

INVESTIGATION OF HYDROGENATION IN LIQUID PHASE. XVII.*

THEORETICAL MODEL OF HYDROGENATION IN A LIQUID FILM ON A VERTICAL COLUMN OF SPHERES

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A theoretical model of an isothermal trickle bed reactor, consisting of a vertical column of spherical particles of catalyst is examined. A solution of pertinent partial differential equation describing convective-diffusional mass transfer in a film of liquid trickling down the surface of the sphere is presented. The solution was attempted in order that the values of conversion of a first-order reaction taking place on the surface of the sphere are obtained. Special attention was paid to the problem of mixing of the reaction mixture in the point of contact of two adjacent spheres and to the problem of attainment of the limiting state in a vertical column of spheres.

In the preceding paper¹ a plane model of a trickle bed reactor was investigated. In comparison with a real column reactor with random packing, however, we were not able to examine on our model the flow of liquid over the curved surface of a packing element and possible mixing of the reaction mixture in the point of contact of two catalyst pellets.

Problems connected with the hydrodynamics of the flow of liquid on a sphere or a vertical column of spheres were studied to date only in connection with absorption processes²⁻⁷. These papers study mostly the laminar regime of the film flow. The mass transfer in the examined spheric film at absorption of a gas is caused by convective diffusion and the solution of this problem has been presented in preceding papers^{2,3,5,8}. There are relatively few works devoted to the study of the properties of trickle bed reactors. Satterfield, Pelosof and Sherwood⁹ analyzed major effects on mass transfer in these reactors, which are utilized for, among other things, refining hydrogenation of organic intermediate products (*e.g.*¹⁰⁻¹²) and confronted the conclusions with their experimental results obtained at hydrogenation of α -methylstyrene in a laboratory model reactor. These results were further compared with their own solution of pertaining transport equations. The solution however, was published for only a limited range of characteristic dimensionless parameters of the system.

The purpose of this work is to provide a complete numerical solution of a reactor model consisting of a vertical column of spheres in a wide range of parameters

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characterizing a given system and to determine major factors affecting the reaction conversion in a given equipment. The assumptions made are analogous to those used in the cited paper⁹.

THEORETICAL

THE ASSUMPTIONS OF THE REACTOR MODEL

1. Let us consider a steady, isothermal and isobaric system consisting of a vertical column of spheres with constant radii in a hydrogen atmosphere, wetted by a liquid reaction mixture containing dissolved hydrogenated substrate. 2. The liquid flows down the outer surface of spherical catalyst particles in the form of a laminar film. Occasional changes of the transverse velocity profile have little effect on the resultant mass transfer in the film (see preceding paper¹). 3. The liquid is introduced on the first sphere with perfectly uniform initial concentration of dissolved hydrogen c_0 . 4. The concentration of the dissolved hydrogen in the film at the gas-liquid interphase is equal to its equilibrium value for a given temperature and pressure. 5. The transport of hydrogen across the film is induced by molecular diffusion and in the direction of the film flow by convection only (diffusion transport in the direction of the film flow can be neglected¹). 6. The reaction taking place on the surface of the wetted sphere is irreversible, first order with respect to the dissolved hydrogen and zero order with respect to the hydrogenated substrate. 7. The region of contact between two adjacent spheres, filled with liquid meniscus is symmetric with respect to a horizontal plane through the point of contact and the volume of the meniscus V (see Fig. 1) is independent of the density of wetting. 8. The average thickness of the film is of much smaller order than the radius of the sphere.

Statement of the Problem

The thickness of a film flowing down the surface of a sphere $s(\beta)$ and its surface velocity $w_{\max}(\beta)$, depend on an angular coordinate β . They are defined by following relationships³:

$$s(\beta) = (3\mu G/2\pi R g \varrho)^{1/3} \sin^{-2/3} \beta = s^0 \sin^{-2/3} \beta, \quad (1)$$

$$w_{\max}(\beta) = (3G/4\pi R s^0) \sin^{-1/3} \beta = w_{\max}^0 \sin^{-1/3} \beta. \quad (2)$$

Dimensionless parameters characteristic for the studied system are analogous to those for a wetted wall¹. In this case, however, they become functions of angular coordinate β .

Geometric simplex:

$$P(\beta) = s(\beta)/R = P^0 \sin^{-2/3} \beta, \quad (3)$$

Peclet number:

$$N_{\text{Pe}}(\beta) = w_{\text{max}}(\beta) s(\beta)/D = N_{\text{Pe}}^0 \sin^{-1} \beta, \quad (4)$$

Sherwood number:

$$N_{\text{Sh}}(\beta) = K s(\beta)/D = N_{\text{Sh}}^0 \sin^{-2/3} \beta, \quad (5)$$

where

$$P^0 = s^0/R = (3\mu G/2\pi R^4 \rho g)^{1/3}, \quad (6)$$

$$N_{\text{Pe}}^0 = w_{\text{max}}^0 s^0/D = 3G/4\pi R D, \quad (7)$$

$$N_{\text{Sh}}^0 = K s^0/D = K/D(3\mu G/2\pi R \rho g)^{1/3}. \quad (8)$$

The mass balance written for an element of volume of liquid in the film (see Fig. 1) for $\bar{P} \ll 1$ in dimensionless form yields following partial differential equation governing the mass transfer in the film:

$$\left(\frac{\partial^2 C}{\partial Y^2}\right) + P^0 N_{\text{Pe}}^0 \sin^{-5/3} \beta (Y^2 - 1) \left(\frac{\partial C}{\partial \beta}\right) = 0. \quad (9)$$

Equation (9) has to be supplemented with boundary conditions according to the assumptions 4 and 6, determining the solution of the problem:

$$\beta = \beta_0, \quad C = C_0(Y), \quad (10)$$

$$Y = 0, \quad C = 1, \quad (11)$$

$$Y = 1, \quad \left(\frac{\partial C}{\partial Y}\right) = -N_{\text{Sh}}^0 \sin^{-2/3} \beta \cdot C_m \quad (12)$$

where $\beta \in \langle \beta_0, \pi - \beta_0 \rangle$, $Y \in \langle 0, 1 \rangle$.

Condition (10) specifies concentration profile across the film introduced on a given sphere. This concentration profile is a constant in the case of the first sphere, in accord with the assumption 3.

Reaction Conversion

According to the assumption 6, following equation for the reaction rate is valid:

$$r = dx/d(W/F) = Kc^* C_m(\beta), \quad (13)$$

where $C_m(\beta)$ stands for dimensionless concentration of dissolved hydrogen in the reaction mixture at the surface of the sphere. For porous catalysts, where the reaction itself takes place predominantly within the pores, it is necessary to calculate the reaction-rate constant K , related to the geometrical surface of the sphere from the relation:

$$K = (ES_p/4\pi R^2)\bar{K}. \quad (14)$$

The effectiveness factor E can be replaced, for large spherical particles, by the following equation^{13,14}, *i.e.*:

$$E = 3/[R(\bar{K} a/D_{ef})^{1/2}]. \quad (15)$$

The reaction conversion can be obtained by integration of Eq. (13), where dW is substituted by the relation:

$$dW = 2\pi R^2 \sin \beta \, d\beta. \quad (16)$$

For the conversion in the film by the constant feed of the substrate we thus obtain:

$$\Delta x_1 = 2\pi R^2 K c^* / F \int_{\beta_0}^{\pi - \beta_0} C_m(\beta) \sin \beta \, d\beta. \quad (17)$$

Integration limits of Eq. (17) are determined by an angle β_0 , which is assumed to be identical with a static angle of the end of the meniscus at the lower sphere (see Fig. 1); a plane symmetry of the meniscus has already been assumed. Malcor¹⁵ has calculat-

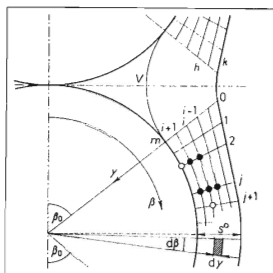


FIG. 1
Sketch of Section of Film with Flow Diagram
of Computation

ed and experimentally verified the dependence of this angle on the Bond number which is defined by the relation:

$$N_{Bo} = \rho g R^2 / \sigma . \quad (18)$$

Chemical reaction, however, can also occur in principle in these regions between the spheres where the liquid forms a meniscus. Two limiting cases will be examined in this work:

a) The reaction rate and hereby the reaction conversion is proportional to the average concentration of the dissolved hydrogen in the inlet film, *i.e.* the reaction mixture is perfectly mixed in the region of the meniscus.

b) The conversion is proportional to the concentration of the dissolved hydrogen in the inlet film at the surface of the upper sphere, *i.e.* $C_m^{(n-1)} (\pi - \beta_0)$ and the reaction mixture is not mixed within meniscus. Thus the radial concentration profile in the film does not change here.

In the first case we shall obtain for the reaction conversion in the meniscus:

$$\begin{aligned} \Delta x_2^{(n)} &= 2\pi R^2 K c^* / F \left[\int_0^{\beta_0} \bar{C}^{(n-1)} \sin \beta \, d\beta + \int_{\pi - \beta_0}^{\pi} \bar{C}^{(n)} \sin \beta \, d\beta \right] = \\ &= 4\pi R^2 K c^* / F [(\bar{C}^{(n-1)} + \bar{C}^{(n)})/2] (1 - \cos \beta_0) . \end{aligned} \quad (19)$$

Assuming a parabolic velocity profile in the flowing film, following relation for the average concentration of the dissolved gas on the n -th sphere is valid:

$$\bar{C}^{(n)} = 1.5 \int_0^1 (1 - Y^2) C^{(n)} \, dY . \quad (20)$$

where Y is a radial dimensionless coordinate, defined as a ratio of the distance from the gas-liquid interphase and the thickness of the film.

The total reaction conversion on the sphere is given by the sum:

$$\Delta x_{sum} = \Delta x_1 + \Delta x_2 . \quad (21)$$

The maximum conversion at the surface of the sphere is obtained when the concentration of dissolved hydrogen is equal to its equilibrium value (*i.e.* $C_m(\beta) = 1$):

$$\Delta x_{max} = 4\pi R^2 K c^* / F . \quad (22)$$

Similarly as in our previous paper¹, it is advantageous to define a reduced conversion

(analogous to the utilization factor) as a ratio of the actual conversion to the maximum conversion, *i.e.*:

$$\begin{aligned} \Delta X_{\text{red}}^{(n)} &= (\Delta x_1 + \Delta x_2) / \Delta x_{\text{max}} = F \Delta x_{\text{sum}} / 4\pi R^2 K c^* = \\ &= 1/2 \left[\int_{\beta_0}^{\pi - \beta_0} C_m(\beta) \sin(\beta) d\beta + (\bar{C}^{(n)} + \bar{C}^{(n-1)}) (1 - \cos \beta_0) \right]. \end{aligned} \quad (23)$$

In the second case the reduced conversion is also expressed by equation (23) if the quantity $\bar{C}^{(n)}$ is there changed by concentration $C_m^{(n)}(\pi - \beta_0)$.

Solution

The nonlinear diffusion equation (9) cannot be solved analytically. A numerical solution was furnished by a finite difference method^{16,17}, using an explicit computational scheme applied to a curvilinear net, as it is seen from Fig. 1. On substituting the difference operators for differential ones in Eqs (9), (12), following set of algebraic equations is obtained:

$$C_{i,j+1} = \frac{k \sin^{5/3}(\beta_0 + kj)}{h^2 p^0 N_{\text{pe}}^0 (1 - i^2 h^2)} [C_{i+1,j} - 2C_{i,j} + C_{i-1,j}] + C_{i,j}, \quad (24)$$

$$C_{i,0} = C_0, \quad (25)$$

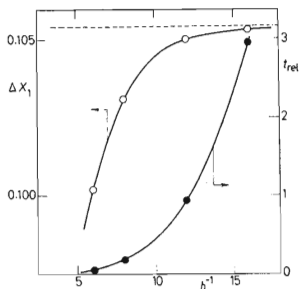


FIG. 2

Dependence of Accuracy of Solution and Relative Computational Time on Size of Mesh of Computational Grid ($N_{\text{pe}}^0 p^0 = 10$; $N_{\text{sh}}^0 = 1$; $\beta_0 = 0.5$; $C_0 = 0$).

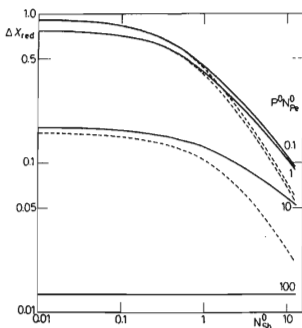


FIG. 3

Dependence of Reduced Conversion on the First Sphere on Parameters $N_{\text{pe}}^0 p^0$ and N_{sh}^0 , for $C_0 = 0$ and $\beta_0 = 0.5$.

$$C_{0,j} = 1, \quad (26)$$

$$C_{m,j} = [2h N_{Sh}^0 \sin^{-2/3} (\beta_0 + kj) + 3](4C_{m-1,j} - C_{m-2,j}). \quad (27)$$

The stability of the set of equations (24)–(27) is determined by the inequality:

$$h^2 k N_{Pe}^0 (1 - i^2 h^2) - 2h^2 P^0 \sin^{1/3} \beta \geq 2k^2 \sin^{5/3} \beta. \quad (28)$$

From condition (28) it is apparent that the least favourable case which has to be respected in computation arises when $\beta = \pi/2$ and $i = (m - 1)$, where m is the number of layers into which the film was divided for computational purposes. On the basis of this result we were able to determine the increment k in the direction of the film flow from a given value of the increment h in the radial direction. Solution of the presented set of equations was performed on an Elliott NCR 4130 computer.

The inaccuracy of the solution was investigated by computing the reaction conversion in the film for different values of the increment in the radial direction h . Fig. 2, plotting the dependence of the result on the inverse value of h clearly shows that a sufficient accuracy ($\epsilon < 1\%$) is attained when $h = 0.1$. Apart from that, the dependence of the relative computational time t_{rel} is plotted in the same figure for illustration. From both of these dependences it follows that additional requirements on accuracy of the solution (*i.e.* for $h < 0.1$) sharply increase the computational time and, therefore, a compromise between both effects has to be found. Consequently most of the computations were performed for $h = 0.1$ or 0.0833 .

RESULTS AND DISCUSSION

Many parameters may affect the value of the reduced conversion on a given sphere. These are: The above given criteria N_{Pe}^0 , N_{Sh}^0 , simplex P^0 , the initial concentration of the dissolved gas in liquid C_0 , the sequence number of the sphere in the vertical

TABLE I

Effect of Angle β_0 on Total Reduced Conversion on the First Sphere for $M = 1$ (for case a))

C_0	$N_{Pe}^0 P^0$	N_{Sh}^0	β_0		
			0.3	0.5	0.7
			conversion		
0	10	1	0.1204	0.1295	0.1384
0	10	0.01	0.1675	0.1715	0.1654
0	1	1	0.4066	0.4115	0.4113
0	1	0.01	0.7945	0.7696	0.7260
1	1	1	0.5059	0.5458	0.5995
1	1	0.01	0.9900	0.9906	0.9915
1	10	0.01	0.9927	0.9948	0.9951

column n , angle β_0 , and, last but not least, the effect of the degree of mixing of liquid in the region of contact between the spheres M . Not all of these parameters affect the result to the same extent and an attempt was made to find the most important of them.

Table I summarizes the results of reduced conversion on the first sphere for selected combinations of dimensionless parameters in the dependence on the value of the angle β_0 (given in radians). From the results it is apparent that for $\beta_0 = 0.3$ or 0.7 , the resultant reduced conversion does not deviate too much from that for $\beta_0 = 0.5$ (the maximum deviation $< 10\%$, the average deviation 3.4%). Quite analogous result was obtained for the second sphere in the sequence and for other combinations of dimensionless parameters both in the case of mixing in the meniscus and in the case of eliminated mixing. From the presented results can thus be concluded that the value of the angle β_0 does not affect appreciably the total reduced conversion and the following computations were therefore performed for one value of this angle $\beta_0 = 0.5$.

Figs 3 and 4 depict the dependence of the reduced conversion for the first sphere on the Sherwood number N_{Sh}^0 and the product $N_{pe}^0 P^0$, for boundary conditions $C_0 = 0$ and $C_0 = 1$. Full lines in both figures show the respective dependence at perfect mixing in the point of contact of the spheres, while broken lines show that dependence in the absence of mixing. It is obvious that the results are lower for the latter case. This difference is especially large for high values of the Sherwood number ($N_{Sh}^0 > 1$). Reduced conversion for low values of this criterion is not affected by an eventual reaction taking place in the meniscus.

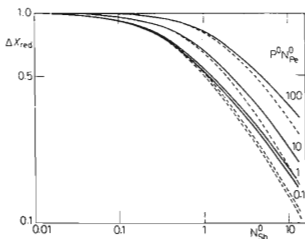


FIG. 4

Dependence of Reduced Conversion on the First Sphere on Parameters

$N_{pe}^0 P^0$ and N_{Sh}^0 , for $C_0 = 1$ and $\beta_0 = 0.5$.

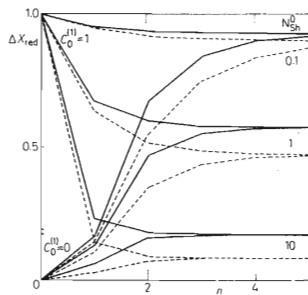


FIG. 5

Course of Reduced Conversion on Vertical Column of Spheres for Some Values of Parameter N_{Sh}^0 , for $N_{pe}^0 P^0 = 10$ and $\beta_0 = 0.5$

A comparison of Figs 3 and 4 with our numerical results obtained on the plane model of a trickle bed reactor¹ reveals similarity in the character of the dependence of reduced conversion on the product $P^0 N_{Pe}^0$ and criterion N_{Sh}^0 for both models studied. Here again, it is possible to define three basic operational regimes of the reactor (*i.e.* diffusion, kinetic and transient region) under the same conditions as in the preceding paper¹.

An important feature of the studied model, consisting of a vertical column of spheres, is the attainment of the limiting state characterized by a constant values of reduced conversion, independent of the boundary condition (10). Fig. 5 shows typical courses of the dependences of the reduced conversion on the sequence number of a sphere for selected values of characteristic criteria. Dependences with the absence of mixing of the reaction mixture in the points of contact of adjacent spheres are shown again by broken lines. The curves clearly illustrate the character of the transition and attainment of the limiting state. The rate of transition can be defined by a sequence number of a sphere n_{lim} , the reduced conversion of which is sufficiently close to a constant value. The dependence of this quantity (the difference from the limiting state is set equal to 1%) on the $N_{Sh}^0 P^0$ product, for the Sherwood number $N_{Sh}^0 = 0.01$ resp. 10, and for boundary condition (10) $C_0 = 0$ respectively $C_0 = 1$, is shown in Fig. 6. Following conclusions can be drawn from the results:

a) The rate of attainment of the limiting state depends strongly on the product $N_{Pe}^0 P^0$ and with its increasing value sharply decreases (n_{lim} increases).

b) The rate of attainment of the limiting state is higher in the case of the model assuming mixing in the points of contact of spheres in comparison with the model excluding mixing (in Fig. 6 shown again by broken line).

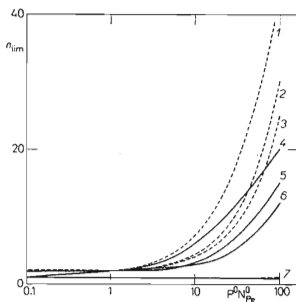


FIG. 6

Attainment of Limiting State on Vertical Column of Spheres for Different Combinations of Parameters of System and for $\beta_0 = 0.5$. $M = 1$ and 0 for a) and b) respectively.

Curve	M	C_0	N_{Sh}^0
1	0	0	0.01
2	0	0	10
3	0	1	10
4	1	0	0.01
5	1	0	10
6	1	1	10
7	0	1	0.01
7	1	1	0.01

c) The value of n_{lim} is higher for the boundary condition $C_0^{(1)} = 0$ than for $C_0^{(1)} = 1$.

d) The dependence of the rate of transition to the limiting state on the Sherwood number is not unique.

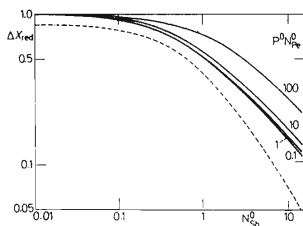


FIG. 7

Dependence of Reduced Conversion on Parameters $N_{Pe}^0 P^0$, N_{Sb}^0 in Limiting State for $n > n_{lim}$ and $\beta_0 = 0.5$

The resultant values of the reduced conversion in the range of the limiting state are shown in Fig. 7 in dependence on characteristic parameters of the system N_{Sb}^0 and $N_{Pe}^0 P^0$. Two extreme cases with respect to the degree of mixing of the reaction mixture in the liquid meniscus are distinguished again. An interesting conclusion was drawn from the case where mixing is neglected, as the results were found independent of the $N_{Pe}^0 P^0$ product.

Solution of the diffusion equation together with the boundary conditions (10)–(12) describing the behaviour and properties of a wetted sphere and/or the behaviour of a column of wetted spheres, provides valuable information about the examined model of a reactor and about complexity of mass transfer in this system. On the basis of submitted results it is possible to determine the character of the dependences between all parameters and criteria controlling the model and to evaluate conversion of a reaction taking place in this type of a reactor, provided that the assumptions (1)–(8) made above are satisfied. The submitted model necessitates however, its experimental verification which will be subject of our next study.

LIST OF SYMBOLS

- a surface area of catalyst related to unit of volume of catalyst pellet (cm^{-1})
 c concentration (mol cm^{-3})
 $C = c/c^*$ concentration

\bar{C}	mean concentration
D	diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)
E	effectiveness factor of catalyst
F	feed of hydrogenated substrate (mol s^{-1})
g	acceleration due to gravity (cm s^{-2})
G	volume flow rate of liquid on sphere ($\text{cm}^3 \text{s}^{-1}$)
h	increment in radial direction
i	sequence number of film layer (see Fig. 1)
j	sequence number of radial section of film (see Fig. 1)
k	increment in direction of flow
K	reaction rate constant related to geometric surface of sphere (cm s^{-1})
\bar{K}	reaction rate constant related to catalyst surface (cm s^{-1})
m	number of film layers
M	degree of mixing in point of contact between two spheres
n	sequence number of sphere
N_{Bo}	Bond number (see Eq. (18))
N_{Pe}	Peclet number (see Eq. (4))
N_{Sh}	Sherwood number (see Eq. (5))
P	geometric simplex (see Eq. (3))
r	rate of reaction ($\text{mol s}^{-1} \text{cm}^{-2}$)
R	radius of sphere (cm)
s	thickness of film (cm)
S_p	internal surface of catalyst pellet (cm^2)
t	time (s)
w	velocity of liquid in film (cm s^{-1})
W	amount of catalyst expressed by corresponding surface area of sphere (cm^2)
Δx	reaction conversion
ΔX_{red}	reduced conversion
y	radial coordinate (cm)
$Y = y/s$	radial coordinate
β	angular coordinate
ε	error of solution
μ	viscosity of liquid ($\text{g cm}^{-1} \text{s}^{-1}$)
ρ	density of liquid (g cm^{-3})
σ	surface tension (g s^{-2})

Superscripts

o	quantity related to sphere equator
*	equilibrium value
n	value for n -th sphere

Subscripts

1	film
2	meniscus
max	maximum value
sum	total value
m	sphere surface

<i>o</i>	boundary value
<i>lim</i>	limiting state
<i>ef</i>	efficient value

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