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Esterification of glycerol and acetic acid in a pilot-scale reactive distillation column: Experimental investigation, model validation, and process analysis

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ABSTRACT

The esterification of glycerol with acetic acid is associated with an unfavorable chemical equilibrium and complex cascade reactions behavior. This results in a challenging and cost-intensive process currently used for triacetin (TAG) production. Reactive distillation (RD) as an integration technology was proposed for TAG production in this paper to improve both efficiency and TAG yield. To design such a column for industrial-scale application, a series of pilot-scale experiments and theoretical investigations were performed. Experiments varying decisive operating parameters were successfully performed showing that complete glycerol conversion and high purity of TAG could be easily achieved, validating reactive distillation as a potential candidate for TAG production. A rigorous model based on the chemical kinetics and phase equilibrium was established and validated by good agreement of the simulation results and the experimental data. The model was then applied to investigate the process synthesis, design and optimization of this integration sustainable process. The results indicate the optimal operating ranges for the design of an industrial-scale RD process to get high TAG purity in the bottom stream with considerably less energy consumption.

1. Introduction

Triacetin, also known as Glyceryl Triacetate, has expanded uses in perfume, coating, pharmacy, cigarette and other fields. So far, the most-used TAG industrial production process is direct esterification of glycerol and acetic acid in the presence of concentrated sulfuric acid [1]. However, glycerol esterification with acetic acid is an exothermic reaction kinetically limited [2] and associated with complex cascade reactions behavior (Fig. 1), which results in the TAG production having many problems such as incomplete reaction, low yield of TAG and long reaction time for traditional production method. In addition, due to concentrated sulfuric acid being employed as catalyst, many disadvantages such as equipment corrosion, side reaction, products separation and environmental risks exist in this process. Combined reaction and separation into a single operation unit, RD is one of the most successful process intensification technologies [3,4]. Compared with traditional reactors, RD allows reaction and separation to happen simultaneously in a single unit, the products being continuously removed from the reactive section and thus leading to an increase of both conversion and selectivity [5]. Another advantage is that, for exothermic reactions, the heat of reaction can be directly used for evaporation of liquid components, which is energy-saving and also could prevent the formation of hot spot [6,7]. Therefore, we propose to produce TAG via continuous RD technology.

The concept of RD was first proposed in 1921 by Backhaus [8]. After a long period, this technology had witnessed its explosive growth in both academic and industrial fields from 1970 to 2000 [9]. Reviews on RD are available from Noeres et al. [10], Taylor and Krishna [11] and Hiwale et al. [12]. The most successful application of RD is the Eastman process for methyl acetate production, ten operation units are replaced by one column and nearly 100% conversion of the reactant is achieved [13]. A research idea in Chua's recent work is useful in the RD process, *i.e.*, excess of either reactant to obtain different objectives [14]. Based on Chua's study, two schemes for retrofitting Isopropyl Alcohol production process were proposed and studied by Niu and Rangaiah [15]. Although shortcomings exist in complex design, difficult scale-up and process control of RD [16], RD is already broadly applied in reversible reaction process such as esterification and etherification reaction [17–19]. However, only a few works have been dedicated to TAG production applied RD technology up to now. Mufrodi et al. [2]

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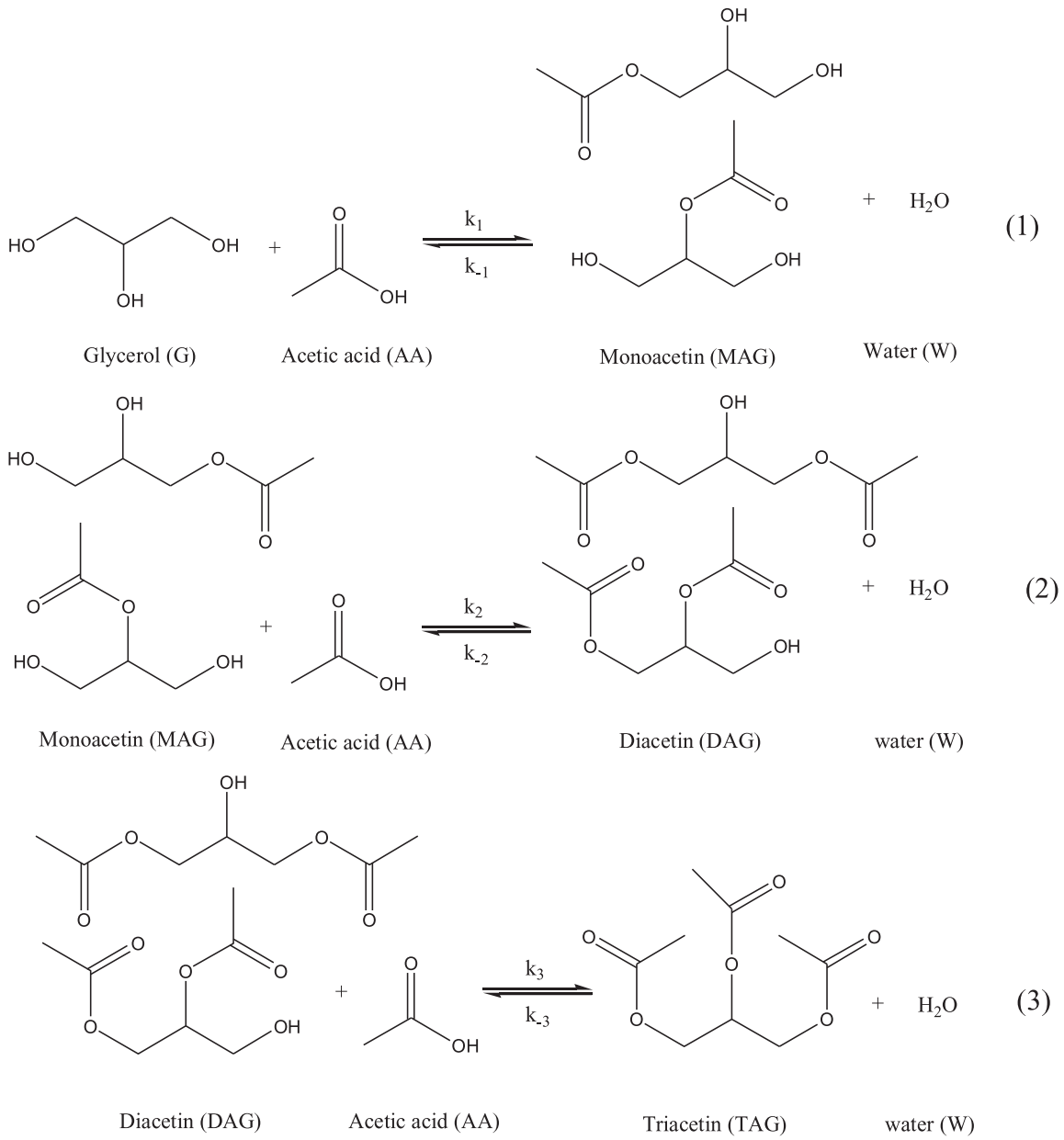

Fig. 1. Mechanism of esterification of glycerol with acetic acid.

reported the reaction kinetics of glycerol acetylation with acetic acid over homogeneous catalyst sulfuric acid. Zhou et al. [20] studied heterogeneous acetylation of glycerol with acetic acid catalyzed by Amberlyst-15 in a slurry reactor and a homogeneous first-order consecutive reaction kinetic model was obtained via reasonable simplification based on LHHW model. The study of Gelosa et al. [21] showed that high purity of TAG and high conversions of reactants could be obtained in a chromatographic reactor. Hasabnis and Mahajani [22] studied TAG production by entrainer-based RD. Ethylene dichloride was employed in their RD column to increase the water removal efficiency and also to keep the temperature below the thermal stability of the catalyst in the reaction zone. Inspired by Hasabnis and Mahajani's work, recent simulation conducted by Huang et al. [23] focused on extending RD for the production of TAG. In this study, pure raw material was replaced by feedstock mixed with a little water and isobutyl acetate was used to separate water. Nevertheless, the production of TAG by RD was only studied theoretically in these publications expected for Hasabnis and Mahajani's work. In addition, the conversion of glycerol and the yield of TAG still remain as an obstacle in these studies, which is not good enough to guide industrial application of RD technology for TAG production.

This paper focuses on the feasibility, optimal design and operation parameters of TAG production by RD technology from glycerol and acetic acid. A novel structured catalytic packing, seepage catalytic packing internals (SCPI), filled with NKC-9 cation exchange resin was used in this study. The SCPI as a high-efficiency catalytic packing was developed in our previous studies and more information about SCPI was described by Gao et al. [24–27]. In the first part, a series of pilot-scale experiments were conducted to investigate the feasibility of TAG production by RD. Secondly, a rigorous model based on the chemical kinetics and thermodynamic method was developed, furthermore the accuracy of the model was validated by comparing with the experimental data. Finally, the

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