

d = density, $1/V$
 d^* = reduced rigid-sphere mixture density, $6y/\pi$
 f = fugacity
 k = Boltzmann constant
 n_i = reduced density of i -molecules, $x_i(\pi N/6V)$
 x_i = mole fraction of i -molecules in system
 y = reduced density in rigid-sphere equations

Greek Letters

β = general coefficient
 ρ = density, $1/V$
 Σ = summation operator
 σ = rigid-sphere diameter
 σ_i = sphere diameter of i -molecules
 σ_{ij} = $1/2(\sigma_i + \sigma_j)$
 ϕ = pressure due to cohesion and soft-repulsion $P - P_{rs}$

LITERATURE CITED

1. van der Waals, J. D., doctoral dissertation, Leiden, Holland (1873).

2. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1967).
3. Barker, J. A., "Lattice Theories of the Liquid State," in *International Encyclopedia of Physical Chemistry and Chemical Physics*, Macmillan, New York (1963).
4. Pierce, F. J., *Microscopic Thermodynamics*, International Textbook Co., Pennsylvania (1968).
5. Ree, R. H., and W. G. Hoover, *J. Chem. Phys.*, **46**, 4181 (1967).
6. Carnahan, N. F., and K. E. Starling, *J. Chem. Phys.*, **51**, 635 (1969).
7. Redlich, O., and J. N. S. Kwong, *Chem. Rev.*, **44**, 233 (1949).
8. Hsu, C. C., and J. J. McKetta, *J. Chem. Eng. Data*, **9**, 45 (1964).
9. Canjar, L. N., and F. S. Manning, *Thermodynamic Properties and Reduced Correlations for Gases*, Gulf Publ. Co., Houston, Texas (1967).
10. Chao, K. C., and J. D. Seader, *AIChE J.*, **7**, 598 (1961).
11. Mansoori, G. A., et al., *J. Chem. Phys.*, **54**, 1523 (1971).

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The Effect of Angular Light Intensity Distribution on the Performance of Tubular Flow Photoreactors

The angular light intensity distribution (ALID) at the surface of several elliptical reflector-photoreactors was determined experimentally using the optically dense potassium ferrioxalate actinometer. The distributions were well correlated by the model

$$I_w(\theta) = \bar{I}_w[1 + \beta \cos \theta]$$

The correlating parameter β was a function of the ratio of the light source and photoreactor tube diameters.

The theoretical effect of ALID on reactor performance was determined for a reaction which proceeded via direct absorption by the reactant. The ALID effect on performance was most pronounced under conditions of high optical densities and low radial mixing rates of reactant.

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SCOPE

The elliptical reflector-photoreactor has been used extensively in the investigation of photoreaction kinetics. The elliptical photoreactor consists of a tubular light source and a quartz reactor tube located at the foci of a reflector cavity whose cross section is elliptical. This construction was suggested by the fact that light rays originating from a light source located at one focus are reflected

through a sink centered along the other focus. The light intensity distribution within the reactor is easily calculated if the light is assumed to enter normal to the reactor surface and is assumed to be uniformly intense about the circumference of the reactor.

Since the source must be of finite size some investigators have questioned this idealized model of light distribution and have proposed more realistic models. However, many such models retain the assumption that the incident light intensity is uniform with respect to the angular direction at the reactor surface.

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This assumption is justified in cases where the reactor performance is independent of the angular light intensity distribution. These cases arise when the reacting fluid is well mixed in the radial direction, and the reaction rate is either first order with respect to the volumetric rate of light absorption or the lifetime of reactive intermediates is long in comparison to their hydrodynamic mixing time in the radial direction. In any other case the angular light intensity distribution will influence the performance of the reactor.

The assumption of uniform angular light intensity distribution at the surface of the reactor has never been experimentally investigated in the literature. Data reported by Jacob and Dranoff (1969) indicates some angular variation of intensity inside the reactor although, by averaging

their data, these authors concluded that the light intensity was essentially uniform over the reactor radius.

The elliptical reflector-photoreactor has proved to be a convenient, easily constructed apparatus for the investigation of photoinitiated reactions. Its continued application in this field requires that the distribution of light intensity entering the reactor be better understood than is presently the case.

It is the purpose of this work to experimentally determine the angular light intensity distribution at the surface of several reactors by the novel means of an optically dense chemical actinometer. These distributions will serve as a basis for computing the theoretical effect of the angular light intensity distributions on the performance of reactors operating over a wide range of conditions.

CONCLUSIONS AND SIGNIFICANCE

The angular light intensity distribution at the surface of several quartz reactor tubes was determined quantitatively by means of an optically dense actinometer. The intensity was determined at eight equally spaced angular positions about the circumference of the reactors.

The intensity distributions were well-correlated for all reactors by Equation (1).

$$I_w(\theta) = \bar{I}_w[1 + \beta \cos\theta] \quad (1)$$

The correlation parameter β was found to depend on the ratio R_r/S_r , the reactor tube radius/light source radius. This ratio was varied from 0.0785 to 1.315 by using reactor tube diameters of 2.5×10^{-2} m, 1.5×10^{-2} m, and 3×10^{-3} m and lamp diameters of 3.81×10^{-2} m and 1.91×10^{-2} m. The parameter β was correlated with R_r/S_r on a semilog plot of β versus R_r/S_r .

The theoretical performance of reactors operating over an optical density range of 0 to 20 was computed using extreme values of β . A reaction model was assumed in which the reaction proceeded via direct light absorption by the reactant. The point reaction rate depended on the square root of the volumetric rate of light absorption and on the first power of the concentration of the absorbing reactant. Such a rate model is realistic in that it represents the form of the rate equation encountered in many chlorination reactions. Perfect axial and radial mixing and laminar motion of a Newtonian fluid were used to repre-

sent two idealized hydrodynamic regimes for the reaction. The internal distribution of light was described separately by a radial model and by a diffuse model.

The performance was most affected by the angular light intensity distribution when the reactor was operated in the laminar regime at optical densities exceeding one. For example, in the laminar regime at an optical density of 10 the mean holding time required to achieve a 50% conversion increases by 20.2% in going from $\beta = 0$ to $\beta = 1$. When the reactant is well mixed under the same conditions the increase of the mean holding time is only 7.4%. In general the angular light intensity distribution had the least effect on performance when the reactant was well mixed in the radial direction, the optical density was low and the internal light distribution followed the diffuse model.

It was concluded that uniform angular distributions can be approached in practice by selecting small values of the ratio R_r/S_r in the construction of the elliptical reflector-photoreactor. Furthermore, operating the reactor at optical densities less than 5 while maintaining good radial and axial mixing ensures that the angular light intensity distribution has little effect on performance even for extremely nonuniform distributions ($\beta = 1$). This result is important since the perfect mixing mode of operation is frequently used to obtain data upon which the kinetic constants of the reaction are based.

The elliptical reflector-photoreactor has been used by Cassano and Smith (1966) in the chlorination of propane, by Matsuura et al. (1969a) in the photolysis of acetone, and by Matsuura and Smith (1970b) in the photolysis of formic acid. These studies assumed the uniform angular distribution of light intensity at the reactor surface. The assumption was justified because the reaction rates were first order with respect to the volumetric rate of light absorption by the reactant. In this case the angular light intensity distribution (ALID) does not affect the reactor performance since the reaction rate can be correctly expressed in terms of the intensity averaged over the reactor

cross section. Other studies have been made in which the reaction rates were not linearly dependent on the absorbed intensity.

Huff and Walker (1962) studied the vapor phase chlorination of chloroform in an elliptical reflector-photoreactor and found the reaction rate to depend on the square root of the absorbed intensity. They assumed a uniform ALID in the analysis of their rate data which were taken at low optical densities. It will be shown subsequently that the ALID does not affect the performance of reactors operating at suitably low values of optical density.

Ragonese and Williams (1971) determined an empirical rate expression for the photolysis of chloroplatinic acid in which the absorbed intensity was raised to the first power. They also assumed a uniform ALID and found that the rate expression could be used to accurately predict the performance of the reactor. A severe test of the effect of ALID on reactor performance was precluded in this case because moderate values of optical density were used.

Cerdá et al. (1972) theoretically investigated the radiation field inside an elliptical photo-reflector using sources of finite spatial dimensions and found nonuniform energy densities about the reactor focus. Their results are limited to the case of a transparent reactor which corresponds to the least likely condition for the existence of angular non-uniformities. It is significant that even under these ideal conditions uniform angular intensities are not possible since an absorbing reactor, encountered in practice, would be expected to accentuate angular nonuniformities.

The extension of elliptical reflector-photoreactor studies to reactions whose rates depend on other than the first power of the absorbed intensity and which are conducted at moderate to large values of optical density requires that the actual ALID and its effect on reactor performance be better understood. In this work the ALID is determined experimentally over a range of reactor-source geometries. The theoretical effect of nonuniform ALID is determined by computation for reactions whose rates depend on the square root of the absorbed intensity. Photoinitiated chain reactions in which termination occurs via a homogeneous second-order process and photodecomposition of initiator in free-radial polymerization are examples of reaction types whose rates depend on the square root of the absorbed intensity.

EXPERIMENTAL DETERMINATION OF ALID

The equipment and procedures used to determine the ALID are described below in some detail. Briefly, an elliptical reflector-photoreactor was constructed to permit the continuous circulation of actinometer fluid through the photoreactor tube. A light shield was mounted concentrically over the reactor tube. This shield contained a narrow rectangular opening (slot) which was oriented along the longitudinal axis of the reactor tube. The light entering through this slot was essentially completely absorbed by the high optical density actinometer fluid within the reactor. The ALID was mapped by rotating the shield about the longitudinal axis of the reactor tube and recording the amount of light absorbed at each angular position. Several reactor tube and light source diameters were used to determine the influence of the internal geometry of the elliptical reflector-photoreactor on the ALID.

Photoreactor. The dimensions of the elliptical reflector and location of the light source and reactor tube are shown in Figure 1. The inside surface of the aluminum reflector was

polished and Alzak treated to provide a brightly reflecting surface. The reactor and light source were held in place by darkened 6.34×10^{-3} m thick Plexiglas covers at each end of the aluminum reflector. This allowed exact and reproducible positioning of the reactor and light source within the reflector. Flat black cardboard light baffles were placed 1.5×10^{-1} m from each end of the reflector to eliminate any end effects due to the light source.

Three cylindrical quartz reactor tubes, with inside diameters of 2.5×10^{-2} m, 1.5×10^{-2} m, and 3.0×10^{-3} m, were used in the investigation. The tubular light sources consisted of a General Electric 1.91×10^{-2} m diam. G36T6 low-pressure mercury germicidal lamp, and a General Electric 3.81×10^{-2} m diam. F40BL blacklight.

Light Shield. The reactor tube was completely shielded with a slotted polyvinyl chloride tube which could be rotated over the circumference of the reactor tube. This section is shown schematically in Figure 2 while the dimensions of the three shields used in this work are given in Table 1.

Chemical Actinometer. The potassium ferrioxalate system was used in this work. This system, first proposed by Parker (1953), has been studied over a wide variety of operating conditions by Baxendale and Bridge (1955), Hatchard and Parker (1956), and by Lee and Seliger (1964).

The actinometer solution was prepared according to the procedure outlined by Baxendale and Bridge (1955) and then

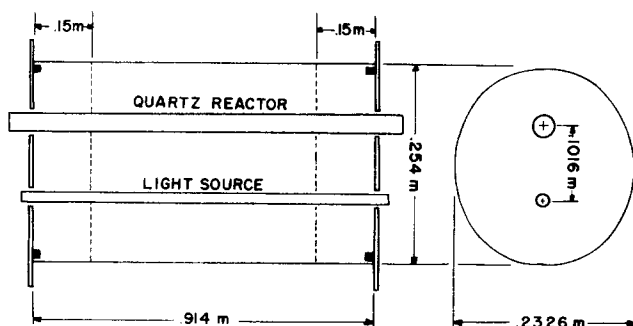


Fig. 1. Schematic diagram of elliptical reflector-photoreactor.

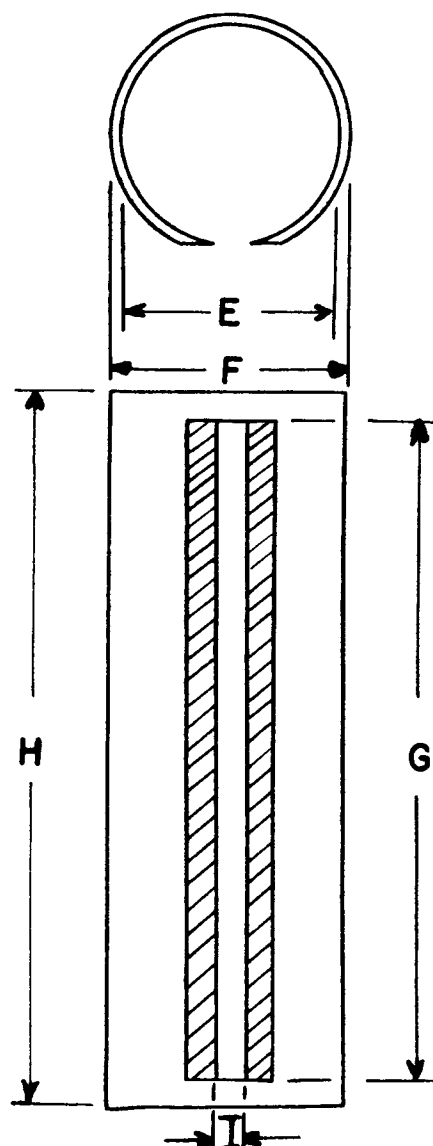


Fig. 2. Schematic diagram of angular shield.

TABLE 1. ANGULAR SHIELD DIMENSIONS

Shield number	Dimension ($m \times 10^2$)				
	E	F	G	H	I
1	2.92	3.33	9.00	10.16	0.30
2	1.88	2.23	9.00	10.16	0.20
3	0.45	0.56	9.00	10.16	0.10

TABLE 2. POTASSIUM FERROXALATE ACTINOMETER

0.005 Molar

 2.41×10^{-3} kg $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ 2.76×10^{-3} kg $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ 2.78×10^{-6} m³ H_2SO_4 (18 Molar)diluted to 1×10^{-3} m³ with distilled water

stored in darkened polyethylene containers. The composition of the actinometer solution is given in Table 2. When the actinometer is exposed to ultraviolet light ferrous ions are produced at a rate proportional to the volumetric rate of light absorption. The concentration of ferrous ions can be determined spectrophotometrically using the procedure outlined by Hatchard and Parker (1956).

Procedure. The light source was stabilized prior to exposure of the actinometer fluid which was recirculated continuously through the reactor tube. The slot in the light shield was positioned at the desired location. During this operation light was prevented from entering the reactor through the slot by means of a temporary, exterior shield. This shield was quickly removed to initiate the experimental run. Since the potassium ferrioxalate system exhibits an extremely large absorption coefficient in the ultraviolet range nearly all radiation entering through the slot was absorbed. After a predetermined time the experimental run was terminated by placing an exterior light shield over the slot. The light intensity at the slot position was calculated from knowledge of the ferrous ion concentration, quantum yield, exposure time, and the slot area. The ALID was determined by locating the shield slot at eight equally spaced circumferential positions about the reactor.

RESULTS

A typical set of experimental angular light intensity measurements are presented as circles in Figure 3. In this polar coordinate representation the zero radian axis lies along the straight line perpendicular to the foci of the elliptical reflector and is directed toward the source. A dimensionless light intensity $I_w(\theta)/\bar{I}_w$ is plotted at each angular position. This dimensionless light intensity is calculated by dividing the experimentally measured light intensity $I_w(\theta)$ by the average light intensity \bar{I}_w where

$$\bar{I}_w = \frac{1}{2\pi} \int_0^{2\pi} I_w(\theta) d\theta. \quad (2)$$

When the ALID is uniform, the distribution is represented by the dashed line in Figure 3.

Figure 3 shows that a nonuniform ALID is possible at the surface of the elliptical reflector-photoreactor. The light intensity is stronger for points on the reactor circumference located closer to the light source and weaker for more distant points. This is the result of a shadowing effect where the reactor prevents light from reflecting off the elliptical reflector onto the distant side of the reactor wall. The symmetric property of the experimental ALID is a

result of the symmetric geometry exhibited by the elliptical reflector, light source, and reactor tube.

A complete set of data is given in Table 3 for various combinations of reactor tube diameters and light source diameters. The model given by Equation (1) was proposed to correlate the data in Table 3. The model parameter β is calculated using a least-squares procedure to best approximate the experimental ALID. In Figure 3 this model is represented by the solid line.

This model was selected for several reasons. First, it is periodic in nature and is symmetric about the zero-radian axis as is the experimental ALID. Secondly, the angular distribution is characterized by a single parameter which is bound by the limits of 0 and 1 for all physically realizable situations. Thirdly, the average incident light intensity \bar{I}_w is independent of the parameter β . This property facilitates the theoretical investigation of the effect of ALID on reactor performance under the condition that the total energy entering the reactor remains constant.

Figure 4 presents the model parameter β as a function of the reactor-to-source radius ratio. A quantitative measure of the shadowing effect is obtained from this representation. As the reactor-to-source radius ratio approaches zero the model parameter β approaches zero. This limit

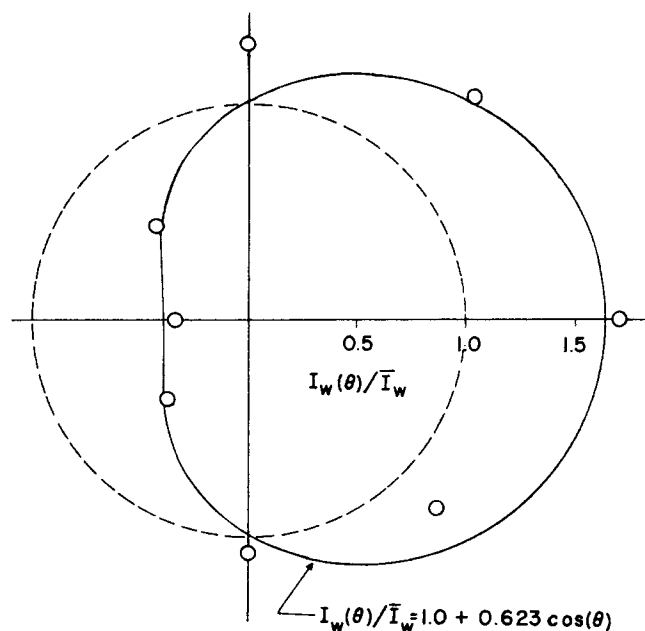


Fig. 3. Dimensionless angular light intensity distribution for $R_r/S_r = 1.31$.

TABLE 3. EXPERIMENTALLY DETERMINED ANGULAR LIGHT INTENSITY

Angular position, rad	Intensity, keinsteins/m ² s $\times 10^7$			
	$R_r/S_r = 1.315$	$= 0.785$	$= 0.157$	$= 0.0785$
0	3.106	3.336	2.780	0.926
0.785	2.666	2.535	2.445	0.880
1.570	2.333	2.615	2.382	0.837
2.356	1.097	1.048	1.583	0.723
3.141	0.648	0.927	1.520	0.653
3.927	0.945	1.040	1.818	0.745
4.712	1.975	2.148	2.320	0.838
5.497	2.233	2.600	2.511	0.903

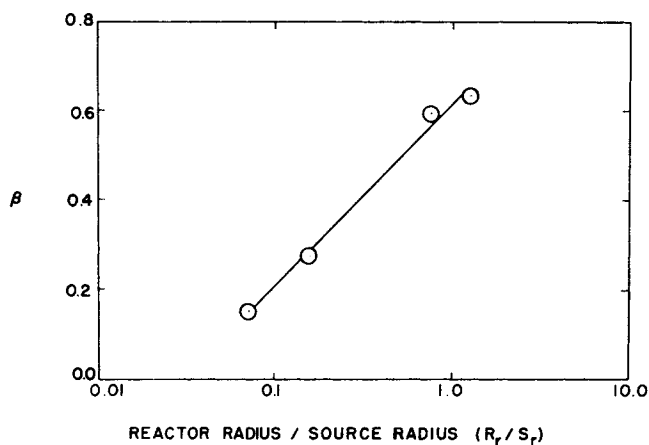


Fig. 4. The parameter β versus R_r/S_r .

corresponds to the case of uniform ALID. As the ratio increases, the shadowing effect also increases as reflected by a corresponding increase in the parameter.

While the relationship presented in Figure 4 is not expected to be valid for all elliptical reflector-photoreactors, it should be valid for arrangements geometrically similar to that used in this work. The importance of the relationship is that it can be used as a guide in the design and application of geometrically similar elliptical reflector-photoreactors such that ALID effects are minimized.

ALID EFFECT ON REACTOR PERFORMANCE

The limiting effect of a nonuniform ALID on performance were determined by computation for a wide variety of hypothetical operating conditions. The considerations made in the selection of a reaction rate model, fluid mixing regimes within the reactor, mode of light distribution through the cross-section of the reactor, and range of optical density employed are discussed below.

Rate Model. It was assumed that the reaction proceeds via direct absorption of monochromatic light by reactant A and that the rate could be represented by Equation (3).

$$\Omega_A = k I_a^n C_A^m \quad (3)$$

The values of n and m are related to the mechanism associated with the overall reaction. For example Cassano and Smith (1966) use a form of Equation (3) where $n = 1$, $m = 1$ to represent the photochlorination rate of propane. Felder and Hill (1970) have shown that the reaction rate for a two-center regenerative chain reaction, such as the chlorination of tetrachlorethylene to hexachlorethylene, can be represented by a form of Equation (3) when thermal ignition effects are negligible.

The specific rate model used in this work was

$$\Omega_A = k I_a^{1/2} C_A \quad (4)$$

although the existence of an effect on reactor performance due to nonuniform ALID is not limited to this model as has been shown by Zolner (1971).

Fluid Mixing. The fluid mixing regime in the cross section of the reaction tube greatly affects the reactor performance with respect to the ALID. When the fluid is well mixed in the radial direction and the life times of the reactive intermediates are long compared to their mixing time, then the reaction rate can be expressed in terms of the light intensity averaged over the cross section. In this case the reactor performance is independent of the ALID

for all values of n . If the life times of the reactive intermediates are short compared to the mixing time then the reactor performance is independent of the ALID only for $n = 1$. In this work two mixing regimes were studied. 1. perfect radial and axial mixing of reactant where the life times of the reactive intermediates are short, and 2. laminar flow of a Newtonian fluid with no radial movement of reactant or reactive intermediates.

Light Intensity Distribution. Two modes of light distribution within the reactor tube were studied. These were the classical radial intensity distribution model and the diffuse model of Matsuura and Smith (1970a). In both cases the incident light was assumed to be distributed angularly at the surface of the reactor tube according to Equation (1) where β was assigned values of 0 and 1 in order to determine the extreme effect of ALID.

Computed Results. The conversion achieved in the reactor was computed for a range of values of the optical density using the equations and methods given in the Appendix. The Beer-Lambert equation for intensity attenuation was used in the derivation of these equations. The results of the computations are given in Figures 5, 6, and 7 where the dimensionless reactor group ψ is plotted against the optical density σ for parameters of fractional conversion X_A . The two cases of ALID are presented where $\beta = 0$ represents uniform distribution and $\beta = 1$ represents extreme nonuniformity.

Several general observations for all flow regimes are indicated. Since the reactor group ψ is proportional to the n th power ($n > 0$) of the average incident light intensity and directly proportional to the reactor space time, it is desirable to operate at the minimum value of the reactor group for a given optical density and fractional conversion. In all cases investigated, the reactor group is insensitive to the ALID for optical densities less than one. However for optical densities greater than one, a larger value of the reactor group is required for a nonuniform ALID than for a uniform ALID in order to obtain the same fractional conversion. This observation applies to all flow regimes investigated. The greatest effect on the reactor group due to nonuniform ALID was observed in the case of laminar flow. Operation of the reactor with perfect mixing resulted

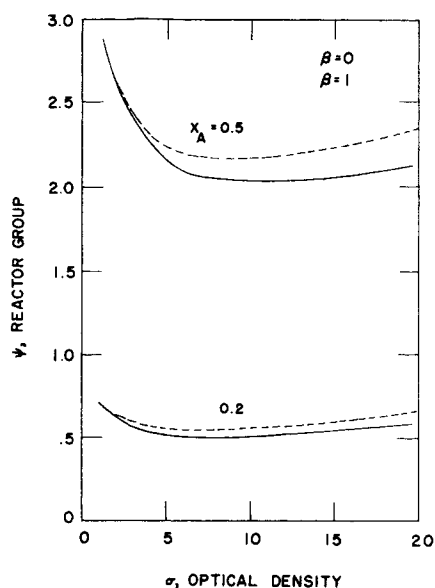


Fig. 5. Reactor group as a function of optical density and fractional conversion for the case of perfect mixing and radial light.

in the minimum effect on the reactor group.

Figure 7 presents the results for perfect mixing operation using the diffuse light model. In general, the observations made above are also valid for this case. There is no effect on the reactor group due to nonuniform ALID at optical densities less than one, while the effect increases with increasing values of the optical density. Reactor group differences due to nonuniform ALID are less in the case of the diffuse model than the radial model over the range of fractional conversions and optical densities investigated. It was not possible to extend the computations for the diffuse model to the laminar flow case because of the excessive computing time required.

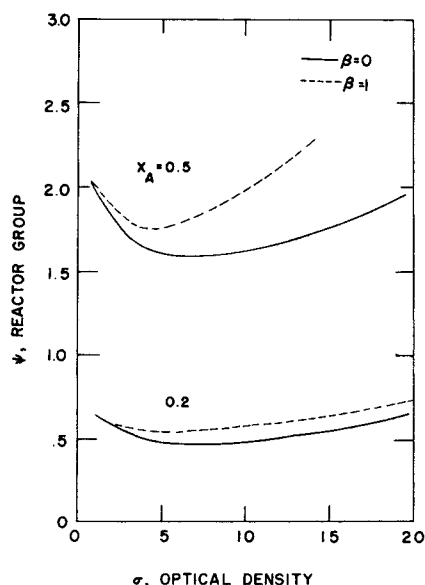


Fig. 6. Reactor group as a function of optical density and fractional conversion for the case of laminar flow and radial light.

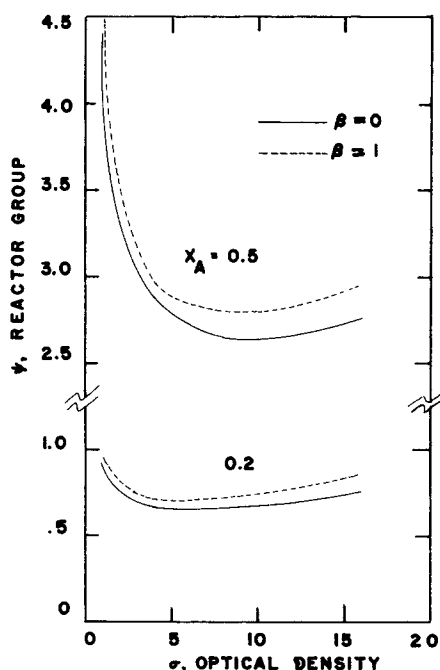


Fig. 7. Reactor group as a function of optical density and fractional conversion for the case of perfect mixing and diffuse light.

This work has demonstrated the existence of a nonuniform ALID in an elliptical reflector-photoreactor. The ALID was well-correlated by a one-parameter model where the parameter was closely related to the internal geometry of the elliptical reflector-photoreactor.

Theoretical computation of the reactor performance under conditions of extreme nonuniform ALID revealed regions of reactor operation where the performance was insensitive to the ALID. It was also shown that the reactor could be designed, by choice of the ratio (R_r/S_r), so as to minimize the effect of the ALID on performance.

NOTATION

- C_A = concentration of species A, kmol/m³
 C_{A0} = initial concentration of species A, kmol/m³
 D = reactor diameter, m
 I_a = absorbed light intensity, keinsteins/m²s
 I_w = incident light intensity directed into the photoreactor, keinsteins/m²s
 \bar{I}_w = incident light intensity averaged over reactor surface, keinsteins/m²s
 k = reaction rate constant, (kmol)^{1-m}(keinsteins)⁻ⁿ(m³)^{m+n-1}(s)ⁿ⁻¹
 L = reactor length, m
 m = reaction rate concentration order, dimensionless
 n = reaction rate absorbed light intensity order, dimensionless
 r = reactor radial position variable, m
 R_r = reactor radius, m
 S_r = light source radius, m
 X_A = flow-averaged fractional conversion of reactant A at reactor outlet, dimensionless
 x_A = pointwise fractional conversion of reactant A, dimensionless
 z = reactor length variable, m

Greek Letters

- α_A = absorption coefficient for species A, m³/kmol m
 β = parameter in Equation (2), dimensionless
 γ = angle of rotation with coordinate center at radius r , rad
 γ' = angle of rotation, rad
 ξ = z/L , reactor length variable, dimensionless
 θ = reactor angular position variable, rad
 ρ = r/R_r , reactor radial position variable, dimensionless
 ρ' = dummy integration variable
 σ = $\alpha_A C_{A0} D$, optical density, dimensionless
 τ = reactor space time, s
 ψ = $4k \bar{I}_w^n \tau / C_{A0}^{1-m} D^n$, photoreactor group, dimensionless
 ω = dummy integration variable
 ω' = $-\rho \cos \gamma + (1 - \rho^2 \sin^2 \gamma)^{1/2}$, dimensionless
 ω'' = $\rho \cos \gamma + (1 - \rho^2 \sin^2 \gamma)^{1/2}$, dimensionless
 Ω_A = reaction rate of species A, kmol/m³s

Subscripts

- d = diffuse light intensity distribution model
 r = radial light intensity distribution model

LITERATURE CITED

- Baxendale, J. H., and N. K. Bridge, "The Photoreduction of Some Ferric Compounds in Aqueous Solution," *J. Phys. Chem.*, 59, 783 (1955).

Cassano, A. E., and J. M. Smith, "Photochlorination In A Tubular Reactor," *AIChE J.*, **12**, 1124 (1966).

Cerdá, J., H. A. Irazoqui, and A. E. Cassano, "Radiation Fields Inside an Elliptical Photoreactor with a Source of Finite Spatial Dimensions," *Photochem. Reaction Eng. Symp.*, **71st National Am. Inst. Chem. Engrs. Mtg.**, Dallas, Texas (1972).

Felder, R. M., and F. B. Hill, "Mixing Effects in Chemical Reactors: Chain Reactions in Batch and Flow Systems," *Ind. Eng. Chem. Fundamentals*, **9**, 360 (1970).

Hamming, R. W., *Numerical Methods for Scientists and Engineers*, p. 206, McGraw-Hill, New York (1962).

Harano, Y., and J. M. Smith, "Tubular Flow Photoreactors for Complex Nonchain Kinetics," *AIChE J.*, **14**, 584 (1968).

Hatchard, E. G., and C. A. Parker, "A New Sensitive Chemical Actinometer: II Potassium Ferrioxalate as a Standard Chemical Actinometer," *Proc. Roy. Soc.*, **A235**, 518 (1956).

Huff, J. E., and C. A. Walker, "The Photochlorination of Chloroform in Continuous Flow Systems," *AIChE J.*, **8**, 193 (1962).

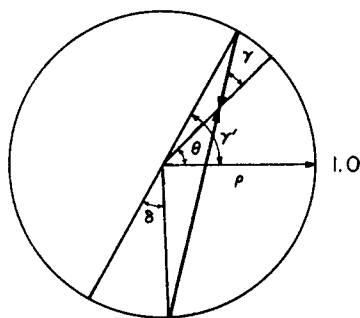
Jacob, S. M., and J. S. Dranoff, "Light Intensity Profiles in an Elliptical Photoreactor," *ibid.*, **15**, 141 (1969).

Lee, J., and H. H. Seliger, "Quantum Yield of the Ferrioxalate Actinometer," *J. Chem. Phys.*, **40**, 519 (1964).

Matsuura, T., A. E. Cassano, and J. M. Smith, "Acetone Photolysis: Kinetic Studies in a Flow Reactor," *AIChE J.*, **15**, 495 (1969).

Matsuura, T., and J. M. Smith, "Light Distribution in Cylindrical Photoreactors," *ibid.*, **16**, 321 (1970).

———, "Photodecomposition Kinetics of Formic Acid in Aqueous Solution," *ibid.*, 1064.



PHOTOREACTOR CROSS-SECTION

Fig. 8. Angles in the diffuse light intensity distribution model.

Parker, C. A., "A New Sensitive Chemical Actinometer: I Some Trials with Potassium Ferrioxalate," *Proc. Roy. Soc.*, **A220**, 104 (1953).

Ragonese, F. P., and J. A. Williams, "Application of Empirical Rate Expressions and Conservation Equations to Photoreactor Design," *AIChE J.*, **17**, 1352 (1971).

Zolner III, W. J., "Light Intensity Distribution in an Elliptical Reflector-Photoreactor," Ph.D. thesis, Northeastern Univ., Boston, Mass. (1971).

APPENDIX

The equations used to describe the performance of the reactor and the methods used to solve them are described here.

The radial model and the diffuse model represent two modes of light intensity distribution whose mathematical development has been presented in the literature; hence, only the relationships pertinent to this work are given here.

Radial Model. The equation describing the radial distribution of light intensity under conditions of uniform angular intensity have been developed by Harano and Smith (1968) and is presented in Table 4. When the light intensity is distributed angularly according to Equation (1) the radial distribution is altered as shown in Table 4.

Diffuse Model. The model equation for the diffuse light distribution within the reactor has been given by Matsuura and Smith (1970a) for the case of uniform ALID. This equation is given in Table 4. The equation for the case of nonuniform ALID is also given in Table 4. The relationships among the angles θ , γ , γ' are shown schematically in Figure 8.

Continuity Equations. Steady state continuity equations were written for the reactant, species A, in the case of perfect mixing and in the case of laminar flow of a Newtonian fluid.

These equations are shown in Table 5. In the laminar flow case it is assumed that there is no radial movement of reactant. The continuity equations are combined with the appropriate light intensity distribution equation and solved to describe the photoreactor performance. Numerical solution was required in all cases. The partial differential equation of Table 5 for laminar flow was approximated by a set of ordinary differential equations which was solved using the Hamming Predictor-Corrector method. In the case of diffuse light the continuity equation for laminar flow was not solved due to excessive computing time requirements. The details of the solution procedure are given by Zolner (1971).

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TABLE 4. LIGHT INTENSITY DISTRIBUTION EQUATIONS

ALID	Radial model	Diffuse model
$\rho = 0$	$I_r(\rho) = \frac{2I_w}{\rho} \exp\left[-\frac{\sigma}{2} \int_0^1 (1-x_A) d\rho\right] \cdot \cosh\left[\frac{\sigma}{2} \int_0^\rho (1-x_A) d\rho'\right]$	$I_d(\rho) = \frac{I_w}{\pi} \int_0^\pi \left\{ \exp\left[-\frac{\sigma}{2} \int_0^{\omega'} (1-x_A) d\omega\right] + \exp\left[-\frac{\sigma}{2} \int_0^{\omega''} (1-x_A) d\omega\right] \right\} d\gamma$
$\rho \neq 0$	$I_r(\rho, \theta) = \frac{2I_w}{\rho} \exp\left[-\frac{\sigma}{2} \int_0^1 (1-x_A) d\rho\right] \left\{ \cosh\left[\frac{\sigma}{2} \int_0^\rho (1-x_A) d\rho'\right] + \beta \cos\theta \sinh\left[\frac{\sigma}{2} \int_0^\rho (1-x_A) d\rho'\right] \right\}$	$I_d(\rho, \theta) = \frac{I_w}{\pi} \left\{ \int_0^\pi (1 + \beta \cos\gamma') \exp\left[-\frac{\sigma}{2} \int_0^{\omega'} (1-x_A) d\omega\right] d\gamma + \int_0^\pi [1 + \beta \cos(\gamma' + \pi + \delta)] \exp\left[-\frac{\sigma}{2} \int_0^{\omega''} (1-x_A) d\omega\right] d\gamma \right\}$

TABLE 5. CONTINUITY EQUATIONS

Perfect Mixing	Laminar Flow
$X_A = \frac{\psi}{4\pi} \sigma^n (1 - X_A)^{m+n} \int_0^1 \int_0^{2\pi} \int_0^1 \left[\frac{I}{I_w} \right]^n \rho d\rho d\theta d\xi$	$\frac{\partial x_A}{\partial \xi} = \frac{\psi \sigma^n}{8} \frac{1}{1 - \rho^2} [1 - x_A]^{m+n} \left[\frac{I}{I_w} \right]^n$
	$x_A = 0 \text{ at } \xi = 0 \text{ for all } \rho \text{ and } \theta.$