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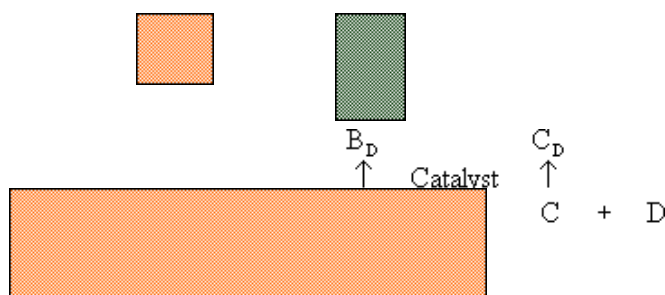
Runaway Studies and Global Kinetic Model Development of Complex Reaction Systems: Case Study *N*-Oxidation of Alkylpyridines

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The assessment of the consequences of reactor runaways is a very important in the chemical industry. However, although quantities such as MTSR (Maximum Temperature attainable by the Synthesis Reaction) can be assessed quite easily, quantities like TMR (Time to Maximum Rate) require a thorough kinetic study of the reaction of interest, before evaluating the consequences of a potential runaway. Additionally, if a reaction does suffer an unwanted runaway and decomposition reactions start, venting of the reactor will almost certainly be necessary. There is a wide range of theoretical work on vent sizing, which, unfortunately, is lacking experimental verification.

The current research addresses the problems of reliable evaluation of the consequences of a reactor runaway and provides good quality experimental data for the validation of the kinetics and reactor vent models.

Reactions of industrial interest have to be studied at conditions similar to the industrial ones in order to provide safe-for-scale-up purposes information. The kinetics of a complex reaction system can be studied well using good quality calorimetric data. The current work focuses in the study of a complex reaction system of competitive reactions, of the type:



In this system, reactants A (2-methylpyridine) and B (hydrogen peroxide) react to form the desired product C (2-methylpyridine *N*-oxide). However, under special (e.g., catalyst, higher temperatures) or normal circumstances reactants participate in parallel unwanted reactions (suffix B) and/or decompose (suffix D), higher temperatures resulting to gas formation and elevated pressures.

The current study involves extensive use of calorimetric techniques for the study of the reactions at normal and runaway conditions. Isothermal calorimetry has been used to develop a global kinetic model for the synthesis reaction of *N*-oxidation of 2-methylpyridine, and the parallel unwanted decomposition of hydrogen peroxide (orange box).

*The kinetics model has been completed with the addition of the kinetics of the thermal decomposition of the produced *N*-oxide (green box) which is presented in the current article; moreover, the model is used*

assess runaway scenarios and the results are validated using adiabatic calorimetry. It will be further used for the experimental validation of venting models.

This model is currently being expanded to cover the whole family of alkyipyridines, namely α -picolines, lutidines and collidines, substances that are extensively used in the pharmaceutical industry. Preliminary work has demonstrated, this research is also expected to result in a concrete methodology, development of global kinetic models and in the improvement of calorimetric experimental techniques.