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A systematic framework for the feasibility and technical evaluation of reactive distillation processes

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ABSTRACT

This study presents a novel design methodology for the feasibility and technical evaluation of reactive distillation (RD), and discusses the applicability of various design methods of RD. The proposed framework for the feasibility evaluation determines the boundary conditions (e.g. relative volatilities, target purities, equilibrium conversion and equipment restriction), checks the integrated process constraints, evaluates the feasibility and provides guidelines to any potential RD process application. Providing that a RD process is indeed feasible, a technical evaluation is performed afterward in order to determine the technical feasibility, the process limitations, working regime and requirements for internals as well as the models needed for RD. This approach is based on dimensionless numbers such as Damkohler and Hatta numbers, as well as the kinetic, thermodynamic and mass transfer limits.

The proposed framework for feasibility and technical evaluation of reactive distillation allows a quick and easy feasibility analysis for a wide range of chemical processes. In this work, several industrial relevant case studies – e.g. synthesis of di-methyl carbonate (DMC), methyl acetate hydrolysis, toluene hydrodealkylation (HDA) process, fatty acid methyl esters (FAME) process and unsaturated polyesters synthesis – clearly illustrate the validity of the proposed framework.

1. Introduction

Reactive distillation (RD) combines reaction and separation into a single operating unit, and represents one of the most important industrial applications of the multifunctional reactor concept. Recently, RD has drawn increased attention due to its key advantages over conventional processes, such as (1) economical profit: significant reduction of capital and operating costs, major energy savings, (2) environmental gains: emissions reduced by 20% or more as compared to a classic setup (e.g. reactor followed by distillation column) and (3) social benefits: improvement on safety, health and society due to the reduced reactive holdup, low chances of runaway sensitivity and lower space footprint [17,18,50,23,12,37,53,52,56].

Scientific literature and patents on RD are abundantly published since the early 20th century. Extensive overviews of industrial application, feasibility analysis, design and synthesis methods, retrofit, modeling strategy and internal design of various distillation systems were reported in several papers [17,18,20,55,56,33,51,6]. RD process design is carried out either by simulation or by synthesis design. Simulation involves specifying the inputs, operating variables and equipment sizes and solving for the resulting outputs. In contrast, synthesis design involves specifying the inputs and selected outputs, operating variables and also design variables, and determine whether a feasible set exits for the given product specifications. Thery et al. [57,58] gave an overview of the state-of-the-art methods available in the literature for the feasibility analysis and the design of RD processes. Although simulation and synthesis design are two different approaches, they are complementary to determine the design parameters. Remarkable, using first synthesis design methods to determine the design parameters enables the chemical engineers to perform more effective simulations [4,42,15,16,21,41,57,58].

Mixed-integer nonlinear programming (MINLP) and fixed-point methods are two approaches used for the synthesis design methods. Ciric and Gu [7], Jackson and Grossmann [22] and Gangadwala et al. [13] used a MINLP model for synthesizing a reactive distillation column by minimizing the total annual cost. Buzad and Doherty [4] have proposed a fixed-point based design method for equilibrium reactive distillation processes which is further extended to non-reactive and reactive residue curve maps (RCM). Venimadhavan et al. [60] have studied the effects of kinetics on reactive distillation residue curve maps. They have identified singular points of the fixed-point method as a function of Damkohler number (*Da*) which is used in combination with the chemical equilibrium constant

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to describe the feasibility of RD applications. From the synthesis design method, the feasibility of applying RD and the process limitations can be easily identified and the suitable model for the simulation studies can be selected [60,14,1].

Simulations are currently based on either equilibrium (EQ) modeling or rate-based modeling. Equilibrium modeling and rate-based modeling were extensively studied by Baur et al. [3], Higler et al. [19], Katariya et al. [24], Kiss [29], Peng et al. [40], Shah et al. [47,48], Sundmacher and Kienle [55] and Taylor and Krishna [56]. In equilibrium modeling, the vapor and liquid are assumed to be in equilibrium. In practice, the theoretical number of stages obtained from equilibrium model calculations is converted to the required real number of stages, either through the overall efficiency of a tray or by the height equivalent of a theoretical plate (HETP) for packed columns. This is a useful approach to simulate a binary system or an existing column. However, this approach is not reliable to simulate a multi-component system or an existing column with different operating conditions [3,24,40]. Compared to equilibrium modeling, rate-based modeling offers accuracy in design of a column as it accounts for: (1) vapor–liquid equilibrium only at the interface between the bulk liquid and vapor phases, (2) a transport-based approach to predict the flux of mass and energy across the interface, and (3) the real hydrodynamic situation of either a tray or a packed column. For these reasons, over-design and under-design are avoided, there is no need for efficiencies and HETPs and the column is designed more realistic as compared to EQ modeling, thereby reducing the capital and operating costs. However, the establishment of a detailed rate-based model is complex since it requires a significant amount of input data, which can be reduced by adopting the model according to the process limitations of reactive distillation [56,40].

2. Problem statement

Currently, the typical design of RD is still based on extensive simulation studies followed by expensive and time-consuming sequences of laboratory and pilot plant experiments. The main reason for this development inefficiency is the absence of an established RD design procedure that is suitable for a straightforward technical evaluation. Hence, the problem is how to determine quickly but reliably when RD is a technically feasible alternative for an existing or a new chemical process. To solve this problem a systematic framework is developed in this work through which the technical feasibility, the process limitations, the working regime, internal and model requirements for RD process can be quickly and reliably evaluated. A major advantage of this approach is its applicability to a wide range of all-scale processes and multiproduct environments. The systematic approach proposed in this work first provides screening criteria for checking the technical feasibility based on types of reactions involved in a process, reaction kinetics, temperature and pressure, types of heat involved during the process, relative volatilities, target purities, equilibrium conversion and equipment restrictions. If all conditions are satisfied in the screening test, the proposed systematic framework in this paper can be used for the detailed technical evaluation. The framework for technical evaluation provides guidelines for the process limitations, the working regime, internal and model requirements for RD process. In order to illustrate the applicability of the screening test for the technical feasibility of RD process, several industrial relevant case studies are examined. The modeling and simulation has been performed for the unsaturated polyester synthesis by reactive distillation in order to demonstrate the applicability of the developed framework for the detailed technical evaluation of RD process.

3. Feasibility analysis of RD processes

The proposed criteria for the technical feasibility of RD is based on industrial applications of RD reported in the scientific literature as well fundamental explanations [1,10,14,25–29,31,35,36,43,45,47–49,54–56].

3.1. Framework for feasibility evaluation

According to the proposed framework, the left hand side of Fig. 1 checks whether a RD process is technically feasible, while the right hand side of the same figure gives an indication whether RD process is also economically attractive or not. In order to perform this technical evaluation, some basic information on the chemical process is required, such as vapor liquid equilibrium (VLE data), stoichiometry of reactions, kinetics, enthalpy of reactions.

The first step is to check the number of products and the reaction type. If there is only one product present, the last step of the main reaction is irreversible and when there are no side reactions present, then there is no advantage of using RD over a simple reactor [27]. One must not forget that the main advantages of RD rely on overcoming the equilibrium limitations and enhancing the selectivity towards the desired product [56,2,17].

As both operations occur simultaneously in the same unit, there must be a proper match between the temperatures required for reaction and separation [26,56]. If there is no significant overlapping of the operating conditions of reaction and separation, then the combination of reaction and distillation is not possible (e.g. a high pressure reaction cannot be combined with a vacuum distillation). Moreover, one must also consider that working in the limited overlapping window of operating conditions of reaction and separation is not always the optimal solution, but merely a trade-off. For example, in the conventional hydro-dealkylation (HDA) process the temperature difference between the reaction and the separation process is 120 °C. In this case, RD was found to be technically applicable, yet it was not economically attractive [54]. Therefore, for a feasible RD process the temperature difference between separation and main reaction should be lower than about 50 °C [9]. Note that this value, as well as the following ones mentioned in this feasibility framework, should be only taken as guideline figures and not interpreted as very strict limits of the RD process.

Moreover, the operating pressure and temperature should not be close to the critical region of the key components, since that would potentially lead to one supercritical phase [25]. If the column operates at the critical pressure of key components, these will be present in the vapor – while in the vast majority of RD processes the reaction takes place in liquid phase [17]. For example, the synthesis of di-methyl carbonate (DMC) by catalytic esterification of carbon dioxide and methanol occurs in the near critical region of CO_2 at 73 bar and 80–100 °C [5]. For this reason, the RD alternative is not applicable in this process as the main reaction takes place in gas and not in the liquid phase.

Relative volatility of key chemical components is also a crucial parameter for the feasibility analysis of RD [59]. Temperature dependence of vapor pressure of individual components can results in decreased relative volatility as temperature increases in multicomponent systems. This can create a mismatch of favorable temperature for kinetics and relative volatilities which can make the RD process unattractive [36]. A relative volatility of minimum 1.1 was chosen here, as this is the typical minimum value for distillation process [36,55]. For instance, in the hydrolysis reaction of methyl-acetate, the reactant (MeAc) is the lightest component and therefore it is difficult to keep it in the reactive zone. Hence, a conventional reactive distillation process is not applicable in this case.