Contents lists available at ScienceDirect

Process Safety and Environmental Protection

journal homepage: www.elsevier.com/locate/psep

Causes and consequences of thermal runaway incidents—Will they ever be avoided?

Rim Saada, Dipesh Patel[1], Basudeb Saha*

Centre for Green Process Engineering, School of Engineering, London South Bank University, 103 Borough Road, London SE1 0AA, UK

ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form 9 January 2015
Accepted 4 February 2015
Available online 12 February 2015

Keywords:
Inherent safety
Hazard identification
Health and environment
Process design
Risk assessment
Thermal runaway reactions

ABSTRACT

A study of runaway incidents involving thermal chemical reactions in the UK over the past 25 years (1988–2013) has been carried out. The objective of this study is to determine possible causes of thermal runaway incidents. A statistical analysis of the underlying problems that led to thermal runaway incidents has been provided. A comparison of the current study on thermal runaway incidents with those identified prior to 1988 has been carried out. This study clearly shows that lessons have not been learnt from thermal runaway incidents caused by operator errors, management failures and lack of organised operating procedures. These factors have been the possible causes of about 77% of all the thermal runaway incidents analysed in this study. The number of fatalities and injuries as a result of thermal runaway incidents has increased by ~325% and ~279%, respectively, in the last 25 years even though the number of incidents was significantly less. On the basis of this analysis, several recommendations have been proposed that could help to minimise the risks associated with any thermal runaway incidents in the future.

1. Introduction

Thermal runaway reactions are characterised by progressive increase in the rate of heat generation, temperature and pressure (Barton and Nolan, 1991). Heat generation increases exponentially with an increase in the system temperature. It also increases due to other factors including the lack of process control and failure to cool the reaction system. An increase in the system pressure could occur due to vapourisation of some of the components in the reaction mixture and decomposition of some of the gaseous products at the elevated temperatures.

In batch operations, the rate of reaction and production are controlled by maintaining the amounts of the reactants, solvents, catalyst and non-reacting chemicals charged to a reactor. Generic batch reactors are usually used for different types of chemical reactions in an industry rather than being specifically designed for a particular reaction due to economic factors. This increases the possibility of thermal runaway as it could be ignored that the heat of some of the reactions may exceed the existing cooling capacity of the reactor. Semi-batch operations tend to be used for specific unit processes that are inherently hazardous such as halogenation, nitration, polymerisation and sulphonation reactions. Similarly, thermal runaway could be a particular problem in unsteady-state batch reactors as reported by Barton and Rogers (1997). This is mainly due to a difficulty in specifying the design, operation and control of a stirred reactor, heating/cooling coils, reflux facilities and emergency relief venting, which would require a systematic approach.

Chemical reactions conducted in batch reactors may get out of control due to other reasons including change in an operating conditions and usage of inappropriate materials (Gillard, 1998). Since batch operations involving exothermic reactions are common in industries, precautionary measures

* Corresponding author. Tel.: +44 0 20 7815 7190; fax: +44 0 20 7815 7699.
E-mail address: b.saha@lsbu.ac.uk (B. Saha).
[1] Present address: School of Engineering, University of Hull, Cottingham Road, Hull HU6 7RX, UK.
http://dx.doi.org/10.1016/j.psep.2015.02.005

Nomenclature

HSE	Health and Safety Executive
ΔH	enthalpy change (J)
LPB	Loss Prevention Bulletin
SDS	safety data sheet
SOPs	standard operating procedures

are necessary to minimise the risks associated with thermal runaway. Some reactions may constitute reaction hazards due to the complexity of the reaction, e.g., nitration reactions are considered to be the most destructive reactions in the present chemical industries as it involves exotherms and heat-sensitive products (Mannan, 2012).

Good control and hazards associated with the chemical reactions are essential aspects of chemical manufacturing. Therefore, the aim of this work was to study runaway incidents for the last 25 years, i.e. 1988–2013 and to compare it with the findings reported by Barton and Nolan (1991) for the thermal runaway reaction incidents occurred between 1962 and 1987. It is envisaged that lessons could be learned from the recently reported incidents and those identified before 1988. The findings in this article include a detailed analysis of the type of industries, unit processes, causes and consequences. It is expected that the information provided in this paper would incorporate the changes within numerous industries to minimise the risks associated with thermal runaway reactions.

2. Incident statistics

2.1. *Case histories pre-1988 (1962–1987)*

Barton and Nolan (1991) studied case histories for industrial incidents in batch reactors involving thermal runaway reactions from 1962 to 1987. They reported that the main causes of thermal runaway incidents were process chemistry and plant design and operation. The lack of understanding of reaction chemistry, temperature control and mischarging of reactants were the main causes for 20%, 19% and 21% of the incidents, respectively.

2.2. *Case histories post-1987 (1988–2013)*

Possible unit processes have been identified for 30 incidents involved in thermal runaway reactions. However, it was not possible to obtain detailed analysis of every incident due to lack of information in the public domain. Nine unit processes that were involved in the incidents are shown in Table 1. It is evident from Table 1 that one third of the incidents have been contributed by polymerisation process followed by decomposition process (13.3%).

2.3. *Causes of the incidents studied*

The possible causes that lead to an overheating and eventual thermal runaway for 30 incidents are classified under "Technical and Physical Causes" and "Human and Organisational Causes". These causes are explained in detail in Sections 2.3.1 and 2.3.2, respectively.

2.3.1. *Technical and physical causes*

Most of the incidents reported in this study have multiple causes, i.e. some of the incidents initiated due to a technical or physical cause were extended to a thermal runaway due to a human cause (LPB, 1995). Fig. 1 represents the number of incidents occurred in the last 25 years with technical and physical causes. It is evident from Fig. 1 that mischarging the reactor has contributed to five incidents. This includes addition of incorrect amount of chemicals and charging chemicals or catalysts in an inappropriate order. In one incident (LPB, 1994b) the root cause of the incident was an overcharge of vinyl acetate during the monomer emulsion make-up for the batch. This was accompanied by inadequate management of a change in the operating procedures.

In this study, four incidents have been caused due to the failure of agitator device (Fishwick, 2004, 2008; LPB, 1993b, 1994a). In one incident the agitator seal ring blew due to an increase in pressure in the reactor (LPB, 1993b). In another incident, the agitator failed causing a cooling at an early stage in the nitration reaction (LPB, 1994a), whereas, in one incident the propeller failed to start and therefore caused a build-up of the temperature in the upper part of the reactor content leading to a thermal runaway incident (Fishwick, 2004). During an incident, the agitator started to slip when a fault occurred in the connection or linkage between the agitator and its drive mechanism and hence the agitator lagged behind and failed to stir properly (Fishwick, 2008).

Trace quantities of impurities could greatly affect a chemical reaction either by reducing the rate of reaction (Ahmad and Baloch, 2007) or increasing the rate of the reaction (Gustin, 2002). During an incident traces of water were retained after washing the reactor that caused an unexpected thermal runaway reaction (Kletz, 1995). The contamination of pure chemicals by trace impurities could lower their thermal stability to a larger extent and cause an unexpected decomposition under normal process conditions (Gustin, 2002). In this study, three incidents were caused as a result of contamination that contributed to thermal runaway and has been reported under 'Quality Control' sub-heading of 'Technical and Physical Causes' (Fig. 1). One incident could have been prevented if the solvent was not contaminated with acetic acid (Kletz, 1991; Van Reijendam et al., 1992).

Reactor design and temperature control are important in a chemical plant to ensure safety of both the operators and the plant. Temperature inside the reactor may deviate due to changes in the heat input/output, heat transfer, pressure and due to thermal lags and hot spots. In this study, four incidents occurred due to a poor plant design (Lindley, 2001; LPB, 1993b, 1994a, 1996) and five other incidents were caused as a result of failure in the process control (FACTS, 1988, 1990, 1991, 1994; LPB, 1993b). Hence, it is vital that mechanical design of all reactors is completed to highest standard. In one incident (LPB, 1996), the reactor failed due to a stress rupture because the reactor was allowed to operate at excessive temperatures beyond its safe operating envelope. This could have been prevented if operating limits were checked beforehand by the operator or the reactor could have been designed to withstand such excessive conditions.

Malfunction, technical failure, venting, leakage, loss of process control and power cut together have possibly contributed to sixteen incidents. All these causes could have been avoided in the process industry if the operator knows beforehand how to deal with a particular situation.