



## Mathematical modelling and simulation for decomposition of agro-herbicide in accelerated reaction calorimeter to avoid water pollution

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### ABSTRACT

Many pesticides, widely used in agriculture, are produced in semi-batch-reactors which involve strong exothermic reactions and show thermal runaway which are difficult to control. In case of failure of cooling systems, the runaway gets triggered. This results in uncontrolled increase in temperature for adiabatic systems with consequent reactor pressurization due to uncontrollable formation of gases. Finally, safety of the reactor becomes questionable with release of hazardous gases to the environment increasing the pollution. Simultaneous decomposition of the product may lead to an accident requiring emergency environmental disaster management plan. In this work, decomposition of 4-chloro-3-nitro benzene tri fluoride in batch reactors is considered. for which a mathematical model has been formulated and is validated. Simulation results comprising of both reactor temperature and pressure profiles are obtained for the effect of cooling failure and other accidental scenarios. This study is helpful to understand possibilities of environmental hazards and increase in the level of air and water pollutions.

*Keywords:* Agro-herbicide; Semi-batch reactor; Mathematical modelling; Runaway reaction; Water; Pollution

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### 1. Introduction

Accidental releases of toxic chemicals will create dangerous environmental and health hazards problem due to release of toxic chemicals. Batch and semi-batch (Fig. 1) reactors are used to produce or store such agrochemicals where probabilities of occurrence of runaway reactions are increased due to failure of some essential components. According to Barton and Nolan [1], thermal runaway reactions create havoc in continuous and batch processes. Due to economic considerations, many reactions are conducted in batch reactors. However, due to operational constraints, these reactors face vulnerabilities of hazardous release while processing pharma/agrochemicals [2]. Hazardous explosions generally

occur in polymerization, batch reactors where the rate of rise in temperature goes beyond control due to non-stoppable exothermic reactions. Some agro-herbicides decompose and release toxic gases that pollute environment. Strong runaway reactions can lead to accidents which the world has observed among about 200 accidents in the past, such as in the study by Theofanous [3] and Bowonder [4], etc. The latter author Bowonder [4] reported accidents in Bhopal in 1984 where methyl isocyanide gas got released from reactors causing hazards to environment. The thermal runaway was caused due to lack of maintenance which allowed entrance of large amount of water into Methyl Isocyanate tank causing forceful release of toxic gas through valve which polluted the environment. According to Bhatluri et al. [5], the hazardous

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accident claimed about 3,800 lives. The ground water (Bhopal) remained contaminated with di and tri chloro benzenes [6]. In Florida on December 2007, the report mentioned that soil and groundwater were still contaminated with manganese and benzene, along with that the chemical accident killed four and thirty-two were injured [7]. The above events indicate that there is a lack in tools to find onset of exothermic runaway and maximum temperature rise due to the fact that contents are not completely mixed [8]. At the same time decomposition of product also releases heat as it is exothermic in nature. The reactors should be designed in such a way that in worst situation, it should allow the evolved gases to exit through vent so as to release the build-up pressure in the reactor and to avoid explosion.

Batch reactors allow both the reactants to be in the reactor so that conversion of product happens from the reactants. In case of decomposition, the compound is taken in the reactor and is slowly heated while the gases formed are allowed to exit with coolant on. In case of failure of instruments/components, the reactants start reaction with already available reactant until they get consumed by the other reactant in the container and proceeds for completion. Due to lack in coolant, produced gases develop pressure which forces the vent/reactor wall to burst. As it is difficult to experiment such hazardous situation, simulations become alternate tool to find out the aftermath and effects of runaway reactions. Reaction kinetics is important which helps in determining the rate of heating/cooling in the reaction. It also helps in finding the operating strategy of the reactor. To study runaway reaction system, the reaction kinetics needs to be known. Many researchers have worked on runaway reactions [5,9–22].

In case of coolant failure, exothermicity of the reaction leads to product decomposition evolving gases which rises pressure in the reactor leading to an accident and environmental hazards. In this paper, CNTBF is chosen as raw material for the decomposition reaction of CNBTF. In this reaction, heat is evolved due to exothermic undesired reactions above maximum allowable temperature. Thus, desired temperature time profile determines the operating conditions of the reaction which is rather in a lower limit and thus may lower the productivity. This motivates the necessity of a mathematical model for the decomposition reaction. Models are helpful for safe-design, scale-up and optimisation studies. Thus, the remaining paper is organized as follows: section 2 deals with development of mathematical model for the decomposition in batch reactor. Description of the experimental set-up is presented in section 3. Experiments in accelerated reaction calorimeter (ARC) are stated in this section. The theoretically simulated profiles of reactor temperature and pressure are validated with experimental data in section 4. Effect of normal parametric values on the profiles of decomposition temperature is discussed in section 5. At the end, conclusion from the study is drawn.

## 2. Mathematical modelling

Let us consider a reaction  $A \rightarrow G$ . Compound A is decomposed to gases G and residues through heating through in homogeneous medium.

The decomposition condition is being modelled by the following ordinary differential equations which represent

energy balance and mass balance equations during production of the product G from A. During decomposition, the pressure evolution into the reactor is governed by Eq. (6). The following assumptions are assumed in the modelling.

- The properties of gas are ideal.
- The reactant mass is in macro and is mixed correctly.
- The impacts of thermal removal are associated with both cooling and ambient dissipation.
- The impact on the quantity of the liquid phase of all chemical reactions is negligible.
- The impacts of temperature generation are only due to chemical decomposition.
- The backward reaction does not occur and inversion of reaction phase does not usually happen.

Let us assume that C denotes its concentration. Let  $m_A$  be mass of sample A with specific heat  $c_{pA}$  taken in sample holder of mass  $m_h$  with specific heat  $c_{ph}$ . Let  $k$  be rate constant ( $\text{kmol}/\text{m}^3\text{s}$ ) and it has been observed [20,21] that the rate equation is given by

$$r_A = k_0 \exp\left(-\frac{E}{RT}\right) C_A^2 \quad (1)$$

where reaction rate  $k = k_0 \exp(-E/RT)$  with  $k_0$  as pre-exponential factor,  $E$  is activation energy ( $\text{J}/\text{kmol}$ ),  $R$  ideal gas constant =  $8,314 \text{ J}/(\text{kmol K})$ ,  $T$  is the dimensionless temperature (K),  $C_A$  is concentration of species A ( $\text{kmol}/\text{m}^3$ ) at any time.  $C_{Af}$  be concentration at final of component A. The conversion  $X_A$  of reactant into product becomes as follows:

$$X_A = \frac{C_{Af} - C_A}{C_{Af}} = 1 - \frac{C_A}{C_{Af}} \quad (2)$$

The material balance in this decomposition may be written as follows:

$$\frac{dX_A}{dt} = \text{Da}_{\text{dec}} \left( \exp\left(\left(\frac{E}{RT}\right)\left(1 - \frac{1}{T}\right)\right) (1 - X_A) \right) \quad (3)$$

where  $\text{Da}_{\text{dec}}$  - Damkoloer number for the decomposition reaction, and may be given by  $\text{Da} = k(\rho_s) / (PM_c)$ , where  $M_c$  is thermal inertia factor,  $P$  is the pressure,  $\rho_s$  is the density of component A.

The energy balance equation for reactor or reactant mass becomes

$$\frac{dT}{dt} = \frac{1}{M_c} (\Delta T) \frac{dX_A}{dt} \quad (4)$$

where

$$M_c = \frac{(m_A c_{pA} + m_h c_{ph})}{m_A c_{pA}} \quad (5)$$

where  $\Delta T$  is change in adiabatic temperature in decomposition,  $m_A$  is the mass of species A (kg),  $c_{pA}$  is specific heat of

sample (J/kg K),  $c_{ph}$  is the mass specific heat of sample container (J/kg K),  $m_h$  is the mass of the sample container (kg).

Let  $P$  be pressure,  $V_L$  be volume of liquid sample,  $V_R$  be volume of reactor and  $n$  be number of moles of gas in the empty space of reactor. Initially, empty space contains air and few moles of  $A_0$ . Then by gas law

$$P(V_R - V_L) = nRT \quad (6)$$

Or

$$\frac{dP}{dt}(V_R - V_L) - P\left(\frac{dV_L}{dt}\right) = RT\frac{dn}{dt} + nR\frac{dT}{dt} \quad (7)$$

Introducing dimensionless variables,  $p = P/P_r$ ,  $\tau = t/t_r$ ,  $\theta = T/T_r$  where subscript  $r$  refers to reference state. The above equation can be written as follows:

$$\frac{dp}{d\tau} = \frac{p}{V_R - V_L} \frac{dV_L}{d\tau} + \frac{dX_A}{d\tau} (2.2)n_{A0} \frac{RT_f}{P_f V_0 (V_R - V_L)} \theta + (n_a + (2.2)n_{A0} X_A) \frac{RT_f}{P_f V_0 (V_R - V_L)} \frac{d\theta}{d\tau} \quad (8)$$

The first part of RHS of above equation can be neglected (as  $V_L \ll V_R$ ) and then the equation reduces to a form which gives the pressure dynamics as

$$\frac{dp}{d\tau} = (2.2)n_{A0} \frac{dX_A}{d\tau} \frac{RT_f}{p_f V_r} \theta + \left[ (n_a + 2.2n_{A0} X_A) \frac{RT_f}{p_f V_r} \frac{d\theta}{d\tau} \right] \quad (9)$$

where  $p$  is dimensionless pressure,  $n_{A0}$  is the number of moles in species A (kmol),  $T_f$  is the reference temperature (K),  $P_f$  is the reference pressure,  $\theta$  is the dimensionless temperature,  $n_a$  is the number of moles in air (kmol)

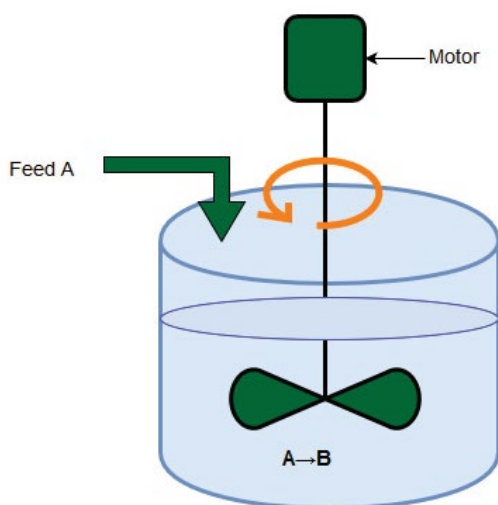


Fig. 1. Schematic of a semi-batch reactor.

With initial conditions as

$$\text{at } t = 0, X_A = 0 \text{ and at } t = 0, \theta = \theta_0 \text{ or } T = T_0$$

Energy balance for the decomposition reactor can be simplified as

$$T = T_0 + \frac{\Delta H_R X}{M_c} \quad (10)$$

where  $\Delta H_R$  enthalpy of the reaction,

In a batch reactor (BR), highly exothermic processes induce the loss of thermal control in case of any operational issues. In this scenario, the online-based monitoring of chemical reactors plays a great role. In this work, the mathematical model of a batch reactor is designed for estimating reactor temperature, coolant temperature (during formation) and pressure for predicting runaway condition and to give prior warning of hazardous states and also a model is developed for an Inlet coolant failure in the reactor is simulated where the nitration of 4-chlorobenzo tri-fluoride can be tested. The advancement of this design in predicting the runaway condition enables the safe operating condition of the BR.

### 3. Experimental set-up

BR is used in the pesticides industry, for the production of CNBTF where large masses get exchanged/converted with release of huge amount of heat. The reactor is equipped with a cooling jacket. In order to carry out the reaction in a laboratory set-up, an ARC is chosen at thermochemical lab, CSIR-CLRI, Chennai. CNBTF is used as reactant (A) which is taken in sample hold and heating started. Temperature and time are recorded. A self-heating rate of  $0.02^\circ\text{C}/\text{min}$  is maintained in the ARC (Fig. 2). The reaction becomes as follows:

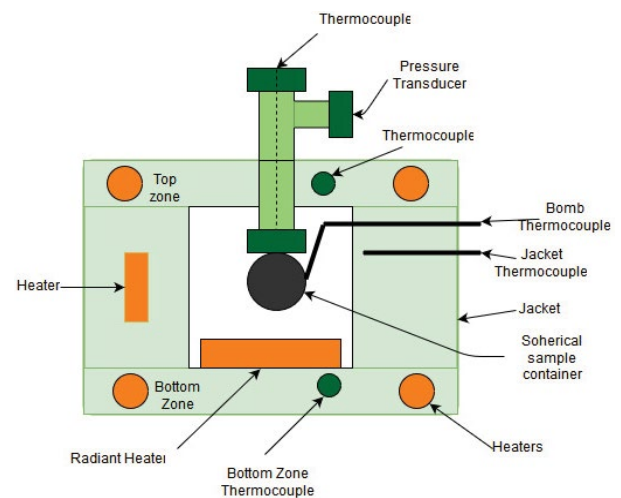
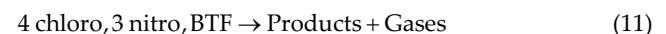


Fig. 2. Schematic representation of the experimental (ARC) set-up.

There are two phases involved, where, reactant A decomposes through interface and intra phase diffusion takes place. Next, interphase diffusion of component A takes place towards the gaseous formation.

3.1. Arc studies

In the present situation, the operating region of heterogeneous system involves hazardous slow reactions. The decomposition reaction calorimeter data were plotted and the micro kinetic (as explained in Eq. (12)) was found to follow the following equation.

$$r_B = -\frac{dC_A}{dt} = 2.718 \times 10^7 \times e^{-108279/8.314T} C_A^2 \text{ kmol/m}^3\text{s} \quad (12)$$

where  $C_A$  is concentration of BTF.

Temperature recorded in the ARC can be seen in Fig. 3a. A reference temperature and pressure profile showing the strategies (guidance) of operation of the reaction calorimeter is also shown in Fig. 3b.

It can be observed from this Fig. 3b that initial heating in ARC started at 15°C, followed by a waiting for 5 min at 40°C, then step heating was done till it reaches 50°C. Thus three cycles of waiting–heating were done till adiabatic condition reached (at 114°C) and then decomposition started to take place at about 255°C. Adiabatic temperature rise was observed at 324°C and finally continued up to 465.8°C. After the end of reaction, the results observed are as follows (Table 1).

4. Results and discussion

The mathematical model equations from (1) to (7) are simulated using ODE solver in MATLAB with initial conditions. Properties of material are obtained from Copelli et al. [20]. These data are substituted in Eq. (1) to find the rate

Table 1  
Operating conditions in ARC due to consumption of reacting mass

Item	Reading
Initial effect temperature $T_0$ (°C)	141
Final instrumental temperature $T_f$ (°C)	255.45
Instrumental adiabatic temperature rise (°C)	114.1
Instrumental inertia factor $M_c$	2.846
Correct adiabatic temperature rise (°C)	324.8
Correct final temperature (°C)	465.8

equation of decomposition reaction. Fig. 3 shows profile of reactor temperature with time during progress of decomposition reaction.

These temperature profiles need to be validated against experimental data. Experimental data under operating conditions (Table 1) are obtained and plotted. Simulation of the model equations for the decomposition reaction is also carried out and temperature profile is compared in Fig. 4a. The pressure profile is also simulated using Eq. (9) and is shown in Fig. 4b. Measured pressure data are also plotted in this Fig. 4b. It can be observed that simulated and measured values are almost very close in case of temperature as well as in case of pressure. The rate of change of pressure with rate of change of temperature during the course of decomposition reaction is shown in Fig. 4c. Pressure rate with temperature rate shows that the function of pressure rate will not gradually vary with temperature rate, it will scatter over temperature rate. Changes in the rate of rise in temperature with temperature of the reactor can be visualized in Fig. 4d. It can be seen that till 335°C, the rate of change in temperature increases, after which the rate declines due to complete decomposition. The operating thermodynamic properties of reaction mass decomposition and all initial and final values are given in Table 2.

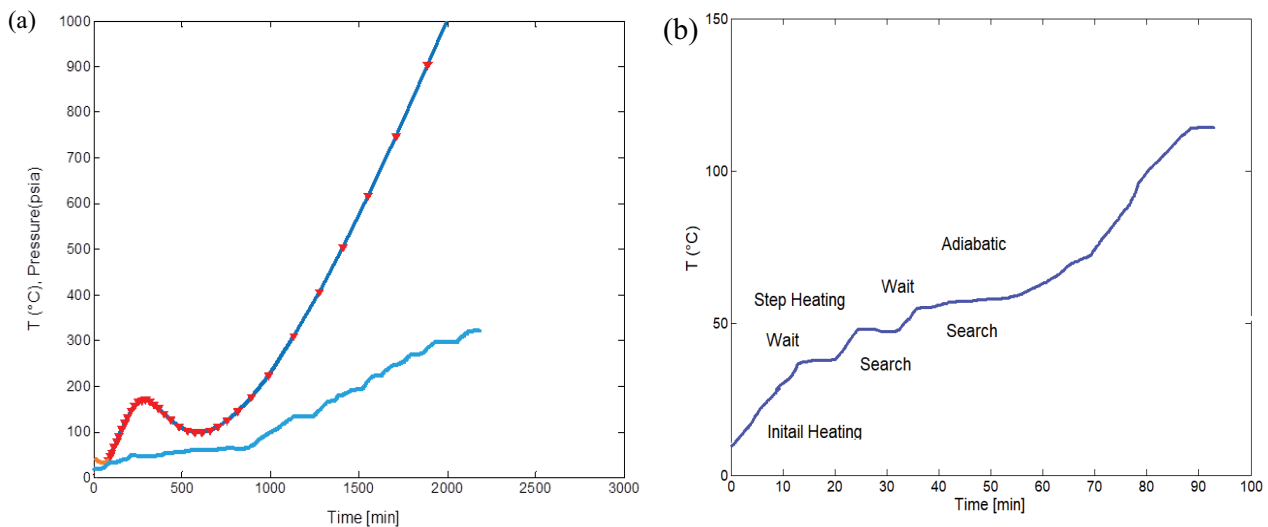


Fig. 3. (a) Temperature (with triangular symbols on line) and pressure (solid line) profiles of decomposed mass as recorded in ARC and (b) strategy (guidance) of operation of decomposition in ARC.

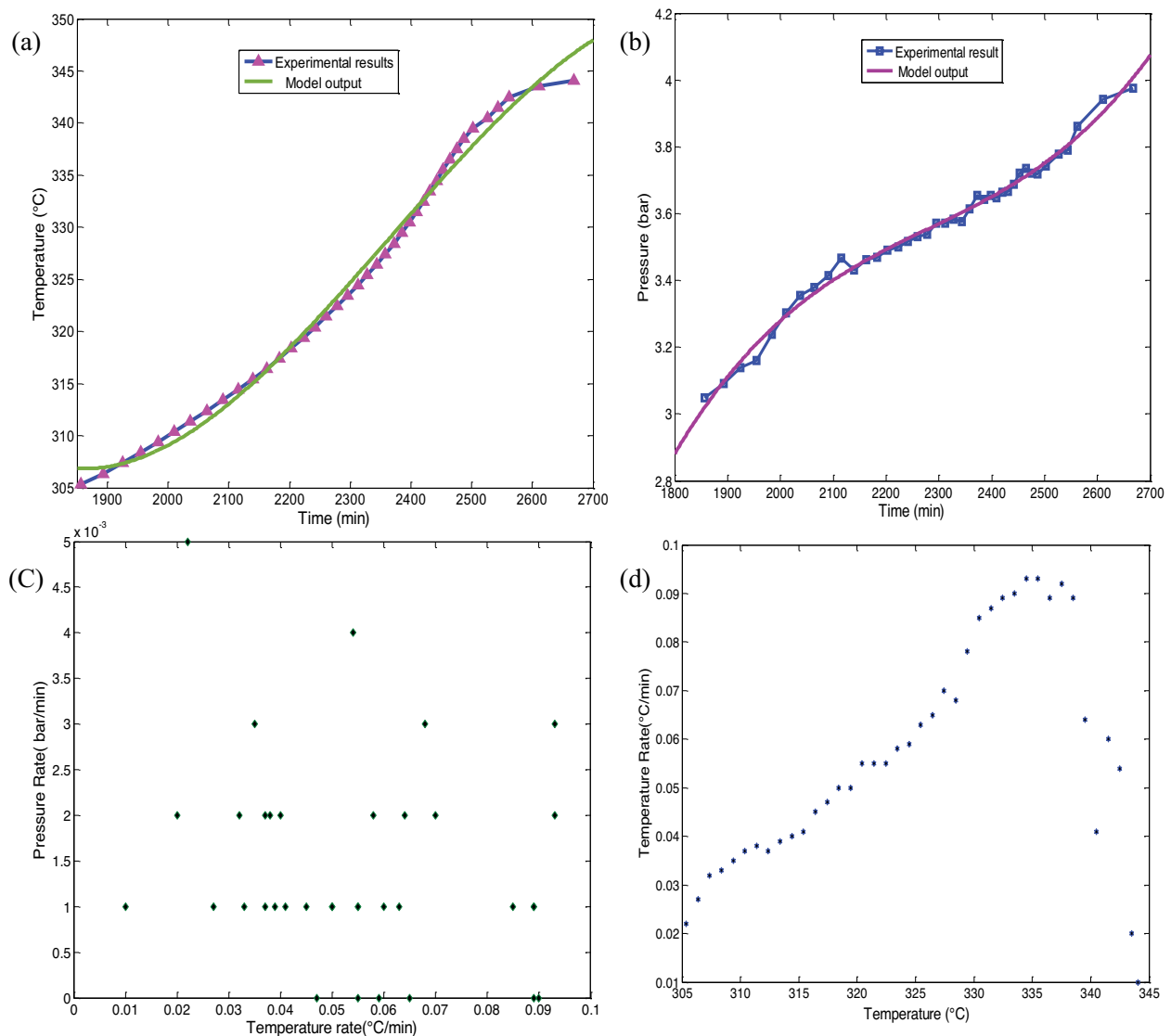


Fig. 4. Profiles of (a) temperature and (b) pressure rate vs. temperature rate and (c) temperature rate vs. temperature during decomposition of CNBTF.

The proposed method of estimation helps in accurate modelling and giving MSE which are shown in Table 3 for temperature and pressure. By estimating open loop pressure and temperature profiles, for a certain operating condition, it is possible to estimate the reactor's runaway conditions, which is used to design reactor emergency situation to avoid very dangerous agro-herbicide (CNBTF) blast conditions.

A sharp temperature profile is obtained, but it reaches maximum value which is lesser than the critical value. It is

noticed that the temperature increases during the decomposition of reactants to products but as soon as the decomposition is completed the temperature decreases gradually due to the proper working of cooling system. Correspondingly the pressure increases along with temperature and also it runs out when temperature decreases due to completion of decomposition of products. Thus, the information and results from the experiment suggest the strategy of designing the reactor (in case of failure, to avoid accident).

It is well-known that the product CNTBF is formed by nitration of 4-Cl-benzotrifluoride (BTF) in semi-batch reactors where BTF is dosed slowly as it is highly exothermic. In case there is a failure in cooling system or valve, there may be self-heating leading to decomposition of product and runaway reactions. From this fact, it is necessary to assume that, if there is no intrusion such as stopping the dosing at the moment of failure of cooling facility, an accident is very probable and critical in  $1/3 t_d$  period, where  $t_d$  is the dosing period

Table 2  
Model validation with mean square error

Sl. No	Profiles	MSE
1	Pressure	0.5338
2	Temperature	0.3771

Table 3  
ARC test: thermodynamic properties of reaction mass decomposition

Operating parameters	Value
Sample mass (g)	0.9988
Sample heat capacity (kJ/kg K):	0
Test cell type	Titanium
Test cell mass (g)	6.9182
Start temperature (°C)	50
End temperature (°C)	450
Temperature step (°C)	5
Temperature rate sensitivity (°C/min)	0.02
Wait time (min)	15
Calculation temperature step (°C)	0.2
Cool temperature (°C)	35
Door release temperature (°C)	50
Maximum safety pressure (bar)	200
Maximum temperature drop (°C)	25
Maximum pressure drop (bar)	20
Maximum exothermic rate (°C/min)	1,000
Maximum pressure rate (bar/min)	100,000.00
Driver heater power (%)	10
Data logging temperature step (°C)	1
Data logging time step (min)	0.5
Exothermic logging temperature step (°C)	1

of the reactant during nitration. The reactor may explode if the dosing is not stopped.

## 5. Conclusion

Batch and semi-batch reactors need precaution in design as they are vulnerable to accidents caused by runaway reactions. Generally, the thermal runaway will not occur in the reactor during normal operating condition because the product obtained will not decompose during the reaction. A thorough study on the decomposition of 4-Cl-3-nitrobenzotrifluoride has been carried out in an ARC thinking an adverse situation of coolant failure. Decomposition of CNTBF creates hazards in environment. The material and energy balances with decomposition kinetics for the reactor are formulated. The mathematical model for the batch reactor is simulated under normal conditions. Experimental studies have been carried out to find the decomposition kinetics and validation of temperature and pressure build-ups in the reactor. This study will be helpful in designing the reactor and taking precaution/planning through environmental disaster management.

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