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Analysis of potential singular point surface of reactive stripping processes

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Abstract

Reactive stripping involves non-condensable gas phase that not only removes the condensable components from the liquid phase but also is used as educt. To analyse the feasible products of reactive stripping process, a model is presented. The potential singular point surface (PSPS) is used as a tool to analyse the feasibility of products. Reactive distillation and reactive membrane process are regarded as two limiting cases of this model with fully condensable gas phase without stripping gas and with infinite gas flow rate, respectively. The influence of the mass transfer conditions and gas flow rate on the PSPS of special and general reactive stripping processes is investigated through hypothetical ternary systems. As expected, location and shape of the PSPS can be dramatically changed at different operating conditions of the process and of the physical properties of the involved components, which is helpful for optimising the suitable parameters for the desired product.

Keywords: Reactive stripping; Reactive distillation; Reactive membrane separation; Feasibility analysis; Potential singular point surface; Continuation

1. Introduction

In chemical industries there are numerous gas–liquid reactions and liquid phase reactions accomplished in the presence of an inert gas. One challenge of improving the existing industrial processes is the combination of multiple reactions in one apparatus. Usually, the terminology “reactive stripping” is used in scientific literature for processes of removing one of the products of chemical reaction from the liquid phase by the inert gas, e.g. removal of water in the solid-acid catalysed esterification of 1-octanol with hexanoic acid (Nijhuis et al., 2002; Schildhauer et al., 2005). Here, we extend it to processes where the gas phase not only removes products from the liquid phase but also supplies reactants for the liquid phase reaction. Typical examples of such important industrial reactions are the liquid phase oxidation of hydrocarbons such as cyclohexane, *p*-xylene, cumene (Suresh et al., 2000), hydrogenation of olefins (e.g. partial hydrogenation of natural oils to edible products) and of nitro aromatic components for producing of key intermediates, dehydrogenation of ethyl benzene to styrene and of alkanes to aromatics (Rylander, 2000), and alkylation of benzene to ethyl benzene or cumene, of isobutene to highly branched parafinic fuel and of phenol to *o*-cresol (Podrebarac et al., 1997; Röper et al., 2000).

For reactive stripping processes, design methods are very important like other reactive separation processes, for example, reactive distillation, reactive membrane separation and reactive crystallization, etc. So far such knowledge is very limited and there is strong need to develop a simple method to quickly predict the possible products based on information of the physical properties, chemical stoichiometric coefficient, and mass transfer coefficients.

For reactive distillation, residue curve maps (RCM) is a widely used tool for designing a potential product, which has been applied for both homogeneous (Venimadhavan et al., 1994, 1999; Thiel et al., 1997) and heterogeneous systems (Qi et al., 2002; Qi and Sundmacher, 2002; Steyer et al., 2002). Specially, singular points play a crucial role, which change with reaction conditions. Song et al. (1997) proved experimentally the existence of these stationary points. Recently, Chadda et al. (2001) reported a method based on two flash cascades, i.e., vapor-fed flash cascade and liquid-fed flash cascade, the stable nodes of which can be taken as the top and bottom products of a fully reactive distillation column. Their results implied that the

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singular points of batch reactive distillation cannot be applied for the rectifying section (or top products). For this purpose, Qi et al. (2004) presented a new feasibility analysis approach based on batch reactive distillation processes (i.e., reactive condenser and new concept of reactive reboiler). They extended the transformed variable based condition for reactive azeotropes presented by Doherty and his coworkers (Barbosa and Doherty, 1988; Ung and Doherty, 1995) to describe and link all kind of singular points and pure components in both reactive condenser and reactive reboiler. They, for the first time, presented the mathematical method to predict the potential singular point surface (PSPS). The PSPS is very helpful for the feasibility analysis due to its important properties: depends only on reaction stoichiometrics and physical thermodynamics; independent on the reaction rate expression; valid for equilibrium controlled as well as for kinetically controlled reactions. Very recently, Qi and Sundmacher (2005) applied PSPS for azeotrope locating using these properties.

For processes controlled not only by chemical reaction but also by mass transfer, the influence of mass transfer on singular points are important. Recently, Nisoli et al. (2004) investigated the effects of the vapor–liquid mass transfer on the feasibility of the reactive distillation. Moreover, Qi and Sundmacher (2004) applied the PSPS approach to study the influence of mass transfer on the feasible products of countercurrent reactive separation processes by using PSPS, where reactive pervaporation was considered. Huang et al. (2004) extended it to a more general case and applied their method to reactive membrane separation process.

For reactive stripping processes, several important factors, i.e., the mass transfer of the components in the liquid and gas phases, volatilities of the components and the gas flow rate, lead to different effects on the process. Therefore, a simple method is strongly needed to quickly predict the potential final product and to optimise proper conditions for a desired product. In this contribution, a model for reactive stripping is presented and the condition for the PSPS is derived. Through ternary systems, the influence of different factors on the PSPS is illustrated.

2. Reactive stripping process description

The process of reactive stripping is shown in Fig. 1. The gas is fed into the vessel and enters the liquid phase by diffusion. The product of chemical reaction is stripped into the gas phase and withdrawn by the gas. In order to analyse the feasibility of such processes, a model is presented here based on the following assumptions:

- The pressure inside the vessel is constant.
- The gas phase is continuous and the liquid phase is batch.
- Heat transfer is much faster than mass transfer such that the temperature is the same in the whole system and is dependent on the physical equilibrium at the interface.
- The mass transfer between the two phases is described by the two films model.
- The chemical reaction takes place only in the liquid bulk.

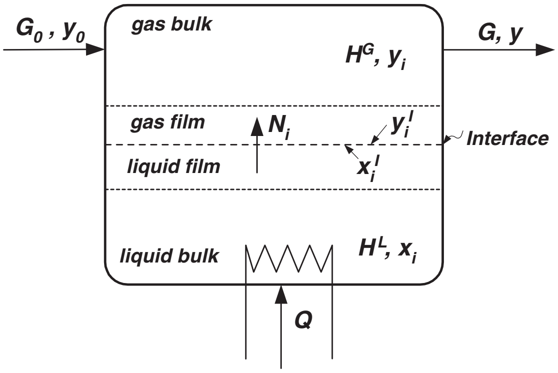

Fig. 1. Scheme of the reactive stripping reactor.

2.1. Model equations

2.1.1. Mass transfer kinetic

The gas–liquid mass transfer is described by the two-films theory (Baerns et al., 1999; Taylor and Krishna, 1993). The mass transfer from the liquid bulk to the gas–liquid interface and from the gas–liquid interface to the gas bulk can be accordingly described with an approximate Maxwell–Stefan equation developed by Schlünder (1984)

$$N_i^L = A^L c_T^L \beta_i^L n_i^L \ln\left(\frac{n_i^L - x_i^I}{n_i^L - x_i}\right), \quad i = 1, \ldots, NC, \tag{1}$$

$$N_i^G = A^G c_T^G \beta_i^G n_i^G \ln\left(\frac{n_i^G - y_i}{n_i^G - y_i^I}\right), \quad i = 1, \ldots, NC, \tag{2}$$

where N_i is the molar flow rate of component i through the interface, and $n_i = N_i/N_T$ with $N_T = \sum N_i$. These equations describe rigorously the non-equimolar mass transfer in binary mixtures. They also apply to multi-component mixtures if all binary diffusion coefficients β_{ij} are equal. Eqs. (1) and (2) yield relatively good approximations for slightly different diffusion coefficients, for dilute mixtures with one key component and also for pseudo binary mixtures. More important is that the above equations include the so-called Stefan-flux and describe the interaction between the diffusion and convection due to the total flux. The approximation is suitable with respect to the aim of the work, which is the development of a simple method for quick feasibility study.

At steady state mass transfer it holds that $N_i^G = N_i^L = N_i$, $N_T^G = N_T^L = N_T$ and $n_i^G = n_i^L = n_i$. Therefore, the mole fractions of the gas and the liquid phases at the interface follow from Eqs. (1) and (2):

$$x_i^I = \frac{K_i^L - 1}{K_i^L} n_i + \frac{1}{K_i^L} x_i, \quad i = 1, \ldots, NC - 1, \tag{3}$$

$$y_i^I = K_i^G y_i + (1 - K_i^G) n_i, \quad i = 1, \ldots, NC - 1, \tag{4}$$