Analysis of an axially irradiated photochemical reactor*

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Abstract

An idealised analysis has been presented for as yet unexplored axially irradiated photoreactor in its two natural configurations. Reactant mixing and levelling of radiation intensity gradient (which may or may not be interrelated, depending on the nature of photochemical reaction considered) in the direction of irradiation, have been already shown to always improve the performance of a transversely irradiated photoreactor, when mixing at all has any effect on the performance. It is concluded from the present analysis that for the axially irradiated reactor, however, mixing effects are not always beneficial.

Potentials for the industrial use of such a reactor in certain cases and possibility for its use in laboratory kinetic studies have been indicated.

Key words: Photosensitisation, Photochemical reaction, Photoreactor, Transversely irradiated photoreactor (T.I.R.), Axially irradiated photoreactor (A.I.R.), Light intensity distribution.

1. Introduction

Photochemical reactions are most commonly carried out in a cylindrical flow reactor enclosed in an elliptical assembly keeping the cylindrical lamp and the reactor at the two focii, or in an annular flow reactor installing the lamp along the central axis. The first type has also been used extensively for kinetic studies of most liquid and gas phase photochemical reactions[1-7]. And the second type has come in for quite a few experimental and theoretical studies[8-11]. Both these types can be grouped under a common title of transversely irradiated reactor (T.I.R.) as the directions of flow and irradiation are transverse to each other. However, both the kinetic studies and analysis of performance have come up against the uncertainties regarding the proper model of incident radiation intensity distribution for a finite non-line source in either of the above two T.I.R. configurations. In particular, for kinetic studies errors due to these uncertainties in the light intensity measurements and the rate, especially when the optical thickness for reactant and for actinometer are considerably different, have been pointed out in the literature[12-14].

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In this communication we propose to analyse the hitherto unexplored axially irradiated cylindrical reactor (A.I.R.) where a beam of parallel rays of light is incident on the reactor parallel to the axial direction. Two alternative configurations PF I and PF II (Fig. 1) arise depending on whether the directions of flow and irradiation are identical or opposite.

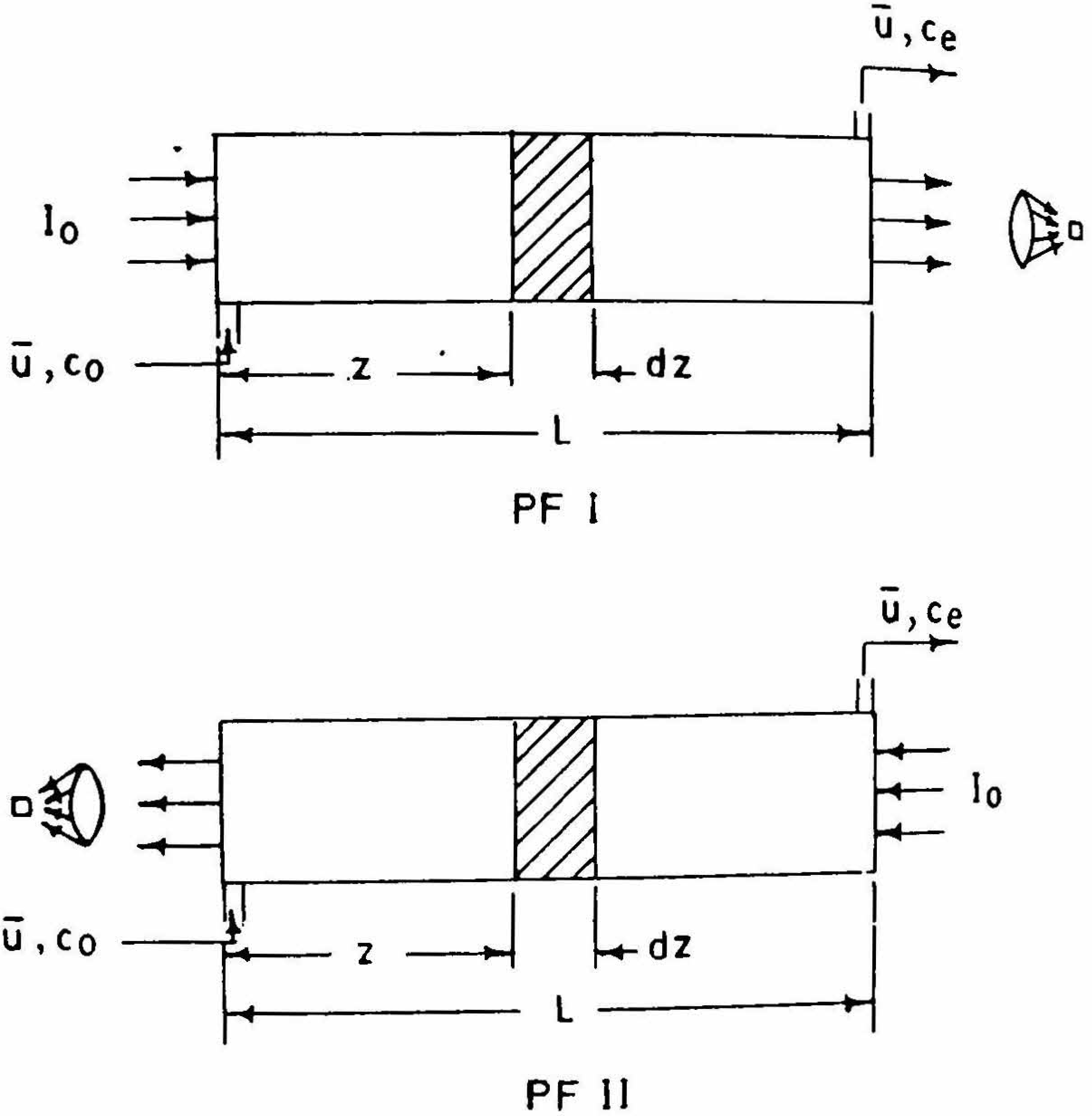

FIG. 1. Basic features of the plug flow model of an axially irradiated photo reactor.

The purpose of the present simplified analysis is three fold:

(i) to set up a simple model of A.I.R. which could be used in an experimental verification of its efficacy in photokinetic studies;

(ii) to compare the performances of configurations PF I and PF II based on such a model; and

(iii) to answer a pertinent question regarding the effect of mixing in photochemical reactors: It has been shown[15] that in a transversely irradiated flow photochemical reactor (T.I.R.) carrying out a reaction whose power law rate expression includes the absorbed radiation intensity with a positive exponent, reactant mixing and levelling of intensity gradient in the direction of radiation always improve the performance, in cases where mixing at all has any effect. But if the irradiation is in the longitudinal direction it would be interesting to know how the levelling of the concentration and intensity gradients in the direction of radiation affect the reactor performance.

2. Analysis

The analysis is restricted by the following assumptions:

(i) I_0 is uniform over and perpendicular to the reactor cross-section;

(ii) radiation is monochromatic;

(iii) reactions follow power-law type rate equation;

(iv) lateral mixing for the absorbing and reacting species is complete over the entire reactor length;

(v) idealised boundary conditions at $z = 0$ and/or $z = L$ exist.

With these assumptions, two ordinary differential equations describing the mass, the radiation balances are to be solved simultaneously, as they are, in general, coupled. Two broad classes of photochemical reactions are considered.

Photochemical reaction with sensitiser absorption (*SA*)

For this class of photochemical reactions where some added substance which absorbs the irradiation and passes the energy to the actual reactant, remains, usually, unchanged in concentration, the mass and radiation balances are decoupled.

The differential equations to be solved are,

$$-\bar{u}\frac{dc}{dz} = r_A \; ; \quad c = c_0 \text{ at } z = o \tag{1}$$

and

$$\begin{aligned} -\frac{dI}{dz} &= \mu I \; ; \quad I = I_0 \text{ at } z = o \text{ (PF I)} \\ \frac{dI}{dz} &= \mu I \; ; \quad I = I_0 \text{ at } z = L \text{ (PF II)} \end{aligned} \tag{2}$$

The intensity profiles, rate equations and their solutions for PF I and PF II are presented in Table I. For the mixed flow extreme (MF), where the reactants are completely mixed

Table I

Photosensitiser absorption; plug flow

	Configuration I	Configuration II
Radiation intensity profile, $I(z)$	$I_0\, e^{-\mu z}$	$I_0\, e^{\mu(z-L)}$
Volumetric rate of absorption of radiation, $I_a(z)$	$\mu I_0\, e^{-\mu z}$	$\mu I_0\, e^{\mu(z-L)}$
Reaction rate r_A	$k\,[I_a(z)]^p\, c^n$	$k\,[I_a(z)]^p\, c^n$
Concentration profile, $a(t), n = 1$	$a = \text{Exp}\left\{\frac{-1}{\tau_s pB_s}(1 - e^{-pB_s t})\right\}$	$a = \text{Exp}\left\{-\frac{1}{\tau_s pB_s}\, e^{-pB_s(1-t)}(1 - e^{-pB_s t})\right\}$
$X_A(\theta), n = 1$	$\frac{\theta}{\theta_{msp}} = \frac{-pB_s t\ \ln(1 - X_A)}{1 - e^{-pB_s t}}$	$\frac{\theta}{\theta_{msp}} = \frac{-pB_s t\ \ln(1 - X_A)}{e^{pB_s(t-1)} - e^{-pB_s}}$
$X_A(\theta), n \neq 1, n > 0$	$\frac{\theta}{\theta_{msp}} = \frac{pB_s t\left\{\frac{(1 - X_A)^{1-n} - 1}{n - 1}\right\}}{1 - e^{-pB_s t}}$	$\frac{\theta}{\theta_{msp}} = \frac{pB_s t\left\{\frac{(1 - X_A)^{1-n} - 1}{n - 1}\right\}}{e^{pB_s(t-1)} - e^{-pB_s}}$

both in lateral and axial directions, the corresponding expressions are given in Table II. For the latter case only an averaged intensity and exit conversions are meaningful.

$$F_1 = a_{PI}/a_{PII} = \frac{\exp\,(-m_1)}{\exp\,(-m_1/F_1')}, \tag{3}$$

for $0 \leqslant t \leqslant 1$ for any n and p.

where

$$m_1 = (1/\tau_s\, pB_s)\,(1 - e^{-pB_s t})$$

and

$$F_1' = e^{pB_s\,(1-t)}$$

Since F_1' is always greater than unity for $t < 1$, F_1 will be less than unity for all $t < 1$. The difference in concentration which is large at the inlet side will diminish gradually to zero at the exit, since at $t = 1$, F_1 will be unity and hence

$$a_{PI} = a_{PII} = (a_e)_{PF} \tag{4}$$

Table II

Photosensitiser absorption; mixed flow

Radiation intensity (spatially averaged), $\bar{I}$	$I_0\,(1 - e^{-\mu L})$
Volumetric rate of absorption of radiation, $\bar{I}_a$	$\frac{I_0}{L}\,(1 - e^{-\mu L})$
Reaction rate, r_A	$k\,[\bar{I}_a]^p\, c^n$
Exit concentration, $a, n = 1$	$\frac{1}{1 + \frac{\tau_s}{B_s^p}(1 - e^{-B_s})^p}$
$X_A,\ n = 1$	$\frac{\tau_s}{B_s^p} = \frac{X_A/(1 - X_A)}{(1 - e^{-B_s})^p}$
$X_A,\ n \neq 0$ $n > 0$	$\frac{\tau_s}{B_s^p} = \frac{X_A/(1 - X_A)^n}{(1 - e^{-B_s})^p}$

One can compare the performances of plug and mixed flow reactors by the ratio

$$F_2 = \frac{\bar{\theta}_M}{\bar{\theta}_P} = F\,\frac{X_A/(1 - X_A)}{-\ln\,(1 - X_A)}, \quad n = 1,\ p \neq 1 \tag{5}$$

$$= F \frac{X_A/(1 - X_A)^n}{\frac{(1 - X_A)^{1-n} - 1}{1 - n}}, \quad n \neq 1, \; p \neq 1 \tag{5 a}$$

at any given X_A and where

$$F = \frac{B_s^{p-1}\,(1 - e^{-pB_s})}{p\,(1 - e^{-B_s})^p}, \quad p \neq 1 \tag{6}$$

$$= 1, \; p = 1 \tag{6 a}$$

Table III shows the variation of the factor F with dimensionless optical thickness B_s for $p = 0·5$.

Table III

Numerical value of F as a function of B_s $p = 0·5$.

B_s	F
0·01	1·0001040
0·1	0·9999023
0·5	0·9974084
1·0	0·9897840
2·0	0·9613717
3·0	0·9202530
5·0	0·8237882

Photochemical reaction with reactant absorption (RA)

In this case, generally one of the actual reactants absorbs the radiation. Since the radiation attenuation then becomes a function of the reactant concentration the mass and radiation balances are coupled:

$$- \bar{u}\,\frac{dc}{dz} = \phi\,(acI)^p\,c^n \tag{7}$$

and

$$(-1)^i\,\frac{dI}{dz} = acI \tag{7 a}$$

where $i = 1$ and 2 for PF I and PF II respectively. Solutions for a few typical cases are considered below:

Case A ($n = 0$, $p = 1$)

For this case, equations (7) and (7 *a*) can be solved simultaneously using proper initial and boundary conditions, for different values of the parameters.

For PF I the boundary conditions are, $z = o$, $c = c_0$, $I = I_0$. The concentration and intensity profiles are given by,

$$a = 1/(1 + Bt), \quad B\tau = 1 \tag{8}$$

$$= (1 - B\tau)/\left\{\exp\left[-B\left(1 - \frac{1}{B\tau}\right)t\right] - B\tau\right\}, \quad B\tau \neq 1 \tag{8 a}$$

$$b = 1/(1 + Bt), \quad B\tau = 1 \tag{9}$$

$$= \frac{(1 - B\tau)\exp\left[-B\left(1 - \frac{1}{B\tau}\right)t\right]}{\exp\left[-B\left(1 - \frac{1}{B\tau}\right)t\right] - B\tau}, \quad B\tau \neq 1 \tag{9 a}$$

For PF II the boundary conditions are, $z = o$, $c = c_0$; $z = L$, $I = I_0$. The profiles are given by,

$$a = \frac{U/B\tau}{1 + \left(\frac{U}{B\tau} - 1\right)e^{Ut/\tau}} \tag{10}$$

$$b = \frac{U\left(\frac{U}{B\tau} - 1\right)e^{Ut/\tau}}{1 + \left(\frac{U}{B\tau} - 1\right)e^{Ut/\tau}} \tag{10 a}$$

where U is the only positive root of the following transcendental equation,

$$e^{-U/\tau} = (1 - U)\ (1 - U/B\tau) \tag{11}$$

which is greater than $B\tau$ in order for the solution to be physically meaningful at every point within the reactor.

In the corresponding mixed flow (MF) extreme, exit concentration $(a_e)_M$ which is the physically significant root of the transcendental equation,

$$e^{-Ba_e} = 1 - B\tau\,(1 - a_e) \tag{12}$$

is obtained by using spatially averaged rate, *Case B* ($n = 0, \ p \neq 1$)

For this case, the solution of equations (7) and (7 *a*), with $p = 0{\cdot}5$, a very common encountered exponent value, for PF I, is given by

$$t = (2/B)\, C_2^{2/3} \left[\frac{1}{2} \ln \frac{(1+\gamma)^2 \ (a - \gamma\sqrt{a} + \gamma^2)}{(\sqrt{a}+\gamma)^2 \ (1 - \gamma + \gamma^2)} + \sqrt{3}\ \mathrm{arctg}\, \frac{2-\gamma}{\gamma\sqrt{3}} - \sqrt{3}\ \mathrm{arctg}\, \frac{2\sqrt{a} - \gamma}{\gamma\sqrt{3}} \right]$$

The mixed flow exit concentration $(a_e)_M$ is given as the root of the equation

$$1 - a_e = \left(\frac{1}{B^p \tau}\right) (1 - e^{-Ba_e})^p$$

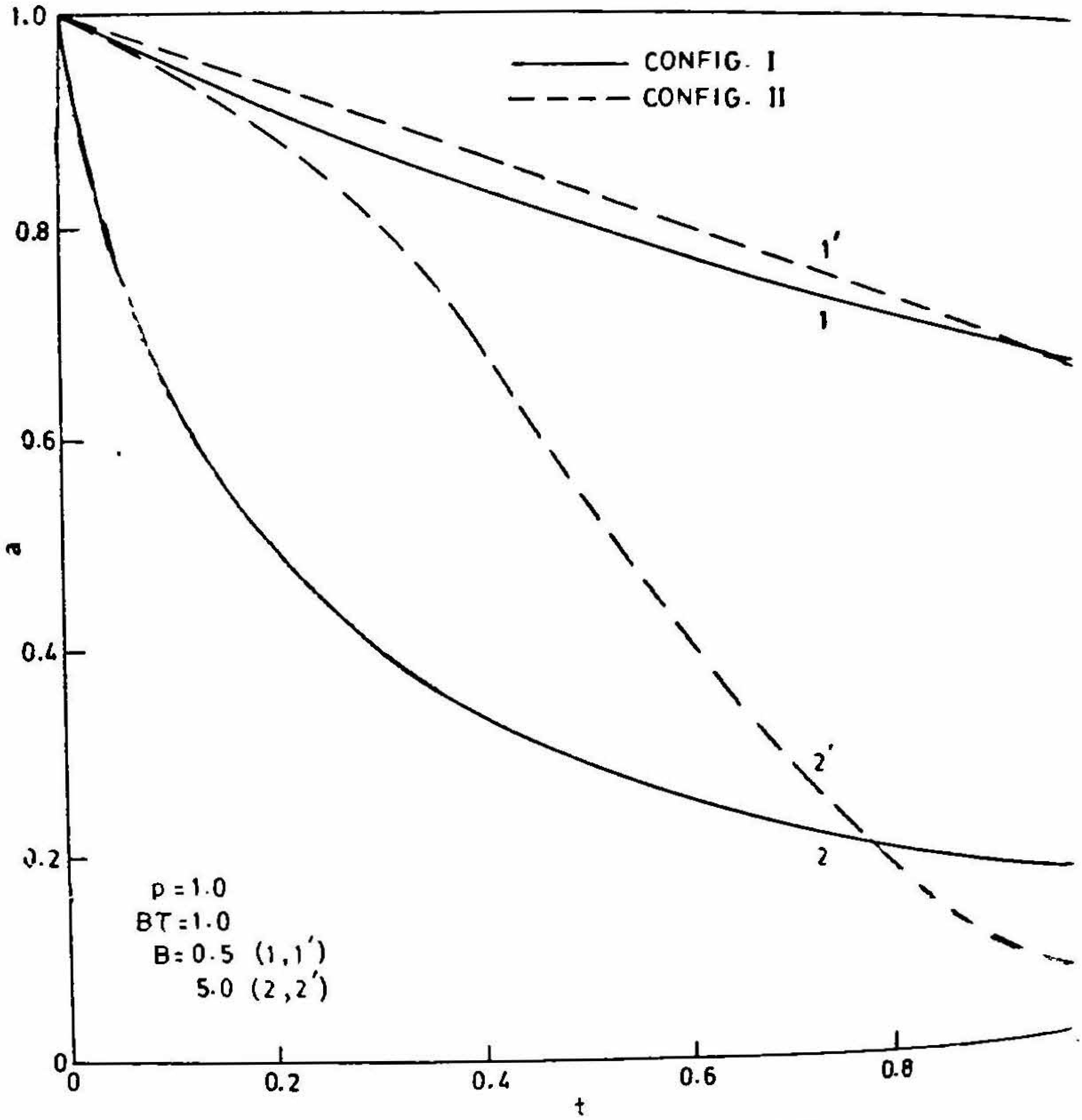

FIG. 2. Comparison of profiles a between PF I and PF II ($B\tau = 1{\cdot}0$).

For RA, however, the profiles intersect each other within the reactor, the point of intersection being closer either to flow outlet or inlet depending on the values of B and/or τ (*eg*., Figs. 2 and 3). Correspondingly the exit concentrations in PF I and PF II may become closer to each other or PF II may give lower exit concentrations. As expected, PF I maintains a lower value of concentration in the early part of the reactor, analogous to the case of SA.

Thus PF I would be more efficient than PF II in the early stages for both SA and RA due to the high values of concentration and intensity available. The identity of exit concentrations for both the configurations in case of SA is probably physically fortuitous as in the more general case of RA they are found to be in general different.

(*b*) Comparison between exit concentrations in PF and MF yield following general results for both SA and RA.

For $p = 0 \cdot 5$, at high absorption and low conversion range, MF is more efficient than PF, while the reverse is true in the case of low absorption and high conversion range. This is clear from the values of the factor F in Table III for SA and from Fig. 5 for RA. For $p = 1 \cdot 0$, however, PF is always more efficient than MF for the entire range of absorption and conversion (for SA, F is unity; *see* also Fig. 4 for RA).

The above results are physically explainable. For the photochemical reactions of positive orders with respect to both reactant concentration and the absorbed light intensity, levelling of their gradients (these are coupled for RA but for SA intensity gradient is independently established) in the axial direction affects the reaction rate in two counteracting ways. Axial mixing of the reactant, considered in isolation, would always lower the local rates as is well known. But in cases where reactant concentration and absorbed light intensity are interrelated the overall effect has to take into account the effect of absorbed light intensity on the rate. Light intensity gradient, formally, on the one hand allows the reaction to occur at different reactor sections at local rates which are always at the maximum level based on reactant concentration alone and implies on the other hand, that gradually less intensity will be available for the activation of the reaction, bringing down the local rates.

Thus depending on the sharpness of the intensity gradient (whose effect on the rate, for any optical thickness is determined by the exponent p), the intrinsic rate parameters and incident intensity level, a situation may arise where the advantage gained by not levelling the intensity and/or concentration gradient is outweighted by the advantage of levelling it. For $p < 1$, greater the value of p, other quantities remaining constant, the more restricted will be the region (of low conversion and high absorption) where MF will have an edge over PF, until for $p = 1$ or more, PF will always be superior to MF as usual.

For SA the effects of changes in concentration and intensity gradients on the performance can be separated and hence one can illustrate the aforementioned point clearly.

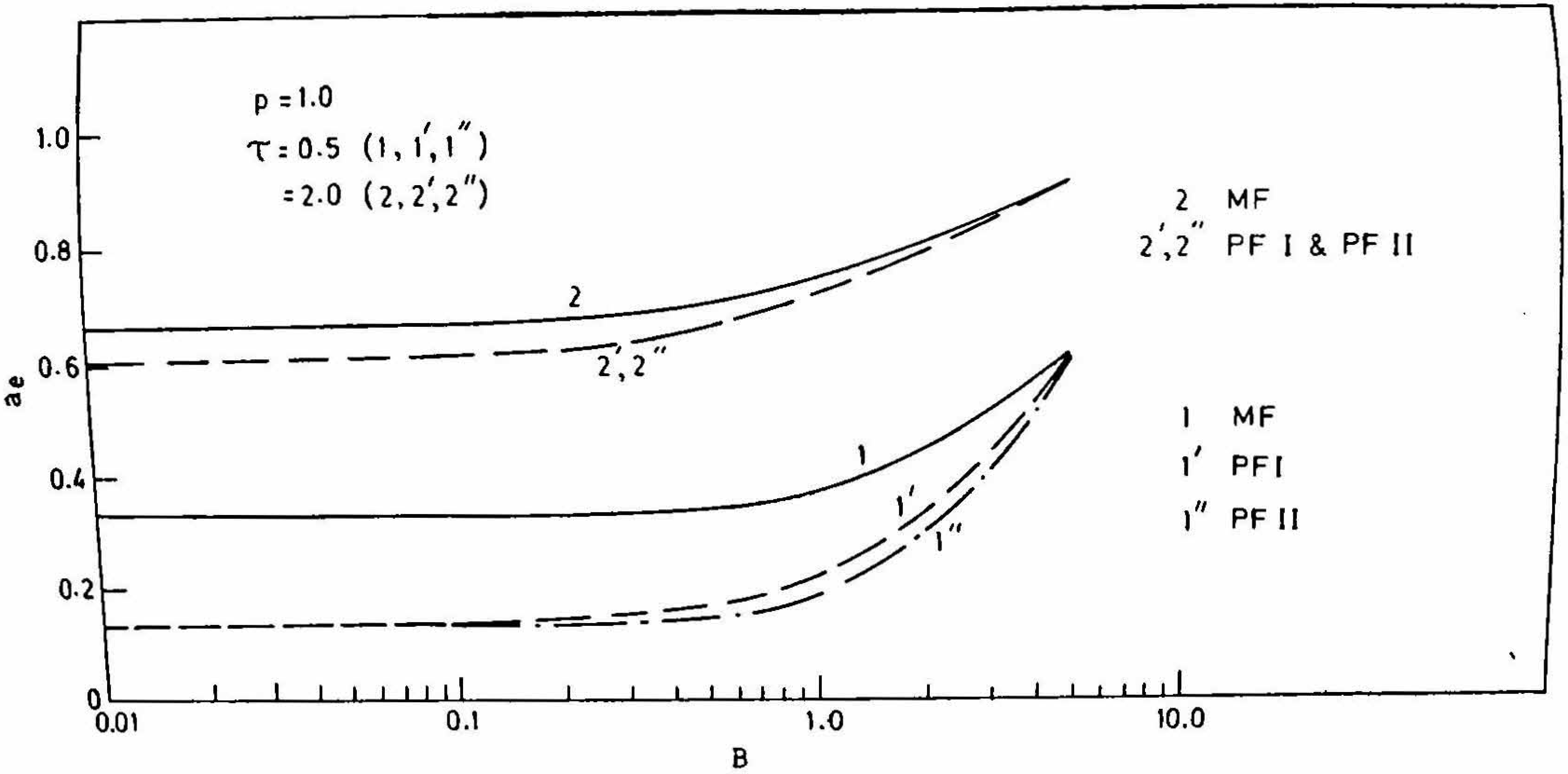

Fig. 4. Comparison of exit concentrations among MF, PF I and PF II ($p = 1\cdot0$).

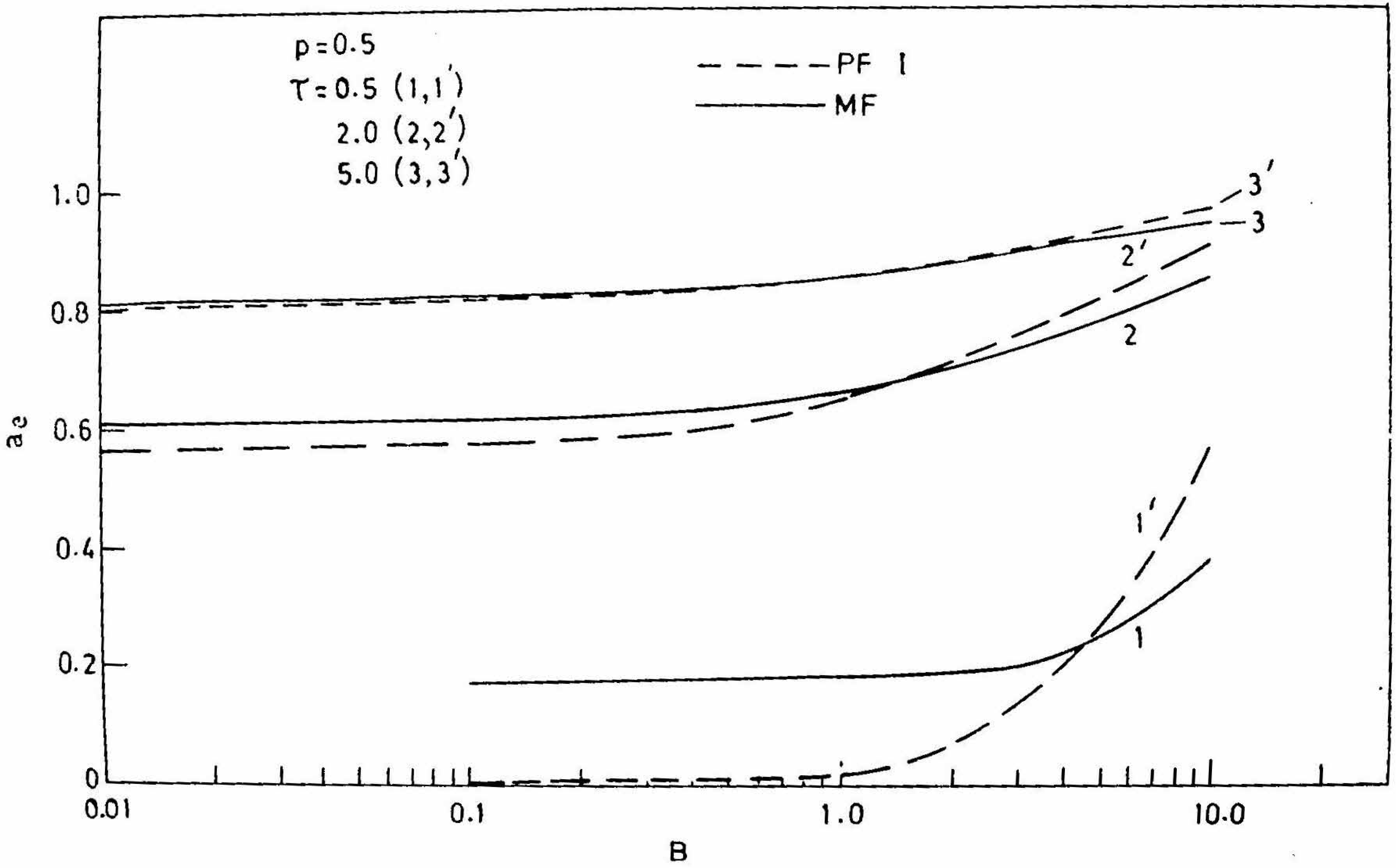

FIG. 5. Comparison of exit concentrations among MF, PF 1 ($p = 0\cdot5$).

It will be seen, that the factor F in equations (5) and (5 a) contains the effect of intensity gradient on the performance explicitly, while the other term (always > 1) in those equations determines the effect of concentration gradient. When $p = 1$ for any value of B_s, F is unity and hence under this condition the usual effect of axial reactant mixing would always be predominant. But for $p = \frac{1}{2}$ the calculated values of F, in Table III, show that there is a certain range of parameter values where the overall effect of reactant mixing and levelling of intensity gradient is to improve the performance.

It can also be shown that in cases of weakly absorbing photochemical systems or of partially illuminated reactors where the so-called 'constant energy loss' radiation attenuation mode can be employed as a good approximation[16] instead of exponential attenuation as assumed here, PF will always be more efficient than MF: intensity profile being essentially flat the usual effect of axial mixing of reactants would show up.

Thus it is clear that unlike in T.I.R. levelling of concentration and intensity gradients in A.I.R. is beneficial only in certain specific ranges of parameter values.

It may be interesting to note that while for SA there is no practical means to control the light intensity gradient for a given B_s, it is possible to do so for RA by devising the reactant mixing.

4. Concluding remarks

Of the three main objectives of the present analysis the second and third, we believe, have been more or less achieved as seen from the last section. A few more points can be made.

(i) Hill and coworkers[15, 17] have shown that, in T.I.R. higher extent of radiation absorption always calls for reactant mixing and levelling of intensity gradient for better performance, when mixing has at all any effects (*eg*., for $p = 0 \cdot 5$). For SA, where intensity gradient cannot be controlled by introducing reactant mixing a low extent of absorption alone can give a relatively more uniform gradient, which in turn will entail low light utilisation efficiency.

For A.I.R. however, there exists a range of extents of absorption and conversion over which reactant mixing and levelling of intensity gradient should rather be avoided in order to operate the reactor at its maximum performance level. Thus it may be possible to tolerate, in A.I.R. a higher optical thickness even without the necessity of mixing for the best performance, than possible in some T.I.R's.

Among the commonly used photoreactor geometries, cylindrical, annular and slab, the first one having the highest surface area of source to reactant volume ratio certainly gives the highest absolute performance, operated as a T.I.R. for identical I_0. But it can be shown from simple calculations that relative rate of fall in performance due to a rise in optical thickness is sharper in this case than for slab geometry, (to which A.I.R. corresponds) at least over a range of B_s. A.I.R. is likely to give a better performance than annular T.I.R. over the entire range of B_s both absolutely and relatively.

(ii) The potential of A.I.R. for its industrial use in the near future can be visualised. The present use of T.I.R. configurations, namely the cylindrical and the annular, has been dictated by the selection of the lamps, which are cylindrical in shape, from quantum yield considerations. But very high pressure, intense, near continuum lamps in the visible and near UV region (*eg*., very high pressure Hg lamps, Xe, Xe–Hg point source lamps) whose shapes might preclude a cylindrical configuration, would become more popular for industrial photochemical use—*eg*., in cases where the absorbing species have a continuous absorption over much of the UV and visible region but one would like to eliminate the shorter wavelengths for better control of product distribution. Also A.I.R can curtail the use of costly transparent quartz as the exposure surface—a suitable inert and transparent material can substitute the quartz windows if necessary. Such a point source lamp along with a paraboloid reflector would probably be utilised in A.I.R. better.

As for the possibility of this reactor arrangement to be used for laboratory photokinetic studies as the alternative to the conventional arrangement, the following comments are perhaps in order:

(i) A monochromatic, collimated, uniformly intense incident light can be realised with more certainty and enables a simpler interpretation of data than the so-called radial, diffused, partially diffused or a host of other models of incident intensity distribution.

(ii) Realisation of the idealised end conditions to be used in the integral analysis of kinetic data poses some practical difficulties. However, the above analysis does allow one to tentatively choose the more suitable configuration and conditions of extent o absorption and of conversion for which the end effects could be minimised. So-calle entrance length calculations suggested in literature[18, 19] also may assist one in the prope choice of length to diameter ratio and other operating conditions, given the optical thickness of the system.

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Nomenclature

A	Reactant A (may or may not be absorbing the radiation).
a	Dimensionless concentration, c/c_0.
a_{PI} or a_{PII}	a for PF I or for PF II.

a_e	Dimensionless exit concentration; may have a suffix PF or M indicating plug flow or mixed flow.
B	Dimensionless optical thickness, in case of reactant absorption, $ac_0 L$.
B_s	Dimensionless optical thickness in case of photosensitiser absorption, μL.
b	Dimensionless radiation intensity, I/I_0.
$B\tau$	(B) (τ).
c	Concentration of the reactant A, g mole/c.c.
c_0	Inlet concentration of reactant A, g mole/c.c.
C_2	A dimensionless constant appearing in equation (13) given by $(B/3)/(1/\tau - B/3)$.
c_e	Exit concentration of the reactant A, g mole/ c.c.
F, F_1, F_1', F_2	Factors defined by equations (3) through (6 *a*).
I	Intensity of radiation, quanta/(cm^2)/(sec).
I_0	Incident intensity of radiation, quanta/cm^2/sec.
I_a	Volumetric rate of absorption of radiation, quanta/c.c./sec.
$\bar{I}_a$	Spatially averaged I_a, quanta/c.c./sec.
k	Specific rate constant in the rate equation describing photosensitisation reaction, $(cc)^{(n+p-1)}$ $(\text{sec})^{p-1}/(\text{g mole})^{n-1}$ $(\text{quanta})^p$.
L	Reactor length, cm.
n	Order of photochemical reaction with respect to the reactant A.
p	Order of photochemical reaction with respect to I_a.
r_A	Reaction rate, g mole/c.c./sec.
t	Dimensionless axial distance, $\theta/\bar{\theta}$.
$\bar{u}$	Average linear velocity, cm/sec.
U	Given by the equation (11).
X_A	Fractional conversion $(c_0 - c)/c_0$.
z	Axial distance cm.
a	Absorption coefficient, cm^2/g mole.

γ	A constant given by $\gamma = \cdot 1 \sqrt[3]{C_2}$.
μ	Attenuation constant for the sensitiser absorption, cm^{-1}.
τ	Dimensionless rate parameter for the reactant absorption, $\left(\frac{\bar{u}}{L}\right)\left(\frac{c_0}{\phi\,(aI_0)^p\,c_o^p}\right)$, with $n = 0$.
τ_s	Dimensionless rate parameter for the photosensitisation, $\left(\frac{\bar{u}}{L}\right)\left(\frac{c_0}{k\,(\mu I_0)^p\,c_o^n}\right)$.
ϕ	Effective quantum yield or combined rate constant to be found in the rate equation of a photochemical reaction involving reactant absorption, $\frac{\text{g mole}}{(\text{quanta})^p}\{(\text{cc})\ (\text{sec})\}^{(p-1)}$ with $n = 0$.
0	$z/\bar{u}$, sec.
0_{msp}	$c_0/k\,(\mu I_0)^p\,c_0{}^n$, sec.
$\bar{\theta}$	Mean residence time, $L/\bar{u}$, suffix M or P refers to mixed flow or plug flow respectively.

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