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Safety evaluating of Beckmann rearrangement of cyclohexanone oxime in microreactors using inherently safer design concept

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ABSTRACT

Beckmann rearrangement of cyclohexanone oxime is an important step to produce caprolactam. Many researches have been devoted to it by using new organic catalysts or new reactors such as microreactor to improve the process efficiency. In this paper, the process was assessed by an inherently safer design (*ISD*) methodology based on risk approach to evaluate the safety effects of new organic catalysts and microreactors. The results show that organocatalyzed Beckmann rearrangement in continuous stirred tank reactors is unacceptable from the view of inherently safer concept due to the large amount of use of organic solvent and the large reactor volume. However, the application of microreactors could significantly increase the safety of both traditional and organocatalyzed Beckmann rearrangement processes with making inventories much smaller. The hazard conflicts that would be transferred to other parts of the process due to the application of microreactors were also evaluated by the Likelihood Index of Hazard Conflicts (*LIHCs*). The high value of *LIHC* because of microreactors indicates that some factors need to be paid more attention at the early design stage.

1. Introduction

Over the last two decades microreactors have gain rapid development and become a new branch of chemical engineering. Due to the dimension up to several hundreds of micrometers, microreactors have the characteristics of fast mixing, excellent heat and mass transfer and inherent safety [1,2]. A lot of dangerous chemical processes have been performed in microreactors, such as nitration [3], fluorination [4], hydrogenation [5], oxidization [6], and rearrangement [7,8]. Compared to the conventional reactors, the application of microreactors can bring many advantages: higher selectivity, faster reaction rate, better process control and increased safety. However, little research on the safety evaluating of the application of microreactors has been reported [9]. Though it is thought to be inherently safe due to the minimal use of reactants and greatly reduced size of process equipment. The use of microreactors may also bring some risks such as easy blockage of channels and the fast dynamics of the process. In addition, microreactors are often used to handle extreme process conditions and involve with numbering-up of the reactors, which require advanced control system [10]. As a result, it is still desirable to evaluate the safety of the application of microreactors to find out that how much the microreactor can improve the safety and to indicate the potential hazards and conflicts at the early design stage.

The Beckmann rearrangement of cyclohexanone oxime (COX) in oleum (Fig. 1) is an important step in the production of ε-caprolactam, the monomer of nylon-6 [11]. Since the rearrangement is very rapid and highly exothermic, it is a serious issue for the process safety. A loop reactor is usually applied for controlling the reaction temperature to avoid the thermal runaway in the reactor. In our previous papers, we tried to carry out the rearrangement reaction in oleum with the microreactor [7,8]. The external circulation was canceled but the cyclohexanone oxime had to be dissolved in the organic inert solvent of *n*-octane to dilute the reactants and remove reaction heat. Furthermore, we have improved a catalytic system [12] based on trifluoroacetic acid (TFA) developed by Ronchin et al. [13,14] which can avoid the side production of ammonium sulfate. The new process which is performed under much milder conditions brings a new safety problem with the large amount use of trifluoroacetic acid and acetonitrile. To improve the efficiency and safety the microreactor was also applied for the organocatalyzed Beckmann rearrangement [15]. As mentioned above, three new processes have been proposed to carry out the rearrangement of which two are in use of microreactors and one is in use of organic catalyst. This typical

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Nomenclature

Notation

AP	Atmospheric pressure (kPa)
AIT	Auto ignition temperature (°C)
C	Concentration of reactant (mol/m^3)
DI	Damage index
DP_{fe}	Damage potential for fire and explosion
DR	Damage radius (m)
df_{pro} and df_{bp}	Design factor for the new process and base process
EF_{co}, EF_{ph} and EF_{re}	Energy factors for combustion, physical and reaction energy
F_1, F_2, F_3 and F_4	Initial energy factors for combustion, physical and reaction energies
FP	Flash point (°C)
FRP	Fire point (°C)
Hc	Heat of combustion (kJ/kg)
ΔHr	Reaction enthalpy (kJ/mol)
INV	Quantity of chemicals involved (tons)
M	Mass of the chemical in use (kg)
N_{df}	Total number of the design factor
NR, NF and *NH NFPA*	Rankings for reactivity, flammability and health of the chemicals
OT	Operating temperature (°C)
pn_1, pn_2, pn_3, pn_4, pn_7 and pn_8	Penalties for temperature, pressure, quantity of chemical stored, hazardous characteristics, type of reaction and side reaction or decomposition
PP	Process pressure (kPa)
V	Volume of reactant (m^3)
VP	Vapour pressure (kPa)

Abbreviation

IRDI	Inherent Risk of Design Index
ISD	Inherently Safer Design
ISI	Inherent Safety Index
I2SI	Integrated Inherent Safety Index
$LIHC_{pro-i}$	Likelihood Index of Hazard Conflicts
LIISD	Likelihood Index of Inherently Safer Design
LSISD	actual Likelihood Score of Inherently Safer Design
PFS_i	Process Factor Score of each design factor
QI2SD	Quantitative Index of Inherently Safer Design
RISI	Risk-based Inherent Safety Index
SWeHI	Safety Weighted Hazard Index
TLS	Total Likelihood Score

process is a good model to do the safety assessment to help to understand the safety effect of the application of microreactors and realize the process optimization and process route selection from the view of safety.

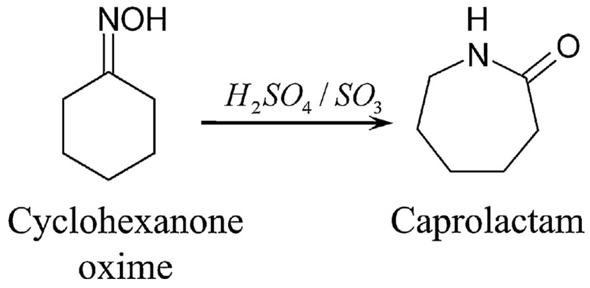

Fig. 1. The Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam.

Inherently Safer Design (*ISD*) aiming to eliminate or minimize the sources of harm by using fewer hazardous chemicals, smaller inventories and milder process conditions have been identified as a reliable technique to design a safer, sustainable and economically viable process plant [16–19]. Inherently safer process means the process is much safer whenever you have chosen any equipment or system. It may be interesting to evaluate the safety of the application of microreactors with the *ISD* concept. There have been many *ISD* methods developed, such as Inherent Safety Index (*ISI*) [20], graphical method [21], Safety Weighted Hazard Index (*SWeHI*) [22] and Integrated Inherent Safety Index (*I2SI*) [23]. Rathnayaka et al. [24] further extended the *I2SI* method, called Risk-based Inherent Safety Index (*RISI*) to analyze and implement inherent safety throughout the process design life cycle. Tugnoli et al. [25,26] proposed a consequence-based tool to assess the inherent safety of process alternatives using the concept of key performance indicators. However, these tools may ignore the risk transferred due to the change of design. Recently, another approach called Quantitative Index of Inherently Safer Design (*QI2SD*) [27], which combined the method of Likelihood Index of Hazard Conflicts (*LIHCs*) [28] and Safety Weighted Hazard Index (*SWeHI*), has been proposed to indicate the potential hazards and conflicts at the early design stage with the *ISD* concept.

In this work, we try to use the method of *QI2SD* to evaluate the safety of Beckmann rearrangement of cyclohexanone oxime. The objective is to find the effect of the microreactors and organic catalyst on the safety and identify the inherently safer process option. The potential damage indices of the conventional process and the three new ones were first estimated and then hazard conflicts of the three new ones were evaluated.

2. Methods

The *QI2SD* method includes three steps: quantify inherent hazards, evaluate inherent safety conflicts and rank the *ISD* alternatives. The details are given as follows.

2.1. Quantify inherent hazards

The quantification of hazards is based on the tools of Safety Weighted Hazard Index (*SWeHI*) [22] and *I2SI* [23], in which the potential energy is first calculated and then correlated as the potential damage as damage radius (*DR*). The damage index (*DI*) is evaluated at last. *DI* index is calculated as follows.

$$DI = \mathrm{Max}\ (5, \mathrm{Min}\ (100, DR/2)) \tag{1}$$

The estimation of *DR* is according to Eq. (2) to represent 50% probability of fatality or damage, which is the common calculation method [22,23].

$$DR = 4.76(DP_{fe})^{1/3} \tag{2}$$