Chemical Engineering and Processing 102 (2016) 27–36

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

journal homepage: www.elsevier.com/locate/cep

Membrane reactors for isoamyl acetate production

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ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form 14 November 2015
Accepted 14 January 2016
Available online 16 January 2016

Keywords:
Membrane reactor
Energy integration
Economic evaluation
Isoamyl acetate

ABSTRACT

In our previous paper (*Chem. Eng. Process.*, 76 (2014) 70), a comprehensive study of conventional and hybrid membrane processes for isoamyl acetate synthesis, using experimentally certified models, was presented. Here, as an extension of that previous work, the performance of membrane reactors was analyzed, using the same thermodynamic, kinetic, and membrane transport models. Two different configurations were investigated by simulation using ASPEN Plus® together with a homemade Excel®-MatLab® interface for membrane reactor modules simulation. The goal was to gain more insight into the isoamyl acetate synthesis using membrane reactors, as a prelude to a detailed experimental research. The analysis procedure includes both the optimization of membrane reactor performance and the minimization of process energy consumption, including the energetic integration using the pinch point methodology. Total annualized costs were estimated and compared with the conventional and hybrid membrane schemes.

1. Introduction

One of the mostly used esters in food industry, due to its characteristic banana flavor, is isoamyl acetate ($C_7H_{14}O_2$, E). It can be obtained from the liquid phase esterification of acetic acid ($C_2H_4O_2$, HAc) with isoamyl alcohol ($C_5H_{12}O$, ROH). This reaction, in which water (H_2O, W) is obtained as a byproduct, presents serious complications including limited chemical equilibrium and challenging product purification [1]. The combination of reaction and pervaporation in a single unit (membrane reactor) allows to shift the conversion for equilibrium limited reactions by removing, selectively, one (or more) products. This type of application is an example of relatively new use of membrane technology, which traditionally had been applied as a tail process solution, and not as an essential part of it. Wynn [2] referred to some examples in this regard. Additionally, membrane technologies are attractive since process efficiency is not limited by the phase equilibrium. Thus, both production costs, due to higher conversion, and efforts in the separation stage can be reduced (this last one is usually energyvore in conventional technologies).

Membrane reactors have been already used to perform many carboxylic acid–alcohol reactions, such as acetic acid with methanol [3], ethanol [4], isopropanol [5], and *n*-butanol [6]. The reaction-pervaporation scheme can be implemented in various configurations [7,8]. Among them, one can distinguish between the systems where the membrane and the reactor are one unit (integrated scheme) and those where pervaporation modules and the reactor are arranged in series (hybrid scheme). In our previous work [9], four process alternatives for isoamyl acetate production were evaluated. It included the transition from conventional to hybrid membrane processes. It was shown that hybrid membrane processes allows obtaining the specified product purity with lower energy duties and economical compromises than the conventional ones.

In this paper, our previous analysis [9] is extended for the integrated membrane reactor schemes. They were studied by simulation using ASPEN Plus® together with a homemade Excel®-MatLab® interface for membrane reactor modules simulation. The design procedure includes the optimization of membrane reactor performance, the minimization of distillation column energy

Abbreviations: ACC, annualized capital cost; HAc, acetic acid; E, isoamyl acetate; gas, gaseous; hom, homogeneous; het, heterogeneous; liq, liquid; MR1, membrane reactor scheme 1; MR2, membrane reactor scheme 2; NRTL, non random two liquid; RCM, residue curve map; ROH, isoamyl alcohol; TAC, total annualized cost; W, water.

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http://dx.doi.org/10.1016/j.cep.2016.01.008
0255-2701/

Nomenclature

Symbols

a	NRTL parameter
a_c	Liquid phase activity
b	NRTL parameter
B	Exponential interaction parameter
c	NRTL parameter
C	Concentration
C_p	Heat capacity
D	Diffusion coefficient
D_0	Pre-exponential factor for diffusion coefficient
F	Molar flow
i	Fractional interest rate
k	Rate constant
K_{eq}	Chemical equilibrium constant
n	Number of years of the project
N	Membrane flux
r	Reaction rate
R	Recovery fraction
T	Temperature
W	Catalyst loading
x	Molar fraction
X	Fractional conversion
z	Membrane thickness

Superscripts

perm	Permeate side
ret	Retentate side

Subscripts

cond	Column condenser
exch	Membrane reactor heaters
i	Component
in	Inlet
j	Component
liq	Liquid phase
m	Membrane
p	Product
preh	Column preheater
tot	Homogeneous + heterogeneous
vap	Vapor phase

Greek letters

α	Specific area
Δ	Difference between inlet and outlet property
λ	Vaporization heat
σ	Stoichiometric coefficient reaction

consumption, and the energetic integration using the pinch point methodology [10]. Total annualized costs (TAC) are also estimated and compared with those of the conventional and hybrid schemes.

2. Isoamyl acetate production framework [9]

Conventional processes for isoamyl acetate production imply the use of one of the reactants in excess and/or the selective recovery of one of the reaction products. Nevertheless, the separation step presents serious complications. According to our previous study [1], the acetic acid–isoamyl alcohol–isoamyl acetate–water mixture presents three binary azeotropes and one ternary azeotrope. From the structure of the residue curve maps for the quaternary mixture, we had concluded that two conventional production schemes imply the use of one reactor and two distillation columns and decanters [1,9]. Thus, if the isoamyl alcohol will be used in excess, after removing the acetate from the products stream by distillation, the remaining alcohol–water mixture will be split in two liquid phases. This mixture can be separated using a distillation column and a decanter. On the other hand, if the acid will be used in excess, the stream of products leaving the reactor will be fed to a first distillation column, where high purity acetate can be obtained at the bottom. A quaternary two-phase mixture is also obtained at the top stream (since part of the alcohol remains after the reaction step and isoamyl acetate is not totally recovered from the bottom), which is fed to a second distillation column and a decanter. In both cases, unreacted reagents are recycled and mixed with the fresh feed.

The use of a membrane process implies two conceptual aspects related to water removal from the reactive mixture: (i) higher overall conversion by equilibrium shift, and (ii) separation of the resulting isoamyl acetate–isoamyl alcohol–acetic acid mixture. In fact, there is not liquid–liquid phase splitting for this ternary mixture, neither homogeneous nor heterogeneous azeotropes are present. Thus, contrary to the conventional processes, in a membrane reactor process a second distillation column and a decanter are no longer needed. Consequently, a sequence of a membrane reactor followed by a distillation column and a recycle loop, to reprocess the unconverted reactants, will be the base for the study proposed in this work.

3. Models for simulation

The esterification under study is a very complex system. In consequence, for this thermodynamically non-ideal mixture, activities are needed in the description of phase behavior and transport (pervaporation) across the membrane. It is also well known that expressing reaction rates in terms of concentrations results in reaction rate constants which often depends on concentrations. Using activities not only corrects this problem, but also provides a unified approach in describing both reaction kinetics and thermodynamic equilibrium [11]. Therefore, we defined previously specific activity, transport, and kinetics models for this system. A brief description of them is presented in the following subsections.

3.1. Thermodynamic model

The NRTL model [12] was used to account for non-ideal phase behavior for the quaternary system. Table 1 lists the NRTL model parameters as previously proposed by us [1]. The considered vapor phase non-ideality is the dimerization of acetic acid, as described by the Hayden–O'Connell model [13].

3.2. Membrane permeation model

In our previous experimental study [14], the permeation model for a silica membrane was defined. Considering the Maxwell–Stefan approach, one can see that the flux through the membrane can be expressed by the following equation:

$$N_i = -c_i \frac{D_{im}}{z} \ln\left(\frac{a_{ci,gas}}{a_{ci,liq}}\right) \quad (1)$$

where D_{im}/z parameters were calculated according to Eq. (2), which corresponding values are presented in Table 2.

$$\frac{D_{im}}{z} = D'_{ij0} \exp\left(\sum B_i a_{ci}\right) \quad (2)$$