Int. J. Heat Mass Transfer. Vol. 26, No. 4, pp. 539–544, 1983
Printed in Great Britain

0017-9310/83/040539-06 $03.00/0
Pergamon Press Ltd.

THE ROLE OF A REFLECTING BOUNDARY IN IMPROVING THE OPERATION OF AN ANNULAR PHOTOREACTOR

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(*Received* 26 *February* 1982)

Abstract—The influence of a cylindrical reflector on a photochemical reaction occurring in an annular photoreactor has been investigated for both batch and continuous operations of the reactor. Absorption of radiant energy has been assumed by the reacting species itself and for each of the operating modes both the extreme conditions of mixing have been considered. Results show that a reflecting wall can be effective in enhancing the conversion only when the optical thickness m (based on the initial conditions and on the inlet) is neither too small nor too large, since in these two cases absorption and reflection, respectively, are negligible anyway. In any case conversion has been found to increase when mixing within the reactor is improved.

NOMENCLATURE

$\dot{a}'''$, dimensionless local rate of radiant energy absorption, $\dot{e}'''/\dot{e}_0'''$;
c_A, concentration of component A;
Da, Damköhler number, $\phi E' c_{A0}^{n-1}/(v_0 R)$;
$\mathscr{D}_e$, reactant effective diffusivity;
$\dot{e}'''$, local rate of radiant energy absorption;
$\dot{e}_0'''$, characteristic scale for $\dot{e}'''$, $\beta c_{A0} E'/R$;
E, power output of the lamp;
E_a, absorbed power;
L, length of the reactor;
m, optical thickness based on initial (batch) or inlet (continuous) concentration, $\beta c_{A0} R$;
n, order of reaction;
Pe, Peclet number, $v_0 R/\mathscr{D}_e$;
r, radial coordinate;
R, outer radius of the annulus;
s, linear coordinate;
S, Strouhal number, $t_r v_0/R$;
t, time;
t_R, characteristic reaction time (batch), $R^2/(\phi E' c_{A0}^{n-1})$;
t_R, residence time (continuous), L/v_0;
$\mathscr{V}$, dimensionless volume, $\pi(1-\xi_i)^2\eta_L$;
v_0, mean axial velocity;
v, axial velocity;
V, dimensionless axial velocity, v/v_0;
$\mathbf{x}$, point;
z, axial coordinate;

Greek symbols
β, molar absorptivity;
γ, dimensionless reactant concentration, c_A/c_{A0};
η, dimensionless axial coordinate, z/R;
ξ, dimensionless radial coordinate, r/R;
ρ, coefficient of reflectivity;
ρ^S, coefficient of specular reflectivity;
ρ^D, coefficient of diffuse reflectivity;
σ, dimensionless linear coordinate, s/R;
τ, dimensionless time, t/t_R;
θ, latitude angle;
ϕ, rate constant (quantum yield for $n = 0$);
φ, equatorial angle.

Subscripts
A, relative to reactant A;
b, relative to bulk quantities;
i, relative to the inner wall of the reactor;
L, relative to the total length of the reactor;
0, relative to the initial (batch) or inlet (continuous) conditions;
r, relative to the reflector.

Superscripts
$\dot{}$, relative to unit time;
$'$, relative to unit length;
$'''$, relative to unit volume.

INTRODUCTION

A LOW yield of the absorption of the radiant energy is quite common in photochemical reactions. The resulting large energy costs have been one of the main obstacles to the development of industrial processes where the most appealing features of photochemical reactivity (high selectivity and low process temperature) could otherwise have been conveniently exploited. In order to increase the radiative power absorbed within the reactor, and consequently the achievable conversion, a reflecting surface is often placed around the lamp–reactor assembly in such a way that at least some of the photons which would otherwise be wasted, having experienced no interaction in their way through the reacting material continuum, could be "recycled" into the reactor and again made available for absorption.

In spite of the practical significance of this policy little attention has been directed to a comprehensive analysis of the role of a reflecting surface in enhancing conversion. Until recently no reliable procedure was available for a quantitative analysis of these situations.

The first attempt to include a reflecting surface in the analysis of a photoreactor (tubular reactor with an elliptical reflector) was made by Cerda *et al.* [1], but the authors assumed a diactinic medium, i.e. with no reaction within the reactor. The more realistic case of a participating medium (i.e. a reacting one) has been considered [2] where the modelling of photochemical reactors has been recognized as a special case of radiative transfer in participating media. The equations which rigorously govern the modelling of a photochemical reactor, even with a reflecting surface, have been derived for different lamp models, but only the case of photosensitized reactions has been considered as an application. Further progress to a better understanding of the basic mechanisms through which a reflecting surface can affect the absorption of the radiant energy and the progress of the reaction has been made [3] where a scattering absorbing medium undergoing a photosensitized photochemical reaction is considered.

The case where the absorption of the radiant energy occurs by the reacting species itself has not yet been considered. The aim of this paper is to investigate the role that a reflecting surface has in such conditions on the performance of both a batch and a continuous annular photoreactor.

The analysis of these situations is done following the general treatment given in ref. [2] and the stiffness which results for the governing equations, as the effect of the absorption characteristics of the participating medium, is by-passed following the procedure [4, 5] where the case of an annular photoreactor with no reflector is considered for a batch and continuous process, respectively.

BASIC EQUATIONS

Both the batch and the continuous operations of an annular photoreactor have been investigated assuming a cylindrical reflector coaxial with the reactor. The photoreaction A → products according to the overall kinetic equation

$$\dot{n}'''_{Ag} = -c_A^n \int_0^{\lambda_c} \phi_\lambda \dot{e}'''_\lambda \, d\lambda$$

has been considered assuming that only the reacting species absorbs radiant energy.

If a monochromatic u.v. source is considered, or if the participating medium behaves as a gray medium, the molar balance of the absorbing–reacting species for both the batch and the continuous operations of the reactor has been given in refs. [4, 5], respectively. The same equations hold here under the assumption stated there. Their dimensionless form can be written as:

Batch operation

$$\frac{d}{d\tau}\int_{\mathscr{V}} \gamma \, d\mathscr{V} = -m \int_{\mathscr{V}} \dot{a}'''(\mathbf{x},\tau)\gamma^n \, d\mathscr{V}, \qquad \gamma(\mathbf{x},0) = 1. \tag{1}$$

Continuous operation

$$\frac{1}{Sr}\frac{\partial \gamma}{\partial \tau} + V\frac{\partial \gamma}{\partial \eta} = \frac{1}{Pe}\frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \gamma}{\partial \xi}\right) - mDa\gamma^n \dot{a}'''(\mathbf{x},\tau) \tag{2}$$

Initial condition: $\gamma(\eta,\xi,0) = 1$;

Boundary conditions: $\gamma(0,\xi,\tau) = 1$;

$$\left(\frac{\partial \gamma}{\partial \xi}\right)_{\eta,\xi_1,\tau} = \left(\frac{\partial \gamma}{\partial \xi}\right)_{\eta,1,\tau} = 0.$$

The term $\dot{a}'''$ which appears in both the previous equations is peculiar to photochemical processes since it gives the local volumetric rate of the radiant energy absorption. It results from the formal solution of the radiant energy balance equation and therefore accounts also for the effects due to a reflector, which, when present, enter into the radiative transfer problem as a boundary condition.

Since the same geometry is considered in the two operating conditions the same formal expression follows for $\dot{a}'''$. If the lamp is modelled as a linear source emitting in a specular way [6], if the reflectivity of the reflector can be given as $\rho = \rho^D + \rho^S$ (ρ^S and ρ^D being the specular and the diffuse components of ρ respectively) and if, furthermore, no refraction is considered at the walls of the reactor [7], $\dot{a}'''$ is given by

$$\begin{aligned}\dot{a}'''(\mathbf{x},\tau) = {} & \frac{\gamma(\mathbf{x},\tau)}{4\pi\xi} \\ & \times \left\{ \int_{\theta_1(\mathbf{x})}^{\theta_2(\mathbf{x})} \exp\left[-m \int_0^{\bar{\sigma}(\theta)} \gamma(\sigma,\tau)\, d\sigma \right] d\theta \right. \\ & \left. + \rho^S \int_{\theta'_1(\mathbf{x})}^{\theta'_2(\mathbf{x})} \exp\left[-m \int_0^{\bar{\sigma}'(\theta')} \gamma(\sigma,\tau)\, d\sigma \right] d\theta' \right\} \\ & + \gamma(\mathbf{x},\tau)\rho^D \int_0^{2\pi} \left[\int_{\theta''_1(\mathbf{x})}^{\theta''_2(\mathbf{x})} \frac{\dot{Q}''_i(\theta'',\varphi,\xi_r)}{\pi} \right. \\ & \left. \times \exp\left[-m \int_0^{\bar{\sigma}''(\theta'')} \gamma(\sigma,\tau)\, d\sigma \right] \cos\theta''\, d\theta'' \right] d\varphi \end{aligned} \tag{3}$$

where $\theta_1 \leqslant \theta \leqslant \theta_2$ and $\theta'_1 \leqslant \theta' \leqslant \theta'_2$ are the latitude range in which the lamp can be seen from $\mathbf{x}$ directly or through the reflector respectively, while $\theta''_1 \leqslant \theta'' \leqslant \theta''_2$ gives the latitude range through which the reflector is seen from $\mathbf{x}$ for any φ (the equatorial angle in a spherical coordinate system centered in $\mathbf{x}$). $\dot{Q}''_i$ is the dimensionless hemispherical flux of radiant energy incident at the point $\mathbf{x}_r$ of the reflector which is seen from $\mathbf{x}$ along the direction (θ'', φ).

The different structure of the terms which account for the contribution of the specularly and diffuse reflected radiation is the result of the different mechanisms through which reflection occurs in the two cases.

In specular reflection, any beam undergoing reflection maintains its own individuality since it experiences only a change of direction in its propagation path. On the contrary, a diffusely

reflecting surface obliterates the past history of the incident radiation and the energy impinging on the reflector is uniformly redistributed along all the directions.

As is apparent from equation (3), when $\dot{a}'''$ is evaluated, the diffusely reflected radiation requires a much greater computational effort than the direct and the specularly reflected radiation. Since the results [2, 3, 8] suggest that, in the situation examined, the effects due to the reflecting surface are larger for any ρ the larger ρ^D is (i.e. the larger the contribution of the diffuse component is) only the case $\rho = \rho^S$ has been considered as a conservative one for that value of ρ. Computed results are conservative in any case since further reflection of the radiation both at the lamp surface and at the lower and upper plate is not accounted for by equation (3).

It is worth noting that, when a reflector is used, not only must the contributions due to the reflected radiation be taken into account in the evaluation of $\dot{a}'''$, but also the value of the contribution due to direct radiation differs from that occurring for $\rho = 0$, as a result of the changes which the reflector causes in the distribution of γ.

Even under the simplifying assumptions previously made, once the proper expression has been given for $\dot{a}'''$, the stiffness of either equation (1) or equation (2) appears unquestionable and it has been by-passed in the numerical solution following the same procedure used in refs. [4, 5]. For continuous operation the analysis of a transient to the steady state appears the most practical way to obtain the steady state conditions. Success of the procedure is expected since, under the assumptions made, no competitive concomitant phenomena occur and, therefore, there is no opportunity for a multiplicity of steady states.

DISCUSSION

The same geometry (Fig. 1) has been investigated for both the operating conditions and the following values have been assumed for the dimensionless geometric parameters: $\eta_L = 1$, $\xi_i = 0.5$, $\xi_r = 1.1$.

Batch operation

Batch operation has been examined since the investigated configuration can be a satisfactory idealization of practical situations in the small-scale production of fine chemicals. It can furthermore give useful information on the basic aspects of the interaction occurring between the radiation field and the reacting–participating medium without the additional effects due to RTD which occur in continuous operation. The two extreme conditions of perfect mixing (p.m.) and complete segregation (c.s) of the reactant have been considered for two values of the initial optical thickness, m (1 ; 5), which can be assumed representative of moderately and strongly absorbing media.

The distributions of the residual bulk concentration γ_b which occur up to $\tau = 3$ are given in Fig. 2 for $\rho = 0$ and $\rho = \rho^S = 1$. It is apparent that the effectiveness of the reflector is larger for $m = 1$ than for $m = 5$, while the opposite is true for the effectiveness of improving the reactant mixing. The results of Fig. 2 can be discussed on the basis of the time and space evolution of the γ-distribution in the c.s. case since in the p.m. case, even if the local reaction rate depends on the position, composition is always uniform thanks to the mixing of the reacting medium. Figures 3 and 4 give the radial distribution of γ at different times in the mid-length cross section of the reactor ($\eta = \eta_L/2$) where the greatest progress of the reaction occurs.

For $m = 1$ the participating medium does not absorb too much and the γ radial distribution is quite uniform (Fig. 3). A large number of photons are therefore available for reflection and, owing to the optical characteristics of the participating medium, reflected photons have an easy way back through the reacting mixture. For $\rho = 1$ the resulting γ-distributions (dashed lines) differ to a significant extent with respect to those of the $\rho = 0$ case (full lines), the changes being large over all the flow cross section.

For $m = 5$, on the contrary, a large non-uniformity arises in the γ distribution (Fig. 4) as the result of the strong absorptivity of the medium: the number of photons which succeed in reaching the reflector is much

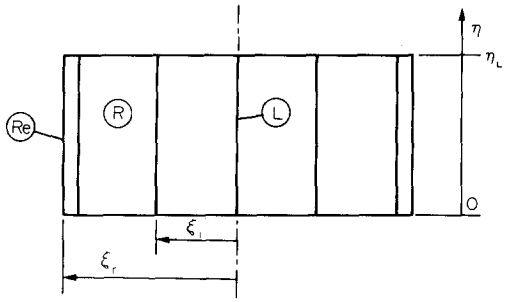

FIG. 1. Schematic drawing of the apparatus: L, lamp; R, reactor; Re, reflector.

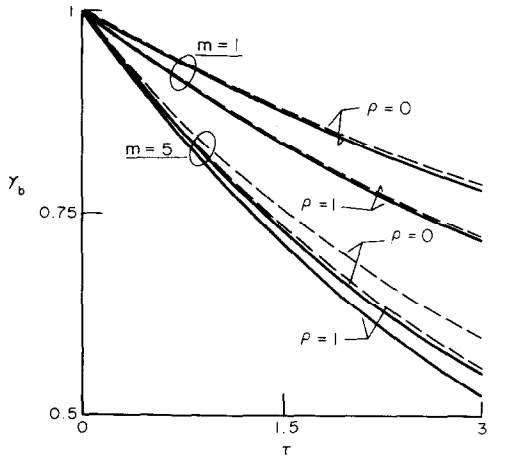

FIG. 2. The batch photoreactor: residual average concentration vs time (—— p.m., ------ c.s.).

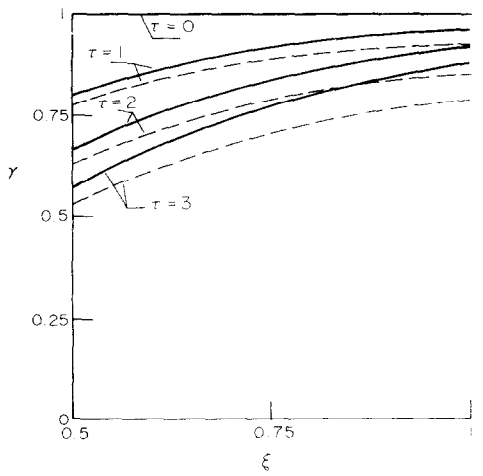

FIG. 3. The batch photoreactor: concentration vs the radial position in the midlength cross section ($\eta = \eta_L/2$) of the reactor in the c.s. case for $m = 1$ (—— $\rho = 0$, ---- $\rho = 1$).

less than in the previous case and those which do are absorbed in the central outer region of the reactor where the highest values of γ occur, while no significant change results in the γ distribution in the region close to the inner wall of the reactor. These arguments suggest that a reflector is more effective the more uniformly the reaction volume is exploited (i.e. the lower the initial optical thickness is) but this conclusion is of no practical consequence when $m \to 0$ since when the optical thin limit is approached the absorption of the radiant energy is always negligible no matter how many photons are travelling through the reaction volume. As it will be confirmed later by a more extensive analysis for the continuous operation case, a reflector can significantly improve the conversion only for intermediate values of m.

With regard to the role of the mixing conditions prevailing within the reactor it must be noted that for the p.m. case conversion is in any case larger than in the corresponding c.s. case since mixing moves the reactant from the outer part of the reactor toward the inner one where the largest values of $\dot{a}'''$ always result. The effect obtained improving the mixing conditions within the reactor is, of course, larger the larger the value of m is whether a reflector is used or not. Figure 2 shows furthermore that for $m = 5$, even in the most favorable reflection conditions ($\rho = 1$), the conversion achieved in the c.s. case is lower than the one resulting, at the same time τ, in the p.m. case with no reflector ($\rho = 0$), while at any τ, the evaluation of the radiant power absorbed within the reactor gives a higher value for the first than for the latter case.

This result confirms the statement [4, 9] that a more effective use of the absorbed power occurs under good mixing conditions and suggests that, when the initial reaction mixture is optically thick, the improving of mixing conditions can be the most effective action to enhancing the conversion.

Continuous operation

In this case the absorbing–reacting fluid is flowing through the reactor and, therefore, the velocity field too (assumed here to be 1-dim. laminar) affects the results at least in the c.s. case and in poor mixing conditions, while in the p.m. case (perfect radial mixing here) the averaging of equation (2) shows that the distribution of γ does not depend on the velocity distribution assumed [5].

The trends exhibited by the results closely follow those obtained in the batch operation case and therefore confirm the conclusions drawn in the previous section.

The values of the residual bulk concentration at the reactor exit (γ_{be}) and of the efficiency of the absorption process (E_a/E, i.e. the ratio between the absorbed and the emitted radiative power) are given in Figs. 5 and 6 as functions of m for $Da = 5$ and $\eta_L = 1$.

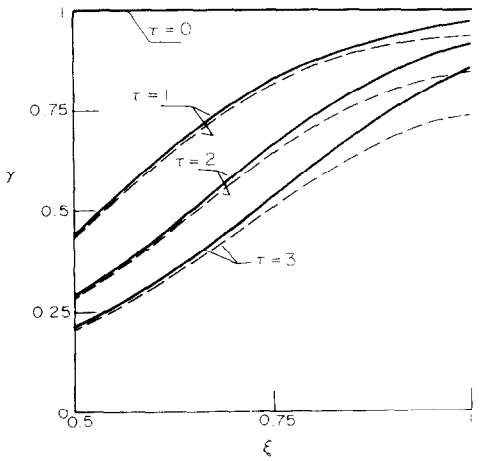

FIG. 4. The batch photoreactor: concentration vs the radial position in the midlength cross section ($\eta = \eta_L/2$) of the reactor in the c.s. case for $m = 5$ (—— $\rho = 0$, ---- $\rho = 1$).

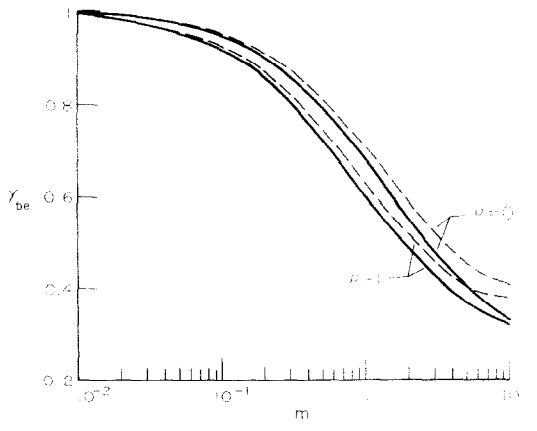

FIG. 5. The continuous photoreactor: the residual bulk concentration at the reactor outlet cross flow section as a function of m for $Da = 5$ and $\eta_L = 1$ (—— p.m., ---- c.s.).

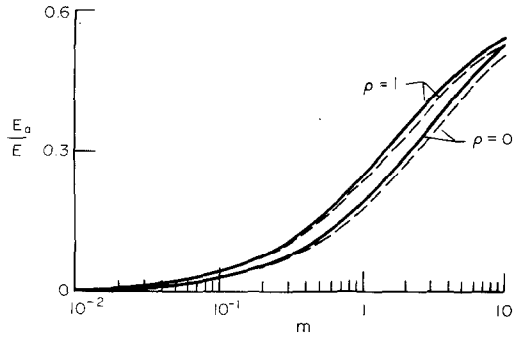

FIG. 6. The continuous photoreactor: the efficiency of the absorption process as a function of m for $Da = 5$ and $\eta_L = 1$ (—— p.m., ---- c.s.).

With regard to the role of a reflector it is apparent that appreciable improvements result only when m is neither too low nor too large since in these two extreme conditions absorption and reflection are respectively negligible. The useful m range depends, of course, on the values of the relevant parameters such as Da, Pe, η_L. Both the figures confirm, furthermore, the relevance of a good mixing to an effective use of the absorbed power.

It must be noted that for the continuous operation too, at high values of m, even in the most effective reflection conditions ($\rho = 1$), the resulting conversion in the c.s. case is lower than the one achievable in the p.m. case with no reflector ($\rho = 0$). The spatial evolution of the γ radial profile is given in Figs 7 and 8 for $m = 1$ and 10 in the c.s. case: the resulting curves can be interpreted on the basis of the same arguments used in batch case, once it has been recognized that the reactant concentration falls to zero at the reactor walls as the result of the large residence times occurring close to them and that large residence times are the only cause of the large conversion which results near the outer wall of the reactor where, at least for $\rho = 0$, the lowest values of $\dot{a}'''$ occur.

With regard to the dimensionless number defined as Da in equation (2), it can be interpreted as a Damköhler

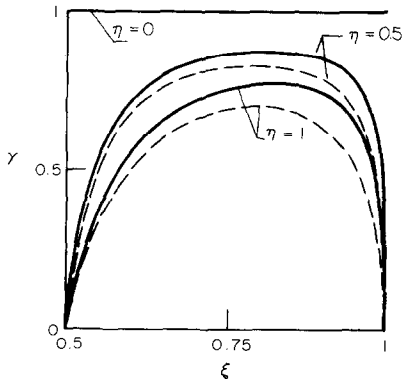

FIG. 7. The continuous photoreactor: the radial distribution of the reactant concentration at different cross flow sections of the reactor for $m = 1$, $Da = 5$, $\eta_L = 1$ (——$\rho = 0$, ----$\rho = 1$).

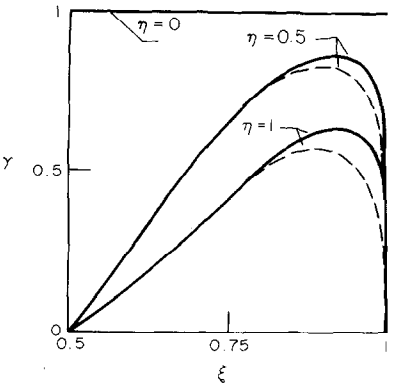

FIG. 8. The continuous photoreactor: the radial distribution of the reactant concentration at different cross flow sections of the reactor for $m = 10$, $Da = 5$, $\eta_L = 1$ (—— $\rho = 0$, ---- $\rho = 1$).

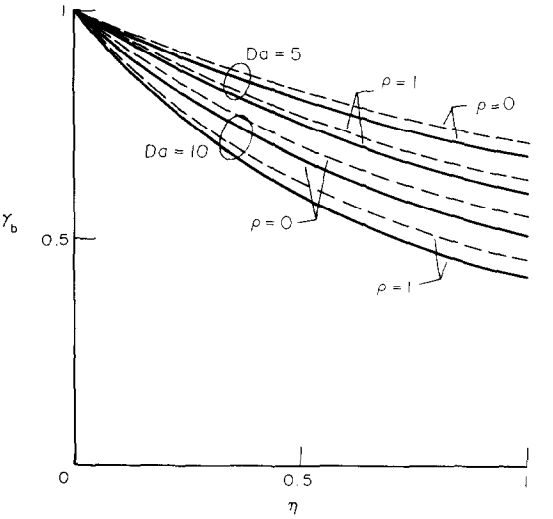

FIG. 9. The continuous photoreactor: the reactant bulk concentration as a function of η for $m = 1$ and $\eta_L = 1$ (—— p.m., ---- c.s.).

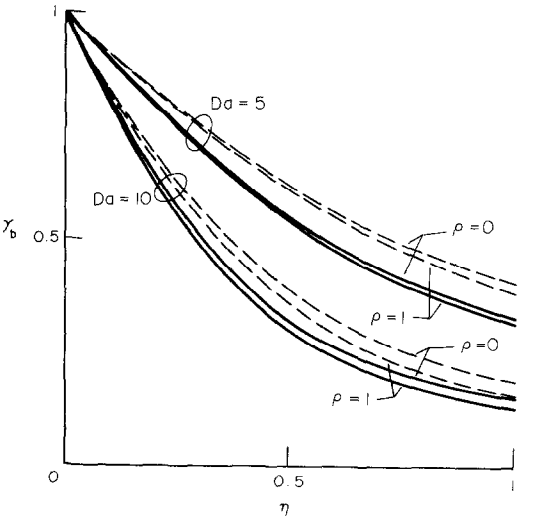

FIG. 10. The continuous photoreactor: the reactant bulk concentration as a function of η for $m = 10$ and $\eta_L = 1$ (—— p.m., ---- c.s.).

number and the usual meaning of the ratio between the reaction characteristic time and the mean residence time can therefore be attached to it. Since an increase of *Da* implies a more effective use of the absorbed power, the influence of *Da* can be predicted on the basis of the previous discussion: Figs. 9 and 10 confirm that, when *Da* is increased, the importance of mixing conditions is reduced and a reflector is slightly more effective.

Acknowledgements—Work supported by C.N.R., Rome, Grant Nos. 78.01030.03/115.3013 and 80.01696.03/115.3013.

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LE ROLE D'UNE FRONTIERE REFLECHISSANTE SUR L'AMELIORATION DU FONCTIONNEMENT D'UN PHOTOREACTEUR ANNULAIRE

Résumé—L'influence d'un réflecteur cylindrique sur une réaction photochimique dans un photoréacteur annulaire a été étudiée à la fois pour des opérations discontinues et continues du réacteur.

L'absoption de l'énergie radiante est évaluée à partir des espèces en réaction et pour chacun des modes opératoires les conditions extrêmes de mélange sont considérées.

Les résultats montrent qu'une paroi réfléchissante peut être efficace dans l'accroissement de la conversion seulement si l'épaisseur optique m (basée sur les conditions initiales et d'entrée) est ni trop faible ni trop grande, puisque dans ces deux cas l'absorption et la réflexion sont respectivement négligeables. En aucun cas la conversion est trouvée augmentée quand le mélange dans le réacteur est accru.

DER EINFLUSS EINER REFLEKTIERENDEN BERANDUNG AUF DIE VERBESSERUNG DER WIRKUNGSWEISE EINES RÖHRENPHOTOREAKTORS

Zusammenfassung—Es wurde der Einfluß eines zylindrischen Reflektors auf die photochemische Reaktion in einem ringspaltförmigen Photoreaktor sowohl bei diskontinuierlicher als auch bei kontinuierlicher Arbeitsweise des Reaktors untersucht. Es wurde angenommen, daß die Absorption der Strahlungsenergie durch die reagierenden Teilchen selbst erfolgt. Für jede der beiden Arbeitsweisen wurden beide extremen Mischungsbedingungen betrachtet.

Die Ergebnisse zeigen, daß eine reflektierende Wand nur dann eine Verbesserung der Umwandlung bewirken kann, wenn die optische Dicke m (basierend auf den Anfangsbedingungen und den Eintrittszuständen) weder zu klein noch zu groß ist, da in diesen beiden Fällen die Absorption bzw. die Reflexion ohnehin vernachlässigbar ist. Es zeigt sich, daß die Konversion auf jeden Fall zunimmt, wenn die Vermischung innerhalb des Reaktors verbessert wird.

РОЛЬ ОТРАЖАЮЩЕЙ ГРАНИЦЫ В УЛУЧШЕНИИ РЕЖИМА РАБОТЫ КОЛЬЦЕВОГО ФОТОРЕАКТОРА

Аннотация—Исследовано влияние цилиндрического рефлектора на протекание фотохимической реакции в кольцевом фотореакторе как в периодическом, так и непрерывном режимах его работы. Предполагалось, что лучистая энергия поглощается только реагирующими компонентами. Для обоих режимов рассмотрены экстремальные условия смешивания. Результаты показывают, что отражающая стенка может интенсифицировать химические превращения только в том случае, если оптическая толщина m (зависящая от начальных условий и условий на входе) имеет не слишком высокое и не слишком низкое значение, поскольку в этих случаях можно соответственно пренебречь поглощением и отражением. Найдено, что в любом случае фотоконверсия ускоряется при более тщательном перемешивании компонентов в реакторе.