Journal of Loss Prevention in the Process Industries 43 (2016) 147–157

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

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

Cooling and stirring failure for semi-batch reactor: Application to exothermic reactions in multiphase reactor

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ARTICLE INFO

Article history:
Received 7 March 2016
Received in revised form
24 April 2016
Accepted 15 May 2016
Available online 17 May 2016

Keywords:
Liquid-liquid reactions
Cooling failure
Accelerating rate calorimeter
Thermal risk assessment
Stirring failure
Epoxidation

ABSTRACT

Thermal safety assessment for multiple exothermic reaction systems in multiphase reactors is challenging. One of the first step is to determine the presence or absence of secondary reactions producing non-condensable gaseous products. Then, a kinetic and thermal study should be performed to evaluate the value of the heat-flow rates due to chemical reactions. Epoxidation of a free fatty acid by a percarboxylic acid produced *in-situ* was studied. A classical approach by determining the adiabatic temperature rise (ΔT_{ad}) and the time to maximum rate under adiabatic conditions (TMR_{ad}) by microcalorimetry was used. Then, different cooling and stirring failure scenarii in a semi-batch lab-scale reactor under isoperibolic mode were performed. It was confirmed that the formation of peroxyformic acid governs the overall reaction kinetics and the reaction temperature. It was confirmed that in case of cooling failure, mechanical agitation should be maintained.

1. Introduction

Since the first oil crisis in the 1970's, academic, political and industrial communities have decided to focus their efforts to diminish the energy consumption. Furthermore, environmental concerns have pushed these communities to minimize the amount of industrial waste. Biomass valorization into chemicals and fuel components can contribute to overcome this challenge through the philosophy of green chemistry (Anastas and Warner, 2000). The advantage of using biomass as raw material is to diminish the dependency on the crude oil resources, using renewable materials and biodegradable ones.

Biomass valorization includes several steps of pretreatment, transformation and separation. To determine whether a biomass process is less energy demanding than its oil-based concurrent, intrinsic kinetic parameters and thermodynamic constants should be determined. The book of Sengupta and Pike (2013) giving different biomass valorization process simulation shows the complexity of this research activity.

Two major questions remain:

- Biomass valorization processes are greener but are they safer?
- How to make a thermal safety assessment in presence of consecutive reactions in multiphase reactor?

These are the crucial issues to be considered.

Thermal risk assessment of chemical processes could be difficult to carry out because the knowledge of reaction kinetics and thermodynamics are required. Due to the high industrial competition and the time consumed in the estimation of kinetic and thermodynamic parameters, safety criteria are usually determined based

Abbreviations: ARC, accelerating rate calorimeter; ARSST, advanced reactive system screening tool; DSC, differential scanning calorimeter; EpOA, epoxidized oleic acid; FA, formic acid; HP, hydrogen peroxide; MTSR, maximum temperature for synthesis reactions; MTT, maximum temperature for technical reasons; OA, oleic acid; PFA, peroxyformic acid; TMR_{ad}, time-to-maximum-rate under adiabatic conditions; T_{D24}, process temperature when TMR_{ad} is 24 h; T_{D8}, process temperature when TMR_{ad} is 8 h; T_P, process temperature; W, water.

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http://dx.doi.org/10.1016/j.jlp.2016.05.011
0950-4230/

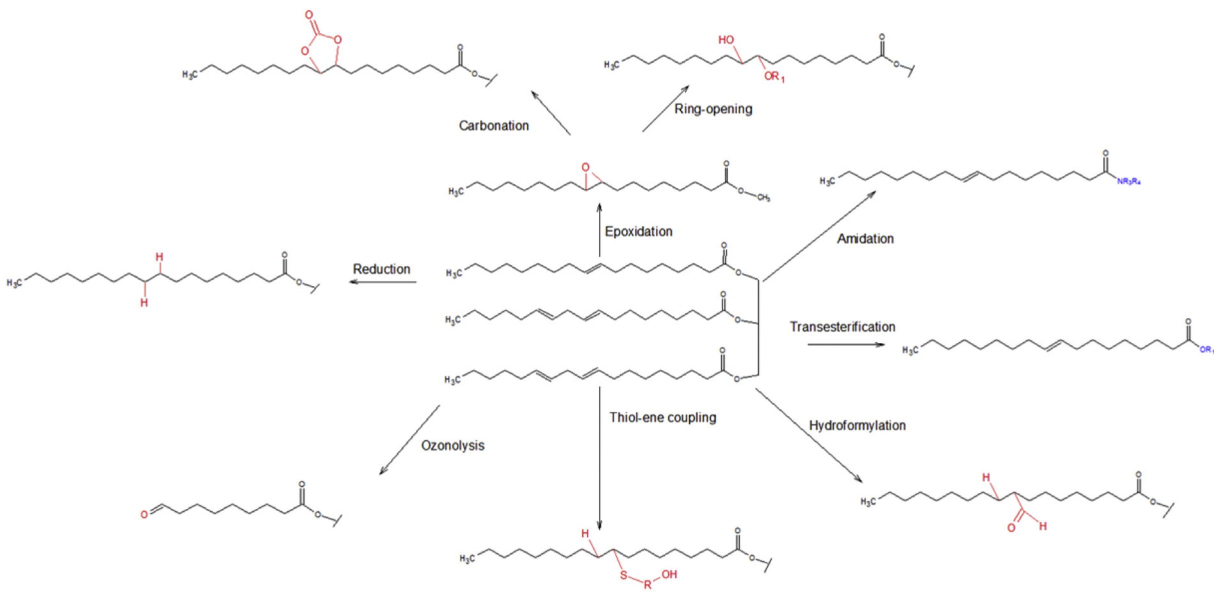

Fig. 1. Different ways of vegetable oil valorization (Nohra et al., 2013).

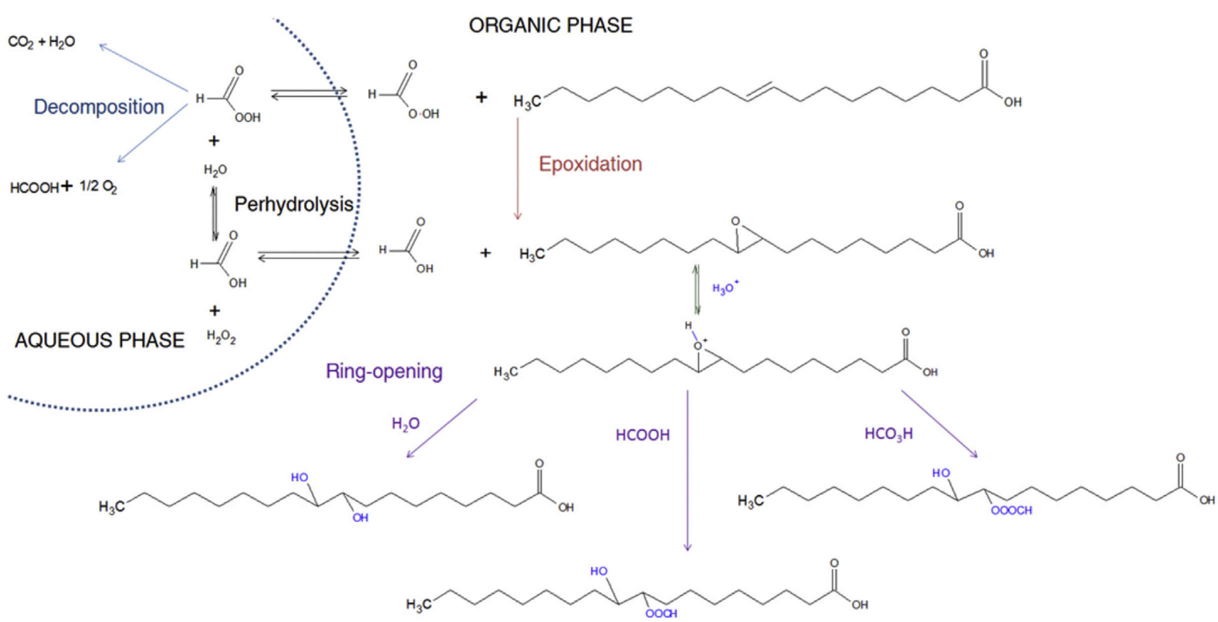

Fig. 2. Simplified mechanism of oleic acid epoxidation by PFA.

on rapid microcalorimetric and calorimetric analysis.

In case that kinetic data are not accurately determined, some authors have developed the concept of boundary diagram for semi-batch reactors for liquid-liquid reaction systems (Steensma and Westerterp, 1988, 1990; Van Woezik and Westerterp, 2002; Maestri and Rota, 2006) by defining some dimensionless quantities.

The other issue for a liquid-phase reaction system is the presence of secondary reactions producing non-condensable gaseous products. These reactions can take place during the loss of the heat control. To evaluate the importance of these secondary reactions, different adiabatic reactors have been developed to follow as well the evolution of gas pressure such as Accelerating Reactor

Table 1
Experimental matrix for oleic acid epoxidation by peroxyformic acid in ARC with a reaction mixture mass of 2.04 g.

Compounds	Weight percentage	Molar percentage	Compounds	Concentration [mol/L]
Formic acid	16.16	10.56	$[HCOOH]_{aq}$	5.21
Hydrogen peroxide	12.52	11.07	$[H_2O_2]_{aq}$	5.46
Water	45.25	75.60	$[H_2O]$aq	37.29
Oleic acid	26.07	2.77	$[OA]_{org}$	3.26