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EFFECTS OF SCATTERING AND REFLECTION OF RADIATION ON BATCH PHOTOCHEMICAL REACTION IN A SLAB GEOMETRY

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Abstract—Effects of scattering of radiation within the medium, boundary surface reflectivity and initial optical thickness of the medium on the conversion occurring in a batch photochemical reaction in plane-slab geometry are investigated analytically. Results are presented for the local and average conversion within the medium, reflectivity and transmissivity of the medium, and normalized optical thickness of the medium as a function of time. The scattering is found to reduce the conversion and tends to increase the uniformity of the distribution of the reactant within the medium.

NOMENCLATURE

$C(x,t)$,	local molar concentration of the reactant;
C_0,	initial molar concentration of the reactant;
$\dot{e}'''$,	local rate of energy absorption;
$I(x,\mu,t)$,	radiation intensity;
I_0,	intensity of diffuse radiation at the emitting boundary;
R,	hemispherical reflectivity of the slab;
T,	hemispherical transmissivity of the slab;
t,	time;
x,	space coordinate.

Greek symbols

K, K^*,	volumetric and molar absorption coefficients respectively;
σ, σ^*,	volumetric and molar scattering coefficients respectively;
γ,	$=C(x,t)/C_0$, dimensionless concentration of the reactant;
γ_b,	dimensionless average concentration of the reactant;
μ,	cosine of the angle between the direction of radiation intensity and the positive x axis;
ρ,	reflectivity of the boundary surface at $x = L$;
τ,	optical coordinate;
$\tau_0(t)$, $\bar{\tau}_0$,	optical thickness and the initial optical thickness of the medium respectively;
ϕ,	reaction rate constant.

INTRODUCTION

The main feature of a photochemical process is that the chemical reaction within the medium takes place as a result of irradiation of the medium by a u.v. source. Radiation entering the medium is absorbed and scattered by the material volume as well as reflected from the boundary surfaces. The absorption, scattering and reflection phenomena play an important role in the obtainable conversion. Recently photochemical processes have been under consideration in the development of solar chemical reactors [1, 2]. The photochemical approach has also been used in the purification of polluted water [3–5]. The rate of photochemical reactions always depends upon the distribution of radiation intensity within the medium. Therefore, to analyze data or to predict the reaction rate in a reactor, it is necessary to know the distribution of light intensity within the medium. In the design of photochemical reactors it is also desirable to know the relative importance of parameters such as the scattering and absorption of radiation within the medium and its reflection from the boundaries on conversion. Some work towards this objective has already been reported in the literature [6–9]. Since there is growing interest in heterogeneous photochemical reactions [10–11] where scattering effects are important, in the present work we examine the effects of scattering and reflection of radiation on conversion in a photochemical process.

ANALYSIS

We consider a reacting medium contained between two parallel plates at a distance L apart. The photochemical reaction takes place in the medium as a result of a diffuse radiation source of constant intensity, I_0, located on the boundary surface at $x = 0$, which is assumed to be transparent. The boundary surface at $x = L$ is assumed to be diffuse reflector, having a reflectivity ρ. The medium absorbs and scatters radiation, and has volumetric absorption coefficient K and scattering coefficient σ, which are assumed to be proportional to the local concentration, $C(x, t)$, of the reactant. Therefore we can write

$$\mathrm{K}(x,t) = \mathrm{K}^* C(x,t), \tag{1a}$$

$$\sigma(x,t) = \sigma^* C(x,t), \tag{1b}$$

where K^* and σ^* are the molar absorption and scattering coefficients which remain constant.

It is also assumed that the rate of photochemical reaction is fast compared to the diffusion of the reactants in the medium, hence the molecular diffusion term in the mass conservation equation can be neglected.

Let the initial concentration, C_0, of the reactant be uniform throughout the medium. For times $t > 0$, the photochemical reaction takes place within the medium. In the present analysis we are concerned with the determination of the concentration of the reactant, $C(x,t)$, as a function of time and position in the medium. The mathematical formulation of this problem is now given.

The equation for the conservation of mass is taken as

$$\frac{\partial C(x,t)}{\partial t} + C(x,t)\,\phi\,\dot{e}'''(x,t) = 0, \quad t > 0, \tag{2a}$$

$$C(x,0) = C_0 \tag{2b}$$

where ϕ is the reaction rate constant and $\dot{e}'''(x,t)$ is the energy absorption rate by the medium, which is related to the radiation intensity, $I(x,\mu,t)$, by

$$\dot{e}'''(x,t) = \mathrm{K}^* C(x,t)\left[2\pi \int_{-1}^{+1} I(x,\mu,t)\,\mathrm{d}\mu\right]. \tag{3}$$

Here the term inside the bracket represents the radiation energy incident per unit volume in the medium and $\mathrm{K}^* C(x,t)$ is the volumetric absorption coefficient.

The radiation intensity $I(x,\mu,t)$ is to be determined from the solution of the equation of radiative transfer. For an isotropically scattering, plane-parallel medium, with a diffusely emitting source at the boundary $x = 0$ and a diffusely reflecting surface at $x = L$, the radiation problem is given in the optical variable, τ, in the form

$$\mu\frac{\partial I(\tau,\mu,t)}{\partial \tau} + I(\tau,\mu,t) = \frac{\omega}{2}\int_{-1}^{+1} I(\tau,\mu',t)\,\mathrm{d}\mu' \tag{4a}$$

$$\text{for } 0 \le \tau \le \tau_0(t),\ -1 \le \mu \le 1,$$

$$I(0,\mu,t) = I_0, \qquad \mu > 0 \tag{4b}$$

$$I(\tau_0, -\mu, t) = 2\rho \int_0^1 I(\tau_0,\mu',t)\,\mu'\,\mathrm{d}\mu', \qquad \mu > 0 \tag{4c}$$

where $\omega = \sigma^*/(\mathrm{K}^* + \sigma^*)$ is the single scattering albedo, μ is the cosine of the angle between the direction of radiation intensity and the positive x axis, and the optical variable τ is related to the physical coordinate x by

$$\mathrm{d}\tau = (\mathrm{K}^* + \sigma^*)\,C(x,t)\,\mathrm{d}x \tag{5a}$$

or

$$\tau(x,t) \equiv \tau = (\mathrm{K}^* + \sigma^*)\int_0^x C(x',t)\,\mathrm{d}x'. \tag{5b}$$

Based on the definition (5b), the optical thickness, $\tau_0(t)$, of the medium at any instant t becomes

$$\tau_0(t) = (\mathrm{K}^* + \sigma^*)\int_0^L C(x,t)\,\mathrm{d}x, \tag{6a}$$

and the initial optical thickness, $\bar{\tau}_0$, of the slab is given by

$$\bar{\tau}_0 = (\mathrm{K}^* + \sigma^*)\,C_0 L. \tag{6b}$$

From equations (5b) and (6b) we write

$$\frac{\tau}{\bar{\tau}_0} = \frac{1}{L}\int_0^x \frac{C(x,t)}{C_0}\,\mathrm{d}x = \int_0^\xi \gamma(\xi,t)\,\mathrm{d}\xi, \tag{7a}$$

where

$$\gamma(\xi,t) = \frac{C(x,t)}{C_0}, \quad \xi = \frac{x}{L}. \tag{7b}$$

Clearly, the ratio $\tau/\bar{\tau}_0$ is related to the normalized average concentration of the reactant at any instant, t, in the medium over the distance $x = 0$ to x.

In the radiation problem defined by equations (4), the time variable, t, is merely a parameter which enters the problem through the dependence of $\tau_0(t)$ on t. Therefore, it can be solved for any given value of $\tau_0(t)$ by a variety of analytical techniques which are well documented in the literature [12, 14]. Here we used the approach described in the reference [14] to solve the radiation part of the problem. The general procedure for the solution of the complete problem was as follows.

The calculations were started with the solution of the radiation problem (4) for the initial optical thickness $\bar{\tau}_0$ and the incident radiation term appearing inside the bracket in equation (3) was computed. The resulting energy absorption term, $\dot{e}'''(x,t)$, was used in the mass conservation problem (2) and $C(x,t)$ was determined at a small time step Δt. This concentration distribution $C(x, t)$ was used in equation (5b) and the optical thickness, $\tau_0(t)$, of the medium at the end of time step Δt was determined. Then the radiation problem (4) was solved for this value of $\tau_0(t)$ and the calculations were repeated.

RESULTS AND DISCUSSION

The calculations were performed for the dimensionless form of the mass conservation problem (2), by using dimensionless time increments $\Delta\eta = 0.005$, where the dimensionless time η is defined as

$$\eta = \frac{\pi\phi I_0}{L}\,t. \tag{8}$$

To illustrate the effects of scattering and reflection of radiation on reaction, we have chosen the numerical values of various parameters in the calculations as $\omega = 0, 0.2$ and 0.8; $\bar{\tau}_0 = 1$ and 5, and $\rho = 0$ and 1. Here, the case $\omega = 0$, a purely absorbing medium, is considered as the reference case. Then, $\omega = 0.8$ represents a highly scattering medium for the physical problem considered here. The values of $\bar{\tau}_0 = 1$ and $\bar{\tau}_0 = 5$ characterize a medium which is initially optically thin and optically thick respectively.

Figure 1 shows a plot of the normalized optical thickness, $\tau/\bar{\tau}_0$, of the medium against the dimensionless space coordinate ξ for different values of ω and $\bar{\tau}_0$, for two values of the dimensionless time, $\eta = 1$ and 3. The normalized optical thickness, $\tau/\bar{\tau}_0$, according to its definition given by equation (7a), is related to the normalized average concentration of the reactant in the region, $\xi = 0$ to ξ, and the value of $\tau/\bar{\tau}_0$ at $\xi = 1$ represents the normalized average concentration of the reactant in the reactor. Scrutinizing the results presented in Fig. 1 reveals that increased scattering reduces the conversion rate achieved over a given period of time and tends to make the concentration of the reactant more uniform over the region. Also, the concentration of the reactant is more uniform with smaller initial optical thickness ($\bar{\tau}_0 = 1$) than with the larger initial optical thickness ($\bar{\tau}_0 = 5$) of the medium.

Figures 2 and 3 better illustrate the physical significance of the conclusions drawn from the results in Fig. 1. The average concentration, γ_b, of the reactant is plotted as a function of time in Fig. 2. The quantity $(1 - \gamma_b)$ represents the conversion, which increases with increasing initial optical thickness and decreasing scattering. Figure 3 shows the combined effects of scattering and the initial optical thickness, $\bar{\tau}_0$, of the medium on the local concentration of the reactant. With smaller value of $\bar{\tau}_0$ (i.e. $\bar{\tau}_0 = 1$), the mean free path of photons is of the same order of magnitude or larger than the geometrical dimensions of the medium. As a result, the scattered photons are likely to escape from the medium and the reaction rate is reduced. As illustrated in Fig. 3a, for the case of $\bar{\tau}_0 = 1$, the reaction rate is reduced almost uniformly over the entire region, resulting in an increased value of γ with increased scattering. On the other hand, with $\bar{\tau}_0 = 5$, as illustrated in Fig. 3b, at early times the reaction takes place to a greater extent in the region near the emitting boundary due to the large initial optical thickness of the medium. Scattering, although reduces reaction in the front region, slightly improves the conversion in the rear region, because forwardly scattered photons cannot escape from the medium. For later times (i.e. $\eta = 3$), the medium becomes sufficiently thin as a result of continued reaction and the effects of scattering on γ distribution obey a similar behaviour to that for the case of $\bar{\tau}_0 = 1$.

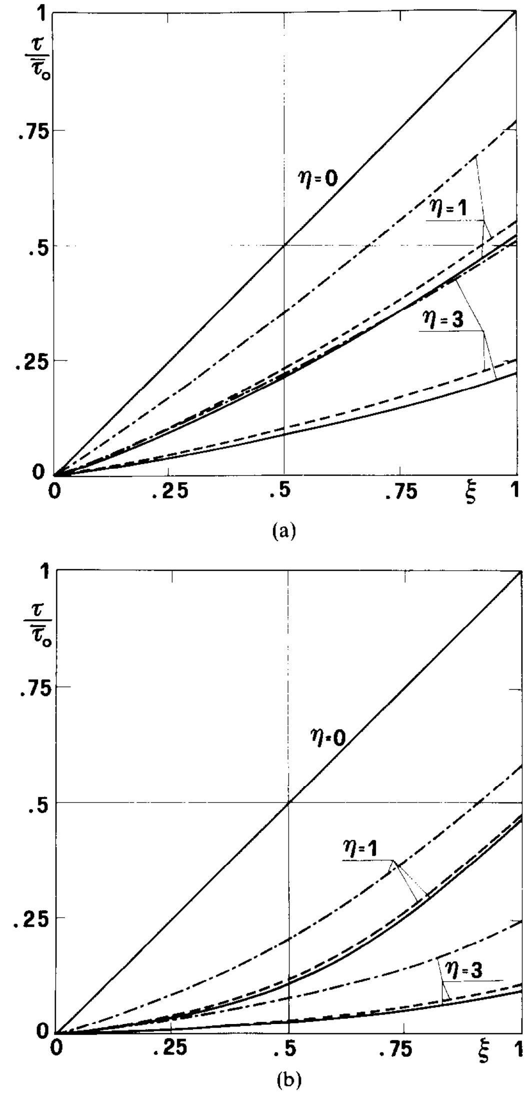


FIG. 1. Normalized optical coordinates vs position at different time for $p = 0$ (—— $\omega = 0$, - - - $\omega = 0.2$, -·-·- $\omega = 0.8$). 0.8). (a) $\bar{\tau}_0 = 1$, (b) $\bar{\tau}_0 = 5$.

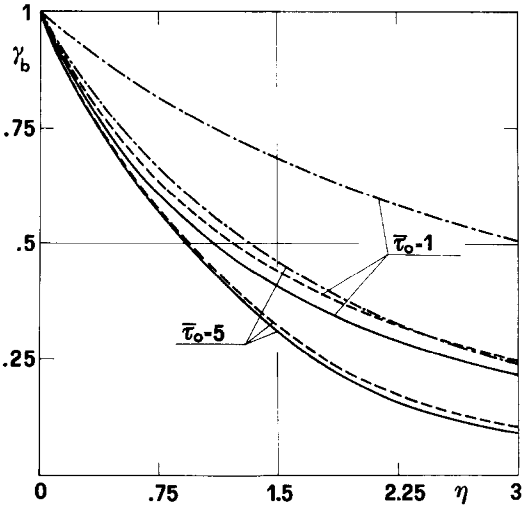
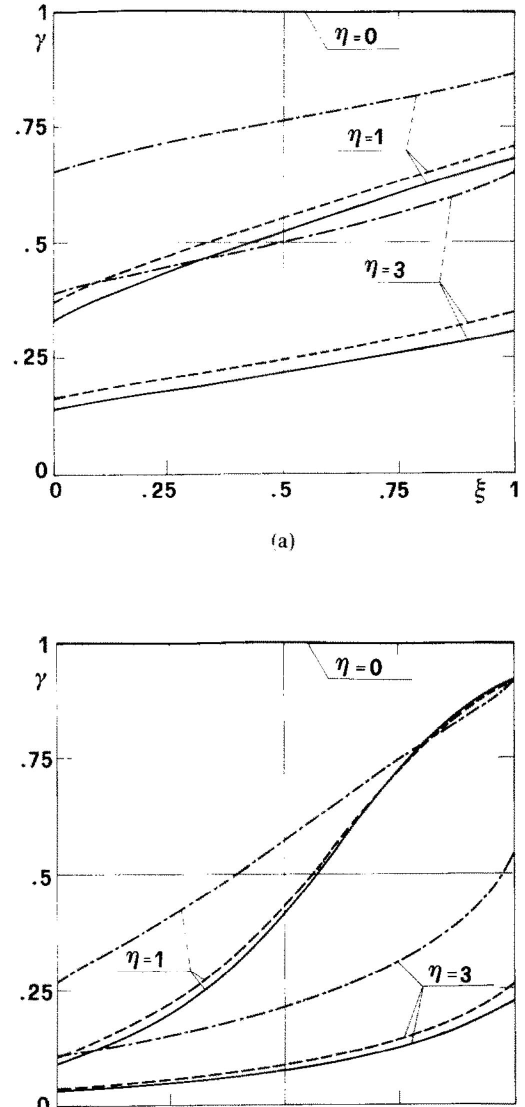


FIG. 2. Average concentration of the reactant vs time for $\rho = 0$ (—— $\omega = 0$, - - - $\omega = 0,2$, -·-·- $\omega = 0.8$).



(a)

(b)

FIG. 3. Reactant concentration vs position at different times for $\rho = 0$ (—— $\omega = 0$, - - - $\omega = 0.2$, - · - · - $\omega = 0.8$). (a) $\bar{\tau}_0 = 1$, (b) $\bar{\tau}_0 = 5$.

Figure 4 shows the transmissivity of the medium as a function of time. In this figure, there is a cross-over of the curves for different values of ω, and the cross-over point is shifted to later times with larger value of the initial optical thickness, $\bar{\tau}_0$. For early times, the transmissivity increases with increasing ω, because photons have more chance to escape from the medium. This in turn reduces conversion, and as a result reduces the optical thickness of the medium to a lesser extent. Therefore, in later times, transmissivity is lower with higher ω. Therefore, early times can be characterized as "scattering controlled period" and later times as the "thickness controlled period".

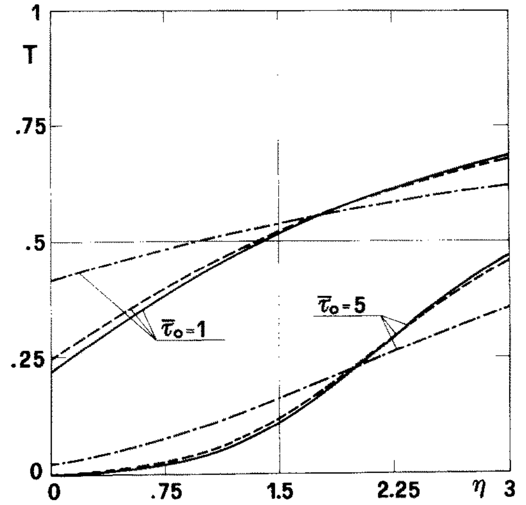


FIG. 4. Hemispherical transmissivity of the slab vs time for $\rho = 0$ (—— $\omega = 0$, - - - $\omega = 0.2$, - · - · - $\omega = 0.8$).

Figure 5 shows the effects of the reflectivity of the rear boundary on the reflectivity of the medium. The cases $\rho = 0$ and $\rho = 1$ characterizes respectively a transparent boundary and purely diffusely reflecting boundary at $x = L$. As expected, the reflectivity of the medium is higher with $\rho = 1$ than with $\rho = 0$, because more photons are reflected backward. This is found to be true in the case of $\bar{\tau}_0 = 1$ over the entire time domain. However, in the case of $\bar{\tau}_0 = 5$, at early times the medium being optically very thick, the reflected photons cannot succeed to reach the emitting boundary and escape from it. Therefore, the reflectivity of the

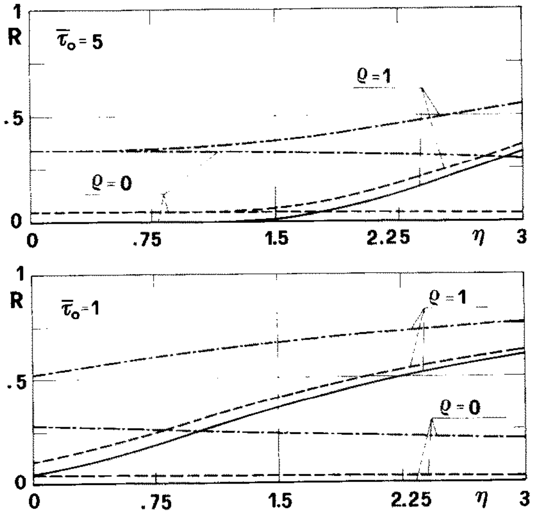


FIG. 5. Hemispherical reflectivity of the slab vs time for $\rho = 0.1$ (—— $\omega = 0$, - - - $\omega = 0.2$, - · - · - $\omega = 0.8$).

rear boundary does not seem to influence the reflectivity of the medium at early times when the medium is optically thick. However, at later times, as the optical thickness of the medium is reduced as a result of chemical reaction, the reflected photons can reach the emitting boundary and escape from it, thus increasing the reflectivity of the medium. The branching of the curves for $\rho = 0$ and $\rho = 1$ is due to this effect. The larger is the value of ω, the earlier is the occurring of this branching. For the case of $\rho = 0$, the reflectivity is increased with increasing ω, because more photons are scattered backward, so having a chance to escape from the emitting surface. There is a slight decrease in reflectivity with time, because more photons are likely to escape from the medium by scattering in the forward direction as a result of decreased optical thickness of the medium.

Figure 6 shows that the dimensionless distribution of the reactant, γ, is lower and more uniform with purely reflecting boundary ($\rho = 1$) than with transparent boundary ($\rho = 0$). This effect is more pronounced with $\bar{\tau}_0 = 1$ than with $\bar{\tau}_0 = 5$, and also with larger values of ω. A similar conclusion can be drawn from Fig. 7, which shows the average concentration, γ_b, of the reactant as a function of time.

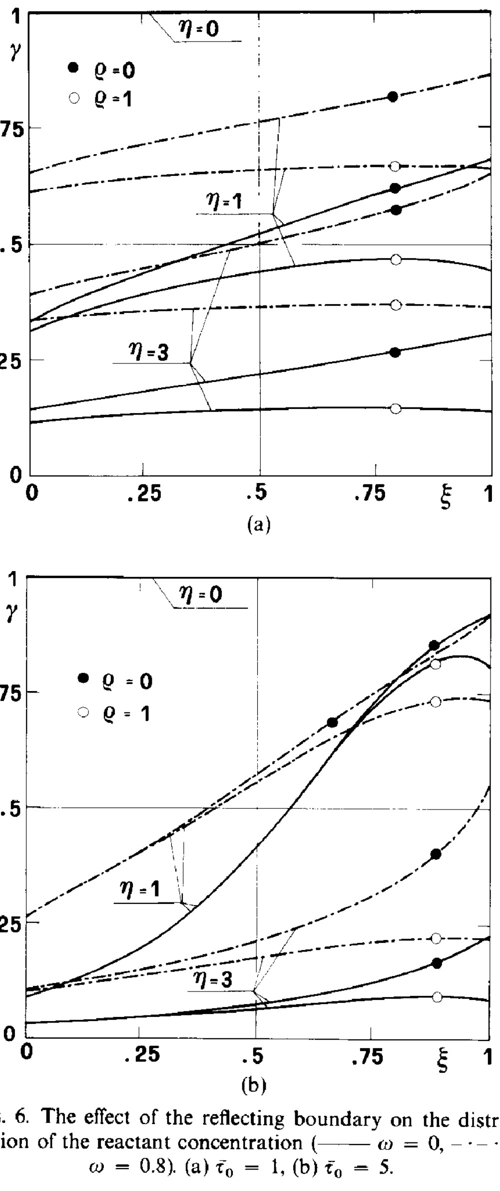


Fig. 6. The effect of the reflecting boundary on the distribution of the reactant concentration (—— $\omega = 0$, –·–·– $\omega = 0.8$). (a) $\bar{\tau}_0 = 1$, (b) $\bar{\tau}_0 = 5$.

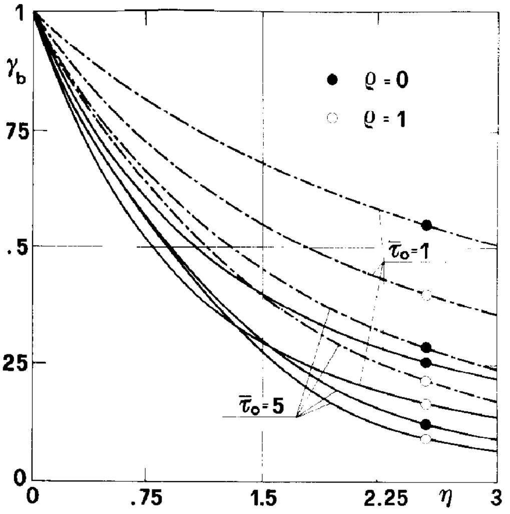


Fig. 7. Average concentration of the reactant vs time (—— $\omega = 0$, –·–·– $\omega = 0.8$).

The foregoing conclusions do not have practical significance for $\tau_0 \to 0$ or $\omega \to 1$, even though they are valid in principle.

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EFFETS DE LA DIFFUSION ET DE LA REFLEXION DU RAYONNEMENT SUR UNE REACTION PHOTOCHIMIQUE DANS UNE GEOMETRIE EN LAME

Résumé—On étudie analytiquement les effets de la diffusion du rayonnement dans le milieu, de la réflectivité de la surface frontière et de l'épaisseur optique initiale du milieu sur la conversion d'une réaction photochimique pour une lame plane. Des résultats sont présentés en fonction du temps pour la conversion locale ou moyenne dans le milieu, pour la réflectivité et la transmittivité du milieu, et pour l'épaisseur optique normalisée. On trouve que la diffusion réduit la conversion et qu'elle tend à accroitre l'uniformité de la distribution du réactant dans le milieu.

AUSWIRKUNGEN DER STREUUNG UND REFLEXION VON STRAHLUNG AUF DIE FOTOCHEMISCHE REAKTION IN EINER SCHICHTGEOMETRIE

Zusammenfassung—Die Auswirkungen der Strahlungsstreuung innerhalb des Mediums, der Oberflächenreflexion und der zeitlich abhängigen optischen Dichte des Mediums auf die Umwandlung bei fotochemischen Reaktionen in einer ebenen Schichtgeometrie werden analytisch untersucht. Es werden Ergebnisse für die örtliche und die mittlere Umwandlung innerhalb des Mediums, die Reflexion und die Transmission und die normierte optische Dichte des Mediums als Funktion der Zeit angegeben. Es stellt sich heraus, daß die Streuung die Umwandlung vermindert und dazu neigt, die Gleichförmigkeit der Verteilung der Reaktionspartner innerhalb des Mediums zu vergrößern.

ВЛИЯНИЕ РАССЕЯНИЯ И ОТРАЖЕНИЯ ИЗЛУЧЕНИЯ НА ФОТОХИМИЧЕСКУЮ РЕАКЦИЮ В СРЕДЕ, ИМЕЮЩЕЙ ФОРМУ ПЛИТЫ

Аннотация — Проведено аналитическое исследование влияния рассеяния излучения в среде, отражательной способности ограничивающих поверхностей и начальной оптической толщины среды на фотохимические превращения, протекающие в среде, имеющей форму плоской плиты. Рассчитаны локальные и средние значения фотохимических превращений, отражательной и пропускательной способности и нормированной оптической толщины среды как функции времени. Найдено, что рассеяние затягивает фотохимическую реакцию и способствует однородному распределению реагента в среде.