Radiation Profiles in an Empty Annular Photoreactor with a Source of Finite Spatial Dimensions

A model of radiant energy emission for tridimensional sources has been developed and used to predict radiation flux density profiles in an annular photochemical reactor. This paper presents results for a reactor without dispersion or absorption effects; that is, reflexions and refractions have been neglected and the energy has been assumed to propagate in a transparent medium.

Computed radiation profiles agree well with published experimental data in a similar lamp-reactor set up.

Also, the formulation does not introduce, as it is the case with all line models, any form of singularities in the prediction of radiation flux density values.

Finally, a parametric study of the effects of lamp dimensions on the shape of the radiation profiles was also made.

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SCOPE

The main distinction between photochemically and thermally activated reactions is the existence of an initiation step which is a function of the distribution of radiation energy inside the reactor. With only a few exceptions, depending upon this distribution, the initiation rates will not be uniform in space and hence the existence of concentration and eventually temperature gradients seem to be almost intrinsic to photoreactors.

This nonuniformity of energy in space is due mainly to the attenuation of radiation produced by absorption of reactants and/or products and the physical and geometrical characteristics of the lamp-reactor system. The latter effect is discussed in this paper.

This aspect has already received attention from previous researchers who formulated some approximate models to evaluate radiation profiles for different types of photoreactors.

A first step in this modeling process considered a line source with emission in parallel planes perpendicular to the lamp axis, the L.S.P.P. Model, (Dolan et al., 1965; Hill and Felder, 1965; Cassano and Smith, 1966; Cassano, 1968; Harris and Dranoff, 1965). A more recent improvement has been the introduction of spherical emission, with or without empirical corrections to account for reflexions and refractions (Jacob and Dranoff, 1966; Jacob and Dranoff, 1968).

All these studies made on the elliptical reflector system (Dolan et al., 1965; Hill and Felder, 1965; Cassano and Smith, 1966; Matsuura et al., 1969; Cassano, 1968; Matsuura and Smith, 1970) or on the annular reactor (Hill and Felder, 1965; Harris and Dranoff, 1965; Jacob and Dranoff, 1966; Jacob and Dranoff, 1968), as well as some new work on radiation yields in photoreactors (Hancil et al., 1972), assumed ideal lamps represented by a straight line (finite or infinite in length depending on the case), which projects as a point on perpendicular planes. These models are attractive due to their simplicity, and they allow a relatively straightforward formulation (and in many cases analytical integration). However, intrinsic to these line models is the existence of singularities for the flux density whenever the distance from a given point to the lamp axis (or to its image at the focal point in the elliptical reflector) approaches zero.

The only exception to this approach has been the tridimensional model for the elliptical reflector (Zolner and Williams, 1971) which substitutes the lamp physically located at one of the focus by a radiating shield surrounding the reactor at the other focus.

In any case, the impossibility of analyzing all the lamp dimensions as design parameters of the photoreactor, as well as of considering the effects of the characteristics of the lamp tube upon the radiation profiles is also implicit in all these models.

A systematic formulation of radiation models seems to be necessary, particularly if the starting point is a more realistic consideration of the energy source.

In this work, an attempt has been made to develop a model for predicting the distribution of radiation in space in the absence of absorption and dispersion (reflexions and refractions) effects as a function of the spatial coordinates of the system. The final objective is the prediction of radiation flux density values at any point inside the reactor, knowing beforehand the characteristics of the lamp (type, size and power output) as well as the dimensions of the reactor. The model called Extense Source Model is then verified with data taken under experimental conditions where those simplifying assumptions may be valid. Theoretical background for this treatment may be found in a previous paper (Irazoqui et al., 1972). The next papers of this series will include reflexion, wall absorption, and refraction effects for the annular reactor, as well as an application of the E.S. Model to the elliptical reflector system.

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CONCLUSIONS AND SIGNIFICANCE

A model of radiant energy emission was developed and applied to a system formed by a cylindrical ultraviolet (U.V.) lamp inside an annular photoreactor.

The computed results agree well with published experimental data for a similar lamp-reactor system but show at the same time that reflexion and refraction effects are not always negligible and should be included in the formulation of a more general theory. This is particularly true for liquid reacting systems.

From the studies reported in this paper it can be concluded that:

1. The extense source model seems to be, at the present, the best theoretical approximation for predicting radiation profiles from a cylindrical source.
2. Departing from pre-existing ones, the model introduces in its formulation all lamp dimensions and thus makes it possible to use them as design parameters.
3. The extense source model approach also allows the full introduction of reflexion, refraction, and wall absorption effects produced by the lamp tube.
4. The emission model (that could be used for other types of photoreactor geometries, for instance, the elliptical photoreflector) does not predict an infinite radiation flux density at the center line of the lamp. This is a significant improvement over all line source models.
5. The model can be easily used to compute volumetric rates of energy absorption; this is the property directly related to the rate of initiation of a photochemical reaction.
6. An approximate analytical solution for the model is useful for analyzing the effects of lamp dimensions upon the radiation profiles. The results indicate that for laboratory size apparatus, the effect of normal changes in the radius of the lamp is almost negligible. On the other hand, it should not be disregarded as a design parameter for large scale reactors. Finally, as it is intuitively predictable, the radiation profiles are sensitive to lamp length only for small values of L.

The results obtained give confidence in the use of the Extense Source formulation for other types of photoreactors, as well as to apply it to directly predicting the spatial distribution of the volumetric rate of energy absorption.

CHOICE OF A MEASURABLE VARIABLE FOR EXPERIMENTAL VERIFICATION OF THE MODEL

It is necessary to choose a convenient experimental variable to evaluate the model. This is particularly true in this case, where the important photochemical property (the volumetric rate of energy absorption, e^a) is not amenable to local and direct experimental measurement. An appropriate choice of a property directly related to e^a will give, by comparison of the predicted values with the actual ones, a good idea about the model per se and about the validity of its assumptions.

With this purpose, the total energy per unit area and unit time impinging on a plane surface was chosen. This surface is placed in such a way that its normal intersects the lamp axis perpendicularly (Figure 2). After this choice, an experimental verification can be made by means of a properly designed thermopile or photocell such that the mean values of the measured property could represent point values within the accuracy of the experimental error. The solid angle of reception of the sensing unit must also be properly chosen such that every possible emitting direction from the source inside the radiation field boundaries is sought by the sensor.

For monochromatic radiation, at a point in space placed in an arbitrary position given by (z_o, r), in cylindrical coordinates, this property can be written as

$$Q = \int_\theta \int_\phi \int_\rho \left| \underline{dq}^{(3)}(\theta, \phi, \rho) \right|_{(r,z_o)} \cos\theta_n \quad (1)$$

θ_n is the projecting angle on the normal to the sensor unit.

A second experimental difficulty to be overcome is related to the calibration of the sensing device in absolute units. For this reason, it is convenient to define a relative value of energy (dimensionless). The reference point is chosen where Q takes the maximum value. This point is defined as the $(z, r)_m$ position and may vary according to the reactor configuration.

Thus, the model will be checked by comparing predicted and actual values for the variable:

$$Q_r = \frac{Q}{Q_{\max}} \quad (2)$$

Nevertheless, it is clear that none of the variables so far introduced will directly enter into the formulation of the reaction rate. In a previous paper (Irazoqui et al., 1972) it was shown, from fundamental principles, that the volumetric rate of energy absorption (e_ν^a) is what really matters. But since e_ν^a can be written in terms of $|\underline{dq}_\nu^{(4)}|$ and the absorbing properties of the reacting medium, Equation (2) should provide enough evidence to use or reject the model.

EMISSION MODEL FOR HOMOGENEOUS EXTENSE SOURCES

Figures 1 and 2 show the main features of the reacting system. The lamp is a cylinder surrounded by an annular photoreactor. The radiation field of interest is limited at the top and bottom positions by opaque zones, as depicted by Figure 1. The most important parameters and nomenclature of the problem are also shown in the figures.

The model is based upon the following assumptions:

ASSUMPTIONS ABOUT THE EMISSION

1. The emitters of the radiation source are uniformly distributed inside its volume.
2. Each elementary volume inside the source has an isotropic emission, that is, the specific intensity associated with each bundle of radiation coming from the same element of volume is independent of direction.
3. Any elementary volume inside the source emits per unit time, at any frequency, an amount of energy proportional to its extension.
4. The energy emitted from any elementary volume of the lamp is due to spontaneous emission, and each of these differential volumes is transparent to the emission of its surroundings.

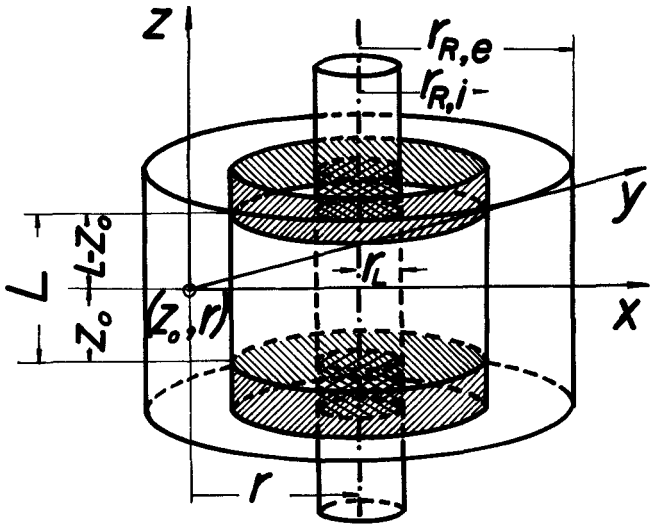

Fig. 1. Photoreactor geometry.

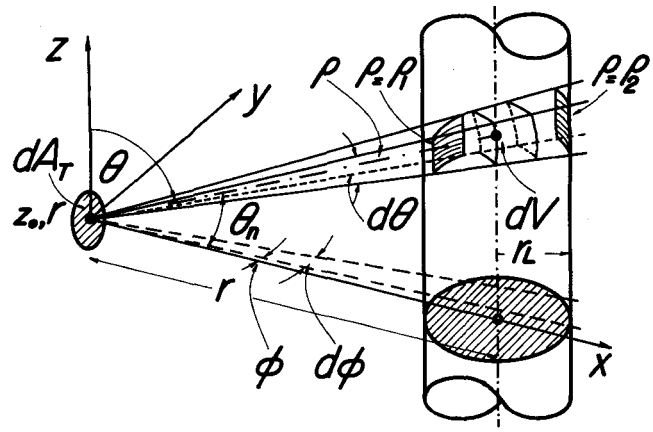

Fig. 2. Variables involved in the theoretical analysis.

ASSUMPTIONS RELATED TO THE SOURCE

1. The lamp is a perfect cylinder, bounded by mathematical surfaces with zero thickness. Thus, any bundle of radiation coming from inside does not change its intensity or direction when it crosses this boundary.

2. The lamp is long enough and it is adequately masked to neglect end effects, that is, the emission characteristics are constant along the z direction. (This assumption does not say anything about the radiation field along the z direction.)

ASSUMPTIONS RELATED TO THE REACTOR

1. The reactor is bounded by two concentric cylindrical mathematical surfaces without thickness, that is, no reflexions, refraction, or absorption occurs at any of the walls of the reactor.

2. The reactor is filled with a transparent fluid, that is, no absorption occurs inside the reaction vessel.

3. The opaque zones at the top and bottom parts of the reactor do not reflect or emit radiation.

THEORETICAL DEVELOPMENT

From the assumptions about the source, the rate of energy emission at frequency ν by a differential volume element is

$$dE_\nu = N_e\, P_\nu\, h\nu\, dV\, d\nu \tag{3}$$

where N_e represents the number of emitters per unit volume of source and $P_\nu\, d\nu$ gives, per unit time, the probability of emission at a given frequency interval $d\nu$. Under previous assumptions (4 and 5 about the emission), N_e and P_ν are related to the emission coefficient j_ν as follows:

$$j_\nu = \frac{N_e\, P_\nu\, h\nu}{4\pi\, \delta} \tag{4}$$

In Equation (4), δ is the density of the emitting medium, and j_ν is a function of frequency as well as of the state variables of the medium; thus, both N_e and P_ν depend upon the operating conditions of the lamp.

From assumption 2 about the emission, the energy emitted in a solid angle $d\Omega$ about a given direction is

$$dE^{(6)}_{\nu,\Omega} = \frac{N_e\, P_\nu\, h\nu}{4\pi}\, d\nu\, dV\, d\Omega \tag{5}$$

which can be written, for a θ, ϕ direction (Figure 2), as

$$dE^{(6)}_{\nu,\theta,\phi} = \frac{N_e\, P_\nu\, h\nu}{4\pi} \sin\theta\, \cos\theta_n\, d\theta\, d\phi\, d\rho\, dA\, d\nu \tag{6}$$

The specific intensity is defined by

$$dE_{\nu,\theta,\phi} = dI_\nu \sin\theta\, \cos\theta_n\, d\theta\, d\phi\, dA\, d\nu \tag{7}$$

which, for the isotropic emission of the differential volume of source at frequency ν gives a specific intensity equal to

$$dI_\nu = \frac{N_e\, P_\nu\, h\nu}{4\pi}\, d\rho \tag{8}$$

At any point in space (z_0, r), the radiation flux density coming from the elementary volume dV with direction θ, ϕ, and for the whole range of frequencies, is given by

$$dq^{(3)}\,(\theta, \phi, \rho)\,]_{r,z_0} = \kappa \sin\theta\, \cos\theta_n\, d\theta\, d\phi\, d\rho \tag{9}$$

where

$$\kappa = \int_{\nu=0}^{\nu=\infty} \frac{N_e\, P_\nu\, h\nu}{4\pi}\, d\nu \tag{10}$$

is a property of the radiation source and its operating conditions.

The total energy per unit area and unit time impinging on the differential area at the point (z_0, r), from all directions in space and from the whole volume of the lamp, can be obtained by proper integration of Equation (9). Substituting $\cos\theta_n = \cos\phi\, \sin\theta$, and performing the integration

$$Q|_{z_0,r} = \kappa \int_\theta \int_\phi \int_\rho \sin^2\theta\, \cos\phi\, d\theta\, d\phi\, d\rho \tag{11}$$

APPLICATION TO THE ANNULAR PHOTOREACTOR

Limits for the Variable ρ

The limits of ρ for any θ, ϕ direction are:

$$\rho_{1\,2} = \frac{r\cos\phi \mp [r^2\cos^2\phi - r^2 + r_L^2]^{1/2}}{\sin\theta} \tag{12}$$

Limits for the Variable θ

From Figures 1 and 3, for the upper and lower boundaries

$$(L - z_0) = \rho_1 \cos\theta_1 \tag{13}$$

$$-z_0 = \rho_1 \cos\theta_2 \tag{14}$$

and using Equation (12), the integration limits as a function of ϕ result

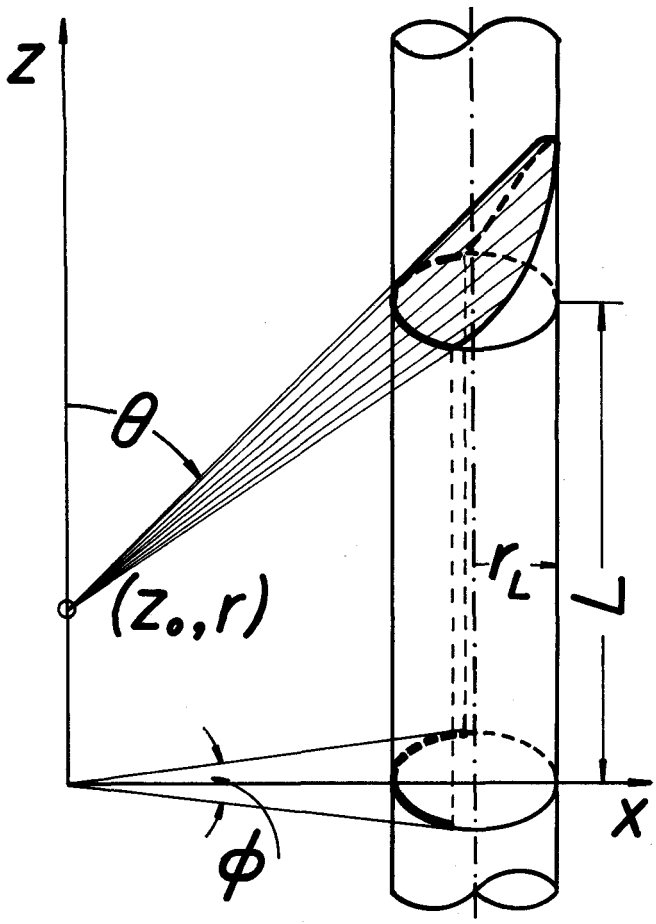

Fig. 3. Limits for θ and ϕ.

$$\theta_1(\phi) = tg^{-1}\left[\frac{r\cos\phi - [r^2(\cos^2\phi - 1) + r_L^2]^{1/2}}{(L - z_0)}\right] \quad (15)$$

$$\theta_2(\phi) = tg^{-1}\left[\frac{r\cos\phi - [r^2(\cos^2\phi - 1) + r_L^2]^{1/2}}{-z_0}\right] \quad (16)$$

Limits for the Variable ϕ

From Figure 3, these limiting values can be obtained by imposing the restriction that both intersections of the ρ coordinate with the lamp boundary must coincide, that is,

$$\rho_1 = \rho_2 \quad (17)$$

With Equation (12) and since ϕ can only take values in the closed interval $[-\pi/2, \pi/2]$:

$$-\phi_1 = \phi_2 = \cos^{-1}\left[\frac{(r^2 - r_L^2]^{1/2}}{r}\right] \quad (18)$$

The final expression results:

$$Q = 2\kappa \int_{\phi_1}^{\phi_2} [r^2\cos^2\phi - r^2 + r_L^2]^{1/2} [\cos\theta_1(\phi) - \cos\theta_2(\phi)]\cos\phi\, d\phi \quad (19)$$

RESULTS: COMPARISON WITH EXPERIMENTAL DATA

Radiation profiles were computed for conditions in which similar experimental information was available. The most significant set of data was found in a work related to the scale up of an annular photoreactor (Jacob and Dranoff, 1970) where radiation profiles for different propagating media were reported as a result of direct experimental measurement. The reactor was irradiated with a cylindrical source. The only difference is that the emission from the lamp is actually coming out from a phosphorescent material covering the inner face of the lamp wall. This phosphorescence is activated by the emission from the lamp volume.

In order to plot Q_r values, two dimensionless position variables were defined as

$$r_a = \frac{r}{r_{R,i} + 1.4\text{ mm}}$$

and

$$z_a = \frac{z}{z_m}$$

where $r_{R,i}$ is the outer radius of the inner wall of the reactor, 1.4 mm is the thickness of the window of the photocell, and z_m is the coordinate of the mid-depth point of the reactor. When $r_a = 1$ and $z_a = 1$, the maximum value of Q_r is obtained ($Q_{r,\max}$).

In Figure 4, Q_r values are plotted as a function of r_a, with $z_a = 1$. It is clear that the best agreement is obtained with the E.S. Model. The air filled reactor is a fairly good approximation to the conditions under which the calculations for the model were performed since it minimizes all types of refraction effects. The same cannot be said about reflexion effects.

On the other hand, if the reactor is filled with water, the radiation profiles seem to be greatly modified, indi-

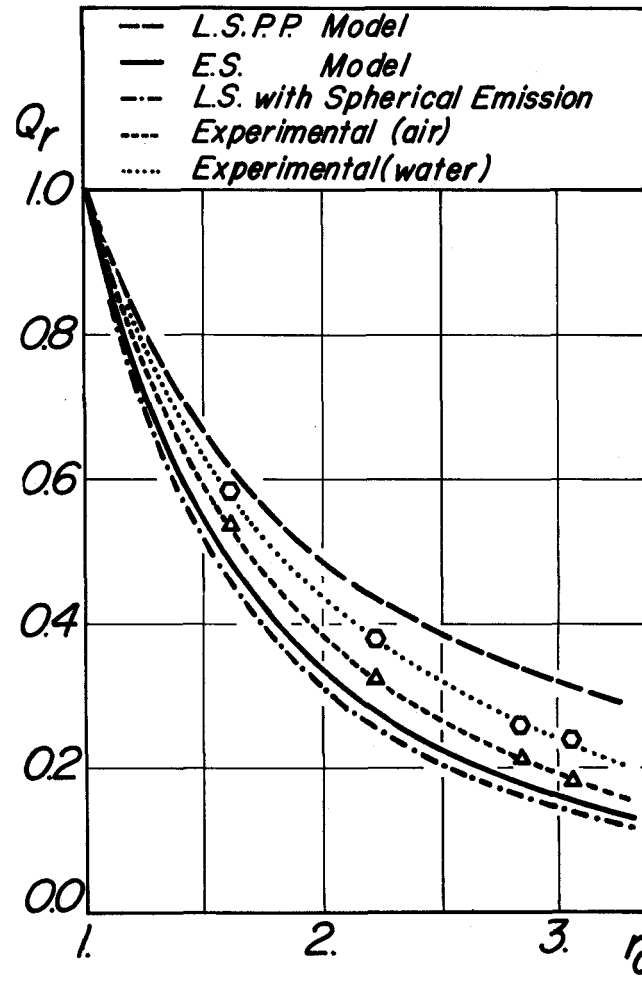

Fig. 4. Results at $z_a = 1.0$.

cating that refraction effects may be significant. If this is the case, the model should be improved to include all these forms of distortions.

Figure 5 shows the variation of the radiation profiles along the z direction. These results are very significant because they illustrate that the assumption of a z independent energy distribution inside the reactor must be handled with great care. In fact, for the short distances used in this work, a variation of 43% was found between the top (or bottom) and the mid-depth portions of the reactor. This effect may be even magnified if the lamp is not long enough to eliminate emission end effects. (The variations reported here with this model are not caused by end effects associated with the emission of the lamp but by the intrinsic geometrical characteristics of the system.)

SENSITIVITY OF THE RADIATION PROFILES TO LAMP DIMENSIONS

It is important to determine the influence of lamp dimensions on the radiation profiles inside the annular reactor. This information could be used directly for reactor design purposes or to decide beforehand when more idealized models (for example, any type of line source model) can be applied because the extension of the lamp has negligible effects.

Derivation of Equations

In order to perform a parametric analysis with the aid of analytic expressions, some simplifying assumptions have been made on Equation (19) to eliminate the relationships given by Equations (15) and (16). This allows a separated integration of the variables θ and ϕ and can be accomplished if it is assumed that the sector of the surface generated by the radius vector ρ when it intersects the limiting circumference of the opaque zone of the lamp (Figure 3) can be substituted by one generated by a radius vector moving at constant θ (Figure 6). This simplification changes slightly the total emitting volume of the lamp, giving a better approach to the exact formulation when the values of θ get closer to $\pi/2$. Also, the larger is the lamp, the smaller will be the error, because the differences between the exact and the approximate formulation will have a negligible effect on the emission volume of the source. With this change in the limits of θ, the results will be

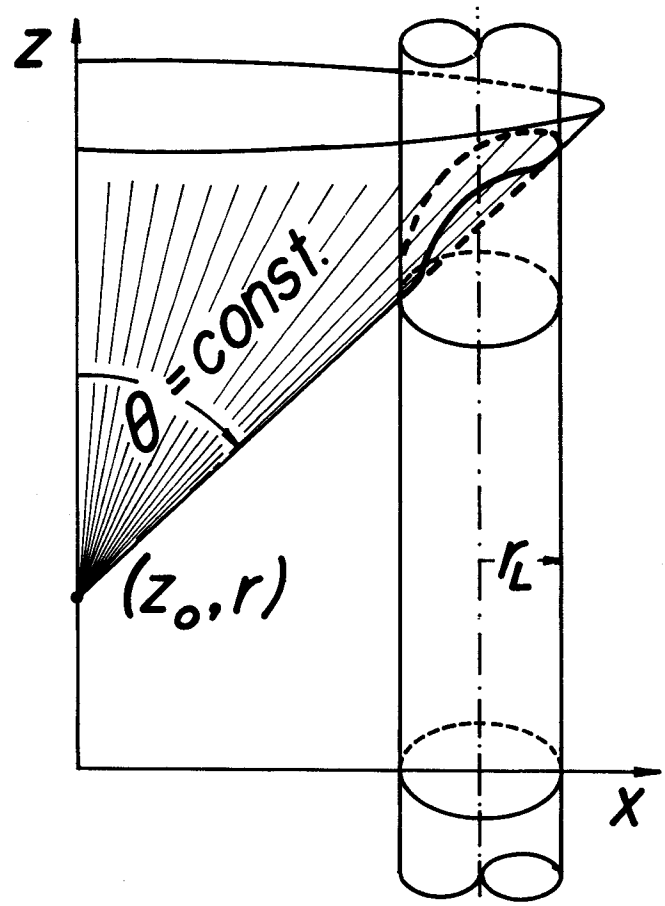

Fig. 6. Simplification of the model.

$$\cos\theta_1 = \frac{|L - z_0|}{[(L - z_0)^2 + (r - r_L)^2]^{1/2}} \tag{20}$$

$$\cos\theta_2 = \frac{-|z_0|}{[(z_0)^2 + (r - r_L)^2]^{1/2}} \tag{21}$$

The final approximate (but analytical) solution is

$$Q = \frac{\kappa \pi r_L^2}{r}\left[\frac{|L - z_0|}{[(L - z_0)^2 + (r - r_L)^2]^{1/2}} + \frac{|z_0|}{[(z_0)^2 + (r - r_L)^2]^{1/2}}\right] \tag{22}$$

The goodness of the approximate solution was checked by comparing it with predictions made with Equation (19). The results (Table 1) show that the errors for lamps of practical size are almost negligible. This verification gives enough confidence for using Equation (22) to carry out the parametric analysis.

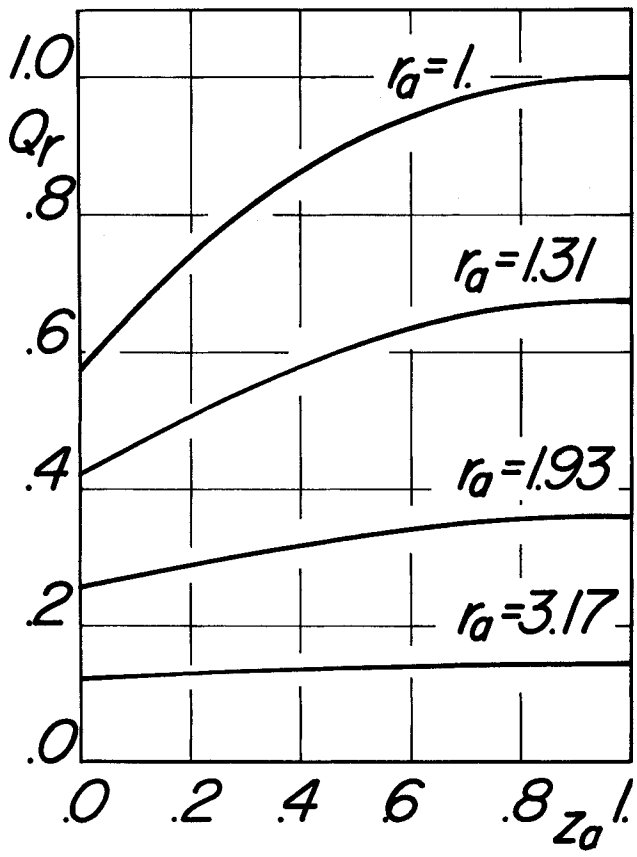

Fig. 5. Variation of Q_r with the z coordinate.

TABLE 1. COMPARISON OF RESULTS OF THE EXACT AND THE APPROXIMATE MODELS

Q_r

	$L = 10$ cm; $r_L = 0.5$ cm				$L = 50$ cm; $r_L = 0.5$ cm			
	$z_a = 0.0$		$z_a = 0.5$		$z_a = 0.0$		$z_a = 0.5$	
r cm	Equation (30)	Equation (35)	Equation (30)	Equation (35)	Equation (30)	Equation (35)	Equation (30)	Equation (35)
4.0	0.5785	0.5760	1.0000	1.0000	0.5037	0.5036	1.0000	1.0000
6.0	0.3577	0.3565	0.5470	0.5474	0.3346	0.3345	0.6573	0.6574
8.0	0.2448	0.2441	0.3384	0.3385	0.2496	0.2496	0.4833	0.4835
10.0	0.1771	0.1769	0.2275	0.2274	0.1984	0.1984	0.3773	0.3775
12.0	0.1338	0.1334	0.1624	0.1622	0.1640	0.1640	0.3055	0.3057
	$L = 10$ cm; $r_L = 1.0$ cm				$L = 50$ cm; $r_L = 1.0$ cm			
	$z_a = 0.0$		$z_a = 0.5$		$z_a = 0.0$		$z_a = 0.5$	
	Equation (30)	Equation (35)	Equation (30)	Equation (35)	Equation (30)	Equation (35)	Equation (30)	Equation (35)
4.0	0.5625	0.5585	1.0000	1.0000	0.5029	0.5026	1.0000	1.0000
6.0	0.3495	0.3476	0.5485	0.5497	0.3341	0.3340	0.6581	0.6584
8.0	0.2398	0.2388	0.3382	0.3389	0.2494	0.2493	0.4845	0.4849
10.0	0.1740	0.1733	0.2263	0.2265	0.1982	0.1982	0.3785	0.3790
12.0	0.1312	0.1307	0.1608	0.1608	0.1639	0.1639	0.3068	0.3072

Effect of the Lamp Radius

Analysis at $z_0 = L/2$. Equation (22), written as shown by Equation (2), gives

$$Q_r = \frac{r_m}{r}\left[\frac{[(L/2)^2 + (r_m - r_L)^2]}{[(L/2)^2 + (r - r_L)^2]}\right]^{1/2} \qquad (23)$$

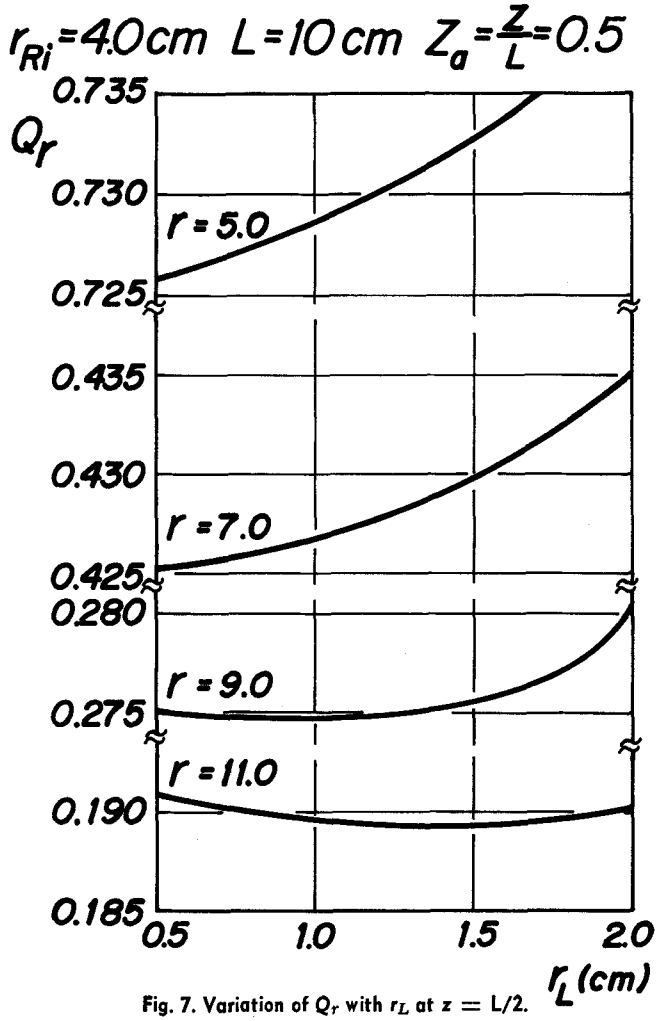

Fig. 7. Variation of Q_r with r_L at $z = L/2$.

The first derivative with respect to r_L has a sign given by that of the numerator, which can be written as

$$(r - r_m)\,(L/2)^2 - (r - r_L)\,(r_m - r_L)\,(r - r_m) \qquad (24)$$

In expression (24), both terms are always greater than zero, indicating that the sign of the numerator depends upon the value taken by r_L. However, since r_L is always smaller than r_m or r, an increase in its value will only change the significance of the second term but not its sign. Thus, if the derivative is originally negative, a change in slope may occur for some values of r_L compatible with the system dimensions. The minimum value of Q_r is obtained for

$$(r_L)_{\min} = \frac{(r + r_m) - [(r + r_m)^2 + L^2 - 4r_m\, r]^{1/2}}{2} \qquad (25)$$

This minimum will not always occur since according to the values of the other variables of the expression (24), the derivative may be also positive originally. Figure 7 illustrates these predictions showing values computed with the exact model for different r positions inside the reactor. At $r = 9$ cm, Equation (25) predicts a minimum for $r_L = 0.9$ cm and this is also depicted in Figure 7.

Analysis at $z_0 = 0.0$. A similar reasoning and mathematical treatment yields a minimum for

$$(r_L)_{\min} = \frac{-[r_m^2 - 3(L/2)^2 - r^2]}{2(r - r_m)} + \left[\frac{[r_m^2 - 3(L/2)^2 - r^2]^2}{4(r - r_m)^2} - \frac{[r_m L^2 + r_m r^2 - r r_m^2 - r(L/2)^2]}{(r - r_m)}\right]^{1/2} \qquad (26)$$

These predictions also agree with computed values.

Effect of the Useful Length of the Lamp

Analysis at $z_0 = 0.0$. Taking the first derivative of Q_r with respect to L, at $z_0 = 0.0$, the following expression is obtained:

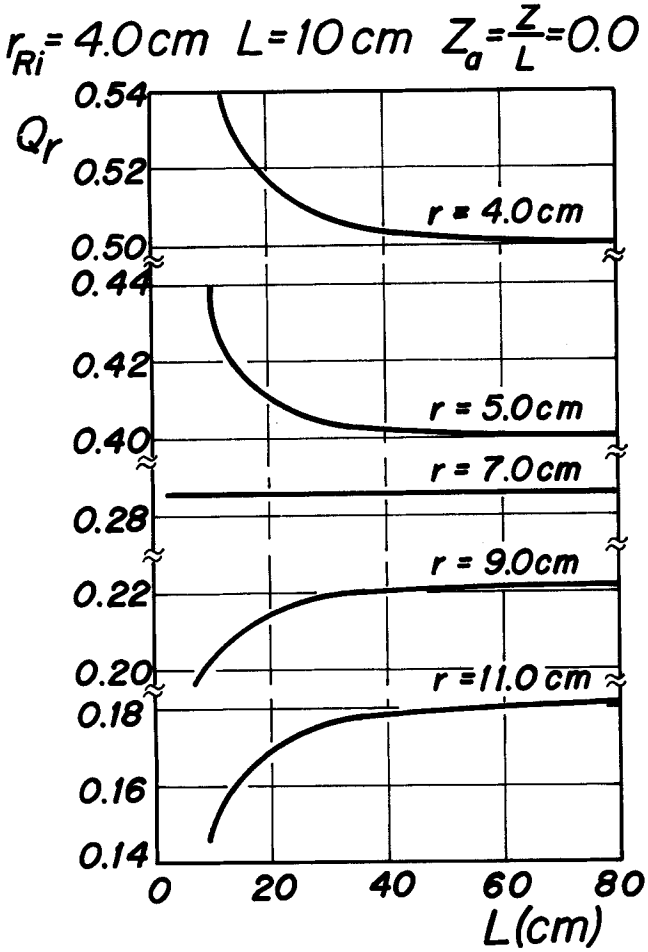

Fig. 8. Variation of Q_r with L at $z = 0$.

$$\frac{dQ_r}{dL} = \frac{r_m L[(r - r_L)^2/2 - 2(r_m - r_L)^2]}{r[(L/2)^2 + (r_m - r_L)^2]^{1/2}\,[L^2 + (r - r_L)^2]^{3/2}} \tag{27}$$

which predicts insensibility of Q_r to variations of L at $z_0 = 0.0$ when $r = r_0 = 2\,r_m - r_L$. For values of $r < r_0$, the first derivative will be negative, and vice versa for $r > r_0$.

As it can be intuitively predicted, the model shows no effects of L when the useful length of the lamp is large enough. Q_r values (computed using the exact model) plotted against L, for several values of r, are shown in Figure 8.

For $r_0 = 7$ cm, the insensibility of Q_r to all values of L is also shown.

Analysis at $z_0 = L/2$. The first derivative of Equation (23) with respect to L gives

$$\frac{dQ_r}{dL} =$$

$$\frac{r_m L\,[(r - r_L)^2 - (r_m - r_L)^2]}{2\,r\,[(L/2)^2 + (r_m - r_L)^2]^{1/2}\,[(L/2)^2 + (r - r_L)^2]^{3/2}} \tag{28}$$

Since $r \geq r_m$, excluding the point where $r = r_m$, the first derivative will increase monotonously. However, again for values of L sufficiently large, in practice, the radiation profile will also be insensible to changes in L. Numerical calculations agree with all these theoretical predictions.

ACKNOWLEDGMENT

The authors thank I.B.M. Argentina S.A. and to FIAT Concord Argentina S.A. for providing some free computing time. Thanks are also given to Mr. Arnaldo O. Valazza for his help in preparing the manuscript.

NOTATION

A = area, cm^2
e^a = volumetric rate of energy absorption, Einsteins s^{-1} cm^{-3}
E = energy flow rate, Einsteins s^{-1}
h = plank constant, erg s
I = specific intensity, Einsteins s^{-1} cm^{-2} sr^{-1}
L = reactor length, cm
N_e = number of emitters per unit volume, cm^{-3}
P_ν = probability density distribution function for emission per unit time at a particular frequency range, dimensionless
q = radiation flux density, Einsteins cm^{-2} s^{-1}
Q = radiant energy flux at the area of reception, Einsteins cm^{-2} s^{-1}
V = volume, cm^3
x = coordinate, cm
y = coordinate, cm
z = coordinate, cm

Greek Letters

δ = density of radiant medium, g cm^{-3}
ϕ = spherical coordinate, rad
ν = frequency, s^{-1}
κ = characteristic property of the lamp emission: defined by Equation (10) (Einsteins cm^{-3} s^{-1} sr^{-1})
Ω = solid angle, sr
ρ = spherical coordinate, cm
θ = spherical coordinate, rad

Subindices

a denotes dimensionless quantity
e denotes outer value
i denotes inner value
L denotes a lamp property
m denotes maximum value
n denotes value measured with respect to the normal
o denotes an arbitrary chosen position
R denotes reactor property
r denotes radial dependency or relative value
T denotes transverse area with respect to the x axis
z denotes z coordinate dependence
θ denotes θ coordinate dependence
ϕ denotes ϕ coordinate dependence
ν denotes frequency dependence

Supraindices

a denotes absorbed value
(j) the number j denotes the order of an infinitesimal quantity

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Manuscript received June 19, 1972; revision received December 7, 1972; paper accepted December 11, 1972.

Observer Theory for Lumping Analysis of Monomolecular Reaction Systems

A new approach for the lumping analysis of reversible and/or irreversible monomolecular reaction systems (MRS) with constant or time-dependent rate coefficients in discrete and continuous mixtures is presented. The observer theory initiated by Luenberger is proposed and extended to obtain the necessary and sufficient conditions of exact and approximate lumping of such systems. Examples are given to illustrate the implications of lumping and to demonstrate the generality and promising aspects of the observer approach. It is shown that this theory is a unifying method for the lumping analysis of MRS. New insights on lumping analysis are discussed.

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SCOPE

Among those chemical reaction systems encountered in chemical processes, the monomolecular reaction system (MRS) is of particular interest to chemical engineers. This follows because many complex reactions such as isomerization and catalytic hydrodesulfurization can frequently be approximated by first- or pseudo first-order reactions. In the kinetic analysis of such reactions which usually contain a large number of distinct chemical species (discrete mixture) or a continuous distribution of components (continuous mixture), it is convenient and practical to lump the species together into kinetically equivalent groups and treat them as independent lumped components. A typical example of this lumping practice is the PONA analysis used in petroleum processing, in which all chemical species in the feedstock to the reformer are lumped into four groups, namely paraffins, olefins, naphthenes, and aromatics.

An important practical question in applying such lumping procedures is whether the kinetic behavior of the original complex reaction system can be satisfactorily represented by the simplified kinetic system described by the lumped components; in an opposite sense the following question may also be raised: if an appropriate lumped kinetic model is known, how can the kinetic parameters of the original system be evaluated from the available measurements of the lumped kinetic system? The latter question has been answered comprehensively by Wei and Prater (1962), Silvestri and Prater (1964), Riekert and Wei (1968), and Prater et al. (1967, 1968, and 1970) by introducing the concept of an experimentally measurable straight-line reaction path for the reversible MRS in a discrete mixture. The former question, however, has been discussed only briefly in the work of Wei and Kuo (1968) and Bailey (1972). Both considered the conditions for the exact and approximate lumping of the reversible MRS in discrete and continuous mixtures, respectively, although the conditions for the exact lumping of a specific class of irreversible MRS in a continuous mixture was also given (Bailey, 1972).

A number of important difficulties, however, prohibit the practical applications of these lumping techniques. All require a priori knowledge of the complete set of kinetic rate coefficients and such information is rarely available in practice. In addition, these results are not applicable for the general irreversible MRS, for the MRS with noisy experimental measurements, or for the MRS with time-dependent rate coefficients such as reactions