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# Practical approach to prediction and prevention of runaway reactions

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## Abstract

A chemical reaction that becomes uncontrollable and escapes may cause a major event involving people, property and the surrounding area. Temperature runaway can be observed as a result of accidents such as overcharging, cooling water failure, pipe obstruction, and excessive initial heating. They can devise various techniques to avoid temperature runaway as a result of events, as well as advise on operational and technical improvements to the process to make it more robust to component failures and accidents. Exothermic methods used in the chemical industry have the potential to cause runaway reactions, resulting in fatalities and damage to infrastructure. Traditional approaches to prevention and prediction of runaway reactions are costly and unsuited to Ministry of Micro, Small & Medium Enterprises (MSME) units. Consequently, we often see incidents in MSME units caused by runway reactions. To reduce such mishaps, a no-cost theoretical prediction system and convenient preventative strategies are recommended.

**Keywords:** MSME; Incident; Exothermic reaction; Temperature Runaway; Precaution

## 1. Introduction

Reactive compounds can release massive amounts of potentially harmful energy under certain conditions, resulting in massive pressure rises. Such risky combinations can result in reactions that vary from the fundamental process reactions, primarily in their pace of progression. Annually, reactive chemicals are implicated in numerous industrial mishaps that endanger people, property, and the environment. The vast majority of chemical reactions in the industry are exothermic. Chemical process industries have substantially helped society throughout the years. Nevertheless, chemical processes can result in accidents such as fires, explosions, and poisonous substance releases. One of the most serious hazards in chemical processes such as polymerization, nitration, sulfonation, epoxidation, and so on This is owing to the exothermic nature of these reactions, which creates considerable heat in the processes. Because of the increased pressure, such a runaway reaction will result in the boiling over of poisonous compounds and their discharge into the atmosphere, as well as the bursting and splintering of reaction vessel fragments.

The MSME segment is estimated to account for 25- 30% of the sector and is critical to domestic chemical manufacturing and job creation. But frequently everyone has witnessed similar catastrophes in MSME chemical process firms, resulting in enormous property losses and injuries or the loss of human life. These units cannot forecast and, as a result, give preventive measures to avert such harmful interactions. It is therefore critical to foresee and avoid such catastrophes caused by runaway reactions using methods available to MSME units. This necessitates the use of simpler heat generation and heat removal prediction algorithms. Modern advanced predictive experimental calorimetric techniques for the determination of heat generation are very costly and also time-consuming, generally suitable for newly developed molecules. Reaction processes carried out in MSME units are usually known and prediction of heat

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generation can also be made by evaluating the thermal kinetics of the reaction theoretically. The heat removal capacity of the cooling system can be calculated with detailed engineering design data calculations or with simple experiments. It is important to remember that perhaps the linkage of mass and energy balance necessitates the solution of complicated differential equations. This resolution is time intensive and may lengthen the time to act in the event of a runaway. Hence, in the case of rapid response rates, it is critical to reducing this energy balance equation to an analytical formula. In the present paper, the application of reaction heats to process safety analysis and simple and reliable methods of computation of heat generation and heat removal by a combination of theoretical estimation and simple experiments are presented that can be easily implemented by MSME units.

## 2. Runaway Reaction

The heat created by an exothermic reaction raises the temperature of the reaction mass in proportion to the amount of heat generated. This temperature rise may trigger the thermal exothermic breakdown of reaction constituents, raising the temperature even higher. Runaway occurs when the total temperature of the reaction mass surpasses a particular limit. The following temperature characteristic values are related to the runaway reaction:

### 2.1. MTT: Maximum Temperature for Technical Reason

This is the temperature of the boiling point of reaction mass constituent in an open system or the temperature of maximum permissible pressure in a closed system. If the reaction mass exceeds this temperature, MTT, runaway will occur either in the form of the release of boiling hazardous chemicals in the atmosphere in an open system or the case of a closed system, leading to rupture of the reaction vessel and splintering of fragments of reaction vessel along with the release of hazardous chemicals in the atmosphere.

### 2.2. $\Delta T_{ad}$: Adiabatic Temperature Rise

The Adiabatic Temperature Rise is a property calculated for any given reaction to indicate the potential severity of a cooling failure or other processes upset. It is determined by the entire amount of energy released (reaction enthalpy), the total mass of the reaction mixture, and the specific heat capacity of the system. This is particularly crucial to determining if it can bring the reaction mixture to a temperature where a secondary reaction or decomposition reaction can eventuate. The adiabatic temperature rise is easily calculated using a Reaction Calorimeter to provide simple 'worst-case' evidence of the temperature rise. This is the increase in temperature of reaction mass only due to the heat of reaction under adiabatic conditions, meaning no heat is given or taken from the reaction mass. This $\Delta Tad$ can be calculated by the following Equation:

$$\Delta Tad = Qr / Cp ..................... (1)$$

Qr is a heat of reaction generally expressed in the unit of Kilo Joules (KJ) or Kilo Calories (KC) per mole of reactant and Cp is the specific heat capacity of reaction mass generally in the unit of Joules/ gm °C or Calories / gm °C.

High $\Delta Tad$ generally means high energies that result in fast runaway or thermal explosion. Assessment of the severity of a runaway reaction based on $\Delta Tad$ is presented in Table 1.

**Table 1** Classification of the Severity of Decomposition Reactions According to the Corresponding Adiabatic Temperature Rise (Assuming a Cp of 2 J/(g K))

| $\Delta H(J/g)$ | $\Delta$ Tad (0C) | Severity |
|---|---|---|
| Less than -500 | >250 | High |
| -500<$\Delta H$ <-50 | 25<$\Delta$ Tad<250 | Medium |
| More than -50 | <25 | Low |

### 2.3. MTSR: Maximum Temperature of Synthetic Reaction

One of the pillars of process safety in a semi-batch reactor is the Maximum Temperature of the Synthesis Reaction (MTSR). It describes the temperature evolution following a cooling failure as a result of the amount of non-reacted material existing at the time of the cooling failure. MTSR is calculated by initiating with the Process Temperature and determining the maximum temperature that the reaction mixture will reach assuming that all of the reaction energy

remains in the reactor (i.e. The system is or becomes adiabatic). The Reaction Calorimeter is an essential tool for the measurement of the heat of the reaction, the reagent accumulation, and MTSR. This is the temperature a synthetic reaction will reach in case of cooling failure and is expressed as

$$\text{MTSR} = T_p + (X_{ac} * \Delta T_{ad}) , \dots\dots\dots\dots\dots\dots \text{(2)}$$

Where;
$T_p$ is reaction process temperature,
$X_{ac}$ is the unconverted fraction of reactant at the time of cooling failure
$\Delta T_{ad}$ is the adiabatic temperature rise of the reaction.

In the worst scenario, MTSR at maximum level will be when cooling failure is at start time and $X_{ac}$ equal to one

$$\text{MTSR} = T_p + \Delta T_{ad} \dots\dots\dots\dots\dots \text{(3)}$$

$T_b$: Boiling Point of the Reaction Mass

$T_d$: Temperature at which rate of decomposition of reaction mass constituent becomes hazardous.

## 3. Application of Reaction Heats to Process Safety Analysis

Stoessel has described the risk associated with chemical processes using five scenarios as shown in Fig. 1. Risk is analyzed concerning the relationship between the desired process temperature, $T_p$, adiabatic temperature rise $\Delta T_{ad}$ for the reaction, boiling point of reaction mass, $T_b$, the temperature of hazardous decomposition, $T_d$, and maximum temperature of the synthetic reaction, MTSR. The potential hazard increases from left to right [2].

In scenario A, even if all the heat is released instantaneously, the temperature will reach MTSR, which is below the boiling point of reaction mass, $T_b$, and hazardous decomposition temperature, $T_d$. So, this is a thermally safe process. In scenario B also MTSR is below $T_b$ and $T_d$, though $T_b$ is higher than $T_d$. This is also a thermally safe process unless the input of extra heat in the reaction mass leads to decomposition.
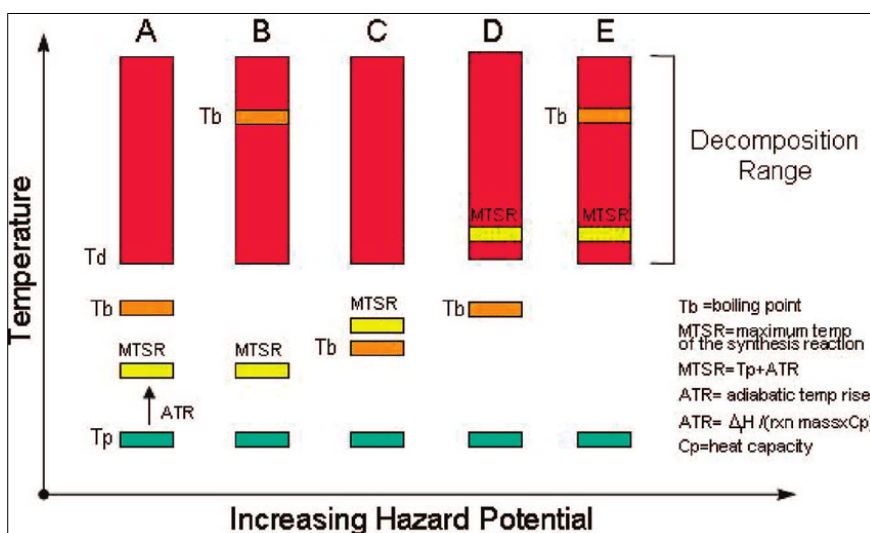


**Figure 1** Five scenarios that depict the relative risk associated with chemical processing [2]

In scenario C, MTSR exceeds boiling temperature $T_b$, and there is the possibility of overpressure in the reactor due to boiling vapor pressure. However, there is no risk of hazardous decomposition since $T_d$ is above MTSR. Controlling reaction rate by measures such as controlled dosing of a reactant may suffice to bring MTSR below $T_b$.

In the case of scenario D, MTSR exceeds both $T_b$ and $T_d$. Hazardous decompositions leading to higher temperature and pressure may take place. Some evaporative cooling may take place since $T_b$ is lower than MTSR. However, reaction controls and protection are necessary. In scenario E, MTSR exceeds $T_d$ but not $T_b$. In the event of loss of control,

significant decomposition will take place leading to the hybrid pressure effect of gaseous decomposition and high-temperature vapor pressure.

### 3.1. Prediction and Prevention of Runaway Reaction

As seen above, the risk assessment prediction of runaways can be made if Tp, Tb, Td, and MTSR, are known. Tp is desired reaction temperature and Tb is known from the reaction experiment. Td can be found from data banks for known reaction ingredients or determined by simple Differential Scanning Calorimetry (DSC) experiment of the reaction mixture. MTSR is determined from Equation (3) by calculation of ΔTad from Equation (1). To calculate ΔTad, the heat of reaction Qr and specific heat capacity Cp should be known. Cp values are readily available from data banks or generally assumed 2.0 joules/ gm K for organic compounds. Thus, if the heat of reaction, Qr, is assessed, ΔTad, MTSR, and thereby severity of runaway reaction can be predicted from the Stoessel diagram.

Once the severity of the exothermic reaction is known, one needs to mitigate the severity by removing heat from the process to keep the temperature of the reaction within safe limits of preventing boiling over, decomposition, and pressurization. To prevent runaway reactions, therefore, the cooling capacity of the process needs to be assessed. And, if this cooling capacity is not adequate, measures to boost the cooling capacity need to be provided for the existing system.

### 3.2. Prediction of Runaway Reaction

As seen above, the severity of the runaway reaction can be assessed if reaction heat, Qr, is known.

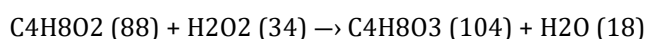Two methods are used to determine this reaction heat, Qr.

- Calorimetric experimental determination.
- Theoretical estimation from thermal data of reaction

Modern advanced predictive calorimetric experimental techniques for the estimation of heat generation are very costly and time-consuming, generally suitable for newly developed reactions. Reactions carried out in MSME units are usually known and the heat of the reaction can be estimated theoretically from the thermal kinetics of the reaction. Both techniques have some limitations and can be considered with a safety margin. Theoretical estimation techniques are more suitable for MSME units and considered here.

### 3.3. Theoretical Estimation of Heat of Reaction, $Q_r$, and Assessment of Severity

Theoretical estimation of heat is long known and is part of textbooks now. It is calculated as the Sum of the Heats of Formations (ΔHf ) of Products of reaction minus that of reactants. Heats of formations, ΔHf, of compounds are readily available from data banks.

For better understanding, we will now work out the theoretical estimation of Qr and assessment of reaction runaway severity with a case example of the heat of epoxidation of Butene Diol with hydrogen peroxide.

Butene Diol + Hydrogen Peroxide —› Epoxy Butane Diol + Water

$C_4H_8O_2$ (88) + $H_2O_2$ (34) —› $C_4H_8O_3$ (104) + $H_2O$ (18)

ΔHf= -342.6 + ΔHf= -187.8 —› ΔHf= -436.3 + ΔHf= -285.4 KJ / M

Therefore, Heat of Reaction, Qr, will be = -436.3 -285.4 + 342.6 +187.8 = -191.3 KJ / M.

A negative sign means that heat will be generated in the reaction.

Thus, 191.3 KJ (45.72 KC) of heat will be produced by epoxidation of one mole, that is 88 gms, of Butene Diol, for a reaction mass of 122 gms.

### 3.4. Runaway Risk Analysis for above example

Calculation of ΔTad once the heat of the reaction is known, ΔTad can be calculated from Equation (1). Assuming Cp for diol of 2 joules / gm K and that of water is 4.182 joules / gm K, specific heat capacity of reaction mass will be (104*2) + (18*4.182) / (104 +18) = 2.322 J / gm K. Therefore,

$$\Delta Tad = (191.3 * 1000) / (122 * 2.322) = 675.3 \text{ K}$$

That is with no heat provided to or removed from the reaction mass, the temperature of reaction mass will increase by 675.30C, assuming a reaction temperature of 250C, MTSR will be

$$MTSR = 675 + 25 = 7000C$$

From the criticality class Table 1 and Stoessel diagram, it is a catastrophic reaction falling under Scenario D of the Stossel diagram. All preventive measures such as efficient cooling controlled dosing etc. need to be provided.

## 4. Prevention of Runaway Reaction

Scientists can model runaway reaction scenarios and determine the best reaction procedure by analyzing reaction dynamics. Measuring, calculating, and comprehending the parameters are critical for assessing and avoiding risk in a chemical process. This enables scientists to forecast temperature and dosing profiles, concentrations, and maximum operating temperatures. Once the severity of the runaway reaction is known, the first step to prevent it is to provide for efficient cooling of reaction mass so that all heat produced in the reaction mass is removed and the temperature of the reaction is maintained at desired process temperature, Tp. This may be achieved by circulating cooling media along the reaction container surface area to remove heat from the reaction by heat transfer from the reaction mass.

The quantification of this heat transfer is provided in the following equation (4).

$$Q = U*A*\Delta Tlm = m*Cp*(T2 – T1) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Where;
Q is heat transferred under a steady state from the reaction vessel, KJ/sec
U is the overall heat transfer coefficient, $KJ/( sec*m^2* °C)$
A is an area available for heat transfer, m2
Δ Tlm is log mean temperature difference = °C
T is the temperature of reaction mass in the vessel, °C
T1 is the inlet temperature of the cooling fluid, °C
T1 is the outlet temperature of cooling fluid, °C
M is the mass flow rate of cooling fluid, kg/sec
Cp is a specific heat capacity fluid, KJ/Kg °C

## 5. Conclusion

Researchers have regularly observed comparable disasters in MSME chemical process enterprises, resulting in massive property damages, injuries, and sometimes the loss of life. It is therefore vital to anticipate and avoid such runaway responses utilizing technologies available to MSME units. The severity of runaway reactions can be assessed if reaction heat, Qr, is known. Two methods are used to determine this reaction heat, Qr. Calorimetric experimental determination and Theoretical estimation from thermal data of reaction. The reaction between Butene Diol and Hydrogen Peroxide can be used as a model system for thermal runaway reactions. The required cooling area for the exothermic reaction can be calculated from Equation 4 and if it is adequate, no runaway will occur. However, if the available cooling area is less, a runaway reaction is predicted and other measures such as cooling media at lower temperature or modifications to the process with reaction mass dilution with high Cp solvent, control dosing of reactant, etc. may be considered to prevent the runaway reaction.

## Compliance with ethical standards

*Disclosure of conflict of interest*

The authors have no conflicts of interest to declare

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