Feasibility studies on preparation of spherical particles of FOX-7 using the novel concept of reverse micelle carried out at laboratory level. Spherical particles of FOX-7, have been successfully prepared in reverse micro-emulsion of triton X 100, cyclohexane, water etc. Analysis of the experimental result revealed that, the particle size and shape of FOX-7 can be varied by changing water to surfactant molar ratio in micro-emulsion. The method describes the process insight about the formation of spherical FOX-7 particles. It is formed within two hours. Spherical particles synthesised in this method are generally in the range of sub-micron and nano-range. Impact sensitivity ( $h_{50}$ ) by fall hammer method is around 45 cm compared to regular synthesised FOX-7 (i.e.  $50 \pm 5$  cm) without altering any change in friction sensitivity i.e. 36 kg. The higher impact sensitivity is attributed due to increase in surface area of the particle size which is the result of the lower particle size achieved in the study. This may be explained because of reduction of the particle size there by increase in, surface area, which makes the particles more active towards impact. Since, the layer structure of the crystal remains unchanged friction sensitivity remains unaffected. Spherical FOX-7 particles are useful for special applications in formulation of high explosive composition.

## 8.6 Polymorphic behaviour of FOX-7

Polymorphic screening of single crystals structure of insensitive high-energy material, FOX-7 was carried out to explore the polymorphic behaviour. This is required to know about the conformational change due to heating while it is being used in high explosive composition or propellant formulations.

The study of FOX-7 by single crystal X-ray diffraction and hot stage microscopy techniques reveals the reversible thermal phase transition of  $\alpha$  form to  $\beta$  form occurs at 390 K and irreversible thermal phase transition of  $\beta$  form to  $\gamma$  form occurs at around 446 K. So, the  $\alpha - \beta$  phase transformation in FOX-7 is reversible and first order. In both the forms the two-nitro groups are deviating from the molecular plane formed by the ethylene carbons and amino groups. The deviation is less in  $\alpha$  FOX-7 but in  $\beta$  FOX-7 both the nitro groups lie much more out of the plane. Also in both the forms the molecules form wavy layers by linking in head-to-tail fashion. Within the layer the molecules are associated via extensive intra and intermolecular H-bonds in both the forms, could be the reason for the unique properties of FOX-7, namely, its high performance and low sensitivity.

During  $\beta$  to  $\gamma$  transition, the crystals jumped and disintegrate into small crystallites. The almost similar unit cell parameters of the  $\gamma$  form compared to  $\alpha$  and  $\beta$  form suggest that the molecular arrangement in  $\gamma$  form is similar to  $\alpha$  and  $\beta$  form, although it has not been able to be solved its crystal structure.

## PUBLICATIONS

### Publications Related to Thesis

1. **A. K. Mandal**, Gauri J Kulkarni, V. B. Sutar and R. K. Pandey, 'Process optimization and kinetics of hydrolysis for 2-dinitromethelene-5,5-dinitropyrimidinedione to prepare FOX-7', 7<sup>th</sup> International High Energy Materials Conference & Exhibition, Pune, India, Dec, 2009
2. **A. K. Mandal**, U.Thanigaivelan, Souraseni Basu and R. K. Pandey, "Thermochemical studies for preparation of 2-methyl-4,6-dihydroxypyrimidine", 7<sup>th</sup> International High Energy Materials Conference & Exhibition, Pune, India, Dec, 2009
3. **A.K. Mandal**, V.B. Sutar and V.L. Narasimhan, "Thermal hazard evaluation of 2-methyl-4,6-dihydroxy-pyrimidine nitration by calorimetric studies", 6<sup>th</sup> HEMCE, Chennai, Dec 2007.
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