Journal of Loss Prevention in the Process Industries 43 (2016) 559–566

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

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

Semi-batch reactors: Thermal runaway risk

Lei Ni [a, b, *], Ahmed Mebarki [b], Juncheng Jiang [a], Mingguang Zhang [a], Zhan Dou [a, b]

[a] Jiangsu Key Laboratory of Hazardous Chemicals Safety and Control, College of Safety Science and Engineering, Nanjing Tech University, Mail Box 13, No. 200, North Zhongshan Road, 210009, Nanjing, China
[b] University Paris-Est, Laboratory Modelisation et Simulation Multi Echelle, MSME (UMR 8208 CNRS), 5 bd Descartes – Bat. Lavoisier, 77454, Marne-la-Vallee Cedex 2, France

ARTICLE INFO

Article history:
Received 3 May 2016
Received in revised form
24 June 2016
Accepted 26 July 2016
Available online 28 July 2016

Keywords:
Thermal runaway
Accident risk
Semi-batch reactors
Boundary diagram
Heterogeneous reaction

ABSTRACT

The paper deals with the thermal safety and the runaway risk evaluation for semi-batch reactors (SBR). The main contributions consist in:

- Construction of a new boundary diagram which describes the reaction temperature vs. target temperature and maximum allowable temperature in order to define the critical conditions for the thermal runaway;
- Identification of the most important governing parameters;
- Evaluation of the risk of accident by a probabilistic description of the prior cooling problem, the appropriate combination of the critical conditions and the assessment of occurrence probability of the thermal runaway accident.

A heterogeneous liquid-liquid reacting system is considered as a case study. A sensitivity analysis is then performed in order to investigate the influence of cooling temperature on the maximum reaction temperature. Monte Carlo simulations are also used in order to calculate the probability of accidents.

1. Introduction

In the fields of pharmaceuticals or organic synthesis, many reactions exhibit excessive heat effects. The reaction cooling becomes a crucial problem (Westerterp et al., 2014). Compared with batch reactors, semi-batch reactor (SBR) not only can control the temperature by coolers, but also can control the feed rate and then control the heat evolutions (Copelli et al., 2014). However in SBR, rapid feed rates or cooling problems may also cause runaway, though safety devices are usually inserted within the semi-batch reactor. Some references (Banerjee, 2002) summarize the causes that may lead to reaction runaway in a generic fault tree. See Fig. 1.

However, it may happen that these safety devices fail due to their weak quality. Such failure could result in accidents causing explosion, blast waves, fragments projection, thermal flux, and products leakage for instance. These subsequent events and hazards may impact and damage the surrounding and may lead to cascading events and domino effect within the whole plant (Mébarki et al., 2009a; Mébarki Nguyen and Mercier, 2009b; Mingguang and Juncheng, 2008; Khan and Abbasi, 2000).

Furthermore, it is still a scientific challenge to reach risk based optimal layout of industrial plants able to take into account potential critical thermal runaway and subsequent domino effect (Nguyen et al., 2009; Mebarki et al., 2012a,b, 2014; Mingguang and Juncheng, 2008).

When dealing with SBR safety, the boundary diagrams method is able to identify the critical runaway condition (Steensma and Westerterp, 1988, 1990, 1991). The key parameters are the "Reactivity number" (Ry), the "Exothermicity number" (Ex), and the target or critical temperature (T_{ta}). This method has actually been adopted for different situations:

- The case of multiple reactions: nitric acid oxidation of 2-octanol to 2-octanone, (van Woezik and Westerterp, 2000, 2002);
- The development of the power-law rate of reaction expressions with (n,m) reaction orders, (Maestri and Rota, 2005a, 2005b).

As the target temperature T_{ta} reflects only the material accumulation in semi-batch reactors, it has also been shown that the reaction may also result in runaway (Stoessel, 2008), as soon as

* Corresponding author. NJTech, Mail Box 13, No. 200, North Zhongshan Road, Nanjing, China.
E-mail addresses: Lei_Ni@163.com (L. Ni), Ahmed.Mebarki@u-pem.fr (A. Mebarki), jcjiang@njtech.edu.cn (J. Jiang), Mingguang_zhang@njtech.edu.cn (M. Zhang).

http://dx.doi.org/10.1016/j.jlp.2016.07.024
0950-4230/

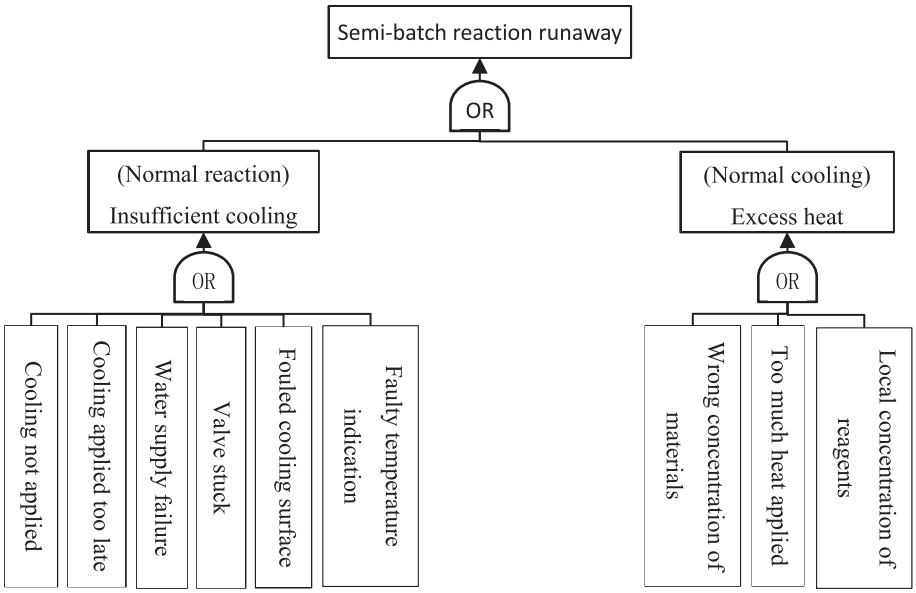

Fig. 1. Fault trees for reactor runaway.

the temperature T_{max} exceeds the maximum allowable temperature (T_{MAT}). Beside the boundary diagram, it is also required to use a temperature diagram in order to check whether the reaction temperature exceeds T_{MAT}, (Maestri and Rota, 2006). Such use of temperature diagram has also been reported for the case of Nitration of 4-Chlorobenzotrifluoride (Maestri et al., 2009a, 2009b).

Rather than using separately the temperature and boundary diagrams, as it is usually done to find the critical runaway condition, the present paper presents a new combined boundary diagrams which considers simultaneously T_{ta} and T_{MAT}. Semi-batch reactors can then be analyzed. A case study is adopted in order to identify the parameters governing the thermal runaway, as well as the indicators and the precursors of imminent accident. The risk of first accident sequence triggered by thermal runaway is also investigated by probabilistic simulation.

2. Framework for thermal safety and risk analysis for semi-batch reactor

The thermal safety and accidents risk in semi-batch reactors are investigated in the case of liquid-liquid reactions. The necessary steps are, see Fig. 2:

- Definition of the initial conditions for the reaction, taking place within the semi-batch reactor,
- Development of the kinetic model for liquid-liquid reactions in SBR,
- Development of the combined boundary diagram,
- Identification of the governing indicators and their critical values,
- Estimation of e the probability for accident occurrence by thermal runaway and prediction of the reactor failure risk.

3. Mathematical model of a SBR for liquid-liquid reactions

For illustration purposes, an exothermic liquid-liquid reaction is considered. The chemical models describing the liquid-liquid reactions, for SBR case, can be summarized as:

$$\upsilon_A A + \upsilon_B B \rightarrow \nu_C C + \nu_D D \quad (1)$$

where: υ_A,υ_B, ν_C *and* ν_D, are the stoichiometric numbers of the components A, B, C and D respectively.

Some important assumptions need to be adopted for the reaction (Steensma and Westerterp, 1988):

(1) The change of reactor volume is the only reason to add a component in the SBR.
(2) No phase inversion occurs during the reaction.
(3) Components A (the dosed co reactant) and C are in the dispersed phase, components B (the initial component when the reaction starts in the SBR) and D are in the continuous phase.
(4) The reaction rate is first order in the concentration of the reactants A and B.
(5) Chemical reaction takes place only in one phase.
(6) Component C is the target product.
(7) The product of heat transfer area and transfer coefficient UA is proportional to the liquid volume in the SBR.
(8) The initial temperature in the SBR is equal to the coolant temperature T_{cool}.
(9) It is a slow reaction.
(10) The initial reaction volume, V_{ro}, is:

$$V_{ro} = \frac{n_{B0}}{C_{B0}} \quad (2)$$

where: n_{Bo} is the number of kilo-moles of B in the reactor at initial time t = 0 s; c_{Bo} is the molar concentration of B in kmol/m^3 at t = 0 s.

The boundary condition between no ignition region and runaway region or between runaway region and "QFS" region (quick onset, fair conversion, and smooth temperature profile) is, see Fig. 3:

$$T_{max} = T_{ta} \quad (3)$$

where: T_{max} is the maximum reaction temperature; T_{ta} is the target temperature.

The dimensionless target temperature becomes, (Steensma and