chemical engineering research and design xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Safety enhancement by transposition of the nitration of toluene from semi-batch reactor to continuous intensified heat exchanger reactor

N. Di Miceli Raimondi[a,b,*], N. Olivier-Maget[a,b], N. Gabas[a,b], M. Cabassud[a,b], C. Gourdon[a,b]

[a] Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4, Allée Emile Monso, F-31030 Toulouse, France
[b] CNRS, Laboratoire de Génie Chimique, F-31030 Toulouse, France

ABSTRACT

The behavior of a continuous intensified heat exchanger (HEX) reactor in case of process failure is analyzed and compared to the behavior of a semi-continuous reactor. The nitration of toluene is considered as test reaction to identify the main failure scenarios that can lead to thermal runaway in both processes using the HAZOP method. No flow rate of process fluid and utility fluid in the continuous process. No stirring during feeding of the reactor followed by normal stirring for the semi-continuous reactor. These scenarios are simulated for both processes and the temperature profiles are observed. This study shows that the temperature is better controlled in the continuous process because of the intrinsic characteristics of the HEX reactor. In fact, this device has a low reactive volume relative to the mass of the reactor, allowing a good dissipation of the heat produced by the reaction, even in case of failure. This characteristic of the intensified reactor is confirmed by an experimental work.

Keywords: Process intensification; Heat-exchanger reactor; Nitration; Safety; Simulation; Failure scenarios

1. Introduction

Process intensification aims at offering drastic improvements in chemical manufacturing particularly in terms of cost, energy consumption, safety, quantity and quality of wastes. The purpose is to develop new media (ionic liquids, supercritical fluids, etc.), new methods of activation (microwaves, ultrasounds, etc.) and new technologies (microreactors, hybrid separators, etc.) to allow these improvements. One of the basic concepts of process intensification is the use of multifunctional apparatuses where more than one unit operation are performed in a unique equipment such as intensified heat exchangers (HEX) reactors (Anxionnaz et al., 2008). These apparatuses are very promising alternatives to batch or semi-batch reactors mainly used in fine chemicals manufacture. Their prospects are a drastic reduction of unit size and solvent consumption while safety is increased due to their remarkable heat transfer capabilities. However, Ebrahimi et al. (2012) pointed out the fact that process intensification by miniaturization improves safety in many cases but that this trend cannot be generalized. Therefore, a safety analysis is required prior to the implementation of an intensified process based on a new technology.

The present work aims to demonstrate the intrinsically safer behavior of a HEX reactor developed by the Laboratoire de Génie Chimique (LGC – Toulouse, France) and the Boostec company specialized in the manufacture of equipments made of silicon carbide (SiC). This material presents excellent chemical resistance, high mechanical strength and stiffness, high thermal resistance and good conductivity (180 $W\,m^{-1}\,K^{-1}$ at 20 °C). The performances of this device have already been demonstrated to handle exothermic reactions such as a direct fluorination (Elgue et al., 2012) and a pharmaceutical application (Despènes et al., 2012). However, its behavior in case

---

* *Corresponding author at*: Université de Toulouse, INPT, UPS, Laboratoire de Génie Chimique, 4, Allée Emile Monso, F-31030 Toulouse, France. Tel.: +33 5 62 25 89 20; fax: +33 5 62 25 88 91.
E-mail address: nathalie.raimondi@iut-tlse3.fr (N. Di Miceli Raimondi).

http://dx.doi.org/10.1016/j.cherd.2014.07.029
0263-8762/© 2014 Published by Elsevier B.V. on behalf of The Institution of Chemical Engineers.

Please cite this article in press as: Di Miceli Raimondi, N., et al., Safety enhancement by transposition of the nitration of toluene from semi-batch reactor to continuous intensified heat exchanger reactor. Chem. Eng. Res. Des. (2014), http://dx.doi.org/10.1016/j.cherd.2014.07.029

Nomenclature

a	interfacial area ($m^2\,m^{-3}$)
A	heat exchange area (m^2)
C	concentration ($mol\,L^{-1}$)
C_P	heat capacity ($J\,kg^{-1}\,K^{-1}$)
d	diameter (m)
D	diffusion coefficient ($m^2\,s^{-1}$)
E	enhancement factor
E_a	apparent activation energy of the decomposition reaction ($J\,mol^{-1}$)
F	molar flow rate ($mol\,h^{-1}$)
h	height (m)
h_{int}	heat transfer coefficient on process side ($W\,m^{-2}\,K^{-1}$)
Ha	Hatta number
ID	molar isomer distribution
K	intrinsic kinetic constant ($L\,mol^{-1}\,s^{-1}$)
L	length (m)
m	mass (kg)
M	molar weight ($kg\,mol^{-1}$)
MTSR	Maximum Temperature attainable by the synthesis reaction (K)
n	number of moles (mol)
N_i	parameter used in the modeling of the kinetic rate
NC	number of compounds
Q_e	heat flux exchanged (W)
Q_p	heat flux produced (W)
r	reaction rate ($mol\,L^{-1}\,s^{-1}$)
R	gas constant ($J\,mol^{-1}\,K^{-1}$)
S	molar selectivity
t	time (s)
t_r	residence time (s)
t_R	reactive medium thickness (m)
t_W	wall thickness (m)
T	temperature (K)
T_b	normal boiling temperature (°C)
T_m	normal melting temperature (°C)
TMR	time to maximal rate (h)
U	heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
V	volume (L)
w	mass fraction
w_R	reactive medium width (m)
W	acid strength

Greek letters

ΔH_r	reaction enthalpy ($J\,mol^{-1}$)
ΔT	temperature rise (°C)
λ	thermal conductivity ($W\,m^{-1}\,K^{-1}$)
ρ	density ($kg\,L^{-1}$)
ε	phase hold-up
χ	conversion rate

Subscripts

ad	in adiabatic conditions
aq	aqueous phase
bulk	bulk
film	film
i	compound i
Ntol	nitrotoluene
R	reactive medium or fluid
tol	toluene
W	reactor wall

Superscripts

0	at the reactor inlet or at initial time
a	in aqueous phase
b	in the bulk
f	in the film
i	at the interface
o	in organic phase

of failure has not been investigated yet. In this context, the nitration of toluene is considered as test reaction. This is a liquid–liquid reaction that presents high risk of thermal runaway due to its exothermicity and the low decomposition temperature of nitro compounds (Chen and Wu, 1996). Aromatic nitration is an intermediate reaction for the production of many compounds such as pharmaceuticals, dyes, pesticides, explosives. At the industrial scale, this reaction is mostly operated in batch or semi-batch reactors (Booth, 2000; Dugal, 2005). It has been used in several works to demonstrate the capabilities of technologies such as micro and millistructured HEX reactors (Burns and Ramshaw, 2002; Henke and Winterbauer, 2005; Halder et al., 2007; Rusli et al., 2013).

In the present work, a safety analysis is conducted to compare the risks associated to the implementation of the nitration of toluene in a semi-batch reactor and in an intensified HEX reactor. For that purpose, further to the reaction description and the presentation of the continuous process, risk assessment by HAZOP method is carried out for both processes in order to identify the failures that can cause the most serious damages. Then, critical scenarios are simulated to observe the temperature increase in both reactors in case of major failures. The inherently safer design of the SiC intensified HEX reactor is then confirmed by experiments in faulty mode.

2. Nitration of toluene

2.1. Reaction description

The nitration of toluene is performed with nitric acid in presence of sulfuric acid and water. This acid mixture is the most common nitrating system currently adopted in chemical industry (Miller et al., 1964; Harris, 1976). The main reaction is the mononitration characterized by a heat of reaction ΔH_r of $-125\,kJ\,mol^{-1}$ (Chen and Wu, 1996):

$$C_7H_8 + HNO_3 \rightarrow C_7H_7NO_2 + H_2O \tag{1}$$

Nitration kinetics and selectivity strongly depend on the sulfuric acid strength W defined as follows (Zaldivar et al., 1995):

$$W = \frac{w^a_{H_2SO_4}}{w^a_{H_2SO_4} + w^a_{H_2O}} \tag{2}$$

where $w^a_{H_2SO_4}$ and $w^a_{H_2O}$ are the mass fractions of sulfuric acid and water in the aqueous phase respectively. A high sulfuric acid strength favors conversion rate but degrades selectivity. Indeed, the dinitration of toluene significantly occurs from

Please cite this article in press as: Di Miceli Raimondi, N., et al., Safety enhancement by transposition of the nitration of toluene from semi-batch reactor to continuous intensified heat exchanger reactor. Chem. Eng. Res. Des. (2014), http://dx.doi.org/10.1016/j.cherd.2014.07.029