



## Secondary decompositions in the *N*-oxidation of low-order alkyipyridines

Lina R. Saenz<sup>1</sup>, William J. Rogers<sup>1</sup>, M. Sam Mannan<sup>1</sup>, and Maria Papadaki<sup>2</sup>

E-mail: [lina.saenz@chemail.tamu.edu](mailto:lina.saenz@chemail.tamu.edu)

<sup>1</sup> Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122, USA.

<sup>2</sup> Department of Environmental and Natural Resources Management, University of Ioannina, Seferi 2, Agrinio, GR 30100, Greece.

### Abstract

The consequences caused by decomposition reactions during runaway scenarios are of significant concern, especially when secondary decompositions develop which can lead to considerable increases of pressure in the system and, in the worst case, to the rupturing of the vessels. As such, the proper identification of secondary decompositions is important in the prevention of undesired events. During the runaway reaction of the *N*-oxidation of alkyipyridines, the unstable hydrogen peroxide starts decomposing at low temperatures, producing oxygen and water. This decomposition can increase the temperature enough to trigger the decomposition of the alkyipyridine *N*-oxide (product of the *N*-oxidation) leading to a subsequent increase in temperature and pressure, which can cause severe consequences due to the continuous production of gases from both decompositions. Because the hydrogen peroxide decomposition is condition sensitive, the runaway behavior of the *N*-oxidation depends on the conditions of the system as well. Thus, changes in concentration, or modifications of operating conditions can affect significantly the onset temperature of the decomposition as well as the Time to Maximum Rate (among other parameters). In order to study the decomposition of low-order alkyipyridines, calorimetric studies for 2-picoline *N*-oxide and 3-picoline *N*-oxide were performed using the Automatic Pressure Tracking Adiabatic Calorimeter (APTAC) in both adiabatic and isothermal modes. The condition-sensitivity of these systems was also studied under different temperatures and concentrations of catalyst, hydrogen peroxide, and the alkyipyridines 2-picoline and 3-picoline. The purpose of this work is to identify the runaway behavior of the *N*-oxidation of low-order alkyipyridines under different scenarios which allow for the development of appropriate safety and control measures.