

Evaluation of diffusional resistances in the process of glucose isomerization to fructose by immobilized glucose isomerase

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Abstract

A kinetic model presented in a previous work is employed to carry out a systematic study dealing with the relative importance of intraparticle and interparticle diffusional resistances in the process of glucose isomerization to fructose by immobilized glucose isomerase. An analytical generalized expression of the effectiveness factor is obtained, which promises to be particularly useful for design purposes. Finally, the role of each of the main parameters influencing the catalyst effectiveness factor is put in evidence and discussed within the whole range of possible operative conditions. © 2001 Elsevier Science Inc. All rights reserved.

Keywords: Glucose isomerization; Glucose isomerase; Immobilized enzyme; Linearized kinetics; Effectiveness factor

1. Introduction

It is well known that high-fructose corn syrup (HFCS) is an interesting alternative sweetener, which is mainly produced by continuous isomerization of starchy syrups in immobilized glucose isomerase (GI) columns. However, the performance of this process is strongly affected by thermal inactivation of the enzyme [1,2], which is responsible for a progressive decrease in the isomerization rate.

The first approaches to describe the related isomerizations kinetics, based on the reversible Briggs-Haldane mechanism coupled with the biocatalyst activity decrease, were successfully applied to both suspended [3] and immobilized systems [4–6]. However, since the concentration distribution along the column or inside the pellet cannot be obtained in an analytical form, due to the problem complexity, numerical methods were firstly utilized by Verhoff and Goldstein [7].

In order to elucidate the role of the most important process variables, a linearization technique has recently been proposed by the authors [8,9], which consisted in linearizing the isomerization rate with respect to substrate concentration within a wide range of conditions of actual interest in industrial processes ($60 < T < 80^{\circ}\text{C}$ and $500 <$

$G_o < 3000 \text{ mol m}^{-3}$). This simplification of the model is expected to give a relevant contribution to the design of a tubular catalytic reactor for continuous HFCS production with constant composition as well as to the process optimization from both technical and economic points of view, provided that a deep knowledge of both inner and outer diffusional resistances is available. In fact, since the enzymes employed for industrial use are immobilized onto supports (usually alumina), diffusional resistances could significantly influence the isomerization kinetics. This effect is usually taken into consideration by introducing a global effectiveness factor, η , which depends on both the intraparticle and interparticle diffusional resistances.

The present study deals with the relative significance of the diffusional resistances in an industrial column for glucose isomerization to fructose by immobilized glucose isomerase.

2. Theory

2.1. Diffusional resistances and catalyst deactivation

The evaluation of the diffusional resistances in a reactor utilizing a catalyst subject to deactivation can be a very hard problem, even from a numerical point of view. A typical situation is schematically represented in Fig. 1, where a

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Nomenclature

D	Mean sugar effective diffusivity through the pellet ($L^2 T^{-1}$)
D^*	Mean sugar effective diffusivity in the fluid phase ($L^2 T^{-1}$)
G	Glucose concentration ($M L^{-3}$)
G_b	Glucose concentration in the fluid bulk ($M L^{-3}$)
G_e	Glucose concentration in equilibrium with the glucose concentration in the feed ($M L^{-3}$)
G_o	Glucose concentration in the feed ($M L^{-3}$)
G_p	Glucose concentration in the fluid film surrounding the particle surface ($M L^{-3}$)
k	Correction coefficient defined in Eq. (32) (-)
\bar{k}	Mean value of the correction coefficient (-)
K	Constant of isomerization equilibrium (-)
k_d	Actual decay constant of the enzyme (T^{-1})
k_i	Kinetic constant of isomerization (T^{-1})
k_L	Coefficient of mass transfer in the fluid phase ($L T^{-1}$)
v	Glucose isomerization rate ($M L^{-3} T^{-1}$)
$v(G_p)$	Reaction rate in the outer surface of the catalyst ($M L^{-3} T^{-1}$)
$\bar{v}[G(r)]$	Mean reaction rate in the particle volume ($M L^{-3} T^{-1}$)
r	Distance from the center of the particle (L)
R	Particle radius (L)
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	Time (T)
T	Temperature ($^{\circ}C$)
t_f	Time of catalyst utilization (T)

Subscripts

b	Value referred to the fluid bulk
e	Value referred to the equilibrium
g	Global value
max	Maximum value
min	Minimum value
o	Inlet value or value referred to the fresh catalyst
p	Value referred to the fluid film surrounding the particle surface

Greek letters

δ	Film thickness (L)
ϵ	Relative error defined in Eq. (20) (-)
η	Effectiveness factor for the catalyst particle (-)
η_g	Global effectiveness factor (-)
η_o	Effectiveness factor for the fresh catalyst (-)
ϕ	Thiele modulus for a catalyst of age t (-)
ϕ_o	Thiele modulus for the fresh catalyst (-)
ψ	Fractional activity of the enzyme (-)
ψ_f	Catalyst fraction, active at the moment of its substitution (-)

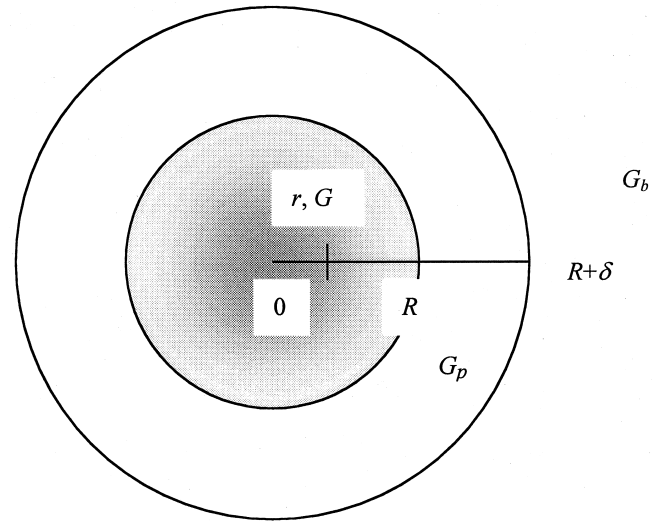


Fig. 1. Schematic representation of glucose diffusion within a spherical pellet of immobilized glucose isomerase. r = Distance from the center of the particle; G = glucose concentration in the particle; G_p = glucose concentration in the fluid film surrounding the particle surface; δ = film thickness; G_b = glucose concentration in the fluid bulk; R = particle radius.

catalyst spherical particle of given radius, R , and age, t , located in a particular position in the reactor is considered.

In the most general case, the mathematical description of the phenomena taking place within the catalyst pellet and around it could be represented as follows (symbols in the appended list):

$$\frac{\partial G}{\partial t} = D \left(\frac{\partial^2 G}{\partial r^2} + \frac{2}{r} \frac{\partial G}{\partial r} \right) - v \quad (1)$$

$$G = 0 \quad \text{at } t = 0 \quad \text{for all } r \text{ values} \quad (2)$$

$$\frac{\partial G}{\partial r} = 0 \quad \text{at } r = 0 \quad \text{for all } t \text{ values} \quad (3)$$

$$G = G_p \quad \text{at } r = R \quad (4)$$

$$\frac{d\psi}{dt} = -k_d \psi \quad (5)$$

$$\psi = 1 \quad \text{at } t = 0 \quad \text{for all } r \text{ values} \quad (6)$$

$$\frac{dG_p}{dt} = \frac{k_L}{\delta} (G_b - G_p) - \frac{D}{\delta} \left(\frac{\partial G}{\partial r} \right)_R \quad (7)$$

Eq. (1), in particular, represents the glucose balance for a generic shell within the catalyst particle, to be integrated with the boundary conditions (2), (3), and (4). Eq. (5), together with the boundary condition (6), describes the rate of enzyme deactivation. The validity of assuming first-order kinetics for the deactivation of immobilized GI was previously demonstrated [4–6]. Finally, Eq. (7) accounts for the time variation of glucose concentration in the fluid film, as a consequence of the diffusion from the fluid bulk to the pellet.

As discussed in a recent study [9], it is practically impossible to obtain a general solution of the above model, since all variables (G_b , G_p , ψ , etc.) can depend on the time and the position within the particle and the reactor. The fractional activity of the enzyme, ψ , for example, generally varies, according to the dependence of k_d on $G(t)$ and $T(t)$, with the distance, r , from the center of the pellet and the history of the particle.

The isomerization rate is given by:

$$v = \psi k_i (G - G_e) \quad (8)$$

where k_i , which generally depends on G and T , is the kinetic constant of isomerization, while G_e is the glucose concentration in equilibrium with the glucose concentration in the feed, G_o , according to the relationship:

$$G_e = \frac{G_o}{1 + K} \quad (9)$$

where K is the equilibrium constant.

By virtue of Eq. (8), Eqs. (1) and (5) are strongly correlated, which represents the strongest difficulty in the model resolution. Nevertheless, the enzyme deactivation is very slow compared with other transient phenomena, so the hypothesis of pseudo steady-state conditions in the catalyst pellet can be applied [9], allowing for a partial decoupling of Eqs. (1) and (5) with respect to the time.

Moreover, owing to the very short biofilm thickness, the accumulation term in Eq. (7) is usually not considered, so the mathematical model can be simplified substituting Eqs. (1) and (7) with the equations:

$$\frac{d^2G}{dr^2} + \frac{2}{r} \frac{dG}{dr} = \psi \frac{k_i}{D} (G - G_e) \quad (10)$$

$$k_L(G_b - G_p) = D \left(\frac{dG}{dr} \right)_R \quad (11)$$

and obviously considering no more the conditions depicted by Eq. (2).

In a previous study it was demonstrated that k_d and k_i are practically independent of G over the whole range of conditions for industrial applications [9]. So, a complete decoupling of Eqs. (5) and (10) is possible for an isothermal process. In this case Eq. (5) becomes:

$$\psi = \exp(-k_d t) \quad (12)$$

and the mathematical model is easily amenable to an analytical solution, as described in the following.

2.2. Diffusional resistances within the catalyst particle

By virtue of Eq. (12), Eq. (10) can be re-written as:

$$\frac{d^2G}{dr^2} + \frac{2}{r} \frac{dG}{dr} = \frac{\phi^2}{R^2} (G - G_e) \quad (13)$$

where:

$$\phi = \phi_o \exp(-k_d t/2) \quad (14)$$

is the Thiele modulus for a catalyst of age t , while:

$$\phi_o = R \sqrt{k_i/D} \quad (15)$$

is the one for the fresh catalyst.

The effectiveness factor for the catalyst particle, defined as:

$$\eta = \frac{v[G(r)]}{v(G_p)} \quad (16)$$

can be easily obtained [10] by integrating Eq. (13) with the boundary conditions (3) and (4):

$$\eta = \frac{3}{\phi^2} (\phi C_{th} \phi - 1) \quad (17)$$

2.3. Combination of inner and outer mass transfer resistances

The combined effect of inner and outer mass transfer resistances can be taken into account by introducing a global effectiveness factor [10]:

$$\eta_g = \frac{\eta}{1 + \epsilon} \quad (18)$$

where:

$$\epsilon = \frac{D}{R k_L} (\phi C_{th} \phi - 1) \quad (19)$$

Being, from Eq. (18):

$$\epsilon = \frac{\eta - \eta_g}{\eta_g} \quad (20)$$

the parameter ϵ represents the relative error introduced by using η instead of η_g .

Eqs. (18) and (19) represent the starting point for the evaluation of the relative importance of the diffusion effects in the industrial process of glucose isomerization. Before discussing this subject by means of experimental results previously presented [9], it is necessary to remember, as pointed out by different authors [10,11], that external transport limitations are not significant whenever the internal ones are absent. Eq. (19), in fact, can be re-written as:

$$\epsilon = \frac{D}{D^*} \frac{1}{Sh} (\phi C_{th} \phi - 1) \quad (21)$$

where D^* is the mean sugar diffusivity in the fluid phase and:

$$Sh = \frac{R k_L}{D^*} \quad (22)$$

is the Sherwood number:

$$Sh = 1 + 0.3 Re^{1/2} Sc \geq 1 \quad (23)$$

Table 1

Values of the kinetic constants for glucose isomerization, k_i (h^{-1}), and for glucose isomerase deactivation, k_d (10^3 h^{-1}), estimated at different temperatures and feed glucose levels

G_o (mol m^{-3})	500	1000	2000	3000
k_i (h^{-1})				
T ($^{\circ}\text{C}$)				
60.0	0.460	0.320	0.199	0.144
70.2	0.770	0.562	0.365	0.271
80.0	1.113	0.847	0.573	0.433
k_d (10^3 h^{-1})				
T ($^{\circ}\text{C}$)				
60.0	0.80	0.72	0.64	0.60
70.2	5.42	4.86	4.32	4.06
80.0	28.46	25.59	22.74	21.33

and Re and Sc the Reynolds and Schmidt numbers.

Since in the situations of practical interest is, according to Froment and Bischoff [10]:

$$\frac{D}{D^*} \leq \frac{1}{6} \quad (24)$$

one can see from Eq. (21) that the value of ϵ cannot be greater than:

$$\epsilon_{max} = (\phi C_{th} \phi - 1)/6 \quad (25)$$

and η_g must correspondingly exceed the value:

$$\eta_{g,min} = \frac{\eta}{1 + \epsilon_{max}} \quad (26)$$

When the inner diffusion resistances are negligible ($\phi \rightarrow 0$), we have:

$$\eta \rightarrow 1 \quad \text{and} \quad \epsilon_{max} \rightarrow 0 \quad (27)$$

so Eq. (26) clearly indicates that:

$$\eta_{g,min} \rightarrow \eta \quad \Rightarrow \quad \eta_g \rightarrow \eta \quad (28)$$

which means that also the outer ones are negligible.

3. Results and discussion

3.1. Kinetic parameters and diffusivity

The evaluation of diffusional resistances significance in glucose isomerization requires, amongst others, the knowledge of the values of parameters k_i , k_d , and D . Table 1 lists the values of the kinetic constants for both glucose isomerization, k_i , and catalyst deactivation, k_d , which were directly calculated from experimental data applying a suitable kinetic model [9]. Table 2, on the other hand, shows the values of the effective mean sugar diffusivity through the pellet, D , which were estimated by putting:

Table 2

Effective mean sugar diffusivity estimated at different temperatures

T ($^{\circ}\text{C}$)	D ($\text{mm}^2 \text{ h}^{-1}$)
60.0	0.1608
70.2	0.1973
80.0	0.2372

$$D = D^*/6 \quad (29)$$

where D^* is the mean sugar diffusivity in the fluid phase [12–14].

3.2. Diffusional resistances in the fresh catalyst

First of all, the case of a fresh catalyst will be considered, in which the diffusional resistances assume the greatest importance, since the reaction rate inside the pellet reaches its minimum value, with respect to that on outer surface.

The values of the Thiele modulus, estimated by Eq. (15), are listed in Table 3, while the corresponding behavior of the effectiveness factor, $\eta_o = \eta(\phi_o)$, obtained by Eq. (17), is shown in Fig. 2.

The results indicate that the inner resistances to diffusion only slightly increase with temperature and decrease with feed concentration, while, as expected, they are strongly related to the particle radius. In particular, the resistances become rather significant ($\eta_o \approx 0.8$) only for $R = 1$ mm, over the whole range of conditions investigated.

Taking into consideration all the mass transfer resistances, the parameter $\epsilon_o = \epsilon(\phi_o)$ must first be determined. For precautionary purposes, only its maximum values are considered:

$$\epsilon_{o,max} = (\phi_o C_{th} \phi_o - 1)/6 \quad (30)$$

Table 3

Values of the Thiele modulus, ϕ_o , estimated by Equation (15) for the fresh catalyst at different values of the particle radius, temperature and feed glucose level

G_o (mol m^{-3})	500	1000	2000	3000
$R = 0.30$ mm				
T ($^{\circ}\text{C}$)				
60.0	0.507	0.423	0.334	0.284
70.2	0.593	0.506	0.408	0.351
80.0	0.650	0.567	0.466	0.405
$R = 0.65$ mm				
T ($^{\circ}\text{C}$)				
60.0	1.099	0.917	0.723	0.616
70.2	1.284	1.097	0.884	0.761
80.0	1.408	1.228	1.010	0.878
$R = 1.00$ mm				
T ($^{\circ}\text{C}$)				
60.0	1.691	1.411	1.113	0.948
70.2	1.975	1.688	1.361	1.171
80.0	2.166	1.890	1.554	1.351

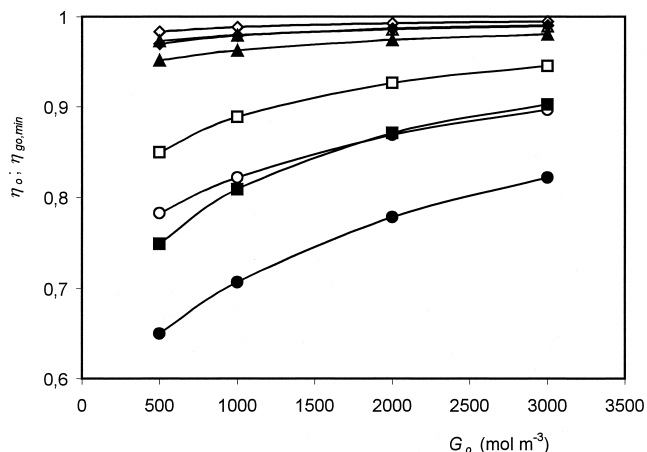


Fig. 2. Dependences of the fresh catalyst effectiveness factor, η_o , and of the global effectiveness factor, $\eta_{go,min}$, on temperature, particle radius, and feed glucose concentration. (\diamond) $R = 0.3$ mm, $T = 60^\circ\text{C}$; (\triangle) $R = 0.3$ mm, $T = 80^\circ\text{C}$; (\square) $R = 1.0$ mm, $T = 60^\circ\text{C}$; (\circ) $R = 1.0$ mm, $T = 80^\circ\text{C}$. Open symbols: η_o ; Full symbols: $\eta_{go,min}$.

the outer diffusional resistances being certainly overestimated in this way. In addition, as pointed out in a previous section, it is expected to be quite low under the conditions considered here, because the most relevant contribution to the global effectiveness factor, $\eta_{go} = \eta_g(\phi_o)$, should be due to inner resistances (η).

The values of $\epsilon_{o,max}$, listed in Table 4, indicate that the relative difference between the global and inner resistances increases with decreasing feed concentration, G_o , and becomes significant (higher than 10%) only when R and T achieve their threshold values of 1 mm and 80°C , respectively. The highest value ($\approx 20\%$) is reached, within the whole domain investigated in this study, at $G_o = 500$ mol m^{-3} , $T = 80^\circ\text{C}$, and $R = 1$ mm, that is under extreme conditions for industrial applications.

Table 4
Maximum values of the relative error, $\epsilon_{o,max} = \epsilon_{max}(\phi_o)$, estimated by Equation (30) for the fresh catalyst at different values of the particle radius, temperature and feed glucose level

G_o (mol m^{-3})	500	1000	2000	3000
$R = 0.30$ mm				
T ($^\circ\text{C}$)				
60.0	0.014	0.010	0.006	0.004
70.2	0.019	0.014	0.009	0.007
80.0	0.023	0.017	0.012	0.009
$R = 0.65$ mm				
T ($^\circ\text{C}$)				
60.0	0.062	0.044	0.028	0.021
70.2	0.083	0.062	0.041	0.031
80.0	0.098	0.076	0.053	0.041
$R = 1.00$ mm				
T ($^\circ\text{C}$)				
60.0	0.135	0.098	0.064	0.047
70.2	0.175	0.135	0.092	0.070
80.0	0.204	0.163	0.117	0.091

Table 5
Values of the time of catalyst utilization, t_f (h), estimated under "extreme" conditions of temperature and residual biocatalyst activity

ψ_f	0.1		0.2	
T ($^\circ\text{C}$)	G_o (mol m^{-3})			
60	3000	3831	2678	
80	500	81	57	

Inserting the values of $\epsilon_{o,max}$ in the Eq. (26), the minimum values of the global effectiveness factor, $\eta_{go,min}$, have been calculated. As shown in Fig. 2, the behavior of $\eta_{go,min}$ is very similar to that of η_o , either from a qualitative or a quantitative point of view. In particular, the global effectiveness factor falls below 0.8 only when $R = 1$ mm and $T = 80^\circ\text{C}$, reaching a minimum value, $\eta_{go,min} = 0.65$, at $G_o = 500$ mol m^{-3} . The most important observation is, however, that at a radius of 0.3 mm, commonly used in industrial application, the global effectiveness factor is subject to very little variations ($0.95 < \eta_{go,min} < 0.99$) within the whole experimental domain investigated.

3.3. Time variations of diffusional resistances

Because the reaction rate of glucose isomerization to fructose decreases with time, due to the progressive thermal deactivation of the catalyst, both η and η_g invariably tend to increase.

The time behavior of the inner and global effectiveness factors will be examined with reference to the following situations:

- temperature and feeding conditions corresponding to the maximum ($T = 80^\circ\text{C}$, $G_o = 500$ mol m^{-3}) and minimum ($T = 60^\circ\text{C}$, $G_o = 3,000$ mol m^{-3}) catalyst deactivation rate;
- particle radius of 0.3 and 1.0 mm, respectively;
- final value of the activity coefficient, that is catalyst fraction still active at the moment of its substitution, $\psi_f = 0.1$ and 0.2 , respectively.

The catalyst utilization times, t_f , corresponding to the last conditions:

$$t_f = \frac{1}{k_d} \ln \left(\frac{1}{\psi_f} \right) \quad (31)$$

have firstly been calculated using Eq. (12), giving the values listed in Table 5, and then used in Eq. (14) to calculate the values of ϕ after different times from the start of utilization, $0 < t \leq t_f$ (Fig. 5). The other parameters, η , ϵ_{max} and $\eta_{g,min}$, have then been obtained as described above.

Figs. 3 and 4 show a comparison of the time behaviors of the inner and global effectiveness factors. As indicated in Table 5, the isomerization process under consideration lasted a time which strongly depended on the temperature and the residual biocatalyst activity, therefore a dimension-

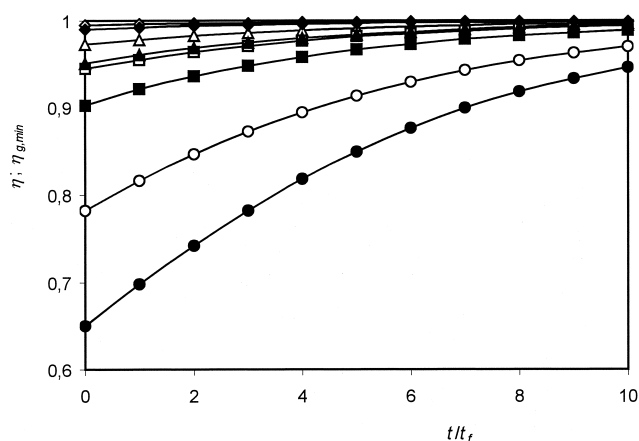


Fig. 3. Time behavior of the inner effectiveness factor, η , and of the global effectiveness factor, $\eta_{g,min}$, at different values of temperature, particle radius, and feed glucose concentration. $\psi = 0.1$. (\diamond) $R = 0.3$ mm, $T = 60^\circ\text{C}$; (\triangle) $R = 0.3$ mm, $T = 80^\circ\text{C}$; (\square) $R = 1.0$ mm, $T = 60^\circ\text{C}$; (\circ) $R = 1.0$ mm, $T = 80^\circ\text{C}$. Open symbols: η ; Full symbols: $\eta_{g,min}$.

less time, t/t_f , has been necessary for comparison. It is evident from these behaviors that both of the effectiveness factors slightly increase with the utilization time. In particular, the global effectiveness factor achieves final and average values always higher than 0.90 and 0.78, respectively, under the whole range of tested conditions. Moreover, as shown in Fig. 6, the relative difference between $\eta_{g,min}$ and η becomes more and more negligible elapsing the time, reaching a value less than 5% at the end of catalyst utilization ($t = t_f$).

From the above results one can conclude that, over a wide range of practical situations, the outer diffusional resistances can be neglected. Alternatively, the global effectiveness factor could be calculated from the inner ones as:

$$\eta_g = k \eta \quad (32)$$

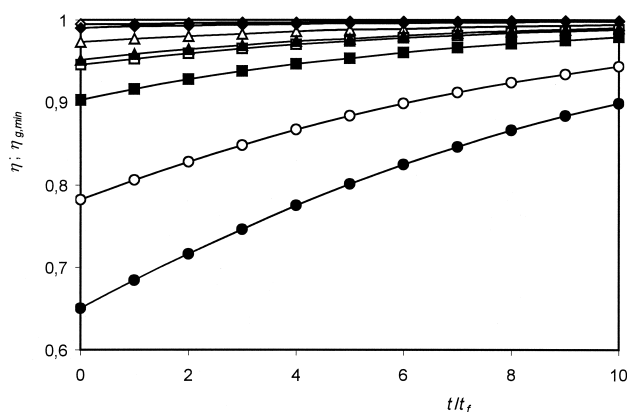


Fig. 4. Time behavior of the inner effectiveness factor, η , and of the global effectiveness factor, $\eta_{g,min}$, at different values of temperature, particle radius, and feed glucose concentration. $\psi = 0.2$. (\diamond) $R = 0.3$ mm, $T = 60^\circ\text{C}$; (\triangle) $R = 0.3$ mm, $T = 80^\circ\text{C}$; (\square) $R = 1.0$ mm, $T = 60^\circ\text{C}$; (\circ) $R = 1.0$ mm, $T = 80^\circ\text{C}$. Open symbols: η ; Full symbols: $\eta_{g,min}$.

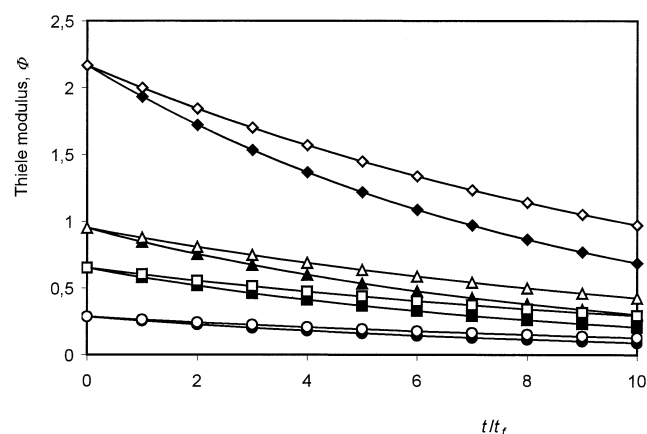


Fig. 5. Time behavior of the Thiele modulus, ϕ , under different conditions of temperature, particle radius, and residual biocatalyst activity. (\circ) $R = 0.3$ mm, $T = 60^\circ\text{C}$; (\square) $R = 0.3$ mm, $T = 80^\circ\text{C}$; (\triangle) $R = 1.0$ mm, $T = 60^\circ\text{C}$; (\diamond) $R = 1.0$ mm, $T = 80^\circ\text{C}$. Full symbols: $\psi = 0.1$; Open symbols: $\psi = 0.2$.

where k is a suitable correction coefficient very close to unity, since:

$$k = \frac{1}{1 + \epsilon} < \frac{1}{1 + \epsilon_{max}} \leq \frac{1}{1 + \epsilon_{0,max}} \leq 0.83 \quad (33)$$

being $\epsilon_{0,max} \leq 0.2$, as shown in Fig. 6.

Taking into account the variations of ϵ with the time, a mean value of the correction coefficient, \underline{k} , can be calculated for a given time of catalyst utilization. The appropriate values of \underline{k} , for the situations considered in this study, are reported in Table 6. Since the values of this correction coefficient are always very close to 1.0, it is evident that considering it for practical purposes is not significant.

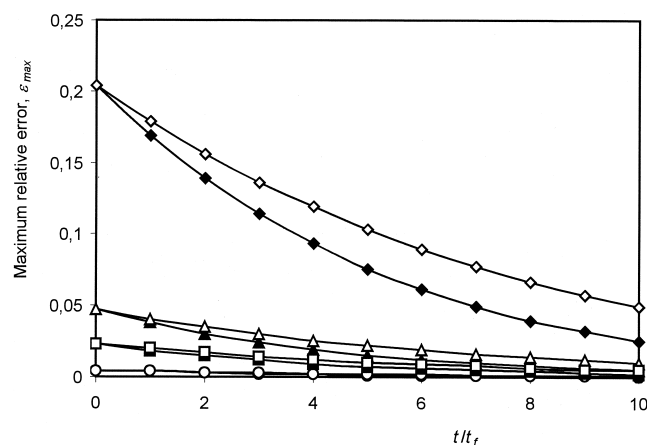


Fig. 6. Time behavior of the maximum value of the relative error, ϵ_{max} , under different conditions of temperature, particle radius, and residual biocatalyst activity. (\circ) $R = 0.3$ mm, $T = 60^\circ\text{C}$; (\square) $R = 0.3$ mm, $T = 80^\circ\text{C}$; (\triangle) $R = 1.0$ mm, $T = 60^\circ\text{C}$; (\diamond) $R = 1.0$ mm, $T = 80^\circ\text{C}$. Full symbols: $\psi = 0.1$; Open symbols: $\psi = 0.2$.

Table 6

Average values of the correction coefficient, κ , estimated under “extreme” conditions of temperature, particle radius, and residual biocatalyst activity

ψ_f		0.1	0.2
T (°C)	G_o (mol m ⁻³)	R (mm)	
60	3000	0.3	0.996
60	3000	1.0	0.965
80	500	0.3	0.988
80	500	1.0	0.903

4. Conclusions

The present study on the kinetics of glucose isomerization to fructose by immobilized GI leads to the following advances in the knowledge of diffusional resistances existing in the immobilized enzyme systems commonly used in industrial processes:

- the application of linearized kinetics allows to find analytical expressions describing the diffusional resistances, which makes the comparison under different conditions easier;
- the outer resistances appear to be very weak, so that they can be neglected in most situations;
- in those cases the outer resistances cannot be neglected, they can certainly be considered in a simplified form by use of Eq. (32), the error introduced by this approximation being very low;
- the approach followed in this study allows to solve in a much simpler way, with respect to the present practice, the design/optimization problems for this isomerization process.

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