Combined Use of Heat Flow Calorimetry and In-situ FTIR Spectroscopy for the Study of Complex Reactive Systems

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ABSTRACT

Alkylpyridines and their $N$-oxides are extensively used in the pharmaceutical industry. Typically the production of these compounds is carried out isothermally, in an open semi-batch reactor, near the mixture normal bubble-point, approximately 373 K, following a protocol described in more detail elsewhere [1]. Phosphotungstic acid, a highly selective complex metal compound, acts as a homogeneous catalyst and an aqueous solution of hydrogen peroxide as the oxidant. Approximately 30% of the added hydrogen peroxide decomposes via a parallel to the $N$-oxidation unwanted reaction, creating an oxygen rich environment in the flammable atmosphere formed by the alkylpyridine, thus compromising the safety of the process. Previous calorimetric studies [2] performed in an open system, suggested that increased temperatures and/or catalyst concentrations can dramatically increase the selectivity towards $N$-oxidation thus reducing the use of hydrogen peroxide and practically eliminating its decomposition. Owing to the complexity of the measurements, their prolonged duration and physical restrictions set by the mixture thermal and thermodynamic properties, previous work was performed in an open system and a narrow temperature and catalyst concentration range. The industrially employed open system ensures the escape of the produced oxygen, but it simultaneously sets an upper limit on the permitted temperature of operation. Given that previous studies indicate practically 100% selectivity towards $N$-oxidation, the current research focused on the study of 3-methylpyridine $N$-oxidation at higher temperatures in a closed system. In-situ infrared spectroscopy was used to determine the maximum conversion of 3-methylpyridine obtained before the hydrogen peroxide decomposition becomes competitive. Based on the results obtained, this paper shows the advantages offered by infrared spectroscopy for the study of complex reaction systems. Additionally, the inherent safety choices made for the open and the closed reactor operation and how they can affect the process efficiency are discussed.

REFERENCES
