Synthesis of n-propyl propionate in a pilot-plant reactive distillation column: Experimental study and simulation

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ABSTRACT

The catalytic esterification of n-propyl propionate using propionic acid and n-propyl alcohol as reactants via a conventional pilot plant reactive distillation column was carried out. The strongly acidic ion-exchange resin Amberlyst46™ was used as the solid acid catalyst. The influence of the reflux ratio (from 2.0 to 2.5), the molar feed ratio (from 2.0 to 2.5), and total feed (from 3.0 to 4.0 kg/h) on the purity and conversion of the species and on the composition and temperature profiles along the column was analyzed. A 23 experimental design with six actual and two simulated experiments was carried out. With the experimental conditions obtained from the simulation results, the experiments showed that a reflux ratio of 2.0, a molar feed ratio of 2.0 and a total feed of 4 kg/h, yielded the largest propyl propionate production (1.60 kg/h). The simulated experiments were carried out using a non-equilibrium model implemented into the simulation environment Aspen Custom Modeler™

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1. Introduction

The structure of chemical process plants may be significantly improved by the integration of chemical reaction and species separation in one multifunctional process unit. This concept, named “reactive separation” may lead to a reduction in equipment and plant size, increased energy efficiency and process safety, waste products reduction, and lower capital investment. Reactive distillation (RD) is one of the most important technologies of this type. In RD the reactants are transformed to products with simultaneous separation of products and recirculation of unreacted reactants to the column. It is also possible to overcome chemical equilibrium limitations, achieve high selectivity towards desired products, integrate the heat of reaction for in situ distillation, and perform difficult separations like binary or ternary azeotropes of multicomponent mixtures with near boiling point (Almeida-Rivera, Swinkels, & Grievink, 2004; Keil, 2007; Sundmacher & Kienle, 2002).

On the other side, the second half of the 20th century has seen a growing awareness of the ecological impact of chemicals production. It is now widely recognized that the development of inherently clean synthesis methodologies can offer process safety, waste products reduction, and lower capital investment. This search for “green chemistry” is a huge challenge for fundamental research in chemical engineering and their neighboring areas (Anastas & Warner, 1998). One important aspect of research towards more sustainable processes for chemical synthesis is the scientific evaluation of potential replacements for volatile organic compounds (VOCs) as solvents.

In this way, the ester n-propyl propionate (ProPro) is an important chemical which is used as an alternative solvent in coatings and printing inks; it is also used in perfumes, fragrances, and as a flavoring in food industry. This solvent is not listed as Hazardous Air Pollutant by the United States Environmental Protection Agency, demonstrating reduced ozone formation potential. The ProPro is not expected to contribute to lower level smog formation, is readily biodegradable, which suggests the chemical will be rapidly and completely removed from water and soil environments, including biological wastewater treatment plants. It can be produced by the esterification of propionic acid (ProAc) with n-propanol (POH),...
producing water as a side product. Since the reaction is reversible and limited by equilibrium, RD may improve the process in comparison with the conventional process, where ProPro is produced in a batch or continuous reactor in a homogeneous or heterogeneous system catalyzed by acids followed by several distillation columns (Duarte, Buchaly, Kreis, & Loureiro, 2006).

However, for the efficient application of RD concepts reliable kinetic and thermodynamic data for the specific reaction system are needed. Thus, the thermodynamic behavior of the VLE and VLLE for an esterification system could be considered through the solution models to represent the non ideality in the liquid phase, while the vapor phase non ideality considering the dimensioning of organic acids may be described by an appropriate equation of state. For the esterification reaction rate equations a pseudo-homogeneous model or a Langmuir–Hinshelwood–Hougen–Watson (LHHW) approach in terms of activities may be used.

From the experimental point of view, it well known that esterification and etherification reactions are promoted by acid catalysis. Particularly, heterogeneous catalysis has the advantage that the solid acid catalyst does not contaminate the process stream. In the last decade, acid ion-exchange resins (Amberlyst 15, 35, and 39) were widely used in several systems (Brehelin et al., 2007; Lee, Chiu, & Lin, 2002; Liu & Tan, 2001; Steinigeweg & Gmeining, 2003; Xu & Chuang, 1997). In the case of esterification reactions, acid ion-exchange resins are good catalyst, but they fail on the thermodynamic stability test (Kiss, Dimian, & Rothenberg, 2006); another important disadvantage of this type of resin is its high affinity for water causing deceleration of the reaction rate. Recently, new acid catalysts have been developed for esterification reactions in order to avoid catalyst deactivation and showing more stability at relatively high temperatures, i.e. zeolite BEA (Schildhauer, Hoek1, Kapteijn, & Moulijn, 2009) and the noncorrosive Bemsted acidic liquid ions (BAlS) (Tao et al., 2011). In summary, still one of the main problems for the application of reactive distillation is to find a suitable solid catalysts which should be active, selective, and stable under the process conditions.

From the modeling and simulation side, commonly the numerical simulation of a RDC is carried out using the equilibrium stage (EQ), or the non-equilibrium stage (NEQ). The simulations are used to identify the role of important operating and design factors, i.e. reflux ratio, reactant ratio, distillate/ feed (D/F) ratio, height of the reactive section, etc. In this context, a considerable number of papers have been published that contain well-documented information on reactive distillation modeling and simulations (Damartzis & Seferlis, 2010; Dimian, Bildea, Omota, & Kiss, 2009; Katariya, Kamath, Moudgalya, & Mahajani, 2008; Lee, Yen, Chien, & Huang, 2009; Tang, Chen, Huang, & Yu, 2005). Svandová, Labovský, Markos, and Jelemský (2009) compared the prediction of the EQ and NEQ models during a RDC safety analysis focusing on the identification of hazardous situations operability problems (HAZOP). The predictive magnitudes of the deviations were different considering the EQ or the NEQ model. Góra and Hoffmann (2001), Hoffmann, Noeres, and Góra (2004) and Pelkonen, Görak, Ohiilischläger, and Kalemsmann (2001) validated the NEQ model with the experimental composition profiles along the column height in a structured-packed distillation column with several non ideal systems. Klöcker et al. (2003, 2004) studied the synthesis of ethyl and hexyl acetates by RD; the experiments were performed using both laboratory scale and semi-industrial scale columns; the simulation results were obtained using the NEQ approach.

Particularly, for the synthesis of the ester n-propyl-propionate, Buchaly, Kreis, and Görak (2007) reported a hybrid process that combines a RD column with a membrane module in the distillate stream in order to selectively remove the produced water without any entrainer. These authors studied the modeling and simulation of the process, and discussed the key issues for the theoretical description of the RD column using a NEQ approach. Altman et al. (2010) studied the synthesis of ProPro in a RDC by coupling a decanter in the distillate stream, in order to recover the products and the unreacted starting materials. The decanter can separate the distillate into two major currents without using any other agents. The aqueous phase is removed from the process and part of the organic phase is used as reflux to the column. The authors noted several operational difficulties, especially in the context of the liquid–liquid phase separator employed; nearly 40% of the experiments failed the data-reconciliation test and thus were not used for model validation.

Therefore, the objective of the present work is to provide reliable experimental data for the ProPro synthesis in a conventional RDC avoiding the operational difficulties found by using a top liquid–liquid decanter. An experimental design based on a factorial arrangement of three variables: the reflux ratio (RR), the molar feed ratio of both reactants (FR), and the reactants total feed (TF) is used to identify the role of these important operating variables on the steady-state reactants conversion, the production rate, and the purity of the products at the top and bottom streams. The predictive capacity of the NEQ model is used to develop the experimental design and to simulate two experiments to complete it. The experimental composition and temperature profiles along the RD column serve to further validate the NEQ model.

2. The reactive system

2.1. Esterification reaction of n-propyl propionate

The heterogeneous catalyzed synthesis of n-propyl propionate (ProPro) is formed by the reversible liquid-phase esterification of n-propanol (POH) and propionic acid (ProAC) with water as an additional product according to following reaction scheme.

In the temperature range of 90–130 °C, several side reactions like self-condensation and dehydration are possible under acidic conditions (see Fig. 1). The self-condensation of the alcohol leads to ethers, whereas the dehydration leads to olefins. In the n-propyl propionate synthesis, these side reactions create di-n-propyl ether and propene, respectively. The di-n-propyl ether is formed from two propanol molecules. Propene can be formed by dehydration of 1-propanol as well as by decomposition of n-propyl propionate. Furthermore, the ether can also be synthesized by an addition reaction if propene is present in the reacting mixture in sufficient amounts (Blagov et al., 2006). In the present work, it is assumed that the RDC operating conditions and the catalyst selected lead to consider that such side reactions do not occur.

2.2. The solid acid catalyst

For the reversible esterification reaction on a solid acid catalyst (SAC), the hydrophobicity of the catalyst surface and the density of the acid sites are highly important, since these aspects determine the catalyst activity and selectivity. The strongly acidic
ion-exchange resin Amberlyst46™ from Rohm and Haas (Lundquist, 1995) was used as the solid acid catalyst in the reactive distillation column. Such ion-exchange resin has been tailor-designed as a heterogeneous acid catalyst for esterification reactions where the undesired side reactions, such as the dehydration of 1-propanol and the self-condensation of 1-propanol, can be suppressed (Blagov et al., 2006). According to the catalyst experiments with Amberlyst46™ carried out by Duarte et al. (2006) and Buchaly et al. (2007), the undesired product reactions were not detected and it was found that this catalyst shows thermal stability up to 120 °C. Also, numerous types of solid catalysts have been proposed for the esterification of different fatty acids with several alcohols: sulfated carbon-based catalysts, heteropoly compounds and mixed metal oxides as niobic acid, sulfated zirconia, sulfated titania, and sulfated tin oxide (Kiss, Omota, Dimian, & Rothenberg, 2006; Kiss, Dimian et al., 2006; Kiss, Dimian, & Rothenberg, 2008; Jitendra, Darbha, & Ratnasamy, 2010; Pietre, Almeida, Landers, Vinhas, & Luna, 2010). Specifically, it has been shown that, at the reactive distillation conditions the metal oxides are even more thermally resistant that the Amberlyst resin. Despite the advances in the catalyst materials, still these catalyst have not been tested in an industrial scale.

2.3. The reaction rate

For the synthesis of n-propyl propionate a pseudo-homogeneous approach of the reaction rates is formulated in terms of activities.

\[
r_i = m_{\text{cat, dry}} \cdot v_i \cdot c_{\text{act}} \left( k_i(T) a_{\text{ProAc}} \cdot a_{\text{POH}} - k_i(T) a_{\text{ProAc}} \cdot a_{\text{H2O}} \right),
\]

\[i = 1, \ldots, n_c\]  

The equilibrium constant \(K_{\text{eq}}\) and the rate constant \(k_1\) [mol s\(^{-1}\) eq H\(^+\)] temperature dependence are modeled via the Arrhenius approach and both parameters have been already reported by Buchaly et al. (2007):

\[
k_1(T) = 7.381 \times 10^7 \exp \left( \frac{-59,630}{RT} \right)
\]

\[
K_{\text{eq}}(T) = 6.263 \exp \left( \frac{4519}{RT} \right)
\]

2.4. The thermodynamic model

The ProPro esterification reactive system is characterized by strong liquid phase non-idealities with several azeotropes, i.e. two homogeneous azeotropes in the binary systems POH/water and ProAc/water, and two heterogeneous azeotropes, one in the binary ProPro/water and a minimum temperature azeotrope in the ternary system water/POH/ProPro. The complete set of binary interaction parameters for the VLE calculation, the azotropic data and the thermodynamic information of the reactive system is given by Buchaly et al. (2007). Table 1 shows the pure component boiling points and the azotropic data.

The UNIQUAC activity coefficient model was applied to evaluate the liquid phase non-idealities and due to the presence of ProAc, the Hayden–O’Connell equation of state is used to account for the non-idealities of the vapor phase incorporating its dimerization.

An analysis of the pure component boiling temperatures shows that for any distillation column a concentrated mixture of the most volatile compounds, POH and water in this case, would be present at the top of the column and at the bottom a concentrated mixture of ProPro and ProAc would exist. However, in order to obtain an appropriate RDC design, careful attention should be paid to the azeotropic compositions. In this way, it is helpful to use the residue

![Figure 1: Reaction path for the synthesis n-propyl propionate.](image)

Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>(T_b) (°C)</th>
<th>Molar weight (kg/kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POH</td>
<td>97.2</td>
<td>60.10</td>
</tr>
<tr>
<td>Water</td>
<td>100</td>
<td>18.02</td>
</tr>
<tr>
<td>ProPro</td>
<td>122.6</td>
<td>116.16</td>
</tr>
<tr>
<td>ProAc</td>
<td>140.9</td>
<td>74.08</td>
</tr>
<tr>
<td>Azeotrope</td>
<td></td>
<td></td>
</tr>
<tr>
<td>POH–ProPro–H2O</td>
<td>86.2</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>POH–H2O</td>
<td>87.6</td>
<td>Homogeneous</td>
</tr>
<tr>
<td>ProPro–H2O</td>
<td>95.0</td>
<td>Heterogeneous</td>
</tr>
<tr>
<td>ProAc–H2O</td>
<td>99.9</td>
<td>Heterogeneous</td>
</tr>
</tbody>
</table>

Table 1: Boiling points of pure components and azeotropic data at 1 atm (Buchaly et al., 2007).
The POH/water systems that span a large part of the phase behavior triangle. Also, it can be noted that the ternary heterogeneous POH/water/ProPro azeotrope is an unstable node in the system with the lowest boiling point \( T_B = 85.82 ^\circ C \) and that the homogeneous binary POH/water azeotrope with a boiling point \( T_B = 87.64 ^\circ C \) is a saddle point. Finally, a distillation boundary due to the three existing azeotropes divides the phase triangle into two distillation regions, labeled as I and II. For the purpose of obtaining high purity ProPro the column should be operated in distillation region I. Notice also that the distillate stream will always contain small amounts of ProPro, depending on the operating conditions of the RDC. To obtain the highest product purity, almost total acid conversion should occur, and thus an excess of alcohol must be used. Also, special attention should be paid to the reactants initial molar ratio in order to prevent two liquid phase formation; as it may be observed in Fig. 2, when most of the acid and POH are consumed in the reactive section, the reactive system would end up close to the binary and ternary azeotropes at the top of the column. In summary, an excess of \( n \)-propanol must be used to ensure a homogeneous distillate stream.

3. Materials and methods

3.1. Reactive distillation process description

The experiments were carried out in a 51 mm ID glass reactive distillation column operating at atmospheric pressure. The column had three packed sections, one condenser, one reboiler, and auxiliary equipment as shown in Fig. 3. The enriching section consisted of two modules of Sulzer\textsuperscript{TM} BX packing with a 2.4 m total height. The reactive section was placed below the enriching section and

![Fig. 2. Residual curve map (RCM) for ternary system (POH–water–ProPro) at atmosphere pressure.](image)

![Fig. 3. Reactive distillation process scheme for propyl-propionate synthesis. Controller (C), indicator (I), mass flow (F), composition (Q), temperature (T), weight (W). The RDC is located at the Chair of Fluid Separation Processes of the Technical University of Dortmund (TUD).](image)

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had two modules of the Katapak SP-11 packing with a 2.2 m total height, where the catalyst was immobilized in wire-gauze bags; the catalyst mass was 0.205 kg of dry catalyst/m3 packing. The stripping section was located below the reactive section and had two modules of the SulzerTM BX packing, with 1.0 m total height. A liquid distributor was installed below each packing module, where the liquid flowing from the module above was collected and redistributed to the packing module below. Two different distributor types with one or six drip points ensured a good liquid distribution on the first packing module of each section. Adiabatic process conditions were achieved by using a heating jacket and a proper insulation of mineral wool.

The column had two feeds. Feed A supplied ProAc at 88.2 °C to the upper part of the reactive section, while feed B delivered POH at 83.9 °C. 1.2 m below feed A. A water-cooled total condenser was used at top of the column to collect a vapor mixture of POH and H2O with a small amount of ProPro. The distillate and the reflux were withdrawn from a holding drum. The ProPro product was obtained at the RDC bottom, and consisted of a mixture of ProPro, ProAc, and POH.

In order to store and monitor all the process variables and to control the operating variables during the experiments, a process control system (MSR-Manager/Labvision, HiTec Zang, Herogenrath, Germany) was installed. The mass flow rates of the feeds, the bottom and the distillate streams were determined with Sartorius MC1 industrial balances via the time derivative of the mass change (in Fig. 3 the balances are indicated as WIC for feeds and W1 for distillate and bottom products). For these accurate balances, the standard deviation of ±0.01 kg/h was used to close the overall mass balance in the data reconciliation.

3.2. Analytical methods

3.2.1. Chemicals

The n-propanol, propionic acid, and n-propyl propionate used for the gas chromatography calibration were supplied by Sigma–Aldrich with a purity of 0.99 g/g and used without further treatment. Acetonitrile (used as internal standard) was obtained from Merck with the same quality. Since the reactive distillation experiments required large amount of chemicals, the n-propanol and propionic acid were delivered in industrial bins by BASF AG, Ludwigshafen. The purity of these chemicals was always determined before each experiment. Normal boiling points and molar weight of the species involved in the RD experiments are given in Table 1.

3.2.2. Gas chromatography

The streams compositions were analyzed off-line using a Shimadzu gas chromatograph (GC-14A) equipped with a flame ionization detector (FID), an autosampler AOC 20i, and a FS-Innopen 1000 capillary column (25 m × 0.25 mm) with a film thickness of 0.27 μm. Helium was used as carrier gas with a gas velocity of 27 cm/s. The split-ratio was set to 1:145; the temperature program for a fast and sharp separation was 333 K for 4.5 min, heat rate of 30 K min−1 to 453 K, and then holding at this temperature for 2.4 min. The method of the internal standard (acetonitrile) was applied to obtain the mass fractions directly from the evaluation of the chromatogram based on single component calibration curves. Each sample was analyzed three times and its average determined. The water composition can only be indirectly calculated by means of the summation conditions. For this reason the Karl–Fischer titration was used to determine the water content.

3.2.3. Karl–Fischer titration

This method is useful for the quantitative determination of the water content in a mixture. The titration was carried out with a titrator from Mettler Toledo DL 31, which is based on a volumetric titration method (reagents: methanol, Hydranal Composite 5, Hydranal-Water Standard 100). The water mass fraction in the sample can be calculated afterwards with high accuracy from the quantity of Hydranal reagent used.

3.3. Reactive distillation experiments

The experimental design was based on a 23 factorial arrangement of the three predominant operational variables: the reflux ratio (RR), the POH/ProAc molar feed ratio (FR), and mass total feed of reagents (TF). The experimental design based on RR, FR, and TF may be represented as the vertexes of a cube, as illustrated in Fig. 4. The experiments were carried out with RR values of 2.0 and 2.5; the FR values of 2.0 and 2.5, and TF of 3.0 and 4.0 kg/h. As mentioned before, an excess of 1-propanol over ProAc was used in order to promote the acid conversion and to prevent the formation of a second liquid phase.

The operating conditions of the reactive distillation column were chosen according with the following considerations: (a) the RR from 2.0 to 2.5 were chosen according to simulation results reported by Buchaly et al. (2007) and Altman et al. (2010), where it was studied the influence of the operation conditions (TF = 3.0–4.0 kg/h, RR from 2.0 to 4.0, and heat duty from 400 to 1200 W) on product purity and acid conversion; (b) the molar FR of reagents between 2.0 and 2.5 was chosen to avoid the two phases in the distillate stream, values less than 2.0 could lead to the formation of two phases (Altman et al., 2010); and (c) the TF from 3.0 to 4.0 kg/h, to observe its effect on conversion and product purity, as well as how long the column takes to reach the stable state. Moreover, under these operating conditions it is expected that the composition and flow rate of distillate could be further processed to remove water and re-circulate the POH to increase the conversion of reactants and product purity (Buchaly et al., 2007).

The actual experiments carried out were E1–E6, while EA and EB cube vertexes were determined by simulation. Since the model was used to establish the experimental design and predict two experiments (EA and EB) by simulation to cover all the cube vertexes, the model should be validated with reliable experimental data to assure predictability under different operating conditions. Thus, the process data was reconciled at steady state. Two requirements had to be fulfilled to determine the existence of a stable state in the RDC: (a) minor change over time in the monitored temperature profile of the column (±0.25 °C), and (b) closed mass balance of the column streams (maximum ±4% in weight). Three temperature and composition profiles were measured to assure the RDC stable state.
Table 2
Summary of mass flow rates and flow ratios of the reactive distillation column experiments.

<table>
<thead>
<tr>
<th>Feed ProAc (kg/h)</th>
<th>Feed POH (kg/h)</th>
<th>TF (kg/h)</th>
<th>FR (mol)</th>
<th>RR (mass)</th>
<th>Distill. (kg/h)</th>
<th>Bottom (kg/h)</th>
<th>Reflux (kg/h)</th>
<th>D/F (mass)</th>
<th>ProPro at bottoms (kg/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>1.32</td>
<td>2.68</td>
<td>4.00</td>
<td>2.50</td>
<td>2.59</td>
<td>1.71</td>
<td>2.27</td>
<td>4.44</td>
<td>0.43</td>
</tr>
<tr>
<td>E2</td>
<td>1.50</td>
<td>2.50</td>
<td>4.00</td>
<td>2.05</td>
<td>2.00</td>
<td>1.90</td>
<td>2.13</td>
<td>3.79</td>
<td>0.47</td>
</tr>
<tr>
<td>E3</td>
<td>0.99</td>
<td>2.01</td>
<td>3.00</td>
<td>2.50</td>
<td>2.00</td>
<td>1.67</td>
<td>1.31</td>
<td>3.33</td>
<td>0.55</td>
</tr>
<tr>
<td>E4</td>
<td>1.14</td>
<td>1.86</td>
<td>3.00</td>
<td>2.02</td>
<td>2.50</td>
<td>1.47</td>
<td>1.51</td>
<td>3.69</td>
<td>0.49</td>
</tr>
<tr>
<td>E5</td>
<td>1.32</td>
<td>2.68</td>
<td>4.00</td>
<td>2.50</td>
<td>2.02</td>
<td>2.03</td>
<td>1.95</td>
<td>4.09</td>
<td>0.51</td>
</tr>
<tr>
<td>E6</td>
<td>1.53</td>
<td>2.47</td>
<td>4.00</td>
<td>1.94</td>
<td>2.45</td>
<td>1.34</td>
<td>2.64</td>
<td>3.29</td>
<td>0.34</td>
</tr>
<tr>
<td>EA</td>
<td>1.14</td>
<td>1.86</td>
<td>3.00</td>
<td>2.00</td>
<td>2.00</td>
<td>1.51</td>
<td>1.49</td>
<td>3.34</td>
<td>0.50</td>
</tr>
<tr>
<td>EB</td>
<td>0.99</td>
<td>2.01</td>
<td>3.00</td>
<td>2.50</td>
<td>2.50</td>
<td>1.34</td>
<td>1.66</td>
<td>3.34</td>
<td>0.45</td>
</tr>
</tbody>
</table>

4. Mathematical modeling

Reliable process models are decisive for RDC design, as they may reduce the process development time, the operation cost, and scale-up to industrial applications. The NEQ model for RDC with peripherals, such as reboiler and condenser used here, was developed at the Chair of Fluid Separation Processes of the Technical University of Dortmund, Germany, and it was implemented into the simulation environment Aspen Custom Modeler™. Also, the model was linked to the Aspen physical properties database.

The specific correlations and parameters employed in the NEQ model for the determination of mass transfer coefficients, specific contact area, liquid hold-up, and pressure drop for the reactive packing Sulzer Katapak™-SP 11 used in the reactive section of the column were developed under the European research project INSERT—Integrating Separation and Reaction Technologies (Brunazzi, 2006). The complete set of equations and the model description can be found elsewhere (Górak and Hoffmann, 2001; Hoffmann et al., 2004; Klöker, Kenig, Hoffmann, Kreis, & Górak, 2005).

4. Results and discussion

This section presents the experimental results obtained in the RDC, as well as those resulting from the simulations with the NEQ model. A summary of the mass flow rates, and flow ratios is given in Table 2. Notice that the operating variable distillate-to-feed mass ratio, (DF)mass is used as an equivalent to the reboiler heat duty. This is due to the fact that thermo-oil was used as heating medium, which itself is heated up electrically in an external heat exchanger. Since the overall efficiency of the system, ηdesign splinted into ηelectricity→oil and ηoil→column was unknown, the adjusted heat input at the evaporator was not equivalent to the heat input in the column.

The distillate and bottom product compositions, as well as reagents conversions for all experiments are given in Table 3. The ProPro composition and reactions obtained by simulation with the model are also included in this table. The status obtained at the end of run experiments is stated in the last column, where it may be noted that experiment E6 was not completely reconciled since there were some problems to account for the distillate stream during the experiment. This behavior is observed on Fig. 5 at plot’s enrichment section, where the simulation and experimental data do not match. For the rest of experiments the status was correct. It may be observed that the simulated composition and conversions are in very good agreement with the experimental data.

4.1. Influence of the reflux ratio

Tables 2 and 3, and Fig. 5 show the effect of changing the RR from 2.0 (experiment E2) to 2.5 (experiment E6), at FR = 2.0 and TF = 4 kg/h. The empty symbols represent the experimental data...
for E2, and the dashed line the corresponding simulation, while full symbols represent the experimental data for E6, and the solid line the corresponding simulation. It may be seen that the chemical species present in the distillate were POH, ProPro and water, while at the column bottom the species were POH, ProPro, ProAc, and small amounts of water. The change in RR from 2.0 to 2.5 caused the distillate stream to change from 1.90 to 1.34 kg/h and the bottom stream from 2.13 to 2.64 kg/h. There were important changes in the distillate composition: POH was diluted from 0.574 to 0.389, ProPro changed slightly from 0.041 to 0.052, and water was concentrated from 0.386 to 0.558. On the other hand, in the bottom stream POH was concentrated from 0.132 to 0.383, ProPro was diluted from 0.643 to 0.461, and ProAc was diluted from 0.225 to 0.156. It was also observed for both experiments that the species compositions were almost similar in the reactive section, which led to conclude that the conversion for both experiments was about the same (see Table 3). All these figures clearly indicate that the change in RR from 2 to 2.5 leads to lower ProPro purity and POH stripping out at the bottom stream, although there is no influence in ProPro mass production at the bottom stream (−1.60 kg/h); the opposite effect is observed at the distillate stream, the POH is stripped out from the reactive section at RR = 2.0 causing the water concentration to diminish in the condensate stream. Moreover, at a RR = 2.5 the amount of water that is returned to the column is larger than at RR = 2.0 causing higher water concentrations in the enrichment section.

Fig. 6 shows the effect of changing the reflux ratio (RR) from 2.0 (experiment E2) to 2.5 (experiment E4), at FR of 2.0; in contrast with experiments E2 and E6, now the TF value is 3 kg/h. The full symbols and solid line represent the experimental data and simulation for E4, respectively, and the dashed line represents the simulated experiment E2. It can be observed that in the bottom stream in both experiments there were only two species present (ProPro and ProAc), this indicates that ProPro purity at bottom stream was larger at TF = 3.0 kg/h than at TF = 4.0 kg/h, and that the mixture would be easier to separate in a second unit. On the other hand, the ProAc conversion in this case was larger than at TF = 4.0 kg/h (see Table 3). Hanika, Kolena, and Smejkal (1999) reported similar results in their study of the synthesis of butyl acetate by RD, when they decreased the feed rate.

Simulated EA vertex showed that the bottom stream composition contains more ProPro and less ProAc (0.790 and 0.209, respectively) in comparison with experiment E4 (0.740 and 0.242, respectively); the production of ProAc at the bottom stream for experiment EA and E4 were almost equal, 1.27 and 1.25 kg/h, respectively. On the other hand, ProAc conversion was higher in experiment EA (see Table 3). This behavior followed a similar trend as that obtained at TF = 4 kg/h, i.e. when the RR was changed from 2 to 2.5, there was a decrement in the ProPro purity and in the POH stripping out of the bottom stream, although there was no influence in ProPro mass production rate at the bottom stream. Moreover, the chemical species behavior in the enrichment zone in both experiments was practically the same. This is because the (DF)mass Values (Table 2) and the water mass flows in both experiments were almost equal (1.319 kg/h in EA and 1.343 kg/h in E4), which means that the heat supplied in the reboiler was almost the same; this was confirmed by the theoretical values of heat calculated with the NEQ model (heat duty was 1291 W for the EA experiment and 1359 W for E4).

Similar results have been obtained by Bucbaly et al. (2007); they reported the influence of the reboiler heat duty (900–1500 W) on the ProPro purity and ProAc conversion at different reflux ratios (1.5–3.0) for the hybrid separation process. At reflux ratio of 1.5 and approximated of 1300 W of heat duty (before reaching the flooding point) the purity of ProPro reported was 0.83, and the ProAc conversion reached was 86%. In our case, the maximum ProPro purity and ProAc conversion were obtained at RR = 2.0 and TF = 3 kg/h, with values of 0.79 and 80.50%, respectively, although in experiment E4 the heat supplied was higher. Altman et al. (2010) reported that at a given RR an increase in the heat duty caused an increase of the acid conversion up to a maximum value. With a further increase of the heat duty, the acid conversion decreased slightly. This is a typical behavior for RD processes because one of the reactants (in this case POH) is stripped off the reactive section at high heat duties.

4.2. Influence of the feed ratio

It is convenient to recall that all experiments were carried out with an excess of POH, in order to promote a larger conversion of ProAc; the POH excess ensured that the reaction was driven in the direction of ProPro (Duarte et al., 2006; Bucbaly et al., 2007). Here we analyze the influence of the feed ratio (FR) of reactants on the column behavior. The FR working range was from 2.0 to 2.5. It may be recalled that experiment E2 yielded a better ProPro bottoms composition than experiment E6. Therefore, for experiments with TF = 4 kg/h, the comparison is made between experiments E2 (FR = 2.05) and E5 (FR = 2.5); meanwhile for experiment with TF = 3 kg/h the comparison will be between experiments EA (FR = 2.0) and E3 (FR = 2.5).

Fig. 7 shows the composition profiles of experiments E2 and E5 at RR = 2.0 and TF = 4 kg/h. It may be observed that the mole fraction of POH in distillate and bottom streams for experiment E5 was larger than in experiment E2. At the bottom stream, the mole fraction of ProPro in E2 was larger than in E5 (0.643 and 0.573, respectively) and also was the ProPro mass production rate (1.60 and 1.37 kg/h, respectively). It may be seen that FR had an impact in the conversion of POH, while the ProAc conversion was almost the same (see Table 3). The POH conversion was lower in E5; as a consequence, the distillate water mole fraction was lower in E5 than in E2.

On the other hand, it may be observed that the molar feed ratio (FR) had a considerable influence on the distillate-to-feed mass ratio, (DF)mass, which affected the POH conversion and composition of both the distillate and bottom streams. Table 2 shows that
Fig. 7. Liquid phase composition profile for experiments where feed ratios (FR) are different. E2 (FR = 2.0, empty symbols and dashed line) and E5 (FR = 2.5, full symbols and solid line). In both experiments the following conditions were fixed at: RR = 2.0; TF = 4.0 kg/h.

The value of (DF)max was larger in experiment E5 (0.51) than in experiment E2 (0.47), meaning that the heat supply and thus the POH distillate mass flow in experiment E5 (1.29 kg/h) were greater with respect to experiment E2 (1.09 kg/h). This is because POH is the lightest component of the mixture with a high evaporation rate, which causes the POH in the reactive zone to be stripped out to the column top (the POH amount was higher in experiment E5); as a consequence, the distillate water mole fraction was lower in E5 than in E2. On the other hand, greater amounts of POH were fed in experiment E5, the excess of which that was not converted or stripped out, accumulated in the bottom of the column, thus lowering ProPro purity.

Fig. 8 shows the composition profiles of experiments EA (FR = 2.0) and experiment E3 (FR = 2.5), at a RR = 2.0 and TF = 3 kg/h. The full symbols and solid lines represent the experimental data and simulation for E3 respectively, and the dashed lines represents the experiment EA simulation.

It may be seen that at TF = 3 kg/h, the mole fraction of ProPro at bottom stream in EA was slightly higher than in E3 (0.790 and 0.771, respectively), as well as the ProPro production rate (1.27 and 1.11 kg/h, respectively). The mole fraction of POH in distillate stream in E3 was higher than in EA, while the mole fraction of POH in bottom stream was almost zero in experiment EA; the conversion of POH in experiment E3 (33.22%) was lower than experiment EA (39.80%). The ProAc conversion was slightly higher in experiment E3 (81.99%) than in experiment EA (80.90%); moreover, the mass flow of ProAc in EA (1.14 kg/h) was larger than in E3 (0.99 kg/h). On the other hand, the value of (DF)max was larger in experiment E3 (0.55) than experiment E2 (0.50).

Hence, at TF = 3 kg/h the column behavior followed the same trends as experiments at TF = 4 kg/h; as POH was the lightest of the mixture present in the reactive zone, it was stripped out to the column top; as a consequence, the distillate water mole fraction was lower in E3 than in EA. On the other side, because experiment E3 was fed with a larger amount of POH, the excess that was not converted or stripped out was accumulated in the bottom of the column and thus diminished the ProPro composition.

Therefore, the column behavior is better at feed ratio of 2.0; it means that if POH molar flow is increased more than twice that of the ProAc, the conversion of POH will decrease because the excess of POH will be stripped-out from reactive zone. At FR = 2, there were a larger ProPro production rate and a higher ProPro concentration at the bottom stream. The D/F ratio impact on conversion was strong: at high D/F ratio, the POH concentration in the rectifying section increased, and thus decreased the POH concentration in the reactive zone and the conversion. Physically, a high D/F ratio implies small bottom product flow; when mass flow of ProAc is higher (experiment EA), it concentrates at the bottom because it is the heaviest component. Similar results were reported by Kolodziej et al. (2004) in their study of synthesis of TAME by RD with a structured catalytic packing.

4.3. Influence of the total feed

In the previous discussions, it was found that for a total feed of 4 kg/h, experiment E2 yielded better results than E5 and E6. For a total feed of 3 kg/h, the simulated experiment EA had better results than E3 and E4 experiments. Therefore, the effect of total feed will be discussed by comparing EA and E2 experiments, at a reflux ratio of 2.0 and feed ratio of 2.0. Fig. 9 shows the composition profiles of EA and E2 experiments.

It may be seen that the mole fractions at the enrichment section and the distillate product were similar for both experiments (see also Table 3), but below the ProAc feed point the composition profiles of POH and ProPro are substantially different. In experiment E2, the bottom stream consisted of a ternary mixture; while in experiment EA the bottom stream was a binary mixture. ProAc conversion was larger in EA than in E2 because of a larger liquid residence time in the reactive zone. Total feed seems to influence productivity and purity of the products. While ProPro throughput was larger at TF = 4.0 kg/h (1.6 kg/h vs 1.27 kg/h), the bottom stream was richer in ProPro at TF = 3 kg/h (0.790 vs 0.643).

In the previous sections differences were observed between experiments at TF = 4 kg/h and TF = 3.0 kg/h; for example, on comparing the effect of RR between (E2 and E6) to (EA and E4), and the effect of FR between (E2 and E5) to (EA and E3), there were pronounced differences. This is because the conversion of the reactants decreases with increasing column load, as the residence time in the
reactive section diminishes at the higher TF. Further, the amount of catalyst is held constant in the column for both experiments while the flow rates are increased. Consequently, the comparison of TF between EA and E2 experiments showed that POH conversion drops from 39.80% to 37.16% while ProAc conversion decreases from 80.90% to 73.44%. Therefore, the ProPro purity decreases significantly from 79.0% to 64.6%.

On the other hand, the total feed also influenced the experimentation time, as shown in Figs. 10 and 11. In these figures we show the behavior of the reflux, distillate, bottom, and condensate mass flows as a function of time for E3 and E5 experiments (TF = 3 kg/h and TF = 4 kg/h, respectively). The plots have three zones: from the beginning until the vertical line (a), corresponding to the start-up period; from line (a) to line (b) which is the transition period towards a stable steady state of the column. In this operation period the compositions of the input and output streams to evaluate the overall mass balance (data reconciliation) were determined; when the error percentage was less than or equal to ±4%, it was considered the beginning of a stable steady state of the column; the period of line (b) to line (c) corresponds to the stable steady state column operation. During this period three composition and temperature profiles were determined to ensure the column steady state operation. Finally, after line (c) the column shut-down is depicted. By comparing the RDC running times, it can be observed that at TF of 3 kg/h the experiment took 13 h to reach the stable steady state, while at TF of 4 kg/h the experiment took 11 h. Therefore, a greater ProPro purity requires more column operation time, which should be considered to evaluate the operation cost with respect to profits.

4.4. The temperature profiles

Fig. 12 shows the behavior of the vapor phase temperature profiles for E2, E5 and E6 experiments, all of which were carried out at TF = 4.0 kg/h. The solid lines represent the simulation of the experiments carried out with NEQ model. The distillate and bottom streams temperature of each experiment is closely related to the composition vector and mass flows. It may be seen that the vapor

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The esterification of propionic acid with 1-propanol to produce n-propyl propionate was studied in a conventional reactive distillation column using the surface-sulfonated catalyst Amberlyst™ 46 immobilized in the structured catalytic packing Katapak™-SP11. The influence of operating parameters, such as: reflux ratio, molar ratio feed of 1-propanol to propionic acid, distillate-to-feed ratio, and the total feed of reactants was analyzed from the results of six actual and two simulated experiments. The experiments covered a broad range of these important parameters. These results may be of help for the analysis and design of n-propyl propionate RDC with more complex configurations. In contrast to Altman et al. (2010), most of the experimental data obtained in the present work were reconciled and the liquid–liquid phase separation operational difficulties at the column top were avoided.

The results show that when the reflux ratio is increased (from 2 to 2.5), the n-propanol concentration increases and the purity of the propyl propionate product at the column bottom diminishes, although the ester mass production rate is unaffected.

On the other hand, the use lower molar feed ratio (2.0) yields greater n-propyl propionate purity at bottom and higher mass production rate. With respect to D/F ratio when this operation parameter decreases the purity of the desired component ProPro is reduced. Also, at higher total feed values the conversion of the reactants decreases. Finally, it was shown that FR and D/F ratio have a considerable impact in the conversion of POH, but not in the conversion of ProAc. The comparatively low sensitivity of the propionic acid conversion to feed ratio variations is caused by the excess of 1-propanol.

The analysis of the experimental and simulated results showed that, in a conventional RDC, at a reflux ratio of 2.0, total feed of 4 kg/h, and a molar feed ratio of 2.0, the n-propyl propionate production rate was highest as was the propyl alcohol recovery. However, at the same conditions and total feed of 3.0 kg/h, the bottoms n-propyl propionate purity was highest and only a binary mixture was formed, although the time to achieve a stable steady state is larger than at total feed of 4 kg/h. Finally, it was shown that through an appropriate thermodynamic analysis and using a NEQ model of the conventional reactive distillation column for the experimental design, similar propionic acid conversions and n-propyl propionate production rate were achieved without a liquid–liquid decanter at the top of the column as proposed by Altman et al. (2010). The NEQ model was further validated with the new experimental data obtained in this work, as the model was capable of properly predicting the experimental data under a variety of conditions with minor deviations.

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References


