Chemical Engineering Journal 331 (2018) 644–651

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Construction of an asynchronous three-zone simulated-moving-bed chromatography and its application for the separation of vanillin and syringaldehyde

Chuanyi Yao[a,b,*], Jinliang Chen[a], Yinghua Lu[a,b], Shaokun Tang[c], Enguo Fan[d,*]

[a] Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
[b] The Key Lab for Synthetic Biotechnology of Xiamen City, Xiamen University, Xiamen 361005, China
[c] Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering & Technology, Tianjin University, Tianjin, 300072, China
[d] Department of Microbiology and Parasitology, Institute of Basic Medical Sciences, Chinese Academy of Medical Sciences/School of Basic Medicine, Peking Union Medical College, Beijing, China

ARTICLE INFO

Keywords:
Asynchronous
Simulated moving bed
Three-zone
Vanillin
Syringaldehyde

ABSTRACT

In the present work, an asynchronous 3-zone simulated moving bed (SMB) has been constructed for the first time and used for the separation of vanillin and syringaldehyde with C18 as stationary phase and ethanol/water = 35/65 (v/v) as mobile phase at 25 °C. The linear model was first used to describe the isotherms of the two compounds. The Henry constants were determined by frontal analysis and the diffusion coefficient as well as mass transfer coefficient were estimated by empirical equations. Then, the triangle theory was used to design the operation conditions of the SMB system with configuration of [1, 1, 2] and followed the operation conditions were further optimized with consideration of the diffusion and mass transfer resistance. The obtained maximum feed flow rate was 0.081 mL min^{-1}, and the experimental purities of extract and raffinate were 97.2% and 96.9%, respectively. Finally, the constructed asynchronous SMB was used to separate vanillin and syringaldehyde with the same apparatus. The optimized average configuration was [1, 1.43, 1.57]. Through an asynchronous switching of inlet and outlet ports, the flow rate of feed was increased to 0.117 mL min^{-1}, which is 44% higher than that of standard SMB. The experimental purities of the extract and raffinate were both higher than 97%. These results clearly demonstrate that the asynchronous 3-zone SMB can give an amiable performance and holds a high potential of wide applications.

1. Introduction

To produce vanillin (4-hydroxy-3-methoxybenzaldehyde), an important compound that is widely used in food, pharmaceuticals and cosmetic industries, either extraction from natural source vanilla beans or chemical synthesis using guaiacol as starting material are usually used [1–3]. Although natural vanillin extracted from vanilla beans is 200 times expensive in price than synthetic vanillin [4], the extraction from natural sources may suffer from low abundance and environmental limitations of natural materials thus it is not economic. While industrial vanillin is mainly produced from guaiacol, the synthetic route is not environmentally friendly. Therefore, the production of vanillin from renewable sources, such as lignin, becomes a promising alternative [5–9]. Unfortunately, the production process of vanillin from lignin, especially from hardwood lignin, produces a complex mixture [9,10]. Although methods such as adsorption using macroporous polymeric resin has been used to recover vanillin from the mixture, the recovered products usually contain vanillin and its structurally similar analogue, syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) [11–13]. Therefore an effective and specific separation of these two compounds is still one of the most important obstacles for vanillin production from lignin [10].

Currently, it is a big challenge to separate vanillin and syringaldehyde using standard methods such as rectification and crystallization from aqueous solutions due to the highly similar chemical structure and close physical properties of both compounds (Fig. 1). Tarabanko et al. [10] performed the separation using extraction with salting out agent and crystallization in water-ammonia media. It was found that the former gives a lower separation factor of 2–2.5 and the latter results in a higher separation factor of ca. 50. Unfortunately the

* Corresponding authors at: Department of Chemical and Biochemical Engineering, College of Chemistry and Chemical Engineering, Xiamen University, 361005 Xiamen, Fujian, China (C. Yao). Department of Microbiology and Parasitology, Institute of Basic Medical Sciences, Chinese Academy of Medical Sciences/School of Basic Medicine, Peking Union Medical College, Beijing, China (E. Fan).
E-mail addresses: cyao@xmu.edu.cn (C. Yao), enguo.fan@ibms.pumc.edu.cn (E. Fan).

http://dx.doi.org/10.1016/j.cej.2017.09.006
Received 14 June 2017; Received in revised form 30 August 2017; Accepted 1 September 2017
Available online 06 September 2017
1385-8947/

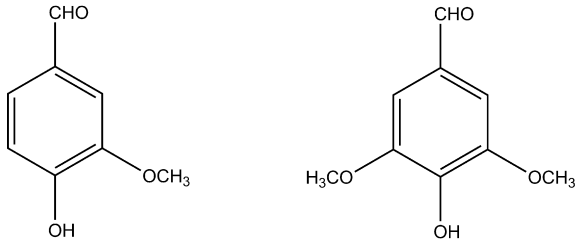

Fig. 1. Chemical structure of vanillin and syringaldehyde.

use of aqueous ammonia and sulphuric acid leads to a significant environmental impact. Therefore, other new separation methods are still highly desired and have to be developed. At this point, one method called simulated moving bed (SMB) chromatography, which is widely used to separate chemically similar compounds in petroleum [14,15], sugar [16,17], and pharmaceutical industry [18–21], should be considered. Thus it is the aim of the present work to pursue the separation of vanillin and syringaldehyde using SMB for the first time.

SMB chromatography is a continuous chromatographic separation technique, in which the inlet and outlet ports are shifted in the direction of liquid phase flow to simulate the counter moving of solid phase [22–26]. Therefore SMB provides a favorable stability of stationary phase because the real movement of solid phase is avoided. Moreover, a further development through non-synchronous shifting of inlet and outlet ports led to the formation of a so-called “Varicol” technology [27], in which a flexible allocation of columns is implemented to different zones. Unlike all the columns in SMB has to be switched simultaneously, this simple non-synchronous shift development makes Varicol to have a better efficiency than SMB, especially when the total number of columns is for example under 8 [27–36].

Both conventional SMB and Varicol comprise 4 zones that form a close-loop, in which a pump (usually located between Zone IV and Zone I) is required to enable the recycling of solvent. However, this usually leads to the formation of a large dead volume. By omitting Zone IV and operating the system as an open-loop 3-zone SMB, the recycling pump can be omitted and the dead volume can be significantly decreased. Another advantage of this open-loop 3-zone SMB is that the contamination of the extract by the light component can be avoided more easily as the solvent is not recycled. Thus, despite a larger solvent consumption is required in 3-zone SMB compared with 4-zone SMB, the 3-zone SMB is preferred usually when a cheaper solvent is used [37], such as in bioseparation processes where inexpensive aqueous solution is commonly applied to maintain the activity of biomacromolecules. To the best of our knowledge, however, an asynchronous 3-zone SMB has not been reported in literature.

In the present work, we not only constructed an asynchronous 3-zone SMB system, but also optimized the system for the separation of vanillin and syringaldehyde. The obtained theoretical conclusions were further verified by experimental results. This is, to the best of our knowledge, for the first time that a 3-zone SMB is used and optimized for the separation of the two aldehydes.

2. Theory

2.1. Column model

The linear driving force model that is believed to be a compromise between efficiency and accuracy [38] was used here to describe the dynamic behavior of vanillin and syringaldehyde in the columns. In this model, the axial dispersion flow in the bulk fluid phase is considered and the mass transfer rate between the fluid phase and solid phase is assumed to be proportional to the difference of equilibrium concentration and actual concentration in the solid phase. The model equations are presented as follows [26].

$$\frac{\partial c_i}{\partial t} + v\frac{\partial c_i}{\partial x} + \frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_i}{\partial t} = D_a\frac{\partial^2 c_i}{\partial x^2} \tag{1}$$

$$\frac{\partial q_i}{\partial t} = k_{e,i}(q_i^* - q_i) \tag{2}$$

where the subscript i stands for components to be separated, $i = A$ (vanillin) or B (syringaldehyde), c (g L^{-1}) and q (g L^{-1}) are the concentrations in the bulk fluid phase and in the solid phase, respectively. q^* (g L^{-1}) is the concentration in solid phase that is an equilibrium with c, v (cm min^{-1}) is the interstitial velocity of liquid phase, ε_b is the external porosity of the packed column, D_a (cm^2 min^{-1}) is the apparent dispersion coefficient, k_e (min^{-1}) is the overall mass transfer coefficient, t (min) is time and x (cm) is the axial distance. Eq. (1) can be obtained by the infinitesimal mass balance. The change of concentration with time (first term $\frac{\partial c_i}{\partial t}$ in Eq. (1)) is determined by the bulk flow (second term $v\frac{\partial c_i}{\partial x}$ in Eq. (1)), transfer to the solid phase (third term $\frac{1-\varepsilon_b}{\varepsilon_b}\frac{\partial q_i}{\partial t}$ in Eq. (1)) and diffusion (fourth term $D_a\frac{\partial^2 c_i}{\partial x^2}$ in Eq. (1)), the transfer rate from liquid phase to the solid phase is described by Eq. (2).

The initial conditions are:

$$t = 0,\ c_i = q_i = 0 \tag{3}$$

And the boundary conditions are:

$$x = 0, D_a\frac{\partial c_i}{\partial x} = v(c_i - c_i^{in}) \tag{4}$$

$$x = L, \frac{\partial c_i}{\partial x} = 0 \tag{5}$$

where c^{in} (g L^{-1}) is the concentration at the inlet of a column, L (cm) is the column length.

Eqs. (1)–(5) construct an partial difference equation system, which cannot be solved analytically. In this work, this equation system was solved numerically by the space-time conservation element/solution element method [39].

2.2. Adsorption isotherms

The equilibrium relationship between q^* and c was represented by a specific adsorption isotherm. The linear model was used in this work:

$$q_i^* = H_i c_i \tag{6}$$

where H_i is the Henry constant, which is obtained by linear regression with experimental data.

2.3. Estimation of dispersion coefficient and mass transfer coefficient

The axial dispersion coefficient, D_a, was estimated by the Chung and Wen Correlation [40]:

$$D_a = \frac{\varepsilon_b d_p v}{0.2 + 0.011(Re)^{0.48}} \tag{7}$$

where d_p is the average diameter of adsorbent particles, Re is the Reynolds number. The value of Re was calculated as follows:

$$Re = \frac{\rho d_p v \varepsilon_b}{\mu} \tag{8}$$

where ρ and μ are the density and viscosity of mobile phase, respectively.

The overall mass transfer coefficient, $k_{e,i}$, was calculated by the following equation [41]:

$$\frac{1}{k_{e,i}} = H_i\left(\frac{d_p^2}{60\varepsilon_p D_{p,i}} + \frac{d_p}{6k_{f,i}}\right) \tag{9}$$