Computer aided design of pellets for fixed-bed reactors performing Michaelis – Menten reactions

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Abstract

The problem of designing the pellet characteristics for existing fixed-bed reactors has been studied. The reactor is assumed to be a unidimensional, plug-flow, heterogeneous type. Three particle shapes, two intraparticle mass transfer mechanisms, two kinds of film resistance to mass transfer and two poisoning patterns have been considered. An economic balance to both product market price and pellet market cost was taken into account. An interactive program (HIMER) containing all these contributions was thus developed, enabling the investigator to follow the reactor performance along the flow coordinate.

Introduction

Most fixed-bed, enzymic reactors included in biochemical industrial processes were designed to perform specific reactions. As time goes by new kinds of enzymes are found and brought to industrial scale, together with new reaction routes leading to a number of new demanded products. Therefore the economic optimization procedure that took place during the former reactor design often loses validity. Instead of having the reactor replaced, a far more attractive solution, ensuring maximum net profit, is exchanging the pellet and eventually creating a void portion on the top of the reactor. The reintegration pattern still continues to take place at the rate initially estimated and the operation costs keep fairly close to the same value, so an economic balance between the market price of the product obtained via the reactor and the market cost of the pellet is shown to be sufficient in the new economic optimization. Several kinds of reactors have been studied and thoroughly reported in the literature. A unidimensional, heterogeneous type, according to Froment (1967) and Froment and Bischoff (1979), consisting of a plug-flow type reactor, with interparticle and intraparticle resistances to mass transfer, was the elected model for the algorithm, a good deal of biochemical reactions catalysed by supported enzymes falling within this hydrodynamic type. Neither heat effects nor pressure drops were taken into account, so a quick, fairly accurate design is obtained. Only minor modifications are, in fact, introduced by such extra effects, as long industrial practice has proved in general. The behaviour of the catalyst particle may be approached in a number of ways, each

one assuming distinct hydrodynamic characteristics and mass transfer behaviours. The effectiveness factor plays an important role in this instance, being able to link the intraparticle averaged behaviour to the bulk behaviour in the reactor (Smith, 1981). A large number of situations are considered in the program, so covering a wide variety of industrial fixed-bed enzymic reactors. A simple, one-substrate Michaelis – Menten kinetic rate equation (Lehninger, 1982) is assumed throughout the program, realizing that other kinetic rate equations could be easily introduced and algebraically treated in quite a similar manner (Durand and Monsan, 1982).

System and methods

The computer program was written in a Hewlett-Packard supported version of Microsoft BASIC. It was implemented at Escola Superior de Biotecnologia (Porto) on a HP-150II, with standard RAM, using a double-sided dual disk drive HP-9123, for 3½ in floppy disks. The VDU hard-copies were taken in a HP-2686A Laser Jet Printer using a RS-232C serial interface to data transfer. A printed listing will be made available to investigators upon request.

Algorithm

The program – HIMER – is designed to study the performance of an existing plug-flow reactor with interchangeable solid-supported enzyme fixed beds. The governing general equation obtained from a differential mass balance in steady-state conditions to the reactor type selected is as follows (Villermaux, 1973):

$$\frac{dC_b^*}{dz^*} + \eta Da(1 - \epsilon)\frac{C_b^*}{K_m^* + C_b^*} = 0 \qquad (1)$$

η being the effectiveness factor, Da the Dahmköler number, ϵ the pellet void fraction. Variables Da, K_m^*, C_b^* and z* are dimensionless variables defined as follows:

$$Da = \frac{Lv_m}{uC_o} \qquad (2)$$

$$K_m^* = \frac{K_m}{C_o} \qquad (3)$$

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$$C_b^* = \frac{C_b}{C_o} \qquad (4)$$

$$z^* = \frac{z}{L} \qquad (5)$$

where L denotes the reactor length, v_m the maximum kinetic rate, u the mean fluid velocity in cross-sectional area of reactor, C_0 the inlet substrate concentration, K_m the Michaelis−Menten kinetic constant, C_b the bulk concentration in the reactor, z the reactor coordinate along flow direction and L the reactor length.

The differential equations as well as the commonly accepted boundary conditions for each particle shape in the pellet, mass transfer behaviour both in interparticle and intraparticle conditions, and poisoning patterns were taken from well established references concerning chemical and biochemical engineering (Smith, 1981; Wingard et al., 1976; Engasser and Horvath, 1976; Goldstein, 1976; Johnson, 1979; Wakao and Smith, 1964; Jackson, 1977; Nir and Pismen, 1976; Satterfield, 1970; Wheeler et al., 1951; Cresswell, 1985). The usual definitions allowing evaluation of the effectiveness factor were used (Mingle and Smith, 1961; Wakao and Smith, 1964; Hougen and Chu, 1962; Schneider and Mitschka, 1965; Aris, 1975; Bischoff, 1965).

Assuming the only relevant contributions to the economic performance of the reactor are the market price of the product obtained, V_p, and the market cost of the pellet, V_c, a dimensionless, time-based cumulative net profit, $\dot{V}_n^*$ may be ascribed to the reactor performance according to:

$$\dot{V}_n^* = \frac{\dot{V}_n}{u\,A\,v_p\,r\,M_m\,(C_o - C_b)} = 1 - \frac{Ma\ z^*}{1 - C_b^*\,(z^*)} \qquad (6)$$

Ma being a dimensionless parameter relating technical to economic features defined as:

$$Ma = \frac{(1 - \epsilon)\,\varrho\,V_c L}{V_p t_{op} r u M_m C_o} \qquad (7)$$

where $\dot{V}_n$ is a time-based cumulative net profit, A the cross-sectional area of the reactor, r the stoichiometric ratio of product to reactant, M_m the molecular weight of product, ϱ the specific density of the pellet solid support, and t_{op} the operating useful life of the enzyme. The dimensionless net profit ranges from unity to lower values, even negative ones. An incremental, time-based dimensionless net profit may be useful, the definition being apparent from Eq. (6).

Implementation

An efficient philosophy when trying to implement a mathematical simulation of supported enzyme reactors is segmenting the whole algorithm into several subroutines, a hierarchical level being defined. Elementary subroutines containing a few input parameters and belonging to the lowest computation level should be able to perform minor actions, being called by the subroutines in the intermediate level whenever required. This is the case of writing a piece of text on the screen in graphical mode, as shown in Figure 1. Note the sequences of ASCII characters preceded by an escape character which enable some features, usually performed at the keyboard, to be done under program control. Intermediate subroutines are directly called by the main program which consists of a number of suitable options. Advantage is taken from the existing user keys on the base of the screen, which send a single suitable character to the buffer where it is eventually accepted and processed through the INKEY$ function. Numeric values are entered via the keyboard through an INPUT function. The different types of menus are shown in Figure 2. A few security facilities have been provided to the program in order to avoid entering wrong data types. Four in-line graphs (see Figure 3) are printed on the screen

```
1000 ' ********************************************************
1001 '
1002 ' Subroutine for labeling under graphics text mode
1003 '
1004 ' SIZE = graphics text size
1005 ' ORIENTATION = graphics text orientation
1006 ' ABCISSA = abcissa for the graphics absolute cursor
1007 ' ORDINATE = ordinate for the graphics absolute cursor
1008 ' TEXT$ = alphanumeric label
1009 '
1010 PRINT CHR$(27)+"*ds"
1011 PRINT CHR$(27)+"*pa"
1012 PRINT CHR$(27)+"*m"+STR$(SIZE)+"m"
1013 PRINT CHR$(27)+"*m"+STR$(ORIENTATION)+"n"
1014 PRINT CHR$(27)+"*d"+STR$(ABCISSA)+STR$(ORDINATE)+"o"
1015 PRINT CHR$(27)+"*pc"
1016 PRINT CHR$(27)+"*l"+TEXT$
1017 '
1018 RETURN
1019 '
1020 ' ********************************************************
```

Fig. 1. BASIC subroutine aimed at writing a piece of text in the graphics screen.

and plotted according to the behaviour of the already integrated portion of the reactor. Technical data are available via the first two graphs (Substrate Dimensionless Bulk Concentration and Pellet Effectiveness Factor) whereas the latter two show the evolution of the Incremental and Cumulative Net Profits. The

economic performance is thus easily followed. A growing oblong is filled up inside the schematic reactor showing the extent of the integration already performed.

Due to the non-linear nature of the differential equations describing the material balance to the reacting substrate inside

a MAIN MENU

Select the shape of the solid support for the enzyme:

| SLAB | CYLINDER | SPHERE |

Select the mass transfer mechanism inside the supported enzyme:

| DIFFUS. | DIFFUS.+ CONVECT. |

Select the importance of film resistance to mass transfer:

| NEGLIGIBLE | EXTERNAL RESIST. |

Select the poisonning pattern:

| NONE | UNIFORM | SHRINK. CORE |

b

PELLET DETAILED MENUS

■ Pellet Geometry

Slab Half Thickness = _____ m

Cylinder Radius = _____ m

Sphere Radius = _____ m

■■ Intraparticle Mass Transfer Mechanism

Effective Diffusivity = _____ m^2/s

Intraparticle Fluid Velocity = _____ m/s

■■■ Film Resistance to Mass Transfer

Film Mass Transfer Coefficient = _____ m/s

■■■■ Poisonning Pattern

Poisonned Fraction = _____

c REACTOR DETAILED MENU

Pellet Void Fraction = _____

Reactor Length = _____ m

Fluid Average Cross-Sectional Velocity = _____ m/s

Inlet Substrate Concentration = _____ mol/m^3

Maximum Kinetic Rate = _____ $mol/(m^3 .s)$

Michaelis-Menten Kinetic Constant = _____ mol/m^3

Specific Density of the Pellet Solid Support = _____ kg/m^3

Molecular Weigth of the Product = _____ kg/mol

Stoichiometric Ratio of Product to Reactant = _____

Operating Useful Life of the Enzyme = _____ s

Market Cost of the Supported Enzyme = _____ $/kg

Market Price of the Product = _____ $/kg

Fig. 2. Listing of the existing menus together with the information asked for by the program. **a.** Main menu, where selection of the mass transfer characteristics is made by pressing the appropriate function key. **b.** Pellet detailed menus where data concerning each of the options chosen in the main menu are entered via the keyboard. **c.** Reactor detailed menu, where both technical and economic characteristics of the reactor are entered via the keyboard.
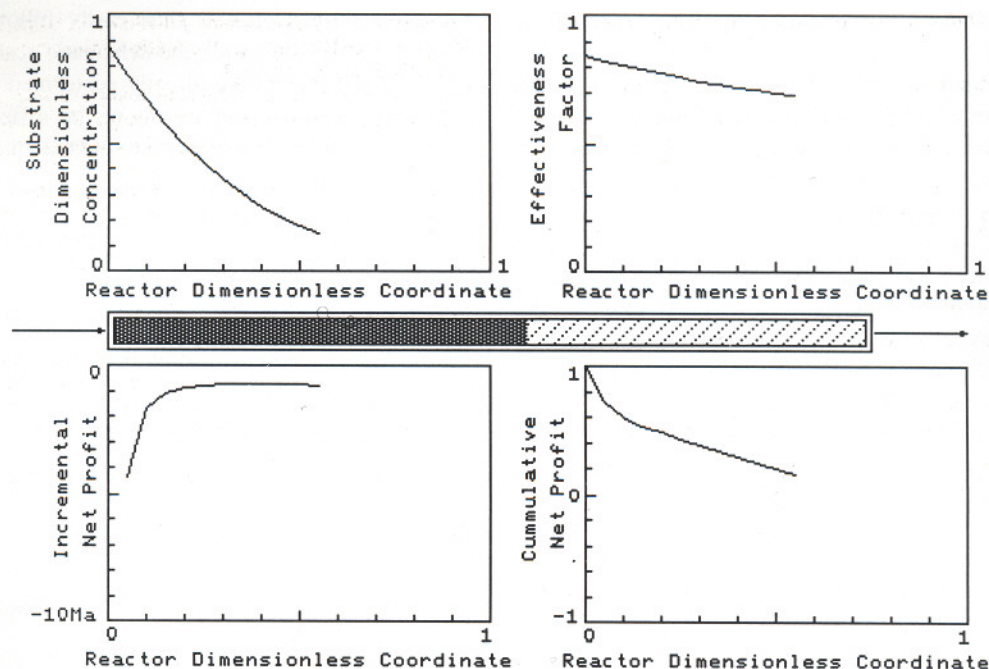
Fig. 3. VDU hard-copy during a run of program HIMER, showing the four in-line graphs reporting as many technical and economic relevant data. The following conditions are assumed: cylindrical geometry (radius = 0.0025 m); diffusional mechanism for mass transfer inside the pellet (effective diffusivity = 0.000 0003 m^2/s); negligible film resistance to mass transfer; no poisoning pattern; pellet void fraction = 0.3; reactor length = 4 m; fluid average cross sectional velocity = 0.12 m/s; inlet substrate concentration = 250 mol/m^3; maximum kinetic rate = 60 mol/(m^3.s); Michaelis−Menten kinetic contanst = 230 mol/m^3; specific density of the pellet solid support = 975 kg/m^3; molecular weight of the product = 0.3 kg/mol; stoichiometric ratio of product to reactant = 1; operating useful life of the enzyme = 200 000 s; market cost of the supported catalyst = 30 000 \$/kg; market price of the product = 35 \$/kg.

the pellet, they are integrated via a numerical method. This decision enables further kinetic equations to be introduced without extensive modifications on the native structure of the program. Integration is developed assuming an initial value problem to stand, from the symmetry condition at the centre of the catalyst particle (whenever this boundary condition is valid), to the catalyst surface (or to the outer surface of active catalyst, in the case of shrinking core poisoning). The other boundary condition is then tested: either unit concentration (for negligible film resistance to mass transfer) or overall molar flux through the pellet outer surface equal to the molar flux through the film (for the opposite situation). If the surface or the bulk concentration is not equal to unity, then another estimate for the concentration at the centre of the catalyst particle is attempted, the integration procedure being iterated until convergence is achieved. A bisection method proved to be effective in the search for the next estimate. The method used for the integration procedure is a Runge−Kutta−Nyström method (Kreyszig, 1979) coupled with an automatic choice of the step size according to a maximum local error criterion. Equation (1) is integrated via a classical Runge−Kutta method of order 4, the step size being controlled in a similar fashion (Conte and Boor, 1983).

Discussion

The use of variable step sizes in the integration of the differential equations adds considerably to the complexity of the pro-

gram and leads to results at a set of nonuniformly spaced points; nevertheless, the automatic step size control provides the user with very good estimates of accuracy, and makes the overall program quite efficient. The substantial additional effort required due to error control may be eventually overcome by using variations to the original Runge−Kutta method (cf. Fehlberg, 1970).

Tests upon the upper boundary for the increment on the independent variable to be accepted during numerical integration of equations were performed. In practice, a 5% increment on the independent variable proved to lead to accurate results on an acceptable industrial scale basis, when dealing with the behaviour of the reacting system. The step size control automatically reduces this value to a lower one in the neighbourhood of the supported catalyst surface and in the first portions of the reactor, where the steepest variations in the concentration profile are likely to occur.

The physical significance of the economic performance characteristics obtained via program HIMER may be enhanced provided a few runs are made for increasing poisoned fractions, according to a given deactivation rate equation. An average value is then to be taken to evaluate the optimal pellet length for the reactor. Moreover, the economic information available proves to be relevant whenever enterprise economic policies are followed concerning extra capital investments. In such cases, a minimum net profit ratio is usually defined, so the actual pellet

length may be evaluated to advantage by using some of the HIMER features.

Although some sophisticated methods were used, allowing some speeding to the integration procedure, program HIMER still requires a few minutes to run, due to the non-compiled nature of the program. Running times depend mainly on the complexity of the mathematical formulae describing the concentration profile inside the pellet, on the maximum local error allowed and on the intrinsic kinetic rate for the enzyme.

Extension of the program to more complex pellet behaviour is a straightforward task, as long as the appropriate differential equations and boundary conditions governing the mass transfer phenomena are available. This is the case with bidispersed porous catalysts (Carberry, 1962; Kuçukada and Dogu, 1985) and supported enzymes performing multiple reactions. Such extended algorithm will readily find an important role as a tool for the investigator, especially because economic constraints are always taken into account. Simulation does advantageously replace laboratory or pilot scale experimentation, thus leading to quick, low cost optimization. The choice of the HP150 series microcomputer for this software represents a compromise between the availability of such systems in industries (often working as intelligent terminals of more powerful minicomputers) coupled with feasibility of operation and the slowness of operation due to interpretative running instead of a compiled one.

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