Separation of tartronic and glyceric acids by simulated moving bed chromatography

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ABSTRACT

The SMB unit developed by the Laboratory of Separation and Reaction Engineering (FlexSMB-LSRE®) was used to perform tartronic acid (TTA) and glyceric acid (GCA) separation and to validate the mathematical model in order to determine the optimum operating parameters of an industrial unit. The purity of the raffinate and extract streams in the experiments performed were 80% and 100%, respectively. The TTA and GCA productivities were 79 and 115 kg per liter of adsorbent per day, respectively and only 0.50 cubic meters of desorbent were required per kilogram of products. Under the optimum operating conditions, which were determined through an extensive simulation study based on the mathematical model developed to predict the performance of a real SMB unit, it was possible to achieve a productivity of 86 kg of TTA and 176 kg of GCA per cubic meter of adsorbent per day (considering the typical commercial purity value of 97% for both compounds) with an eluent consumption of 0.30 cubic meters per kilogram of products.

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1. Introduction

During the last twenty years, biofuels have been considered as one of the best alternatives to replace fossil fuels, to limit greenhouse gas emissions and to diminish the overall pollution in the world. Among the proposed biofuels is the biodiesel [1–3], obtained from oil seeds or animal fat. Biodiesel is generally produced through the so called transesterification reaction in which an alcohol and esters (usually, with long chain hydrocarbons) are obtained from glycerides and another alcohol [4,5]. As usual, when triglycerides are used as reactants, besides the biodiesel, bioglycerol is produced. The increase of the biodiesel production around the world has caused a great surplus of bioglycerol [6]. Besides the environment concerns for this industrial waste, the price for both crude glycerol and refined glycerol has fallen by a factor of 10 [7–9]. Thus, researchers are seeking for new and eco-friendly applications for this low cost raw material.

Many works are being developed aiming to produce added value compounds from bioglycerol [10–23], as tartronic (TTA) and glyceric (GCA) acid. GCA has three functional groups and a great potential as chemical intermediate. It also has anticholesterol activity [24], esters of glyceric acid have antitrypsin activity [25] and it has demonstrated to be able to accelerate ethanol and acetaldehyde oxidation in mice [26]. TTA is also very important for the synthesis of fine chemicals and new polymers in fine chemical industry, where it is used as reactant in catalytic oxidation to produce mesoxalic acid which is a potentially valuable chelating agent also used as intermediate compound [27]. These works show that both TTA and GCA are promising products, however they are not produced industrially and their current price is around hundreds of euros per gram [28]. In order to overcome this issue, these compounds can be obtained from bioglycerol catalytic oxidation [13] with a yield of 50% of GCA and 25% of TTA. It is important to highlight that the production of these acids has been focus of the scientific community at least during the last 20 years [6], however as far as our knowledge goes no publications can be found in the open literature regarding their continuous purification. This is significant, because their production process uses expensive catalysts and the yields usually are not higher than 50%. Hence, this research will have a direct impact in the pharmaceuticals and fine chemical industries producing these organic acids but its impact can also be extended to biodiesel producers at the same time. Nevertheless, the

Nomenclature

List of Symbols

$\bar{C}$	Average concentration in extract and raffinate stream (kg m^{-3})
C	Liquid-phase concentration (kg m^{-3})
C_{ik}	Compound i fluid-phase concentration in column k of the SMB (kg m^{-3})
Dax	Axial dispersion coefficient (m^2 s^{-1})
DC	Desorbent consumption (m$^3_{desorbent}$ kg$_{product}^{-1}$)
d_c	Column diameter (m)
K_{GCA}	Adsorption constant of glyceric acid ($-$)
K_{TTA}	Adsorption constant of tartronic acid ($-$)
k_h	Intraparticle mass transfer coefficient (m s^{-1})
L	Bed length (m)
N_c	Number of columns ($-$)
PU_X	Extract purity (%)
PU_R	Raffinate purity (%)
PR_R	Raffinate productivity (kg m$^3_{ads}^{-1}$ day)
PR_X	Extract productivity (kg m$^3_{ads}^{-1}$ day)
Pe	Peclet number
Q_j	Volumetric flow rate in section j (with $j = I, II, III, IV$) (m^3 s^{-1})
Q_D	Volumetric flow rate of the desorbent (m^3 s^{-1})
Q_{Rec}	Volumetric flow rate of the recycle (m^3 s^{-1})
Q_X	Volumetric flow rate of the extract (m^3 s^{-1})
Q_F	Volumetric flow rate of the feed (m^3 s^{-1})
Q_R	Volumetric flow rate of the raffinate (m^3 s^{-1})
Q_S	Volumetric flow rate of the solid (m^3 s^{-1})
$q^*_{i,k}$	Solid phase concentration in equilibrium with liquid phase concentration (kg m^{-3})
$\bar{q}_{i,k}$	Average solid phase concentration of specie i in column k of the SMB unit (kg m^{-3})
t	Time variable (s)
t_{switch}	Switching time (s)
u^*_k	Interstitial fluid velocity in the kth SMB column (m s^{-1})
V_c	Column volume (m^3)
z	Axial coordinate (m)

Greek letters

ε	Bed porosity
β	Safety factor applied on section velocity ratios ($>$1)
γ_j	Ratio between liquid and solid interstitial velocities in section j of the SMB

similar chemical structure between them represents an important challenge for the implementation of a separation step.

In this sense, separation processes based on adsorption principles, which generally achieve high purities and high efficiencies, even for difficult purifications can be an alternative. One of these approaches includes performing a continuous liquid chromatographic separation in fixed or moving beds. These moving beds, in turn, can be classified as True Moving Bed (TMB) when there is an actual flow of the solid phase inside the column or as Simulated Moving Bed (SMB) when there is an apparent flow of the solid phase. In a previous work [29], a reliable methodology to determine the adsorption isotherms of these organic acids in a cation ion exchange resins based on poly styrene–divinylbenzene (PS-DVB) was reported. These data were used to evaluate the separation by the True Moving Bed technology using Dowex® 50wx-2 as stationary phase.

Both moving bed approaches allow the separation of the compounds when the solid phase moves in the opposite direction of

Table 1
Constraints of Ruthven and Ching for the net fluxes of the species to be separated.

Constraints of Ruthven and Ching, 1989	Regions
$\gamma_I > \frac{1-\varepsilon}{\varepsilon} \frac{q_{A,I}}{C_{A,I}}$;	Regeneration
$\frac{1-\varepsilon}{\varepsilon} \frac{q_{B,II}}{C_{B,II}} < \gamma_{II} < \frac{1-\varepsilon}{\varepsilon} \frac{q_{A,II}}{C_{A,II}}$;	Separation
$\frac{1-\varepsilon}{\varepsilon} \frac{q_{B,III}}{C_{B,III}} < \gamma_{III} < \frac{1-\varepsilon}{\varepsilon} \frac{q_{A,III}}{C_{A,III}}$;	Separation
$\gamma_{IV} < \frac{1-\varepsilon}{\varepsilon} \frac{q_{B,IV}}{C_{B,IV}}$;	Regeneration

the liquid phase, which maximizes the mass transfer driving force, providing a better efficiency than in the batch operation or in the traditional fixed bed techniques. Furthermore, moving beds are also more advantageous due to the continuous operation and the efficient use of the required desorbent. However, the SMB shows additional advantages [30–38] as the ability to overcome the major issues of the TMB, namely, equipment abrasion, mechanical erosion of adsorbent and difficulties in maintaining plug flow for the solid.

Conventionally, an SMB has two inlet streams, feed and eluent, and two outlet streams, extract and raffinate. These streams divide the unit into four sections, each of which responsible for a different function. In Section I the more-retained compound must move with the liquid to be collected in the extract port and to regenerate the solid, while in Section IV the less-retained compound must move with the solid to be collected in the raffinate and to regenerate the liquid. In Sections II and III the more-retained compound must move with the solid to be collected in the extract port and the less-retained one must move with the liquid in the direction of the raffinate collecting point.

From Fig. 1, it is possible to see that in Section I both species must move upward, in Sections II and III the less-retained compound must move upward, while the more-retained component must move downward, and finally in Section IV the net flux of both species has to go downward. In the usual operating mode of an SMB, the inlet and outlet streams move forward to the next column in the direction of the fluid flow at regular time intervals, called the switching time, t_{switch}, and this is how the movement of the solid is simulated. One cycle is completed when the initial location of injection/collection of all the streams is obtained. It can be concluded that, during one cycle, the same column assumes different roles in the separation process depending on the section it is located in.

In order, to achieve a simple and reliable methodology to determine the initial operating condition, usually, the fluid and solid velocities in each section are expressed using a dimensionless parameter, (see Table 1):

$$\gamma_j = \frac{1-\varepsilon}{\varepsilon} \left(\frac{Q_j}{Q_s} \right) \tag{1}$$

In this context, the present work aimed the design of a continuous chromatographic process for the purification of glyceric acid and tartronic acid, based on the SMB technology.

2. Experimental

2.1. Chemicals and materials

DL-glyceric acid (20% in Water, ca. 2 mol/L) was purchased from Tokyo Chemical Industry – TCI (Japan) and tartronic acid >97.0% from Sigma-Aldrich (Germany). Sulfuric acid 95–97% PA from Chem-Lab (Belgium) was used to prepare the eluent solution and for preparation of the studied mixtures. All the water used in this work was deionized, filtered and degassed in our laboratories.