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Towards efficient and inherently safer continuous reactor alternatives to batch-wise processing of fine chemicals: CSTR nonlinear dynamics analysis of alkylpyridines N-oxidation

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HIGHLIGHTS

- Reactor analysis for continuous fine chemicals and pharmaceuticals production.
- CSTR model is developed based upon conservation laws and reaction kinetics.
- Operational parameter space separated by steady-state multiplicity and stability.
- Performance metrics and steady-state/dynamic characteristics identify best designs.
- Impact of initial conditions on safe and efficient start-up of the process is investigated.

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ABSTRACT

This paper demonstrates the integration of process safety concepts (e.g., reactive chemicals, inherently safer design) with classical reaction engineering/system fundamentals (e.g., first-principles reactor modeling, system dynamics and stability) for identifying economically viable and safe continuous stirred tank reactor (CSTR) designs for scale-up of batch-wise fine chemical and pharmaceutical syntheses. As an illustrative and industrially relevant example, the homogeneous catalytic exothermic N-oxidation of alkylpyridines is investigated using a jacketed CSTR model. Reactor steady-state multiplicity and oscillation phenomena, which may bring about serious incidents, are analyzed based upon system equations. Reactor design and operation conditions as well as start-up strategies and worst-case scenarios are systematically investigated to address process safety concerns and balance reactor efficiency.

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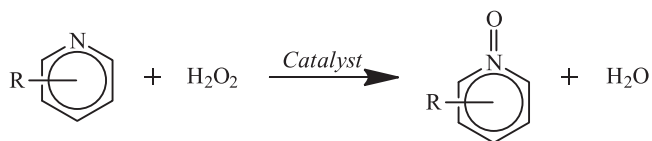
1. Introduction

Pyridine and its derivatives are of considerable popularity within chemical processing industry for their versatile uses, for instance, in the pharmaceutical and agrochemical industries as starting materials for the production of antibiotics, antiulcer medication, herbicides and insecticides, etc (Scriven and Murugan, 1996). Alkylpyridine N-oxides, which are obtained from the liquid phase, homogeneous catalytic N-oxidation of alkylpyridines (Scheme 1) using hydrogen peroxide as the oxidizer and phosphotungstic acid ($H_3PW_{12}O_{40}$) as the catalyst, are important intermediates in these syntheses.

Regarding safety concerns associated with Scheme 1, its large reaction heat release along with the competitive undesired decomposition of hydrogen peroxide, which is exothermic and oxygen-generating, renders the batch and semi-batch reactors where the reaction is traditionally carried out prone to runaway and represents a serious hazard of fires and explosions given the flammability of alkylpyridines. Previous studies (Papadaki and Gao, 2005; Papadaki et al., 2002; Pineda-Solano, 2014; Pineda-Solano et al., 2012; Sempere et al., 1998) of this reacting system mainly dealt with investigation of reaction kinetics and determination of safe operation conditions by means of reaction calorimetry, which represents the first line of defense for batch and semi-batch reactors safety, as discussed in the in-depth review by Westerterp and Molga (2006). For example, Sempere et al. (1998) and Papadaki et al. (2002) developed a kinetic model for Scheme 1 by performing N-oxidation of 2-methylpyridine in an open semi-batch reactor. Calorimetric information was collected and analyzed

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Scheme 1. N-oxidation of alkylpyridines using phosphotungstic acid as the catalyst.

to derive kinetic parameters such as frequency factors, activation energies and chemical equilibrium constants for the formation of intermediates. Papadaki and Gao (2005) extended the model to make it applicable to N-oxidation of other substances in the pyridine family such as 3-methylpyridine, 4-methylpyridine, dimethylpyridines and trimethylpyridines. From a reactor design and operation perspective, Pineda-Solano et al. (2012) established through experiments that running the reaction at elevated temperature and pressure in a closed semi-batch reactor would greatly depress and practically eliminate the exothermic decomposition of hydrogen peroxide. Those kinetic parameters may in turn be used to develop convenient design and operation criteria for chemical reactor safety.

The works of Westerterp et al. (e.g. Steensma and Westerterp, 1991, 1990; Van Woezik and Westerterp, 2002; Westerterp and Molga, 2004; Westerterp et al., 2014) and Maestri et al. (e.g. Maestri and Rota, 2005a, 2005b, 2006, 2007; Maestri et al., 2006) provide a practical tool set for determining inherently safer operation conditions for batch and semi-batch reactors based upon the concept of boundary diagrams. It is especially useful in the fine chemical and pharmaceutical industry for the sake of time and cost savings since it only requires fundamental kinetic parameters obtained from reaction calorimetry rather than investigation of more detailed reaction mechanisms. Specifically, starting from the first-principles liquid–liquid phase heterogeneous semi-batch reactor model, the authors divided the dimensionless parameter space of exothermicity (Ex , the ratio of maximum reaction heat release to cooling capability) and reactivity (Ry , the ratio of reaction rate to cooling rate) into regions featuring different ignition, thermal runaway and productivity characteristics. Operation conditions, including the dosing time and the cooling temperature, could be therefore selected according to the region boundaries together with the critical lines of Ex_{max} (below which heat release is not sufficient for reaction runaway) and Ry_{min} (above which reaction is quickly ignited and an approximately linear conversion profile as well as a smooth temperature profile is achieved, referred to as the QFS condition in the papers) in order to guarantee reactor safety and efficiency. The methodology has since accommodated scenarios such as slow (Steensma and Westerterp, 1990; Westerterp and Molga, 2004)/fast (Steensma and Westerterp, 1991) kinetics, homogeneous reactor (Maestri et al., 2006; Westerterp et al., 2014), arbitrary reaction order (Maestri and Rota, 2005a, 2005b), and parallel/consecutive reaction networks (including autocatalytic reactions) (Maestri and Rota, 2006, 2007; Van Woezik and Westerterp, 2002), and has been verified by several experimental studies (Maestri et al., 2006; Van Woezik and Westerterp, 2002). Meanwhile the concept of QFS is applied in another major series of literatures (e.g. Bosch et al., 2004; Strozzi and Zaldivar, 1994; Strozzi et al., 1999; Zaldivar et al., 2005) that aims to improve the online early warning detection system for reactor safety by employing the divergence criterion developed over years. For practical application, the divergence of the system could be calculated from system state space reconstructed based upon online measurement of some characteristic variable (e.g. temperature in the aforementioned papers). According to these papers, the most proper reconstruction method as well as reconstruction parameters (such as the embedding dimension, the time step, and the number of trajectories of the

characteristic variable) for a specific case can be identified by analyzing the measured data. The criterion has been proved to be able to distinguish accurately and timely between runaway and non-runaway (e.g. QFS) scenarios for different reaction schemes, reactor types, and operation modes for batch and semi-batch processes.

There has been increasing interest from both academia and industry in discovering and manufacturing specialty chemicals, especially fine chemicals and pharmaceuticals, through continuous flow processing, with most declared advantages including but not limited to improved safety and product quality, higher throughput and reduction in the amount of raw materials needed (Anderson, 2001; Calabrese and Pissavini, 2011; Hartman et al., 2011; Mills et al., 2007). Hartman et al. (2011) provided a useful decision roadmap for quick screening of the feasibility of trying out flow reactors. According to the roadmap, flow reactors have the potential of safer and more efficient handling of reactions featuring fast kinetics and large reaction heat release, which is the case for the catalytic N-oxidation of alkylpyridines.

In the present study, a continuous stirred tank reactor (CSTR) is selected for analysis. Among all flow reactors, both conventional ones (e.g., continuous stirred tank reactors and plug flow reactors) and novel ones (e.g., membrane reactors and microchannel reactors), CSTRs are favored for highly exothermic reactions owing to spatially uniform concentration and temperature profiles which facilitate controllability and are thus easier to implement control and instrumentation. Insight obtained from CSTR analysis provides a fundamental basis for subsequent analysis of more complex configurations such as tubular reactors or membrane reactors.

Systematic mathematical approaches have long served chemical reactor design and operation purposes (Liljenroth, 1918). Bilous and Amundson's (1955) landmark paper treated CSTR as a dynamic system and employed Lyapunov's first method of linearization to yield a pair of algebraic conditions for local stability of steady states. It triggered subsequent boom of research with respect to CSTR steady-state multiplicity or dynamics, or both in some cases (Farr and Aris, 1986). On the steady-state branch, Van Den Bosch and Luss (1977) presented very strong necessary and sufficient criteria for unique or multiple steady states of an adiabatic CSTR accommodating an n th-order ($n \geq 0$) reaction, while Tsotsis and Schmitz (1979) and Leib and Luss (1981) established the corresponding exact necessary and sufficient criteria with Leib and Luss (1981) being also applicable to nonadiabatic cases. Based upon singularity theory, which was developed and tentatively applied to CSTRs in Golubitsky and Schaeffer (1979) and Golubitsky and Keyfitz (1980), Balakotaiah and Luss (1982, 1983, 1984) exhibited complex multiplicity features of CSTRs, the steady states of which could be described by a single algebraic equation, by dividing reactor parameter space into different regions corresponding to different numbers of steady states and predicting all possible types of bifurcation diagrams, which depict the dependence of the steady state of a state variable (e.g., concentration, temperature, and conversion, etc.) on a slowly varying design or operation variable (e.g., Damköhler number, residence time, etc.). On the dynamic branch, except from a series of papers by Amundson and his co-workers (e.g., Aris and Amundson, 1958a, 1958b, 1958c) which studied transient behaviors of a CSTR and the effect control systems had on altering the dynamics, a classical paper by Uppal et al. (1974) performed an exhaustive study of the dynamic behavior of a CSTR with a single first-order, irreversible, exothermic reaction, the result of which was the demarcation of the reactor design and operation parameter plane based upon steady-state and dynamic characteristics. It was later complemented by Williams and Calo (1981) and Kwong and Tsotsis (1983) which established finer structure of the parameter plane as well as corresponding new bifurcation

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