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Separation of glucose/fructose mixtures. Analysis of elution of profiles

Lj. Matijašević [a,*], Đ. Vasić-Rački [a], N. Pavlović [b]

[a] *Faculty of Chemical Engineering and Technology, Marulićevtrg 19, 1000 Zagreb, Croatia*
[b] *PLIVA, Ulica gkada Vukovara 79, 1000 Zagreb, Croatia*

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Abstract

In this work, pulse response experiments and mathematical methods for the analysis elution profiles were used for the characterisation of resins and fixed bed columns.

The predicted elution profiles were used for estimation of the column efficiency, for determination of parameters of the fixed bed and particles (the first absolute moment) and for determination of parameter values for analysis of the relative contribution of rate processes (the second central moment). © 1997 Published by Elsevier Science S.A.

Keywords: Separation; Pulse response; Fixed bed; Glucose; Fructose

1. Introduction

Two solutes, glucose and fructose, are considered for chromatographic separation. Lewatit MDS 1368 is used as the chromatographic medium and deionized water as the eluent. In this work, the analysis of the response to input disturbance has been used. The experimental elution profiles of each sugar were used for research of the influence of several parameters on the efficiency of separation, such as the length of the column, retention time and inlet concentration.

The residence time distribution of the various kinds of molecules through the column is the most important criteria in separation efficiency, but we wish to separate two sugar isomers similar in their structure and chemical properties. The moment analysis technique was used for determination of the adsorption equilibrium constant, porosity of particle and voidage of the fixed bed, as well as for the investigation of the effect of flow rate on the relative contribution of each rate process.

Data on the rate of mass transfer between beds of particles and a flowing liquid are needed in the design of the many devices used for adsorption, leaching, ion exchange and chromatography. They are of particular importance in heterogeneous catalysis and catalyst regeneration.

2. Mathematical model

The theoretical analysis of the experiments into fixed beds based on the theories of dispersion in chromatographic columns has been introduced by many authors [1–6]. According to the axial dispersion model the differential equation determining the transport of a tracer through a column is

$$\frac{\partial c}{\partial t}=D_z\frac{\partial^2 c}{\partial z^2}-v_L\frac{\partial c}{\partial z}-\frac{3(1-\epsilon)\epsilon_p}{\epsilon R}D_r\frac{\partial q}{\partial r} \tag{1}$$

The radial dispersion can be neglected because the ratio of column diameter to length is small and the flow is in the turbulent regime.

In general, three steps will determine the rate of mass transfer between a liquid and dispersed solid phase:

- film diffusion, i.e. the transport through the liquid film surrounding the particles;
- particle diffusion, i.e. the transport inside the pores of the particle;
- other physical or chemical processes performed in the liquid or in the solid particles (adsorption in our case).

The film diffusion, i.e. the transport through the liquid film surrounding the particles, is assumed to be:

$$D_r\frac{\partial q}{\partial r}=k_f(c-q) \tag{2}$$

The transport inside the pores of the particles is assumed to be:

$$\frac{\partial q}{\partial t}=D_r\left(\frac{\partial^2 q}{\partial r}+\frac{2}{r}\frac{\partial q}{\partial r}\right) \tag{3}$$

The adsorption process is assumed to be:

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[*] Corresponding author.

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$$\frac{\partial c_p}{\partial t}=k_a\left(q-\frac{c_p}{K_e}\right) \tag{4}$$

The initial and boundary conditions are:

$$c=q=c_p=0 \quad (\text{for } t\leq 0, z>0)$$

$$c=d(t) \quad (\text{for } t>0, z=0)$$

$$c=\text{finite} \quad (\text{for } t>0, z\rightarrow\infty)$$

$$D_r\frac{\partial q}{\partial r}=k_f(c-q) \quad (\text{for } t>0, r=R)$$

$$\frac{\partial q}{\partial r}=0 \quad (\text{for } t>0, r=0)$$

The analytical solution of the above equations is obtained for the first two moments by applying the final value theorem of Laplace transforms (Eq. (3)):

$$\mu_1=\bar{t}=[\epsilon+(1-\epsilon)\epsilon_p(1+K_e)]\frac{V_0}{Q} \tag{5}$$

$$\mu_2=\sigma^2=\frac{2DzV_0A^2\epsilon_p^3}{Q^3}[1+\phi(1+K_e)]^2+\frac{2V_0\epsilon_p}{Q}\phi\left[\frac{K_e^2}{k_a}+\frac{R(1+K_e)^2}{3}\left(\frac{1}{k_f}+\frac{R}{5D_r}\right)\right] \tag{6}$$

where $\phi=(1\text{-}\epsilon)\epsilon_p/\epsilon$.

The unknown parameters K, ϵ and ϵ_p can be obtained by application of equation for the first moment. The second moment consists of separate and additional terms. Dividing both sides by $2V_0Q$ and using the additivity of terms the equation for the second moment may be arranged as:

$$\mu_2\frac{Q}{2V_0}=\Delta(D_z)+\Delta(k_a)+\Delta(k_f)+\Delta(D_r) \tag{7}$$

where the relative contribution of axial dispersion is,

$$\Delta(D_z)=\frac{D_zA^2\epsilon^2}{Q^2}[\epsilon+(1-\epsilon)\epsilon_p(1+K_e)]^2 \tag{8}$$

relative contribution of adsorption,

$$\Delta(k_a)=(1-\epsilon)\epsilon_p\frac{K_e^2}{k_a} \tag{9}$$

relative contribution of film diffusion

$$\Delta(k_f)=(1-\epsilon)\epsilon_p\frac{R^2(1+K_e)^2}{k_f} \tag{10}$$

relative contribution of intraparticle diffusion

$$\Delta(D_r)=(1-\epsilon)\epsilon_p\frac{R^2(1+K_e)^2}{15D_r} \tag{11}$$

The parameter D_z can be determined by a general empirical correlation which was originally proposed by Chung and Wen (1968)

$$\frac{D_z}{v}X=\frac{\text{Re}}{0.20+0.011\text{Re}^{0.48}} \tag{12}$$

$$\text{Re}=\frac{u_Ld_p}{v} \quad X=1 \text{ for fixed bed}$$

The mass transfer coefficient or film diffusion coefficient can be determined by the following correlation

$$\text{Sh}=\left(\frac{d_pk_f}{D}\right)=2+0.76\text{Sc}^{1/3}\text{Re}^{1/3} \tag{13}$$

3. Experimental

A schematic diagram of the experimental apparatus is shown in Fig. 1. The column was packed with Lewatit MDS 1368 by Bayer Leverkusen in a column of 2.5 cm diameter and lengths of 25 and 50 cm. A small portion of different concentration glucose and fructose (about 0.5 ml) was injected into the column at different volumetric flow rate. The eluent was redistilled and deionized water. The column temperature was kept at 313 K by circulating thermostated water through the jackets. Figs. 2 and 3 show examples of elution profiles, obtained in experimental apparatus.

The efficiency of the separation h was defined in this study as port of fructose in mixtures of glucose and fructose. It was calculated as peak area of fructose in sum of areas for fructose and glucose:

$$\eta=\int_{t_1}^{t_2}c(t)\,\mathrm{d}t\bigg/\int_{t_0}^{t_2}c(t)\,\mathrm{d}t \tag{14}$$

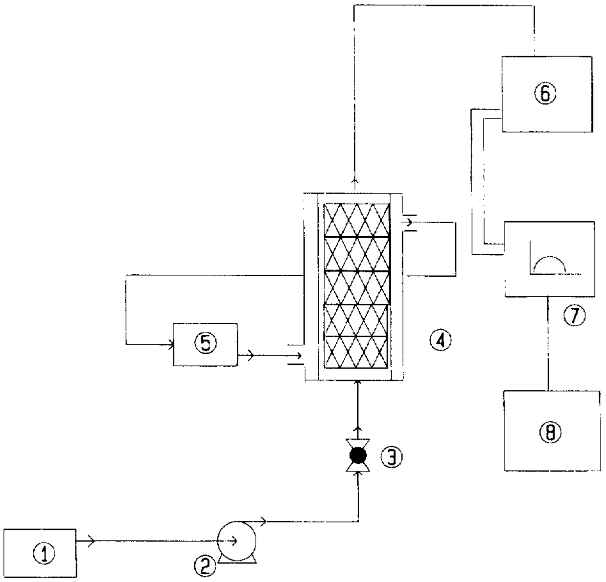

Fig. 1. Experimental apparatus for the pulse response experiment. 1, eluent tank; 2, peristaltic pump Masterflex ColeParmer; 3, injection valve; 4; glass column with double jacket; 5, thermostat WebMLW; 6, differential refractometer; 7, recorder; 8, tank for waste.

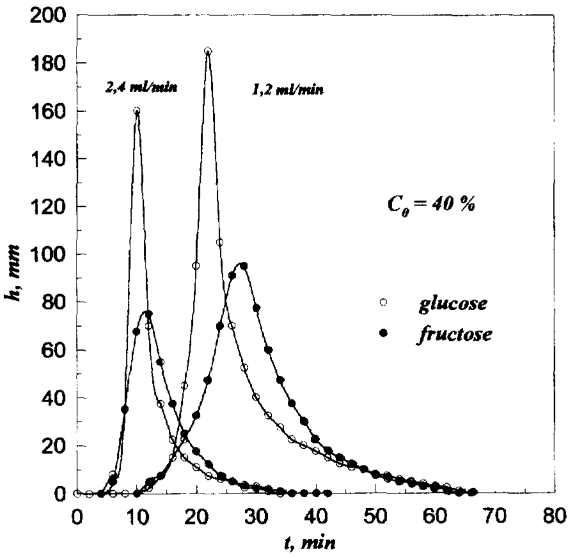

Fig. 2. Example of experimentally obtained response curves for glucose and fructose ($C_0 = 40\%$).

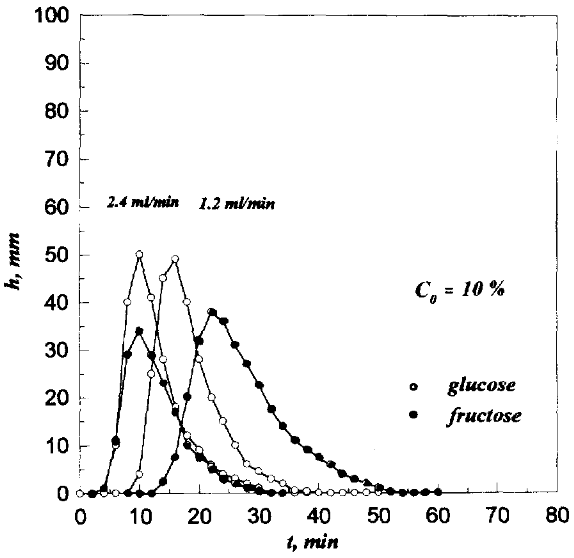

Fig. 3. Example of experimentally obtained response curves for glucose and fructose ($C_0 = 10\%$).

Figs. 4 and 5 show the efficiency of the separation as a function of concentration and of the mean residence time in two different columns.

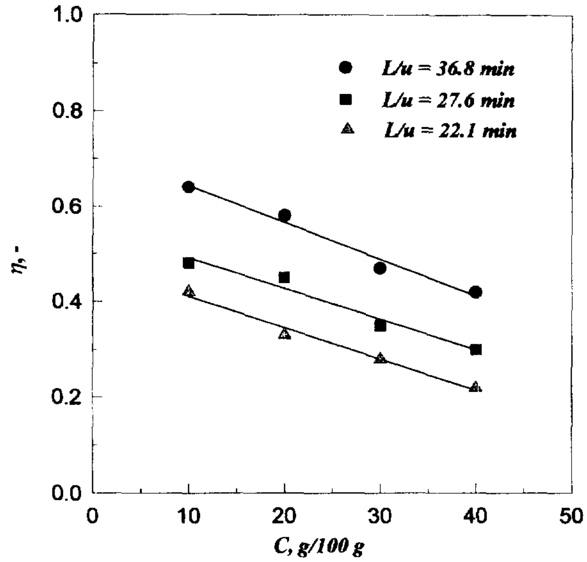

Fig. 4. Effect of mean residence time and concentrations on the column efficiency ($L = 25$ cm, $d = 1.5$ cm).

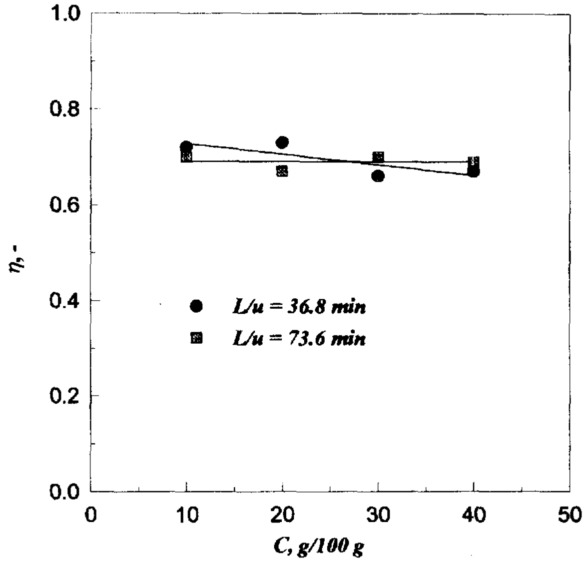

Fig. 5. Effect of mean residence time and concentrations on the column efficiency ($L = 50$ cm, $d = 1.5$ cm).

4. Results and discussion

The purpose of the separation of glucose and fructose from mixtures in order to increase the sweetness by their re-mixture to a desired composition, because fructose is much sweeter than its isomer glucose.

Figs. 4 and 5 show the efficiency of the separation as a function of concentration and of the mean residence time in two different columns. The column efficiency decreases at higher concentration an increases with retention time as shown in Fig. 4. The efficiency of a longer column (Fig. 5) was approximately the same for all concentration and retention times.

The importance of rate processes was evaluated from Eqs. (7)–(11) and their dependencies are illustrated in Fig. 6. If flow rate increases, the resistance of axial dispersion decreases. The film diffusion and intraparticle diffusion resistance do not play a leading part. The adsorption resistance, in most flow rates, plays an important role, characteristic of small particles.

All of the rate processes in Eq. (7) depend on the flow rate. The choice of flow rate, particle size, length and diameter of columns, may influence the priority of any one of these processes.

The data required for analysis of the relative contribution of rate processes are summarized in Table 1. These data were obtained in the earlier experiments [7].

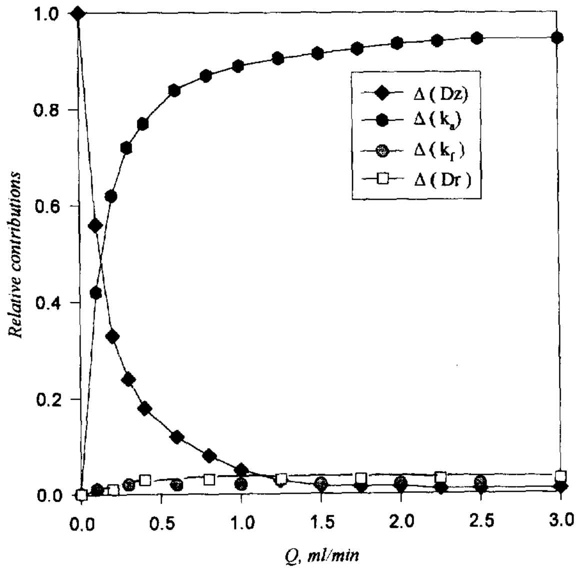

Fig. 6. Effect of flow rate on relative contribution of each rate process to the second moment.

Table 1
Parameter values used for analysis of fixed bed

Parameter	Values
ρ^{40}, kg m^{-3}	992.3
h, Pa s	1.571×10^{-3}
L, m	0.25
d, m	0.015
d_p, m	4.23×10^{-4}
A, m^2	1.767×10^{-4}
V_o, m^3	4.42×10^{-5}
ϵ, –	0.44
ϵ_p, –	0.4
K_e, –	0.187
D_r, m^2 s^{-1}	6.8×10^{-10}

This model can be widely used for turbulent flow of fluids in pipes and flow through packed beds, as well as a spectrum of different MW compounds, whereas the relative contribution of rate processes will be different.

The results reported in this study may used for the design or evolution bioreactor with a fixed bed as well as separation equipment.

5. Symbols

A	cross-section area, m^2
c	concentration of the solute, g dm^{-3}
d_p	particle diameter, m
D	molecular diffusion coefficient, m^2 s^{-1}
D_r	effective intraparticle diffusion, m^2 s^{-1}
D_z	axial dispersion coefficient, m^2 s^{-1}
k_a	adsorption rate constant, min^{-1}
K_e	adsorption equilibrium constant
k_f	mass transfer coefficient, cm min^{-1}
L	bed length, m
q	concentration of the solute in the pore space, g dm^{-3}
Q	volumetric flow rate, cm^3 min^{-1}
R	radius of the particle, m
r	radial coordinate in the particle, m
Re	Reynolds number
Sh	Sherwood number
t	time, min
t	the mean residence time, min
u	interstitial velocities, cm min^{-1}
V_o	bed void volume, m^3
v	superficial velocities, cm min^{-1}
z	axial coordinate in the bed, m
ϵ	void fraction of the bed
ϵ_p	porosity of the particle
μ_1	first moment of the elution curve, min
μ_2	second moment of the elution curve, min^2
η	viscosity
ν	kinematics viscosity
σ^2	variance, min^2

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