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Simulated Moving Bed Technology in the Reactive Process of Glucose Isomerization

EDUARDO A. BORGES DA SILVA, ANTONIO A. ULSON DE SOUZA AND SELENE GUELLI U. DE SOUZA*

Departamento de Engenharia Química e Engenharia de Alimentos, Universidade Federal de Santa Catarina, Laboratório de Simulação Numérica de Sistemas Químicos, LABSIN, Campus Universitário Cx. P. 476, 88.040-900, Florianópolis (SC), Brazil

selene@enq.ufsc.br

ALÍRIO E. RODRIGUES

Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Laboratório de Engenharia de Separação e Reação, LSRE, Rua Dr. Roberto Frias S/N, 4200-465, Porto, Portugal

Abstract. The glucose isomerization process coupled with adsorption using simulated moving bed technology to obtain high/higher fructose syrups (*HFS*) are discussed. The mathematical modeling of this process, based on the equivalence between True Moving Bed Reactor (TMBR) and Simulated Moving Bed Reactor (SMBR) is presented. Reaction and adsorption parameters are determined experimentally. A new configuration of the SMBR is proposed which allows the production of fructose-rich product (90% in purity).

Keywords: simulated moving bed reactor, glucose isomerization, SMBR configuration

1. Introduction

The integration of chemical reaction and adsorptive separations in chromatographic reactors is recognized as one of the promising ways to improve the efficiency of hybrid adsorptive/reactive processes. In the Simulated Moving Bed Reactor (SMBR), counter-current continuous separation occurs simultaneously with reaction; SMBR is a possible alternative to traditional reactors with two distinct units: one for reaction and the other for separation (Meurer et al., 1997; Migliorini et al., 1999).

Some classes of reactions in which SMBR has been applied successfully are: esterification reactions (Kawase et al., 1996), alquylation, hydrogenation, and also enzymatic reactions (Azevedo and Rodrigues, 2001; Ching and Lu, 1997). In this research, the focus is on the process of glucose isomerization, a reversible reaction of industrial interest to produce high/higher fructose syrups (*HFS*).

The amount of fructose produced is determined by the equilibrium constant of the isomerization reaction of glucose to fructose, which results approximately in an equimolar mixture of the sugars. In order to obtain higher fructose syrup, adsorption columns packed with strongly acid ionic resins, or zeolites, in the calcium form, is often used. The technology of simulated moving bed has been used in the separation of glucose and fructose isomers with success since the commercialisation of the SAREX process, developed by UOP (SORBEX processes) (Ruthven and Ching, 1989).

A system requiring a second plant for producing HFS, from a sugar mixture leaving the isomerization reactor, represents an additional cost. Then, research has been made to discover alternatives to obtain 55% w/w fructose syrups or highest fructose contents using only

*To whom correspondence should be addressed.

the enzymatic reactor. The thermodynamics of the system favors the production at higher temperatures and 55% w/w fructose content could be produced directly if enzymatic reactors were operated at 95°C; this road constitutes one of the great challenges for enzyme technology (Chaplin and Bucke, 1990).

The idea of just using one single unit to carry out such process—reaction and separation—opens a window for the application of SMBR technology. It is known that the separation of glucose and fructose in SMB units is already a process well documented in the literature and applied industrially.

The objective of this work is to present and discuss alternative configurations of SMBR units for the separation of sugars and production of *HFS* from glucose isomerization. The case where the feed stream contains only glucose is also analyzed.

2. Mathematical Model

In the process of glucose isomerization, the reaction is reversible and equilibrium limits the conversion with equilibrium constant of the order of one (equilibrium conversion of 50%). In general, an enzymatic reactor, (fixed bed) is used to produce the feed for the SMB unit. This will allow later the recovery of glucose (less retained species) in the rafinate stream and fructose (more retained species) in the extract stream. Probably, both sugars can be obtained with purities higher than 90%. This process is quite flexible, but it is limited by the equilibrium condition of the enzymatic reactor.

A system proposed by Hashimoto et al. (1983) used the SMB technology associated with fixed bed reactors. This hybrid unit showed lower eluent consumption in comparison with the system mentioned above. The enzymatic reactors in the system only appear in Section 3 (reaction section), just after the feed stream—Fig. 1. The reactors switch together with external streams in the switching time intervals (t^*). There are three sections in this system, in which it is convenient to get a maximum conversion of glucose in Section 3 to avoid contamination of the extract stream (where fructose is collected).

Table 1. Identification of terms in generic equation according to the phase considered.

Phase	ϕ	U_k	C_1	S^ϕ
Fluid				
Reactors	$C_{i,k}$	v_k	D_k	$\left(\frac{1}{\varepsilon_r}\delta_i \rho_{fb}\right) r_{i,k}$
Adsorbers	$C_{i,k}$	v_k	D_k	$\left(\frac{1-\varepsilon_a}{\varepsilon_a}\right) k_c(q^*_{i,k} - \bar{q}_{i,k})$
Solid	$\bar{q}_{i,k}$	$-u_S$	0	$k_c(q^*_{i,k} - \bar{q}_{i,k})$

This system was chosen to analyse some interesting aspects of the use of the SMB technology in the glucose isomerization process. The analysis of the system configuration is accomplished by mathematical modeling and dynamic simulation of the reactive unit. The model is based on the equivalence between SMBR and TMBR (Lode et al., 2003). The model equations, using the equivalence strategy, have been obtained from mass balances for chemical species in fluid and solid phases of both adsorbers and reactors. They can be represented by the generic form of Eq. (1). The corresponding terms for the phases are given in Table 1.

$$\frac{\partial \phi}{\partial t} + \frac{\partial}{\partial z}(U_k \phi) = \frac{\partial}{\partial z}\left(C_1 \frac{\partial \phi}{\partial z}\right) + S^\phi \qquad (1)$$

In the above equations $C_{i,k}$ and $\bar{q}_{i,k}$ are the concentrations of species i (i = glucose and fructose) in the

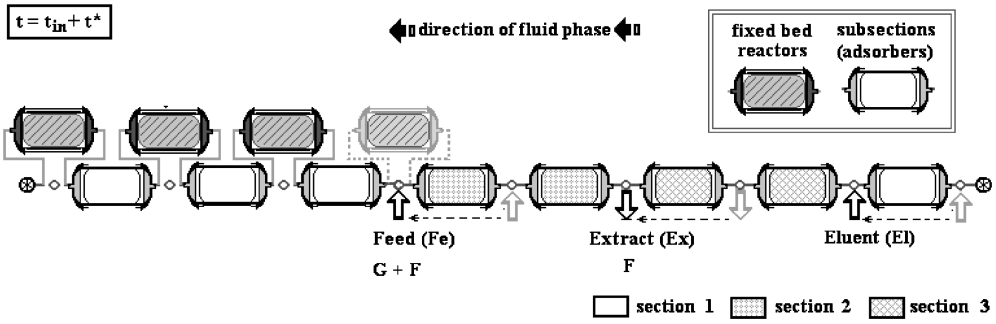

Figure 1. System: SMB unit associated with fixed bed reactors for glucose isomerization (G - Glucose; F - Fructose). (Hashimoto et al., 1983).

fluid and solid phases respectively in section k (k = 1, 2 e 3) of the TMBR. The interstitial fluid velocity and solid velocity are v_k and u_s, respectively. The parameters ε_a and ε_r are adsorber and reactor porosities; ρ_{fb} represents fixed bed density in the reactor. For the solid adsorbent phase, mass transfer resistances have been taken into account by a global rate coefficient k_c using the *LDF* approximation. This model allows the use of any adsorption equilibrium relation ($q^*_{i,k}$) and reaction rate equation (r_i). The value of δ can be -1 to glucose or $+1$ to fructose.

The initial conditions are

$$t = 0: \quad C_{i,k} = \bar{q}_{i,k} = 0 \tag{2}$$

The boundary conditions are specified as

$$v_k C_{i,k}|_{z=0^-} = v_k C_{i,k}|_{z=0^+} - D_k \frac{\partial (C_{i,k})}{\partial z}\bigg|_{z=0^+} \tag{3}$$

$$\frac{\partial (\bar{q}_{i,k})}{\partial z}\bigg|_{z=0} = 0 \quad \text{(except for reaction columns)} \tag{4}$$

$$\frac{\partial C_{i,k}}{\partial^z}\bigg|_{z=L} = 0 \quad \text{(for the Sections 1, 2 and 3)} \tag{5}$$

$$\bar{q}_{i,k}|_{z=L} = \bar{q}_{i,k+1}|_{z=0} \quad \text{(for the Sections 1 and 2)} \tag{6}$$

$$\bar{q}_{i,k}|_{z=L} = \bar{q}_{i,k+2}|_{z=0} \quad \text{(for adsorption columns in section 3; } k+2 = 1 \text{ when } (k+2) \text{ is higher than maximum number of subsections)} \tag{7}$$

The entrance and exit points for the species are located between the various sections of the TMBR unit. Therefore, mass balances at these nodes have to be written to complete the model (L is the length of a subsection).

The equivalence relationships between SMBR and TMBR for the system shown in Fig. 1 should be analysed carefully. In particular in this configuration, the solid phase in the reactors does not present the simulated movement in the adsorber unit, and this means that the equivalence is different for reactors and adsorbers in the equivalent TMBR.

3. Experimental

3.1. Reaction Parameters

To obtain the global reaction rate equation, batch experiments with different initial glucose and fructose concentrations were carried out—0.5 M, 1.0 M, 2.0 M and 3.0 M. The operational temperature of 55°C is maintained in the reactors. The glucose isomerization is catalyzed by the action of the immobilized enzyme *glucose isomerase Sweetzyme IT* (*Novozymes A/S*, Denmark). The sugars solutions (60 mL) contain magnesium sulphate hepta-hydrated (20 g/L) to keep the stability and activity of the enzyme, and the pH is controlled in 7.7/7.8 (for 25°C). The kinetic parameters were obtained by the technique of Lineweaver-Burk and they are: $K_{mr} = 0.46$ mol/L, $K_{mf} = 0.54$ mol/L, $V_{mr} = 260$ μmol/min g_{Enzyme} e $V_{mf} = 316$ μmol/min g_{Enzyme}. The equation of the global reaction rate of the glucose isomerization is (concentration is given in mol/L):

$$r_i = \frac{V_{mf} K_{mr} C_G - V_{mr} K_{mf} C_F}{K_{mf} K_{mr} + K_{mr} C_G + K_{mf} C_F} \tag{8}$$

3.2. Adsorption Parameters

To determine the adsorption equilibrium isotherms and global mass transfer coefficients for fructose and glucose, both chromatographic method and breakthrough curves for each component were obtained. A packed bed column with resin *FINEX CS11GC* (*Finex Co*., Finland) in Ca^{2+} and Mg^{2+} ionic forms was used. The concentration range of 0.2 to 1.0 M was investigated. The temperature was 55°C and the solvent is the same used in reaction experiments. The adsorption kinetics was determined by numerical simulation.

All the chemical reagents were of analytical degree. Fructose and glucose concentrations were determined by HPLC using a refraction index detector. Details on the experimental methods can be found in Borges da Silva (2004).

4. Results and Discussion

To solve numerically the model equations presented, a computational algorithm in FORTRAN language was developed. Partial differential equations are discretized

Table 2. Operational conditions and model parameters of the glucose isomerization in the SMBR.

Operational conditions				Parameters		
	$C_{F,o}$		1.0 M	Ionic form*	Ca^{2+}	Mg^{2+}
	$C_{G,o}$		1.0 M	k_c^F	2.25 min^{-1}	8.85 min^{-1}
Q_{Fe}(Feed)	1.50 mL/min	Q_1	31.10 mL/min	k_c^G	2.92 min^{-1}	9.45 min^{-1}
Q_{El} (Eluent)	5.60 mL/min	Q_2	24.00 mL/min	K_F	0.53	0.35
Q_{Ex}(Extract)	7.10 mL/min	Q_3	25.50 mL/min	K_G	0.27	0.29
t^*			3.84 min	Length (L)	30 cm	
ε_r, ε_a			0.4	Diameter (d)	2.6 cm	

*Ionic form for FINEX CG11CS—cationic exchange resin.

using Finite Volume Method. Modified Strongly Implicit Method (MSI) is used to solve the algebraic equations systems.

The process dynamics of glucose isomerization in SMBR is simulated with the operational conditions and model parameters listed in Table 2. In this Table 2, the flow rate in the section k of SMBR is Q_k. The operational conditions are estimated considering the equilibrium theory. Two cases are shown in Fig. 2: in the first, the unit behavior when the feed is a mixture of fructose and glucose, according to the system of Fig. 1; and the second case, an alternative configuration where the feed is only glucose. The behavior is analyzed through the concentration profiles of the species in the unit sections.

Figure 2(a) shows the concentration profile of the sugars in a SMBR fed with an equimolar mixture of glucose and fructose. In this unit, there are 13 columns (reactors/adsorbers) and 1 adsorber after the feed current. The reactors are packed with the immobilized enzyme and the adsorbers with the resin in Ca^{2+} form. In spite of the degree of purity (85% fructose) and of the eluent economy obtained, the main interest of this process configuration is to allow the use of a feed of pure glucose. This situation is shown in Fig. 2(b), in which the unit shows section 3 beginning with an enzymatic reactor (in this case there are 12 columns instead of 13). The purity degree is maintained (83%), but the product is recovered with low concentration.

The operation of the reactive unit of SMB requires that the ion exchange resin for separation of glucose and fructose is in Mg^{2+} form (Hashimoto et al., 1983). The enzymatic reaction that occurs in the unit does not allow the presence of ions Ca^{2+}, which inhibit the enzyme *glucose isomerase* in the glucose conversion. With the adsorption data obtained for the resin *FINEX CS11CG* in the form Mg^{2+}, the region of the plan (m_2; m_3) was constructed that corresponds to the operational

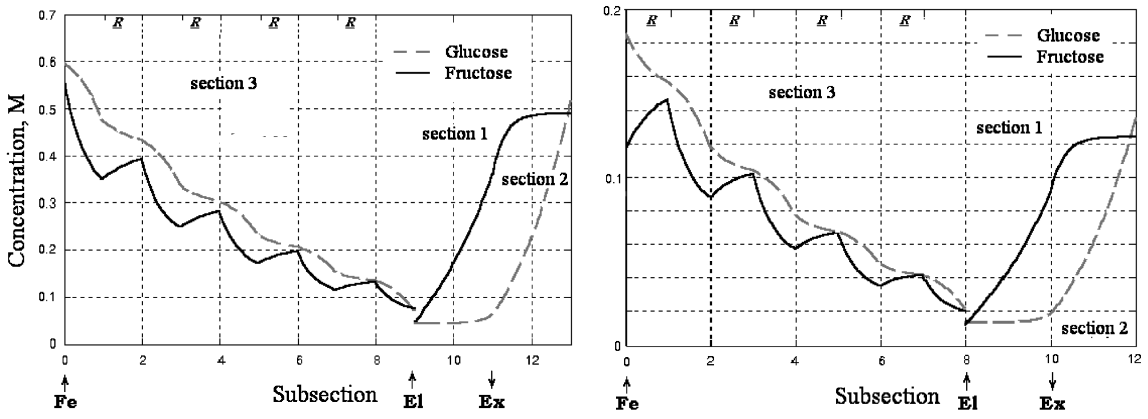

Figure 2. Concentration profiles of sugars in the SMBR in cyclic stationary state: (a) Feed: glucose 1 M and fructose 1 M, configuration—5ads./4reactors-2-2; (b) Feed: glucose 1 M, configuration—4reactors/4ads.-2-2.

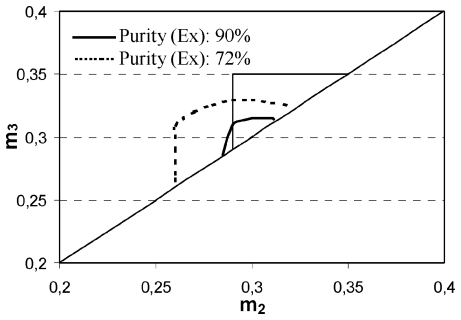

Figure 3. Region of the plan (m_2; m_3) to obtain fructose in purity of (–) 70% and (--) 90% from glucose isomerization process in SMBR (ion exchange resin in form Mg^{2+}).

conditions for which the fructose purities of 70% and 90% in the extract current can be reached. The values of the permutation time and of the parameter m1 are 3.87 min and 0.52, respectively. The feed of the unit consists of glucose solution 1.0 M. The definition of parameter m_k is presented in Eq. (9), where V_c is volume of a subsection.

$$m_k = \frac{Q_k t^* - \varepsilon_a V_c}{(1 - \varepsilon_a) V_c} \tag{9}$$

Figure 3 shows that it is possible to use the SMB technology in the glucose isomerization process to obtain high purity fructose, with a configuration as suggested for the system indicated in Fig. 2(b). Some aspects like productivity and catalyst activity in low concentrations are being investigated.

5. Conclusion

The global rate of the enzymatic reaction of glucose isomerization and adsorption parameters of the sugars were experimentally obtained. Using the numerical simulation with experimentally measured parameters, one can conclude that it is possible to obtain high purity fructose from glucose in the isomerization process coupled with SMB technology. The application of the resin in Mg^{2+} form limits the range of operational conditions that can be applied, but it has been shown that an integrated system of reaction and separation using the SMB technology is capable of producing high-purity HFS from reversible reaction (glucose isomerization).

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