Analysis of a Photochemical Film Reactor

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Photochemical processes involving heterogeneous reactions are gaining importance in the chemical industry (Hacker and Butt, 1975; Brkic et al., 1978; Legan, 1982). Typical processes involving photochemical reactions are chlorination of *n*-alkanes and alkyl aromatics, sulfochlorination and sulfoxidation of *n*-alkanes, nitrosation of cycloalkanes (Prengle et al., 1975; Fisher, 1978), and ozonolysis of waste water (Schorr et al., 1971).

Photochemical gas-liquid reactions can be conducted in elliptical or annular reactors, bubble or spray columns, film-type reactors, or stirred vessels (Doede and Walker, 1955). The radiation field modeling of such reactors has been recently reviewed by Alfano et al. (1986). In all these reactors, the gas diffuses into the liquid and its reaction with the liquid is enhanced by photons through excitation of either the liquid-phase reactant or the dissolved gas. If the enhancement is high, the reaction would be confined to the vicinity of the interface.

In such a situation, it would be advantageous to have a reactor where a thin layer of liquid is brought in contact with gas while passing through an irradiated zone. One way of achieving this is to pass a thin layer of dispersion with a very high gas content through a rectangular reactor irradiated from the top (Doede and Walker, 1955). A similar situation can also be achieved in a falling film reactor where the liquid flows at the wall and the gas through the central core (Shirotsuka and Sudoh, 1978). This reactor, however, has only a limited gas-liquid interfacial area, determined by the wall.

To increase the area available for mass transfer while still having thin liquid films, as well as continuous availability of gas, it may be advantageous to produce the gas-liquid dispersion in the form of foam and irradiate it when it passes through a column. Foam has polyhedral gas bubbles surrounded by a large number of thin films. This provides an adequate gas supply in the vicinity of the liquid that is present in the form of thin films. The main concern would be the irradiation of foam that would be poor because of its complex structure. The foam behavior, however, drastically changes when it passes through tubes of large and small diameters. When the tube diameter is much larger than the size of foam bubbles, the foam moves through the tubes retaining its polyhedral structure. If, however, the tube diameter is comparable to or smaller than the bubble diameter, it transforms itself into thin films (Bikerman, 1973; Rinkes, 1967) that are separated by gas pockets. This would offer a different reactor configuration, in which a liquid moves through a tube in the form of thin films that are perpendicular to the tube axis and separated by gas pockets.

Such a reactor is analyzed in this note. It is assumed that this parallel film reactor is axially irradiated with monochromatic radiation. The gaseous reactant diffuses into the film from the two gas pockets associated with it and reacts there with the liquid-phase component even in the absence of radiation. The rate of reaction is enhanced because the liquid-phase component is excited by radiation. Chlorination of alkanes as well as ozonolysis of phenols proceed even in the dark, and radiation only enhances their rates. Such reaction schemes have been analyzed earlier for simpler geometries (Mahajan and Sharma, 1981). In this research, the scheme of reactions already available in literature has been employed for the analysis of the proposed configuration of a multifilm reactor.

Description of the Physical System

An axially irradiated moving multiple film reactor is shown in Figure 1. It consists of many parallel tubes, each having a number of parallel films. These films, separated by uniform gaps containing the diffusing and reacting gas, move upward axially. As a film passes the top of the reactor, it is ruptured, and the liquid thus released is collected separately. Collimated monochromatic light is supplied at the top of the tube bundle. Radiation, on being absorbed by the liquid, excites the liquid-phase reactant. As the liquid film moves toward the source of radiation, it experiences an increasing intensity of radiation. The gas dissolves and reacts with the liquid component even without radiation. In the presence of radiation, however, an excited species of the liquid reactant is formed, which reacts with the dissolved gas at a higher rate. Thus, the rate of reaction is enhanced significantly. As all the tubes are identical and act in parallel, it is sufficient to analyze one of them.

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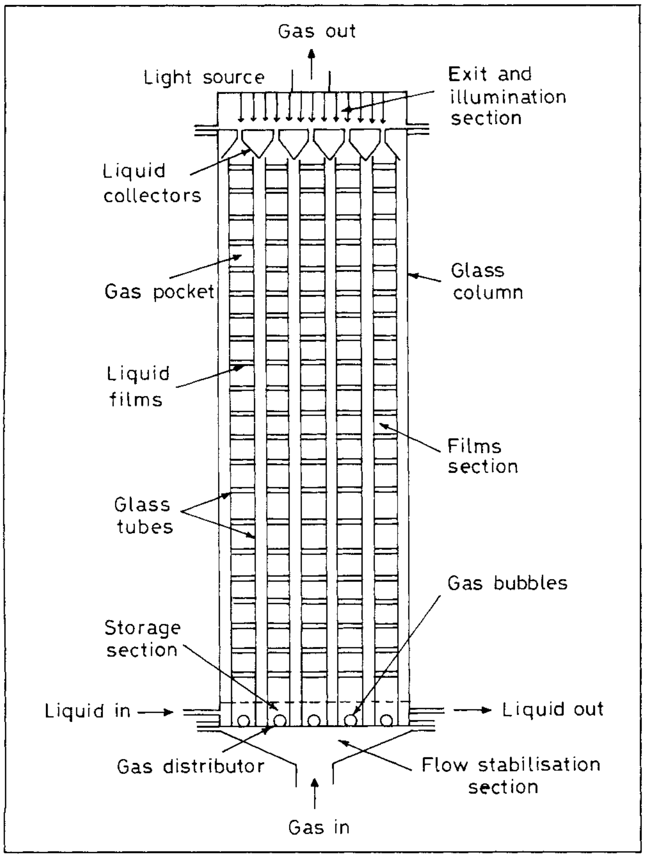

Figure 1. Photochemical film reactor.

The Model

Liquid films of finite thickness are generated either by passing the foam of requisite bubble sizes through a set of narrow tubes or by the formation of bubbles (larger than the tube diameter) at the nozzle tip located under each tube. The films, thus generated, are already separated by finite gas pockets, from which the reactive component diffuses into the film and reacts there. As the film moves upward, it encounters a varying intensity of radiation. As the light absorption occurs mainly in the liquid, the intensity varies in a discontinuous way. Every rupture of the film at the top of the reactor suddenly causes a step change in the intensity that remains constant until the next film ruptures.

Looking at a frozen intensity profile, one would find that the intensity decreased continuously in each film while remaining virtually constant in the gas pocket, Figure 2. As the number of films is large, we have approximated the actual discontinuous intensity variation by a continuous one which is also shown in Figure 2. The Beer-Lambert's law is assumed to be applicable, but with a modified extinction coefficient that can be related to the true extinction coefficient through a number of films and gas pockets and their respective thicknesses. The radiation attenuation through a liquid medium in the absence of gas pockets is given by:

$$I = I_o e^{-\alpha Z} \tag{1}$$

If we split the liquid into films and separate them through gas pockets, we obtain a new extinction coefficient related to the true extinction coefficient by:

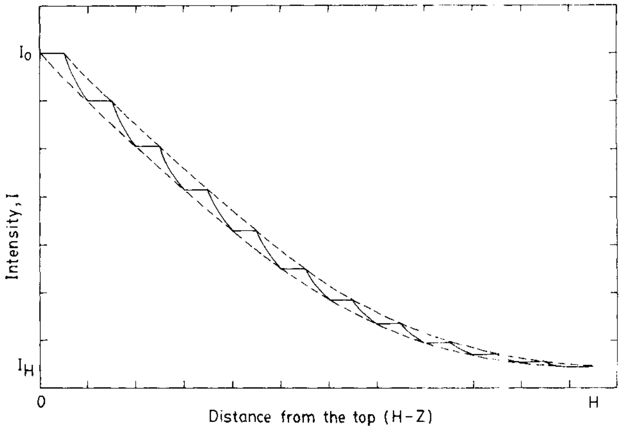

Figure 2. Attenuation of light intensity in multiple films.

$$\alpha' = \frac{\alpha n_f \delta_f}{[n_f \delta_f + (n_f - 1)\delta_p]} \tag{2}$$

This expression for α' yields the correct value of α, if the gas pockets are missing, as a limiting case. In an actual contactor, there will be both absorption and scattering of radiation. In the present analysis, attenuation has been assumed to due only to absorption. Separate experiments may be needed to obtain the extent of scattering of radiation. Further, formation of stable films involves the use of surfactants that may also absorb radiation. It is assumed that this contribution can be neglected, because of the very low concentration of surfactants required for film stabilization.

The basic unit of the reactor of this kind is a liquid film of uniform thickness surrounded on each side by limited amount of gas, corresponding to half the size of the gas pocket. The film is assumed to be flat having no internal flow. There could be small section adjacent to the wall where the thickness of the film would be larger. Further, during movement there will be circulation in this small section. In this model, the film is assumed to be of uniform thickness without any circulation, because of the very small fraction of the film area, to which the above effects are confined. The film, along with its surrounding gas pockets, moves upward as a plug until it reaches the top where it is ruptured and the liquid withdrawn.

As every unit moves with the same constant velocity, all units spend identical time in the reactor. The radiation received by the film part of the unit varies as a function of time. Thus the analysis of the reactor simplifies to that of a liquid film surrounded by a gas pocket on each side, where the diffusing gas undergoes a chemical reaction that is accelerated due to radiation. We assume that at any particular instant the light intensity is uniform within the thin film, at an average value, although this average intensity changes with time. Averaging of light intensity over the film thickness will cause an error, which can be significant if the light absorption in the films is very high. However, if the absorption is relatively small, the assumption will be reasonable. The assumption, however, leads to a major simplification in the analysis as the concentration of the diffusing species can be assumed to be symmetric around the middle of the film. The diffusion accompanied by chemical reaction in the presence of light in the film is governed by:

$$\frac{\partial C_A}{\partial t_c} = D_A \frac{\partial^2 C_A}{\partial x^2} - K_1 C_A - K_2 I_a C_A \tag{3}$$

where

$$I_a = I_0 \cdot \exp\{-\alpha_\lambda [H - Z(t_c)] C_B\} \cdot \alpha_\lambda C_B \tag{4}$$

For a constant flow rate of gas the film-rise velocity is also constant. Thus,

$$Z(t_c) = u_b t_c \tag{5}$$

The initial and boundary conditions for Eq. 3 are:

$$\begin{aligned} &\text{At } t_c = 0;\ 0 \le x < +a;\ C_A = 0 \\ &\qquad x = +a;\ C_A = C^*_{A0} \end{aligned} \tag{I}$$

$$\text{At } t_c > 0;\ x = 0;\ \frac{\partial C_A}{\partial x} = 0 \tag{II}$$

$$\text{At } t_c > 0;\ x = +a;\ -V_p \frac{\partial C_{Ag}}{\partial t_c} = D_A S \frac{\partial C_A}{\partial x} \tag{III}$$

Boundary condition II is based on the concentration symmetry around the origin (middle of the film) and boundary condition III implicity assumes that gas pockets are well stirred and physical equilibrium prevails at the gas-liquid interface.

The system of Eqs. 3-5 and conditions I-III has, therefore, been nondimensionalized and solved numerically. The following dimensionless variables have been defined:

$$\tau = \frac{D_A t_c}{a^2};\ \xi = \frac{x}{a};\ \overline{C}_A = \frac{C_A}{C^*_{A0}} \tag{6}$$

Combination of Eqs. 3-5 and nondimensionalization using the set in Eq. 6 leads to:

$$\frac{\partial \overline{C}_A}{\partial \tau} = \frac{\partial^2 \overline{C}_A}{\partial \xi^2} - \alpha_1 \overline{C}_A - \alpha_2 \exp\{-\alpha_3(1 - \alpha_4 \tau)\} \overline{C}_A \tag{7}$$

where

$$\alpha_1 = \frac{K_1 a^2}{D_A},\ \alpha_2 = \frac{K_2 I_o a^2 \alpha_\lambda C_B}{D_A},\ \alpha_3 = \alpha_\lambda H C_B, \text{ and } \alpha_4 = \frac{u_b a^2}{H D_A}$$

Similarly, initial and boundary conditions I-III become:

$$\begin{aligned} &\text{at } \tau = 0;\ 0 \le \xi < +1;\ \overline{C}_A = 0 \\ &\qquad \xi = +1;\ \overline{C}_A = 1.0 \end{aligned} \tag{IV}$$

$$\text{at } \tau > 0;\ \xi = 0;\ \frac{\partial \overline{C}_A}{\partial \xi} = 0 \tag{V}$$

$$\text{at } \tau > 0;\ \xi = +1;\ -\alpha_5 \frac{\partial \overline{C}_A}{\partial \tau} = \frac{\partial \overline{C}_A}{\partial \xi} \tag{VI}$$

where

$$\alpha_5 = \frac{V_p}{K_c S a}$$

A simple explicit finite difference scheme is suitable for the above system. The equivalent system of difference equations is used for marching in time to obtain both the transient concentration profile as well as the fractional gas absorption at any given time. The latter is calculated by means of:

$$M_t = \left[\frac{S D_A}{V_p C_{Agi}}\right] \int_0^{t^*_o} \left.\frac{\partial C_A}{\partial x}\right|_{x=+a} dt_c \tag{8}$$

In dimensionless form, Eq. 8 becomes

$$M_f = \mu_0 \int_0^{\tau^*} \left.\frac{\partial \overline{C}_A}{\partial \xi}\right|_{\xi=+1} d\tau \tag{9}$$

where

$$\mu_0 = \frac{S a C^*_{A0}}{V_p C_{Agi}}$$

Results and Discussion

Figure 3 presents the effect of intensity parameter α_2 on the fractional gas absorption, when the kinetic parameter α_1 is held constant at 1.0. At relatively short times of contact ($\tau < 10^{-3}$), the effect of the intensity parameter α_2 is negligible, because the amount of absorbed reactant gas in the film is very small in spite of large diffusional fluxes. The effect of photochemical reaction on gas absorption, like that of ordinary chemical reaction, is negligible at such short times of contact corresponding to enhancement factor of near unity. For larger times, however, there is a significant enhancement in the rate of gas absorption. At still larger times, all curves tend to the same value corresponding to the complete depletion of the limiting gaseous reactant. The effect of α_2 on the gas absorption for a faster reaction ($\alpha_1 = 10$) also shows a similar enhancement due to the photochemical contribution. Differences in the rates of absorption, however, appear at shorter τ values for a faster reaction and the enhancement is more pronounced at the lower

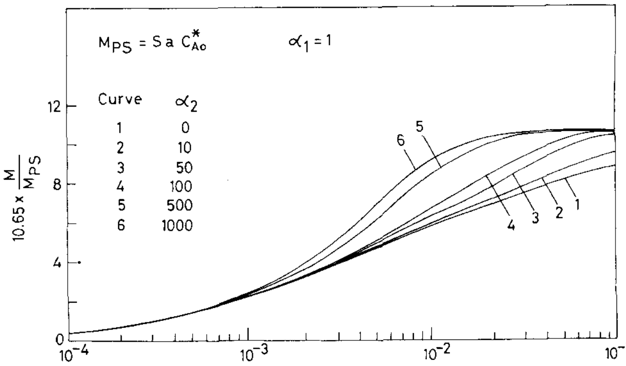

Figure 3. Effect of intensity parameter on gas absorption.

values of intensity parameter. Moreover, the maximum enhancement in gas absorption attainable through an increase in the intensity of illumination is lower at the faster chemical reaction. A simulation for an even faster reaction ($\alpha_1 = 100$) confirms these conclusions.

Contrary to the constant and steady intensity of incident illumination assumed so far, a fluctuating intensity may sometimes be employed. A sinusoidally modulated light intensity has been investigated in the past both theoretically and experimentally (Tomaszewicz, 1990; Schumm and Bauer, 1989; Tolles and Ihrig, 1957). In this study, the effect of intensity fluctuations on gas absorption was explored by employing a sinusoidally oscillating intensity of the incident light. The only change required in the formation of the model corresponds to the replacement of I_o by $[I_{om} + I_a \sin(\omega t_c)]$ in Eq. 4 while all the other aspects remain unchanged. The equivalent dimensionless form of Eq. 7 is:

$$\frac{\partial \overline{C}_A}{\partial \tau} = \frac{\partial^2 \overline{C}_A}{\partial \xi^2} - \alpha_1 \overline{C}_A - [\alpha_2[1 + \beta_5 \sin(\beta_6 \tau)] \exp\{-\alpha_3(1 - \alpha_4 \tau)\}]\overline{C}_A \qquad (10)$$

where

$$\alpha_2 = \frac{K_2 C_B \alpha_\lambda a_2 I_{om}}{D_A}$$

$$\beta_5 = \frac{I_a}{I_{om}}$$

$$\beta_6 = \frac{\omega a^2}{D_A}$$

Figure 4 shows the effect of the frequency parameter β_6 on the gas absorption. The parameters chosen for simulation are $\alpha_1 = 100$, $\alpha_2 = 500$, and the amplitude parameter $\beta_5 = 0.5$. The frequency parameter has been varied in the range 3.14×10^{-2} to 3.14×10^7, corresponding to an equivalent frequency variation from 10 Hz to 1 MHz. It is clear from Figure 4 that the effect of fluctuations in the intensity of light is small. Interestingly, the frequency of oscillations is detrimental to the gas absorption, although only mildly so.

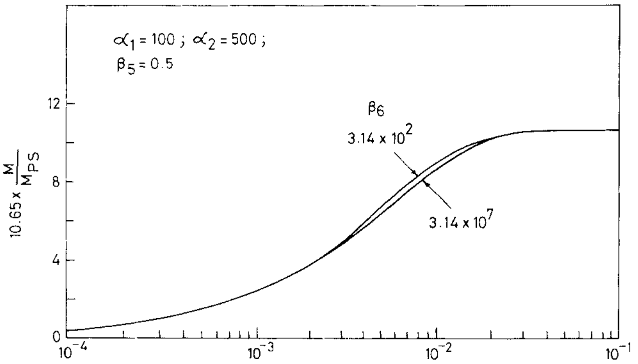

Figure 4. Effect of intensity: modulation frequency parameter on gas absorption.

Effect of the mode of operation

So far the liquid films have been considered to move against the direction of illumination of PCFR. For the situation where films move along the direction of illumination, the nondimensional governing equation is:

$$\frac{\partial \overline{C}_A}{\partial \tau} = \frac{\partial^2 \overline{C}_A}{\partial \xi^2} - \alpha_1 \overline{C}_A - \alpha_2 \exp\{-\alpha_4 \tau\} \qquad (11)$$

where

$$\alpha_4 = \frac{\alpha_\lambda C_B u_b a^2}{D_A}$$

The rest of the formulation remains unchanged.

Numerical simulation of gas absorption through Eq. 11 for identical conditions as for the countercurrent operation shows that the effect of direction of motion of the liquid films with respect to the direction of irradiation has vanishingly small effect. The effect is equivalent to a slightly enhanced gas absorption. Therefore, the effort required to develop a reactor that would permit an effective realization of this mode of operation probably is not worthwhile.

The present analysis can be extended to an actual photochemical foam-bed reactor, if light attenuation in such a system can be estimated either experimentally or theoretically.

Notation

a = half-film thickness, m
C_A = concentration of dissolved unreacted A in the liquid film at depth x and time t_c, kmol/m^3
$\overline{C}_A$ = dimensionless concentration of A in the liquid film defined in Eq. 6
C^*_{A0} = saturation concentration of A at the liquid film surface corresponding to the inlet gas-phase concentration, kmol/m^3
C_{Ag} = concentration of component A in the gas pocket, kmol/m^3
C_{Agi} = concentration of component A in the gas pocket entering the reactor, kmol/m^3
C_B = concentration of component B in the liquid film, kmol/m^3
D_A = diffusion coefficient of component A in the liquid in the film m^2/s
H = height of a tube, m
I = intensity of light at a point in liquid, einstein/s/m^2
I_a = average intensity of light encountered by the film at position $Z(t_c)$, einstein/s/m^2
I_0 = incident intensity of light for illumination, einstein/s/m^2
I_{om} = mean intensity of the incident light around which the sinusoidal fluctuation occurs, einstein/s/m^2
K_1 = pseudofirst-order reaction rate constant ($= K_2 C_B$), s^{-1}
K_2 = second-order reaction rate constant, m^3/kmol·s
M_f = fractional gas absorption
n_f = number of liquid films in the tube
S = surface area of a film, m^2
t_c = time of contact, s
t^*_c = total time of contact, s
u_b = bubble or film rise velocity, m/s
V_p = volume of a gas pocket, m^3
x = spatial coordinate of the system with the origin placed at the center of the foam film, m
Z = depth in liquid, vertical position of the film, m

Greek letters

α = extinction coefficient, m^{-1}
α' = effective extinction coefficient in a film reactor, m^{-1}
$\alpha_1 \ldots \alpha_5$ = constants

α_λ = molar extinction coefficient at wave length of light λ, m^{-1}
β_5, β_6 = constants
δ_f = thickness of a liquid film, m
δ_p = thickness of a gas pocket, m
μ_0 = constant defined in Eq. 9
ξ = dimensionless spacial coordinate defined in Eq. 6
τ = dimensionless time of contact defined in Eq. 6
τ^* = $(D_A t_c^*)/d^2$
ω = frequency of oscillation of light intensity fluctuation, s^{-1}

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