Experimental model validation for *n*-propyl propionate synthesis in a reactive distillation column coupled with a liquid–liquid phase separator

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ABSTRACT

In the synthesis of some organic esters, reactive distillation coupled with a liquid–liquid phase separator is often used to increase the product purity or to recover the reactants. In this article, we present a comprehensive experimental and theoretical study on the heterogeneously catalysed synthesis of *n*-propyl propionate by reactive distillation and a subsequent liquid–liquid phase separator. The experiments were performed in a pilot-scale reactive distillation column. Data-reconciliation tests proved that the experimental results obtained comprise a complete, reliable set of composition and temperature profiles along the pilot-scale reactive distillation column and can be used for further model validation. A nonequilibrium-stage model was applied to predict the experimental results. Simulation studies demonstrated that the composition and temperature profiles in the rectifying section of the column were highly sensitive to the composition of the reflux stream entering the column. Deviations between the experimental and predicted composition profiles in the rectifying section were identified. An explanation for the deviations is given in this article.

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1. Introduction

Reactive distillation (RD), a process in which chemical reaction and thermodynamic separation are integrated in a single apparatus, represents one of the best-known examples of process intensification (Harmsen, 2007; Schoenmakers and Beßling, 2003). It allows for higher reactant conversion, product selectivity and energy savings with favourable investment and operating costs. Despite these advantages, RD has several constraints, such as complex design, difficult scale-up and advanced process control (Sundmacher and Kienle, 2003). Nevertheless, the concept of RD has been industrially applied for certain types of reactions, the most important being esterifications (Agreda et al., 1990), trans-esterifications (Steinigeweg and Gmehling, 2004) and etherifications (Sundmacher and Hoffmann, 1996), in which the maximum reactant conversion is limited by chemical equilibrium.

A reactive distillation column used for esterification reactions can be coupled with a liquid–liquid phase separator at the top of the column. There are two different reasons to use a liquid–liquid phase separator; these in turn depend upon whether the ester is a low- or high-boiling component in the reaction system. In the first case, the

separator can ensure higher product purities by separating the organic ester from the aqueous phase. For example, Kloeker et al. (2003) reported the successful use of a liquid–liquid phase separator in the synthesis of ethyl acetate to further purify the distillate stream. The same reaction system was studied by Lai et al. (2008). They investigated different start-up procedures experimentally in the production of high purity ethyl acetate and demonstrated that initial holdup compositions in the column and in the liquid–liquid separator play an important role for an efficient start-up. Similar results were reported by Forner et al. (2008) in the synthesis of *n*-propyl acetate. In the second case, the ester is a high-boiling component and leaves the RD column with the bottom stream. Here, a liquid–liquid phase split of the distillate stream enables the discharge of the aqueous phase and recycling of the organic phase, the latter mainly consisting of unconverted reactants, back to the RD column. In this context, Schmitt et al. (2004) presented a comprehensive study on the synthesis of *n*-hexyl acetate by reactive distillation coupled with a liquid–liquid phase separator.

In the case of *n*-propyl propionate synthesis, Altman et al. (2010) already performed RD experiments in a pilot-scale column. However, the authors noted several operational difficulties, especially in the context of the liquid–liquid phase separator employed. A data reconciliation test to identify the stationary operating conditions confirmed these difficulties. They reported that nearly 40% of their performed experiments failed the data-reconciliation

test. The reconciliation test is passed if all the measured values can be adjusted within the limits of the experimental error in such a way that physical constraints are satisfied (i.e., mass and component balances and reaction rates). Based on these results, we decided to install a new liquid–liquid phase separator in the pilot plant (Altman et al., 2010) to improve the phase separation and to provide more reliable experimental results for n-propyl propionate synthesis. Especially, the crucial need for experimentally determined column profiles has recently been emphasised by Taylor (2006). The purpose of our article is to fill this gap and to provide reliable experimental temperature and concentration profiles for n-propyl propionate synthesis in a reactive distillation column coupled with a liquid–liquid phase separator. Furthermore, a nonequilibrium-stage model is used to predict the experimental results.

Table 1
Nomenclature and pure component boiling points at $p=1$ atm (NIST, 2009).

Component	IUPAC name	Formula	T_b (K)
POH	1-propanol	C_3H_7OH	370.4
Water	Water	H_2O	373.2
ProPro	Propanoic acid propyl ester	$C_2H_5COOC_3H_7$	396.1
ProAc	Propanoic acid	C_2H_5COOH	414.1

Table 2
Azeotropic data at $p=1$ atm (Gmehling et al., 2004).

Type	Molar fraction (mol/mol)				T_b (K)
	x_{POH}	x_{water}	x_{ProPro}	x_{ProAc}	
Heterogeneous	0.350	0.520	0.130	–	323.4
Homogeneous	0.431	0.569	–	–	390.9
Heterogeneous	–	0.650	0.350	–	363.2
Homogeneous	–	0.950	–	0.050	373.1

The comparison between experimental and simulated column profiles is discussed in detail.

2. Reaction system

The chemical system investigated in this study is the heterogeneously catalysed synthesis of n-propyl propionate (ProPro). It is formed by the reversible, acid-catalysed, liquid-phase esterification of 1-propanol (POH) and propionic acid (ProAc) with water as an additional by-product according to Eq. (1):

$$\text{(1)}$$
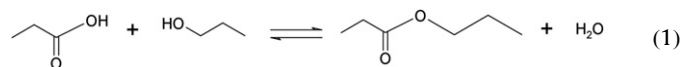
Based on the work of Buchaly et al. (2007), the strongly acidic ion-exchange resin Amberlyst 46™ from Rohm and Haas was selected as a heterogeneous acid catalyst for n-propyl propionate synthesis. Because Amberlyst 46™ exhibits active centres only at its surface, undesired side reactions, such as the dehydration of 1-propanol, leading to the corresponding alkenes, and the self-condensation of 1-propanol, leading to the corresponding ether, can be suppressed (Duarte et al., 2006).

The nomenclature and the boiling points of the pure components at atmospheric pressure are listed in Table 1. The chemical system shows a complex thermodynamic phase behaviour, which is illustrated by the azeotropic data presented in Table 2. In total, two homogeneous and two heterogeneous azeotropes exist. The low-boiler of the system is the ternary, heterogeneous azeotrope consisting of water, 1-propanol and n-propyl propionate.

A large miscibility gap exists in the subsystem consisting of water, 1-propanol and n-propyl propionate. The relevant ternary phase diagram at atmospheric pressure is shown in Fig. 1. Additionally, the distillate compositions of all the experiments performed herein (Exp1–Exp7) are illustrated in Fig. 1. Because the miscibility gap increases with lower temperatures, the distillate
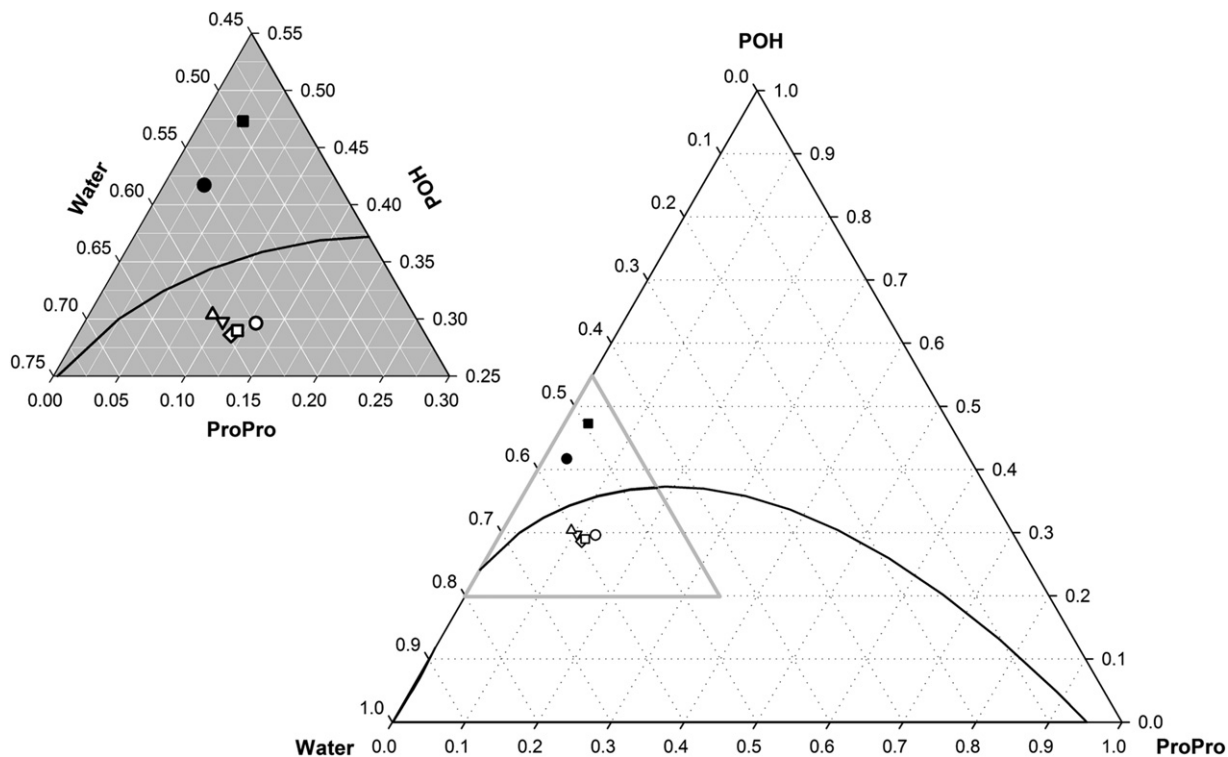

Fig. 1. Ternary phase diagram for the subsystem comprising water, 1-propanol (POH) and n-propyl propionate (ProPro). The miscibility gap is bound by a binodal curve (—), which was calculated at a temperature of 293 K. The distillate stream compositions of all the experiments are indicated as follows: ■ Exp1, ● Exp2, ▽ Exp3, □ Exp4, ○ Exp5, △ Exp6 and ◇ Exp7.