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-dihydroxy-pyrimidine (MDP) (its keto form is 2-methyl-4,6-pyrimidine-dione, MPD) using concentrated nitric acid (HNO₃) and sulfuric acid (H₂SO₄) 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 (°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 (°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 (°C) required for hydrolysis, hydrolysis time (hrs), run away conditions, temperature (°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°C and reaction temperature above 20°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 follows 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.