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# A STUDY OF THE EFFECT OF DISPERSION ON THE ENZYMATIC CONVERSION OF STARCH TO GLUCOSE IN A SMALL PILOT PLANT FLUIDISED BED REACTOR

ESTUDO DO EFEITO DE DISPERSÃO NA CONVERSÃO ENZIMÁTICA DE AMIDO EM GLUCOSE NUM REACTOR DE LEITO FLUIDIZADO À ESCALA PILOTO

The effects of dispersion on the conversion of starch to glucose by amyloglucosidase immobilised on glass beads (ballotini) in a small pilot plant fluidised bed reactor are theoretically studied. This study indicates that, using the correlation of Chang and Wen (1968) to calculate the dispersion number in the reactor, no substantial differences in conversions exist between the dispersed plug flow model and the ideal plug flow model. Using the correlation of Bruinzel (1962) to calculate the dispersion number however, there are some differences between the conversions of the dispersed plug flow and those of the ideal plug flow model.

# 1. INTRODUCTION

The use of immobilised enzymes as industrial catalysts represents an increasingly important aspect of heterogeneous catalysis. Enzymatic reactions are somewhat complex in their kinetic characteristics, the basic reaction rate equation (known as the Michaelis-Menten equation)

$$V = \frac{k'_2 E.S}{K'_m + S}$$
(1)

where

k'2 is a kinetic constant

K'm the Michaelis-Menten constant

E enzyme concentration or activity (units)

S substrate concentration

often being subjected to modification by inhibitory and other effects. For these reasons the choice of reactor configuration is not always straightforward. Further limitations are imposed on reactor design by mass and heat transfer requirements, the need to optimise catalyst life and by practical considerations such as the nature of the feed material, etc.

Immobilised enzymes are already extensively used in the carbohydrate syrup industry, for the manufacture of fructose from glucose, using immobilised glucose isomerase. However, the glucose is still produced by enzymatic hydrolysis of starches using batch methods with the enzyme in solution. Practical progress with an immobilised enzyme has been hampered by factors such as the presence of suspended solids causing blockage in beds and filters. Furthermore to show commercial advantage very high conversions to glucose must be achieved, without the formation of retrograded by-products. Conversions of 90% are relatively simple to achieve but better than 95% must be achieved for commercial success.

At high conversions the reaction is tending to the first order rate control regime and hence a plug-flow reactor would appear desirable. Packed beds have demonstrated disadvantages in blockage and mass transfer limitations and we have therefore been concerned with the use of fluidised beds to achieve high conversions of starch to glucose using a fungal amyloglucosidase immobilised on rigid inorganic carriers. However, the degree of mixing prevailing in the reactor can affect adversely the conversion (4,5) and offset the advantages of this reactor in comparison with the fixed bed reactor.

Here we consider the prediction of conversion in a pilot plant reactor, using measured fluidisation parameters and published predictions of the axial dispersion effects occuring in fixed and fluidised beds.

Non porous glass beads are used as enzyme supports (diameter 0.254 mm  $\rho_{\rm S}=2.925\,{\rm g/cm^3}$ ). Elsewhere we describe methods for the attachment of enzymes to such particles (6). Such beads would in practice be unsuitable since the activity/unit weight is low. However, we used them for this study in order to avoid the internal diffusion effects that would be obtained with more suitable porous materials. We were therefore restricted to low substrate concentrations in order to achieve reasonable conversions within the complete flow range of the reaction system. This is however the range of importance, as shown above. At low starch concentrations not only can the dispersed plug flow model equation be analytically solved since the rate expression according to a Michaelis-Menten kinetic becomes first order if S  $\ll K'_{\rm m}$ , but also the differences between

conversions of the extreme models (PF and CST reactors) increase.

with

$$U_{mf} = 0.155$$
 (cm/s) (5)

Due to the height of the available reactor L,  $(L_{max} = 85 \text{ cm})$  the flow rate through the reactor depends on the weight of glass with which the reactor is loaded. In order to have the maximum number of units of enzyme activity within the reactor to compensate for the low specific activity of the non porous immobilised enzyme preparations but at the same time allowing for a wide range of bed voidages to be covered the weight of glass was fixed at 1500 g. For this weight of glass and using equation (4) the following range of flows through the reactor and appropriate bed voidages were calculated.

## Table 1

## Range of flow (I/ h) across the reactor and corresponding bed voidages for a loading of 1500 g glass particles

Q (I/h)	e	L (cm)
0	0.365	45.3
10 (Q <sub>mf</sub> )	0.365	45.3
74.5 (0 max)	0.662	85.3

# 4. DERIVATION OF THE PLUG FLOW AND CSTR MODEL EQUATIONS

For starch hydrolysis with amyloglucosidase (AG) the kinetic constant in equation (1) are normally determined from measurements of the rate of product formation (ie. glucose), though such constants are more properly defined in terms of the substrate. Thus the rate expression according to Michaelis-Menten kinetics for the non substrate inhibited reaction,

can be written as:

V ( 
$$\mu$$
 mole glucose/min) = k<sup>\*</sup><sub>2</sub> E<sub>W</sub> W  $\frac{C_S}{K'_m + C_S}$  (6)

where

- Cs starch concentration in g/l
- E<sub>W</sub> specific activity of the immobilised enzyme preparation in Units/gram
- $k'_2$  kinetic constant  $\frac{\mu \text{ mole/min}}{\text{Unit}}$
- Km Michaelis-Menten constant g/l

Converting equation (6) to g mole glucose produced per hour we abtain:

$$(-r'_{G}) = \frac{1}{W} - \frac{d N_{G}}{dt} = k''_{2} E_{W} - \frac{C_{S}}{K'_{m} + C_{S}}$$
 (7)

Models for the plug flow and CST reactors are obtained by using the fundamental reactor equations for the respective reactor and the Michaelis-Menten equation. For a liquid fluidised bed reactor the dispersed plug flow model proposed by Levenspiel (1972) (3) has been used by Kobayashi and Moo-Young (1971) (4) and Revel Chion (1975) (5) but its applicability has not been tested. This model is based on the concept of mixing in an analogous manner to molecular diffusion governed by Fick's law and gives conversions in between those of the plug flow and CST reactors, depending on the degree of mixing prevailing in the reactor.

Generally a certain amount of backmixing is encountered in all non ideal continuous reactor but, visually if nothing else, one would expect it to be important for the fluidised bed reactor. The dispersion number  $D_V/vL$  where L is the bed height, v the fluid velocity and  $D_V$  the dispersion coefficient describes quantitatively the mixing effect.

Chang and Wen (1968) (1) have developed the following correlation for the Peclet number Npe for a fixed and fluidised bed,

$$\epsilon N_{\rm Pe}/\chi = 0.20 \pm 0.011 \ {\rm Re}^{0.48}$$
 (2)

where

$$N_{Pe} = \frac{d_p v}{D_v} = \frac{d_p U}{D_{11}}$$

and

- d<sub>D</sub> particle diameter (L)
- v interstitial velocity (Lt<sup>-1</sup>)
- U superficial velocity (Lt<sup>-1</sup>)
- D<sub>V</sub> effective longitudinal dispersion coefficient based on interstitial velocity (L<sup>2</sup> t<sup>-1</sup>)
- $D_U$  effective longitudinal dispersion coefficient based on superficial velocity (L<sup>2</sup> t<sup>-1</sup>)
- χ 1 for fixed bed data, Remf /Re for fluidised bed data, dimensionless

The relationship  $\epsilon N_{Pe}/\chi$  covers the range of  $\epsilon = 0.4$  to 0.8 and particle density range up to 8.07 g/cm<sup>3</sup>. Hence may be derived:

$$\frac{D_{V}}{VL} = \frac{D_{U}}{UL} = \frac{d_{p}}{L} \cdot \frac{1}{N_{P_{\theta}}} = \frac{d_{p}}{L} \times \left[\frac{1}{(0.20 + 0.011 \text{ Re}^{0.48} \chi^{1/\epsilon})}\right] (3)$$

# 3. DETERMINATION OF A RANGE OF FLOWS ACROSS THE REACTOR

A flow diagram of the fluidised bed reactor used is shown in fig. 1. A relationship between the flow across the reactor and the voidage of the bed was determined for the glass support used, with water at 45 °C, and the following equation, of the form  $U = U_i e^n$ according to Richardson (1971) (7), was obtained:

$$U = 4.639 e^{3.374}$$
 (cm/s) (4)

where

$$k''_2 = 10^{-6} \cdot 60 k'_2$$
  
NG = g mole of glucose  
 $(-r'_C) = (g mole glucose/h g support)$ 

The reaction rate as derived (equation 7) gives us the rate of glucose produced (g mole/h)/g support. In order to be able to use the fundamental reactor equations one needs to convert this into a rate of starch disappearance.

Since for each n mole of glucose formed there is one mole of starch consumed the relationship between the two rates is simply:

$$\left(-\frac{1}{W} \quad \frac{d N_{S}}{d t}\right) = \frac{1}{n} \left(\frac{1}{W} \quad \frac{d N_{G}}{d t}\right) = \frac{1}{n} k_{2}^{"} E_{W} \quad \frac{C_{S}}{K_{m}^{'} + C_{S}} \quad (8)$$

where

n = number of g mole of glucose produced per each g mole of starch consumed

$$\left(-\frac{1}{W} \quad \frac{d N_S}{dt}\right) = g \text{ mole of starch consumed per hour and g of support (g mole / h g support)}$$

However the starch molecular weight [M.W.] Starch is unknown and therefore so is n. We can however derive a simple relationship which will enable us to overcome this difficulty. If one considers the polymer starch which is made up of glucose units, its hydrolysis to glucose can be written as:

> 1 mole Starch + (n-1)mole  $H_2 0 \rightarrow n$  mole glucose [(monomer)<sub>n</sub>]

Hence

[M.W.] Starch = n.180 - (n-1).18

and

$$\frac{[M.W.]_{Starch}}{n} = [M.W.]_{Monomer} = \frac{n.180 - (n-1).18}{n}$$
(9)

where

[M.W.] Monomer is the monomer average M.W.

When n is very high:

$$[M.W.]_{Monomer} = \lim_{n \to \infty} \frac{[M.W.]_{Starch}}{n} = 162$$
(10)

This means that, for a high M. W. glucose polymer, the monomer average M. W. contained in the starch polymer is 162. The limit of  $\frac{n-1}{n}$  varies from 0.9 for a 10 monomer polymer to 0.999 for a 1000 monomer polymer and accordingly [M. W.]Starch / n varies from 163.8 to 162.018. Thus provided that [M. W.]Starch is greater than 2000 the error in the assumption that [M.W.]Starch/n is 162 does not exceed 1.11% and will decrease as [M. W.] Starch increases.

# 4.1. DERIVATION OF THE PLUG FLOW EQUATION

Let us consider an isothermal plug-flow reactor. For a reaction rate based on unit weight of catalyst (support containing enzyme in this case) a substrate balance across the reactor gives (Levenspiel (1972) (3)):

$$F_{OS} d X_{S} = (-r'_{S})dW$$
(11)

If COS is the starch concentration in the feed then:

$$F_{OS} = \frac{C_{OS} \Omega}{[M.W.] \text{ Starch}} \quad (g \text{ mole/h}) \qquad (12)$$

where Q is the flow rate across the reactor in I/h.

Substituting equations (8) and (12) into equation (11) one obtains:

$$C_{OS} \ Q \ dX_{S} = \frac{[M.W] \ Starch}{n} \ k_{2}^{"} E_{W} \ \frac{C_{S}}{K_{m}^{'} + C_{S}} \ dW \qquad (13)$$

Since [M.W.] 
$$_{Starch}/n \cong 162$$
 and

$$X_{\rm S} = \frac{C_{\rm OS} - C_{\rm S}}{C_{\rm OS}} \tag{14}$$

we obtain after integrating

$$E_{t} = E_{W} \cdot W = \frac{0}{162 k_{2}'} [C_{OS} X_{S} - K_{m}' \ln (1 - X_{S})]$$
(15)

In the derivation of equation (15) above bulk diffusion effects have been ignored since they can be shown to be unimportant for dilute starch solutions at least up to 10 g/l (see Appendix).

## 4.2. DERIVATION OF THE CSTR MODEL EQUATION

For an isothermal well stirred reactor the rate equation based on a unit catalyst weight can be written (Levenspiel (1972) (3)) as:

$$F_{OS} X_S = (-r'_S) W \tag{16}$$

Using equations (8), (10) and (14) we obtain :

$$E_{t} = E_{W} \cdot W \frac{\Omega}{162 k_{2}''} \left[ C_{OS} X_{S} + K_{m}' \frac{X_{S}}{1 - X_{S}} \right]$$
(17)

## 5. DERIVATION OF THE DISPERSED PLUG FLOW MODEL EQUATION

As before the external diffusion effects can be shown to be insignificant,

The dispersion model of Levenspiel (1972) (3) for the case of an enzymatic reaction following Michaelis-Menten kinetics can be developed for this case as follows:

Consider an element of volume  $\Delta V$  of a heterogeneous reactor at



Since

(out-in) bulk flow + (out-in) axial dispersion + disappearance = 0 by reaction (18)

$$v \frac{d[S]}{dI} - D_v \frac{d^2[S]}{dI^2} + (-r_S) = 0$$
(19)

Now since  $(-r'_S) = \frac{1}{W(g)} \frac{d N_S}{dt}$  and  $(-r_S) = \frac{1}{V_L(I)} \frac{d N_S}{dt}$ 

$$(-r'_{S}) W(g) = (-r_{S}) V_{L}(I)$$
 (20)

W(g) weight in grams of the immobilised enzyme  $V_1$  (1) volume of substrate in litres

Thus

$$(-r_{\rm S}) = (-r_{\rm S}') \frac{W(g)}{V_{\rm L}(I)} = (-r_{\rm S}') \frac{(1-\epsilon)\rho_{\rm S} V_{\rm T} 10^3}{\epsilon V_{\rm T}} =$$
$$= 10^3 \frac{(1-\epsilon)}{\epsilon} \rho_{\rm S} (-r_{\rm S}')$$
(21)

where  $V_T$  is the total volume of the reactor in litres. Taking the value of  $(-r'_S)$  from equation (8) one obtains :

$$(-r_{\rm S}) = 10^3 \frac{(1-\epsilon)}{\epsilon} \rho_{\rm S} \frac{1}{n} k_2^{\prime\prime} \frac{\rm E_W C_{\rm S}}{\rm K_m^{\prime} + C_{\rm S}}$$
(22)

As 
$$[S] = \frac{CS}{[M.W.]_{Starch}}$$
 and  $\frac{[M.W.]_{Starch}}{n} \approx 162$ 

Using the dimensionless distance across the reactor Z = I/L, we obtain :

$$\frac{D_{V}}{vL} \frac{d^{2}C_{S}}{dZ^{2}} - \frac{dC_{S}}{dZ} - \frac{L}{v} \frac{1-\epsilon}{\epsilon} \rho_{S} 10^{3} \cdot 162 k_{2}^{"}E_{W} \frac{C_{S}}{K_{m}^{'}+C_{S}} = 0$$
(23)

Now as  $v = \frac{U}{\epsilon}$ ,  $\frac{L}{U} = \tau$  (mean residence time) and  $1 - \epsilon = \frac{L_0}{L} (1 - \xi_0)$  equation (23) becomes :

$$\frac{D_{V}}{VL} \frac{d^{2}C_{S}}{dZ^{2}} - \frac{dC_{S}}{dZ} - \frac{\tau L_{0}}{L} (1 - \epsilon_{0}) \rho_{S} 10^{3} \cdot 162 \, k_{2}^{"} E_{W} \frac{C_{S}}{K_{m}^{'} + C_{S}^{'}} = 0$$
(24)

In the range of concentrations we are interested in the linear form of equation (1)

$$\frac{c_S}{K'_m + c_S} = k_{0_2} c_S \tag{25}$$

(26)

can be used (see page ) and equation (24) becomes

$$\frac{D_{V}}{VL} = \frac{d^{2}C_{S}}{dZ^{2}} - \frac{dC_{S}}{dZ} - \frac{\tau L_{0}(1 - \epsilon_{0})}{L} \rho_{S} 10^{3} \cdot 162 k_{2}'' E_{W} k_{0} c_{S} = 0$$

If we put

$$\gamma = \frac{L_0 (1 - \epsilon_0)}{L} \rho_{\rm S} \, 10^3 \, 162 \, k_2'' \, {\rm E_W} \, k_{0_2} \tag{27}$$

We finally obtain :

$$\frac{D_{v}}{vL} \frac{d^{2}C_{S}}{dZ^{2}} - \frac{dC_{S}}{dZ} - \tau \gamma C_{S} = 0$$
(28)

or in terms of the fractional conversion XS

$$\frac{D_{v}}{vL} \quad \frac{d^{2}X_{S}}{dZ^{2}} \quad - \quad \frac{dX_{S}}{dZ} \quad + \tau\gamma(1-X_{S}) = 0$$
(29)

As pointed out by Levenspiel (1972) (3) the fractional conversion of the reactant (S) in its passage through the reactor is governed by three dimensionless groups: a reaction rate group  $\gamma \tau$ , the order of reaction n (in the present situation n = 1) and the dispersion group  $D_V$ 

The analytical solution of equation (29) for vessels with any kind of entrance and exit conditions according to Levenspiel (1972) (3) is:

$$\frac{C_{S}}{C_{OS}} = 1 - X_{S} = \frac{4 b \exp(\frac{1}{2} \frac{vL}{D_{V}})}{(1+b)^{2} \exp(b/2 \frac{vL}{D_{V}}) - (1-b)^{2} \exp(-b/2 \frac{vL}{D_{V}})}$$
(30)

where

$$p = \sqrt{1 + 4\gamma \tau \left(\frac{D_V}{vL}\right)}$$
(31)

For small deviations from plug flow expanding the exponentials and dropping higher order terms equation (30) reduces to:

$$\frac{C_{S}}{C_{OS}} = 1 - X_{S} = \exp\left[-\gamma \tau + (\gamma \tau)^{2} \frac{D_{V}}{vL}\right]$$
(32)

Equation (26) as derived is valid both for a packed and fluidised bed reactor.

# 6. LINEARIZATION OF THE MICHAELIS-MENTEN EQUATION

Consider plotted in fig. 2 the equation

ł

$$r = \frac{C_S}{K'_m + C_S}$$
(33)



It can be shown that

$$\left(\frac{\mathrm{d}r}{\mathrm{d}C_{\mathrm{S}}}\right)_{\mathrm{C}_{\mathrm{S}_{2}}} = \frac{\mathrm{K}_{\mathrm{m}}^{\prime}}{(\mathrm{K}_{\mathrm{m}}^{\prime} + \mathrm{C}_{\mathrm{S}_{2}})^{2}}$$
(34)

Now the equation of the tangent to the curve of equation (33) in the range of concentrations we are interested in can be approximately written as:

$$r' = (r) C_{S_1} + \frac{K'_m}{(K'_m + C_{S_2})^2} (C_S - C_{S_1})$$
(35)

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$$r' = k_{0_1} + k_{0_2} C_S$$
 (36)

$$k_{0_1} = (r) c_{S_1} - \frac{K'_m}{(K'_m + c_{S_2})^2}$$
 (37)

and

$$\zeta_{0_2} = \frac{\kappa_m}{(\kappa'_m + c_{S_2})^2}$$
 (38)

If CS1 is taken at point zero then

$$r' = k_{0_2} C_S$$
 (39)

The point  $C_{S_2}$  within the interval 0– $C_S$  can be chosen in order to obtain the lowest differences between values given by equation (33) and (39).

# COMPARISON BETWEEN CONVERSIONS OF THE DEFINED FLOW AND DISPERSED PLUG FLOW MODELS AT 1.0 g/I STARCH SOLUTION

The kinetic constants for the preparation were derived from the work of Revel Chion (1975) (5) for amyloglucosidase covalently immobilised on 1.319 mm diameter glass beads.

$$K'_{m} = 12 \text{ g/l}$$
  
 $k'_{2} = 2.166 \mu \text{ mole glucose/min Unit g support}$ 

According to these values which are assumed to hold for the support used -0.254 mm diameter glass beads - the equations derived for the plug flow and CST reactors become :

Plug Flow 
$$E_t = E_W \cdot W = \frac{\Omega}{0.021} [C_{OS} X_S - 12 \ln (1 - X_S)]$$
  
reactor (40)

$$\begin{array}{c} \text{CST} \\ \text{reactor} \end{array} \quad \text{E}_{t} = \text{E}_{W} \cdot \text{W} = \frac{\Omega}{0.021} \quad \left[ \text{C}_{\text{OS}} \times_{\text{S}} + 12 \quad \frac{\times_{\text{S}}}{1 - \times_{\text{S}}} \right]$$
(41)

The value of  $k_{O2}$  calculated for the value of K'\_m = 12 g/l for the concentration range of 0-1 g/l was  $k_{O2}$  = 0.079 for  $C_{S2}$  = 0.333 with a maximum error of 4.5 %.

Using equations (2), (4) and (5), the Peclet number for a fluidised bed is calculated as

$$N_{Pe} = \frac{10.834 + 0.162 \, \Omega^{0.48}}{1.296} \tag{42}$$

and for a fixed bed as

$$N_{Pe} = 0.5479 + 0.0081876 \, \mathrm{Q}^{0.48} \tag{43}$$

The mean residence time in hours can be computed for a fluidised bed by

$$\tau(h) = \frac{V(I)}{\Omega(I/h)} = \frac{2.798}{\Omega(5.421 - \Omega^{0.2964})}$$
(44)

and for a fixed bed by

$$\tau(h) = \frac{0.8129}{\Omega(1/h)}$$
 (45)

The height of bed L for the fluidised bed can be computed by

$$L(cm) = \frac{155.935}{5.421 - 0^{0.2964}}$$
(46)

Using equations (42) to (46) the value presented in table 2 were calculated.

#### Table 2

## Values for fixed and fluidised beds as introduced in the text

Fixed Bed $d_p/L = 5.695 \times 10^{-1_0}$ $L_0 = 45.3 \text{ cm}$			Fluidised Bed							
Q(I/h)	au (h)	Npe	1/N <sub>Pe</sub>	D <sub>v</sub> /vL	L(cm)	τ(h)	Npe	1/NPe	(d <sub>p</sub> /L) 10 <sup>4</sup>	D <sub>v</sub> /vL
1	0.8129	0,556	1.798	0.00102	-	-	-	-	<u></u>	-
4	0.2023	0.564	1,774	0.00101	-	-	-	-	-	-
8	0.1016	0.570	1,754	0.00100	-	-	-	-	-	-
10	0.0813	0.573	1.746	0.00099	45.3	0.0813	0.573	1,746	5,695	0.00099
20	0.0406	0.582	1.717	0.00098	52.1	0.0468	0.237	4.215	4,952	0.00208
30	0.0271	0.590	1.695	0.00097	58.2	0.0348	0,142	7.039	4,432	0.00312
40	0.0203	0.596	1.678	0:00096	64.0	0.0287	0,0989	10.114	4.031	0.00408
50	0.1630	0.601	1,663	0.00095	69.8	0.0251	0.0747	13,383	3,696	0.00495
60	0.0135	0.606	1.649	0.00094	75.9	0.0227	0.0595	16.813	3.399	0.00571
74.5	0.0109	0.613	1.632	0.00094	85.1	0.0205	0.0454	22.026	3.031	0.00667

According to the values tabulated the dispersed plug flow equation for a 1.0 g/l starch solution was solved for the range of flow rates possible in the fluidised bed reactor. Since the values of the dispersion number are rather low, equation (32) was used. The weight of glass beads is 1500 g and an enzyme activity of 5.33 unit/gram is assumed. The value of  $\gamma$  from equation (27) was computed as

$$\gamma = \frac{738.910}{L \text{ (cm)}}$$

The results obtained for the dispersed plug flow model – fluidised and packed bed – and PFR and CSTR models are presented in table 3. The differences between the extreme models are evident and those between the dispersed plug flow either packed or fluidised beds – and the ideal plug flows are insignificant.

# Table 3

Theoretical conversion for PFR, DPFR (packed and fluidised bed) and CSTR according to equations (40), (28) and (41) respectively. Conditions: 1 g/l starch solution, 8000 Units, 45 °C

Q (1/h)	×	хD	×	
	*PFR	Packed Bed	Fluidised Bed	*CSTR
1	1	1	-	0.933
4	0.967	0.963	-	0.775
8	0.815	0.809	-	0.630
10	0.738	0.734	0,734	0.575
20	0.483	0.484	0.485	0.400
30	0.354	0.357	0.357	0.306
40	0.279	0,282	0,282	0,248
50	0.230	0.233	0.233	0.208
60	0,195	0,198	0,198	0.179
74.5	0.160	0.163	0.163	0.149

## 8. DISCUSSION

Under the range of experimental conditions tested either the ideal PF or dispersed PF packed bed model equations give conversions similar to those of the dispersed plug flow fluidised bed model equation. So the degree of mixing prevailling does not substantially affect the conversion.

The value  $D_v/vL$  was calculated by equation (3) and since it is influenced by the value of  $U_{mf}$  we compared the value used ( $U_{mf} = 0.155$ ) with values calculated as below, from the correlations presented by Richardson (1971) (7).

a) For uniform spherical small particles

$$\begin{split} U_{mf} &= \ 0.00059 \ d_p^2 \ (\rho_S - \rho_f) \ g/\mu \\ giving \ U_{mf} &= \ 0.122 \end{split}$$

b) For large particles, using the Ergun equation

$$Re_{mf} = \frac{U_{mf} \rho_f d_p}{\mu} = 25.7 \left[\sqrt{1 + 5.53 \cdot 10^{-5} Ga} - 1\right]$$
  
giving  $U_{mf} = 0.146$ 

Thus it is likely that a reasonable value for  $U_{mf}$  was used and that the possible errors introduced in  $D_{\rm V}$  /vL would not influence the values of the conversions.

Since the dispersion number as given by equation (3) increases with the flow rate we investigated the effect of dispersion at high flow rates and high conversions. Conversions of 0.90, 0.95 and 0.98 were considered for an ideal plug flow reactor working at a flow rate of 74.5 l/h, (maximum flow rate through the fluidised bed reactor) and the correspondent  $E_W$  values calculated. Then the conversions in the dispersed plug flow models were calculated as presented in table 4:

## Table 4

Comparison between conversions of plug flow and dispersed plug flow models at  $Q = 74.5 \ I/h$ 

E <sub>W</sub> (Unit/gram)	X <sub>PFR</sub>	XDPFR		
		Packed Bed	Fluidised Bed	
64.478	0.900	0.883	0.880	
87.268	0.950	0.945	0.942	
113,344	0.980	0.977	0.976	

It may be seen that both the packed and fluidised bed dispersed plug flow models give again substantially the same conversion as the ideal plug flow model. Although the dispersion in the fluidised bed is higher than that in the packed bed, both conversions are effectively the same. This is due to the fact that although the value of  $D_V$  /vL is higher for the fluidised bed, than for the packed bed, it is compensated by the higher value of  $\tau = \frac{L}{U}$ . Of course the size of

the fluidised bed reactor is  $85/45.3 \approx 1.9$  times higher.

Again either ideal plug flow model or dispersed plug flow model give similar conversions.

Since the effect of mixing is more important for first order reactions it seems that in principle (if the dispersed plug flow model describes the conversion in the fluidised bed reactor) for high starch concentrations this effect will be even less important.

As to the value of  $D_V/vL$ , it is given one for a given reactor operating under given conditions but when designing a reactor it will probably be possible to optimise the value of  $D_V/vL$ .

According to the results obtained using the Chang and Wen correlation the application of the plug flow model to the fluidised bed reactor should be adequate. However, using the correlation presented by Bruinzel et al. (1962) (2) for fluidised beds the values obtained for the dispersion number are much higher than those obtained using equation (3).

The correlation presented by these authors is

$$N_{Po'} = 4.3 \times 10^{-3} R_{B'} 0.18$$
(47)

where

$$N_{Pe'} = \frac{U d_p}{\epsilon D_{11}}$$

and

$$\operatorname{Re}' = \frac{\operatorname{Ud}_p}{\epsilon \mu}$$

and it then follows that

$$\frac{D_U}{UL} = \frac{10^3}{4.3 \operatorname{Re}^{0.18} \epsilon} \qquad \frac{d_p}{L} \qquad (48)$$

As Re' and  $\epsilon$  increase with Q and d<sub>p</sub>/L decreases with Q, D<sub>U</sub>/UL decreases with Q, contrarily to what happens with equation (3) where D<sub>U</sub>/UL(= D<sub>v</sub>/vL) increases with the flow rate.

We have calculated the conversions for the fluidised bed reactor using this correlation for the case considered in table 4 and have obtained:

XPFR	X <sub>DPFR</sub> (Fluidised Bed)
0.900	0.851
0.950	0.917
0.980	0.955

It can be concluded that in this case there are some significant differences between the two models considered. Moreover, since according to equation (47) the dispersion number decreases with Q, for high conversions at low flow rates the effect will even be higher. We are now in a position to test experimentally the models here derived by using amyloglucosidase immobilised on the same beads as those used in the earlier hydrodynamic studies, and will compare the experimental results with those here predicted.

# APPENDIX

According to Pitcher (1975) (8) the effect of external film diffusion in a fixed bed reactor can be estimated from single point reactor performance data by calculating the height of the bed required for the necessary conversion assuming film diffusion to be the controlling step. This height  $L_0$  can be estimated from the correlation given by Satterfield:

$$L_{0} = \frac{\epsilon^{Re^{\frac{2}{3}} N_{Sc}^{\frac{2}{3}}}}{1.09 a} \ln (Y_{1}/Y_{2})$$

where

e	bed voidage
Re	Particle Reynolds number $U \rho_f d_p / \mu$
NSc	Schmidt number $\mu/\rho_{\rm f}$ D <sub>S</sub>
а	ratio of particle surface area to reactor volum
Y <sub>2</sub>	mole fraction of substrate in the product
Y1	mole fraction of substrate in the feed

The diffusivity  $D_{SB}$  for starch (dilute solutions) in water can be approximately computed by the empirical correlation of Wilke and Chang (Treybal (1968) (9)).

$$D_{SB} = \frac{7.4 \times 10^{-8} (\phi M_B)^{0.5} T}{\mu' v_S 0.6}$$

where

D<sub>SB</sub> diffusivity of (S) in diluted solution of solvent B, sq cm/sec

MB solvent M. W. (water in this case)

T Temperature, °K

μ' solution viscosity, centipoise

vs solute molal volume at n bp, cm<sup>3</sup>/g mole

 $\phi$  association factor for solvent (2.6 for water as solvent)

The value of  $\mathsf{D}_{SB}$  was calculated for a  $\mathsf{C}_{OS}$  value of 10 g/l as follows:

$$\phi$$
 = 2.6  
T = 273 + 45= 318 °K  
 $\mu'$  = 0.772 cp  
v<sub>S</sub> = n.v<sub>S</sub> C<sub>6</sub>H<sub>12</sub> O<sub>6</sub>- (n-1) v<sub>S</sub>H<sub>2</sub> O = 162.8 n - 14.6

Thus

$$D_{SB} = \frac{20852.8 \times 10^{-6}}{(n \times 162.8 - 14.8)^{0.6}}$$

 $\mathsf{D}_{SB}$  depends obviously on starch molecular weight. The starch to be used is a thinned starch with its molecular weight assumed not to exceed 4000. Thus

$$n \ge 180 - (n - 1) = 4000 \implies n = 24.6.$$

Then

$$D_{SR} = 0.144.10^{-5} \text{ cm}^2/\text{s}$$

1 365

Now

$$Re = \frac{0.834 \times 0.99523 \times 0.0254}{0.772 \times 10^{-2}} = 2.77$$

$$N_{Sc} = \frac{0.772 \times 10^{-2}}{0.99523 \times 0.144 \times 10^{-5}} = 5.39 \times 10^{3}$$

$$a = \frac{4 \pi r^{2}}{\frac{4}{3} \pi r^{3}} (1 - \epsilon_{0}) = \frac{6 (1 - \epsilon_{0})}{d_{p}} = 147.67$$

Let us calculated now the height of reactor required to achieve a 0.95 conversion in a 10 g/l starch solution with a flow through the packed bed of  $53.9^{\circ}$  l/h. For a 0.95 conversion we have

$$Y_{1} \cong 1$$

$$Y_{2} = \frac{1}{1+19 \text{ n}}$$
and
$$\frac{Y_{1}}{Y_{2}} = 468.4$$
Thus
$$L_{0} = \frac{0.365 (2.77)^{\frac{2}{3}} (5.39 \times 10^{3})^{\frac{2}{3}}}{1.09 \times 147.67} \ln (468.4) =$$

$$= 8.45 \text{ cm}$$

As the available height of the reactor for the fixed bed is 45.3 cm it can be concluded that the diffusion effects are not important for the conditions considered.

Value of Qmax for the fluidised bed reactor for a 10 g/l starch solution.

# NOMENCLATURE

8	External surface area of support per unit volume of reactor ( ${\rm L}^{-1})$
b	$\sqrt{1 + 4 \gamma \tau (D_v / vL)}$ in equation (31)
COS	Initial starch concentration (ML <sup>-3</sup> )
CS	Actual starch concentration (ML <sup>-3</sup> )
do	Particle diameter (L)
Ds	Substrate diffusivity ( $L^2 t^{-1}$ )
D <sub>SB</sub>	Substrate diffusivity in diluted solution of solvent $B(L^2 t^{-1})$
DU	Effective longitudinal dispersion coefficient based on superficial velocity ( $L^2 t^{-1}$ )
Dv	Effective longitudinal dispersion coefficient based on interstitial velocity
E	Enzyme concentration $(ML^{-3})$ or total enzyme activity (Units)
Et	Total enzyme activity
Ew	Specific enzyme activity (Unit/gram)
Fos	Molar Feed rate of substrate (S) (Mt <sup>-1</sup> )
g	Acceleration due to gravity (Lt <sup>-2</sup> )
Ga	Galileo number ( $\rho_f (\rho_S - \rho_f) g d_p^3 / \mu^2$ ), dimensionless
k'2	Reaction rate constant for immobilised enzyme $(t^{-1})$
k2	$60 \times 10^{-6}$ k'2
k <sub>01</sub>	Reaction rate constant, dimensionless
k02	Reaction rate constant, ((concentration) $^{-1}$ )
K'm	Michaelis-Menten constant for immobilised enzyme ( $ML^{-3}$ )
L	Length of expanded bed or reactor
LO	Length of fixed bed or reactor
1	Distance along the bed or reactor
MB	Molecular weight of B
NG	Gram mole of glucose
Npe	Particle Peclet number (U $d_p/D_U = v d_p/D_v$ ) dimensionless
N <sub>Pe</sub> '	Modified Peclet number $(U d_p/e D_U = v d_p/e D_v)$ dimensionless
Ns	Gram mole of starch
Nsc	Schmidt number $\mu / \rho_{\rm f} D_{\rm S}$ , dimensionless
n	Exponent in Richardson and Zaki equation
n	Gram mole of glucose yielded by a gram mole of starch
۵	Flow rate (L <sup>3</sup> t <sup>-1</sup> )
Re	Particle Reynolds number (U dp $\rho_{\rm f}/\mu$ ), dimensionless
Re'	Modified particle Reynolds number (U d <sub>p</sub> $\rho_{\rm f}/$ / $\epsilon_{\mu}$ ), dimensionless
Remf	Particle Reynolds number at minimum fluidisation velocity ( $U_{mf}d_{p} \rho_{f} / \mu$ ), dimensionless
r, r'	Reaction rate, dimensionless
(-r <sub>G</sub> )	Reaction rate of glucose formation (t <sup>-1</sup> )
(-rs), (-r's)	Reaction rate of starch disappearance (t <sup>-1</sup> )
(S)	Substrate
[S]	Molar concentration of substrate (ML <sup>-3</sup> )
S	Substrate concentration
Т	Absolute temperature °K

t	time
U	Superficial liquid velocity (Lt <sup>-1</sup> )
Ui	Constant in Richardson and Zaki equation (Lt <sup>-1</sup> )
Umf	Minimum fluidisation velocity (Lt <sup>-1</sup> )
V	Volume of reactor (L3)
٧.	Velocity of enzyme reaction (ML <sup>-3</sup> t <sup>-1</sup> )
v	Interstitial liquid velocity (U/ $\epsilon$ ), (Lt <sup>-1</sup> )
٧S	Solute molal volume (cm <sup>3</sup> /g mole)
VL	Liquid reactor volume (L <sup>3</sup> )
VT	Total volume of reactor or bed (L <sup>3</sup> )
XS	Fractional conversion, dimensionless
Z	Dimensionless distance along the reactor (I/L)
W	Enzyme preparation weight (gram)
Y	Mole fraction of substrate, dimensionless

## GREEK LETTERS

γ	parameter defined in equation (27)
e	bed voidage of fluidised bed, dimensionless
€O	bed voidage of fixed bed, dimensionless
μ, μ΄	dynamic viscosity (ML <sup>-1</sup> t <sup>-1</sup> )
PS	solid density (ML <sup>-3</sup> )
Pf	fluid density (ML <sup>-3</sup> )
τ	mean residence time (t)
x	Remf/Re for fluidised bed, 1 for fixed bed, dimensionless
ø	association factor for solvent.

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#### RESUMO

Os efeitos da dispersão na conversão de amido a glucose pela amiloglucosidase imobilizada sobre partículas de vidro (ballotini) num reactor de escala piloto de leito fluidizado, são estudados teoricamente. Este estudo indica que, usando-se a correlação de Ćhang e Wen (1968) para calcular o número de dispersão do reactor, não há diferenças substanciais entre as conversões obtidas, quer no modelo de tipo êmbolo com dispersão, quer no modelo de tipo êmbolo ideal. Usando-se a correlação de Bruinzel (1962) para calcular o número de dispersão, verificaram-se contudo algumas diferenças entre as conversões obtidas nos dois modelos.