Isoamyl propionate production by reactive distillation

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ABSTRACT

In this work, the production of isoamyl propionate by esterification of propionic acid with isoamyl alcohol, via continuous reactive distillation was studied. Conceptual design of the reactive distillation system was conceived from the construction of conventional and reactive residue curves maps at 101.32 kPa. The process was modeled using an equilibrium-stage approach and simulated with Aspen Plus® 7.3. Experimental evaluation of the process was carried out in a 8 cm ID × 6 m tall pilot-scale glass reactive-column, using Amberlyst® 70 ion exchange resin as catalyst contained in a KATAPAK® SP-11 structured packing. Reasonably good agreement between experimental and simulation results was observed. For a single equimolar feed, propionic acid conversions over 96% and isoamyl propionate purities over 98 wt.% in the bottoms product were obtained. Results obtained in this work can be used for scale-up studies of an industrial reactive distillation operation as a possible alternative to upgrade isoamyl alcohol from the bio-ethanol industry.

1. Introduction

Bioethanol industry and its by-products have been growing rapidly in the last years as bio-based alternatives for fossil derived fuels and chemicals. One of these potentially valuable by-products is fusel oil, which is obtained as side stream in the ethanol refining process. Fusel oil is primarily composed by isoamyl alcohol and active amyl alcohol isomers, in ranges between 41 and 85 vol% [1]. In general, its composition depends on the fermentation substrate, yeast types and the conditions used during the fermentation process, as well as the proper characteristics of the subsequent ethanol refining processes. Usually, fusel oil is used as fuel in steam boilers or is mixed with fuel ethanol in production plants [2]. However, the fusel oil can be used as raw material for obtaining isoamyl alcohol, which in turn, can be used for the synthesis of value-added chemical derivatives improving the overall economics of the bioethanol industry. Among the variety of derivatives, isoamyl esters can be used as ingredient in fragrances, and flavors, and also as a plasticizer and industrial solvents [3]. Specifically, isoamyl propionate stands out as a high value added component because is used in pineapple and apricot-like flavor formulations. Thus, this work studies the feasibility of using a reactive distillation process for the synthesis of isoamyl propionate, as possible high value-added derivative of the isoamyl alcohol obtained from fusel oil.

One route to produce isoamyl propionate is by the direct esterification of isoamyl alcohol with propionic acid in the presence of an acid catalyst (Eq. (1)). This reaction is limited by chemical equilibrium, and product separation from the reactive media must be considered for obtaining attractive yields.

$$\text{Propionic acid (AC)} + \text{isoAmyl alcohol (OH)} \overset{H+}{\rightleftharpoons}$$
$$\times \text{ isoAmyl Propionate (EST)} + \text{Water} \qquad (1)$$
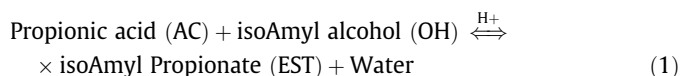
Research on fusel oil and propionic acid derived esters has been active in recent years because of the need for green solvents and biobased chemicals. Küçük and Ceylan [4] carried out fusel oil direct esterification with various carboxylic acids, including propionic acid, for the synthesis of mixed esters with possible direct use in the fragrances market. Yu et al. [5] presented a review on isoamyl propionate production using different catalytic materials such as modified molecular sieves, acid activated carbons and some ion exchange resins. Similarly, Erdem and Cebe [6] reported data for the esterification kinetics of propionic acid with n-amyl alcohol under the catalytic action of Amberlyst®-15, Amberlite®-IR120, and Dowex®-50W ion exchange resins. By using Amberlyst®-46 as catalyst, Kotora et al. [7] provided information on the implementation of propyl propionate synthesis in a reactive distillation system. In the propanol–propionic acid esterification system, Ameri et al. [8] reported the use of membranes as an option for the selective removal of water from the reaction media to improve conversion and to obtain a suitable purity of propyl

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Nomenclature

A	parameter in Table 1
a	activity
B	binary energy parameter in NRTL activity model in Table 3
C	binary energy parameter in NRTL activity model in Table 3
E_a	activation energy (kJ/kmol)
e	euler number
G	binary energy parameter in NRTL model in Table 3
ΔH_{Rxn}	reaction enthalpy (kJ/kmol)
K_{eq}	chemical equilibrium constant
k_o	specific reaction constant (kmol-i/kg-cat s)
R_g	ideal gas constant (kJ/kmol K)
r	reaction rate (kmol/kg-cat s)
ΔS_{Rxn}	reaction entropy (kJ/kmol K)
T	temperature (K)

w	mass fraction in liquid
X	conversion
x	mole fraction in liquid
y	mole fraction in vapor

Greek letters

α	binary parameter for NRTL activity model in Table 3
τ	temperature dependent parameter of NRTL activity model in Table 3
υ	stoichiometric coefficient

Subscripts

i, j	component
cat.	catalyst
$-a$	activity based

propionate as principal product. Ajaikumar and Pandurangan [9] also recognized the importance of water removal and tested some silicon and aluminum based molecular sieves for the esterification of various alcohols and acids, including the isoamyl alcohol and propionic acid.

Taking into account the final use of isoamyl propionate as fragrance and flavoring ingredients in consumer goods, and the need for greener products, some works have also reported the enzymatic action of lipase over various substrates in a direct synthesis option [10–15].

Even though not covering propionates but acetates production, a couple of recent publications have proposed to use reactive distillation technology for the direct esterification of fusel oil using Amberlyst 15 as catalyst [16,17]. In that work, esterification and transesterification reactions were considered, and separation schemes for the complex mixture of ester are discussed.

Finally, in a publication of the authors [18], a kinetics model for isoamyl propionate synthesis using Amberlyst®-70 as catalyst was evaluated. Because this catalyst can tolerate higher temperatures (up to 463 K) than most ion exchange resins, it is suitable to use within a reactive distillation system operating above atmospheric pressure. Under these conditions, boiling temperatures for distilling the reactive mixture are in an appropriate range for fasts reaction rates, making reactive distillation (RD) an attractive processing alternative. Although in these same conditions undesirable side-reaction products such as isoamyl ether can be formed, the absence of this reaction was verified by mole balance in the reaction kinetic studies [18]. Etherification reaction of long chain

alcohols require higher temperatures and higher temperatures [19,20].

In this context, this work describes the conceptual design, modeling and experimental evaluation of a continuous RD column for the synthesis of isoamyl propionate. The RD operation was conceived by the construction of conventional and chemical equilibrium residue curves maps (RCM) at 101.32 kPa, as the two extreme cases for process analysis. Taking into account the RCM results, an equilibrium-stage reactive distillation model was built in Aspen Plus® 7.3 [21], and used to establish the best operating conditions for high reactants conversions and products purities. The experimental validation of the model was performed in a glass pilot scale reactive distillation column operating continuously at atmospheric pressure.

2. Materials and methods

2.1. Materials

Propionic acid (>99.5 wt.%, Merck KGaA), isoamyl alcohol (>99.5 wt.%, J.T. Baker), isoamyl propionate (>99.0 wt.%, SAFC KGaA), and water (HPLC grade, J.T. Baker) were used as standards for calibration of the GC method. The n-hexanol (>99.0 wt.%, SAFC KGaA) and acetonitrile (HPLC grade, EMD) were used as internal standard and solvent for chromatographic analyses, respectively. Amberlyst®-70 ion exchange resin purchased from the Dow Chemical Co. was used as the catalyst in the reactive

Table 1
Parameters for an extended Antoine expression for the calculation of pure-component vapor pressures.

Component Parameter	Isoamyl alcohol[a]	Propionic acid[b]	Isoamyl propionate[b]	Water[a]
$\ln(P_V/Pa) = A_1 + \frac{A_2}{(T/K)} + A_3 \ln(T/K) + A_4(T/K)^{A_5}$				
A_1	117.0700	71.8183	61.5293	73.6490
A_2	−10743.0000	−8019.1195	−7376.4659	−7258.2000
A_3	−13.1650	−6.8021	−5.4343	−7.3037
A_4	1.1670E−17	1.2980E−17	−6.2010E−17	4.1700E−06
A_5	6.00	6.00	2.00	2.00
Minimum temperature (K)	155.95	368.83	381.77	273.16
Maximum temperature (K)	577.20	437.16	461.35	647.10

[a] Taken from Aspen Plus® 7.3 data bases.
[b] Taken from Leyva et al. [25].