

Radiative Transfer in Photocatalytic Systems

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Radiation absorption at the surface of catalytic particles is the initial step of photocatalytic oxidation reactions currently considered for their potential effectiveness in the treatment of polluted water with traces of highly toxic organics. Owing to the presence of catalyst particles within the fluid phase, the radiation field within a photocatalytic reactor results from the absorption and scattering within the participating medium. An annular reactor with a coaxial central lamp was considered, and the resulting 2-D radiation field was analyzed using a Monte Carlo technique to solve the radiative transfer equation. Results are discussed based on the relevant optical parameters, and a heuristic is derived for the design and rating of a photocatalytic reactor. To exploit the reaction volume effectively, the order of magnitude of the optical thickness should be close to unity, and for a given value of the absorption coefficient the catalyst with the lowest albedo should be selected; however, a precise evaluation of the phase function is not crucial to a reliable representation of the radiation field.

Introduction

Photocatalytic oxidation (PCO) has been demonstrated to be a highly effective technique for treating water contaminated with trace levels of refractory organic pollutants (Matthews, 1990, 1992; Ollis and Turchi, 1990). As a wastewater treatment process, it has distinct advantages over its more traditional competitors (such as adsorption, chemical oxidation, and biodegradation) in that PCO can completely degrade many classes of toxic organic compounds, forming only carbon dioxide and mineral acids, and it can achieve this within relatively short treatment times.

Photocatalytic oxidation occurs as a result of the combined action of three components, a semiconductor photocatalyst, a sufficiently energetic photon source, and an oxidizing agent; these components are usually anatase titanium dioxide, near-ultraviolet radiation, and oxygen, respectively. The first step of this process requires the absorption of electromagnetic radiation whose energy exceeds the semiconductor material's band gap, to promote an electron from the valence to

the conduction band. The resulting conduction-band electron and valence-band hole can then promote redox processes, including activation of the oxidizing agent, or alternatively recombine (Bahnmann et al., 1991).

Although many studies have analyzed the mechanisms of the photochemical processes occurring at the catalyst surface, little research has focused on radiative transfer within this type of photoreacting media (Santarelli et al., 1982) and, specifically, on the relevant optical properties of the catalyst particles (Martin et al., 1993). In fact, radiative transfer is crucial in photocatalytic processes, as well as in any other photochemical process, since reaction can occur only if the energy released by absorbed photons is made available to the reacting species. In this respect, absorbed photons should be considered as *nonmaterial* reactants which, like other *material* reacting species, must be present for reaction to occur. To exploit the available reaction volume effectively, the value of the local volumetric rate of radiant energy absorption must be *sufficiently large* at every point within the reactor.

The modeling of the radiation field is crucial in the design and rating of a photoreactor and requires the solution of the radiant energy balance equation (Alfano et al., 1986; Bandini et al., 1977; Spadoni et al., 1980; Yue, 1993a,b), which can be

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carried out once the proper constitutive equations have been chosen for the terms that account for the participation of the medium. Radiative transfer in participating media has been thoroughly investigated with respect to applications in other scientific and technical areas (such as astrophysics and heat transfer). In the wide body of available literature it is worth quoting classic texts (Ozisik, 1973; Siegel and Howell, 1992; Van de Hulst, 1981; Whitaker, 1977) that have provided invaluable support for the *first principles* approach to the problem considered here. In the case of PCO, as far as radiation is concerned, the presence of solid particles within the liquid reaction medium causes scattering to occur in addition to absorption. Furthermore, due to the nature of heterogeneity centers (the catalyst particles), scattering occurs according to mechanisms that are quite different from those in gas-liquid systems that have been considered in the literature and reviewed by Alfano et al. (1986). This article deals with the analysis of radiative transfer in an absorbing-scattering medium flowing in an annular reactor subject to the radiation emitted by a lamp placed on the central axis of the reactor. The analysis also includes an investigation of the roles of the relevant optical parameters (optical thickness, albedo, and phase function).

The influence of the dimension and the concentration of the photocatalyst particles as well as the geometric configuration of the assembly are discussed to determine the conditions for effective operation of the reactor. An initial validation of the model is also presented and discussed.

Model Equations

A general kinetic equation can be used to describe PCO reactions

$$\mathfrak{R} = k_e c_p^n, \quad (1)$$

where k_e is an effective rate constant and c_p is the pollutant concentration. k_e turns out to be

$$k_e = k_e(c_{\text{cat}}, \dot{e}_{\lambda_1}''', \dot{e}_{\lambda_2}''', \dots) \quad (2)$$

that is, it is a function of the catalyst concentration (c_{cat}) and the local volumetric rate of absorption (\dot{e}_{λ_j}''') of those components of the incident radiation whose wavelength (λ_j) is effective in activating the reaction.

These local volumetric absorption rates are related to the radiative transfer within the medium and are key parameters in the derivation of a reliable kinetic equation.

For any effective wavelength λ , the local volumetric rate of radiant energy absorption can be evaluated at each point within an isotropic medium thus:

$$\dot{e}_{\lambda}'''(\mathbf{x}) = k_{\lambda}(\mathbf{x}) \int_{4\pi} I_{\lambda\omega}(\mathbf{x}) d\omega, \quad (3)$$

where $I_{\lambda\omega}(\mathbf{x})$ is the intensity of the radiation of wavelength λ traveling through a point \mathbf{x} along the direction ω and $k_{\lambda}(\mathbf{x})$ is the local value of the absorption coefficient of the medium, assuming that the Lambert-Beer law applies.

$I_{\lambda\omega}(\mathbf{x})$ depends on the geometry of the system, the optical properties of the medium, and the relevant boundary conditions: the emission by the lamp and the reflection and refraction occurring at the walls of the reactor.

The distribution of $I_{\lambda\omega}(\mathbf{x})$ can be obtained from the solution of the radiant energy balance equation which, under the assumptions discussed in Appendix A, can be written as

$$\frac{dI_{\lambda\omega}}{ds} = -(k_{\lambda} + \sigma_{\lambda})I_{\lambda\omega} + \frac{\sigma_{\lambda}}{4\pi} \int_{4\pi} I_{\lambda\omega} p_{\lambda}(\omega' \rightarrow \omega) d\omega' \quad (4)$$

where k_{λ} and σ_{λ} are the absorption and single-scattering coefficients, respectively (the absorption and scattering cross section per unit volume) and $p_{\lambda}(\omega' \rightarrow \omega)$ is the phase function (which accounts for elastic scattering from the direction ω' to the direction ω).

These three parameters describe the optical behavior of the medium: k_{λ} accounts for absorption, while σ_{λ} and p_{λ} account for scattering, both quantitatively and qualitatively, respectively.

The relevance of k_{λ} and σ_{λ} to radiative transfer within a given system may be more easily understood if they are compared with the relevant characteristic geometric length of the system, l_0 . Since k_{λ} and σ_{λ} can be interpreted as the reciprocal of a λ -photon mean free path before an absorption or scattering event, the following dimensionless parameters result, respectively:

$$m_{\lambda} = (k_{\lambda} + \sigma_{\lambda}) \cdot l_0 \quad \text{the optical thickness}$$

$$C_{\lambda} = \frac{\sigma_{\lambda}}{k_{\lambda} + \sigma_{\lambda}} \quad \text{the single scattering albedo.}$$

The former compares the dimension of the system with the mean free path of a λ -photon before an interaction event (irrespective of the type of event), while the latter provides the probability for an interaction event to result in scattering. No recasting is required for the phase function p_{λ} since it is already dimensionless: it determines the probability of a λ -photon being scattered from the direction ω' to the direction ω .

The evaluation of these parameters characterizes the optical behavior of the catalyst particles with respect to radiative transfer. A discussion of the way in which each parameter's value depends on the nature of the particles as well as the links that they establish between the balance equations is presented in Appendix B. It is worth noting that values for all of these parameters can be directly measured, although obtaining a reliable expression for the phase function can be difficult.

As described in Appendix A, the participation of the medium considered here is restricted to particles which do not undergo any change during the process, hence the radiative transfer problem becomes decoupled from the reaction problem. Thus Eq. 4 is independent of the mass balance for the reacting species and can be solved in advance to provide the distribution of \dot{e}_{λ}''' to the latter. Furthermore, if the catalyst particles are assumed to be uniformly distributed within the reactor, then k_{λ} and σ_{λ} (and thus m_{λ} and C_{λ}) turn out to be constant throughout the reactor volume.

Solution of the Radiative Transfer Equation

To obtain the distribution of the local volumetric rate of radiant energy absorption \dot{e}_λ''' , Eq. 4 has to be solved for any direction ω along which the radiation passing through any point x can travel. To circumvent the difficulties that arise if an analytical solution of the resulting integrodifferential equation given in Eq. 4 is sought, a Monte Carlo approach to the simulation of the overall radiative process has been used: the fate of a statistically meaningful number of nondimensional photon bundles (ergons) emitted by the lamp has been followed.

The procedure outlined by Spadoni et al. (1978) has been implemented to account for phase functions different from the isotropic case. In particular diffuse and specular reflection have been considered at the particles' surface, thus allowing systems using "large" particles to be modeled accurately, although the calculation method can cope with any form of anisotropic scattering.

An option to select the lamp emission mode has also been included in the simulation, in order to be able to examine both mercury arc and metal halide fluorescent lamps. Here the lamp has been modeled as a diffusely emitting linear source, and the inner reactor wall, through which photons enter the system, has been considered as a purely geometric surface. Further details on the simulation procedure are described by Pasquali (1992).

Description of the Photoreactor

A cylindrical annular reactor with the lamp placed on the axis has been considered for the purpose of this series of simulations. For subsequent validation of the model, the dimensions of the investigated assembly were used:

- Lamp and reactor's length: 1,200 mm
- Inner radius of the reactor: 20 mm
- Outer radius of the reactor: 57 mm
- Lamp emission source: diffuse emission

Due to the high aspect ratio of the reaction zone, changes along the axial direction are quite small and therefore the following discussion will mainly focus on the analysis of the radial changes in the midlength cross-flow section of the reactor.

Model's Results

The influence of the optical parameters has been investigated using the assumption of monochromatic light (or negligible dependence of the optical parameters on the light wavelength): any reference to a specific wavelength will therefore be omitted in the following. The results for different values of the optical thickness m , at constant albedo ($C = 0.2$), and for diffusely reflecting spheres are shown in Figure 1.

Recalling the physical significance of the optical thickness, it is then not surprising that at low values of m the distribution of \dot{e}_λ''' is quite uniform, but the resulting values are also quite low, since most of the photons succeed in escaping from the system either immediately or after a scattering event. Conversely, for high optical thicknesses the interaction of the photon bundles with the medium is large and the energy is

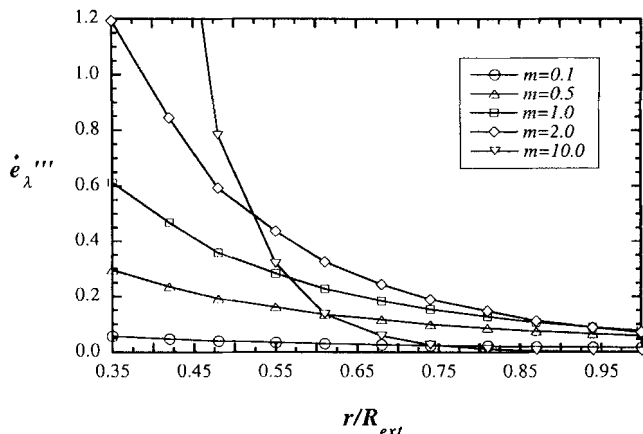


Figure 1. Radial distribution of \dot{e}_λ''' in the midlength cross-flow section of the reactor for different values of m .

$C = 0.2$, particles modeled as diffusely reflecting spheres.

not evenly absorbed within the reactor: at the inner edge of the annulus there is an unnecessary excess of absorbed energy, while the outer edge of the reactor is poorly illuminated and minimal reaction can occur there.

Results show that, in order to exploit the reaction volume effectively, the order of magnitude of the optical thickness should be close to unity. Thus a heuristic for the design and rating of a photoreactor naturally follows: the reactor's dimension and the catalyst concentration should be selected in order to meet the preceding requirement, which can always be met during the design phase, but could conflict with the kinetic constraints determined in the rating phase, requiring a compromise to be made.

Results for different values of the albedo C , at constant m for diffusely reflecting spheres, are given in Figure 2. The curves show that an increase in the albedo reduces the absorption of radiant energy and makes the distribution more even, because of the higher probability that intercepted photons will be scattered.

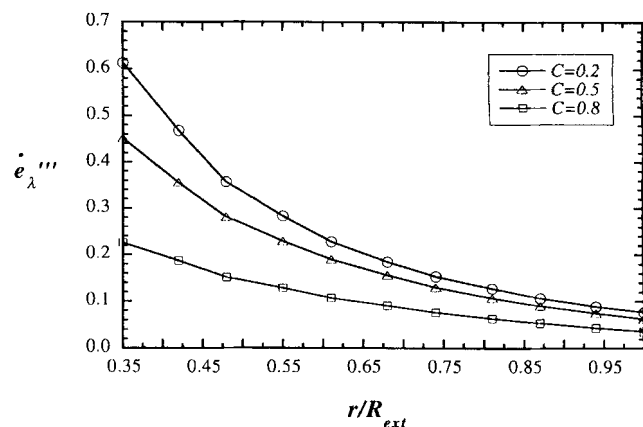


Figure 2. Radial distribution of \dot{e}_λ''' in the midlength cross-flow section of the reactor for different values of C .

$m = 1.0$, particles modeled as diffusely reflecting spheres.

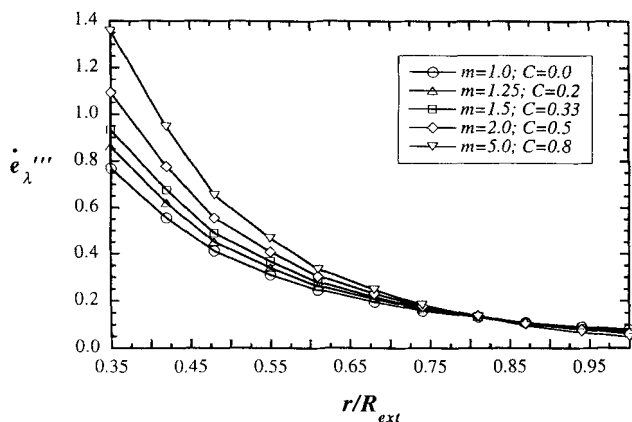


Figure 3. Effect of scattering on the radial distribution of e_{λ}''' in the midlength cross-flow section of the reactor at constant absorption.

$kl_0 = 1.0$, particles modeled as diffusely reflecting spheres.

This could lead to the conclusion that the catalyst with the lowest albedo is the most optically efficient. It must be noted, however, that the curves plotted for different values of C and constant optical thickness do not properly demonstrate the effects of scattering, since as C increases at constant m , the absorbing capability of the medium decreases accordingly. In addition, it is not sensible to apply this kind of comparison in real situations, since the absorbing capability of the medium of higher albedo can easily be increased by using a higher catalyst concentration.

The effects due to scattering may only be more correctly analyzed by keeping absorption—the kl_0 part of m —constant and changing m accordingly for changes in C .

For $kl_0 = 1$, which guarantees a high degree of absorption as well as a reasonably uniform distribution of e_{λ}''' , the effect of different values of σ has been examined. The resulting absorbed energy profiles are shown in Figure 3. It is apparent that, since an increase in σ (and C) also causes m to increase, the catalyst with the lowest albedo provides the most uniform energy profile and the most satisfactory exploitation of the reactor's entire volume. This result is useful in the design and rating of photocatalytic reactors: since the albedo is an intrinsic property of the particles, and thus cannot be adjusted, it follows that the catalyst with the lowest albedo should always be preferred (all other characteristics being similar).

Finally, the role of the phase function was investigated. As previously discussed, the phase function cannot be determined easily, but since scattering is essentially by reflection in large opaque spheres ($\pi D/\lambda > 5$) such as the ones considered here, reference has been made to the two modes of specular and diffuse reflection that may occur at the particle surface as the result of the surface conditions. It should be noted that if the reflection mechanism is specular and the directional reflectivity is uniform, then the scattering is isotropic.

Results for $C = 0.8$, that is, for conditions under which scattering is the dominant mode of interaction, are shown in Figure 4. These demonstrate a relatively low sensitivity of the results to the mode of reflection of the scattered photons, the

differences being not too large and in all cases less than 15%, even in the most affected part of the reactor.

Since the actual behavior of the particles will in some way be intermediate of the two extremes considered here, the previous findings allow one to infer that a precise evaluation of the phase function is not crucial to a reliable representation of the radiation field.

Experimental Results

A series of experiments was conducted in order to obtain a preliminary evaluation of the reliability of the model. The radiative flux emerging from the outer wall of the annulus was measured in a reactor fed with an aqueous suspension of catalyst particles. The catalyst material employed was TiONA VC grade titanium dioxide, with an average particle diameter D_{avg} of $11.93 \mu\text{m}$ (as measured by photon correlation spectroscopy). The reactor's geometric dimensions were as reported in the previous section. The external reactor wall was constructed from Corning QVF borosilicate glass and the internal wall was made of UV grade quartz. The light source used in all the experiments was a 40-W metal halide fluorescent "black light" (NIS model F40T10BL-B), which emitted almost exclusively in the region of the electromagnetic spectrum between 330 and 390 nm.

The radiative flux was measured using a Macam SD102 UV silicon photodiode equipped with a UVA Cos 102 cosine corrector and a SD103 band-pass filter (maximum transmission at a wavelength of 365 nm decreasing by 90% of maximum transmission at 335 and 385 nm) in order to measure only radiation in the region of the spectrum effective for photocatalytic reaction.

Experiments were carried out at different catalyst concentrations across a wide range of optical thicknesses, from optically thin to optically thick media. Since the same catalyst was used in all experiments, the albedo, which is an intrinsic property of the material, was constant. The approximation of constant albedo over the range of wavelengths present in the physical system is reasonable due to the previously mentioned spectral characteristics of the lamp and the detector's filter. Since apparatus to measure the albedo were not avail-

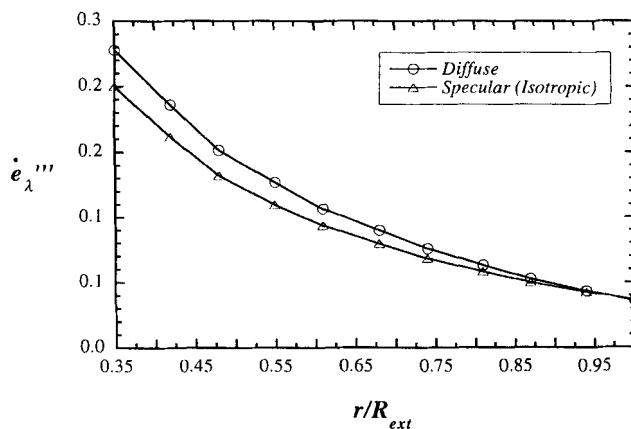


Figure 4. Radial distribution of e_{λ}''' in the midlength cross-flow section of the reactor for different phase functions.

$m = 1.0$, $C = 0.8$.

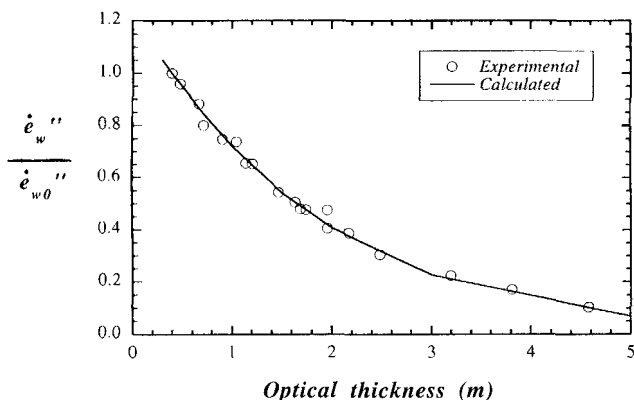


Figure 5. Measured vs. calculated values of radiative flux emerging from the outer wall of the reactor.

$C = 0.5$, particles modeled as *diffusely* reflecting spheres.

able, the latter was treated as a parameter to fit the model to the experimental data.

Figure 5 presents the results for the ratio between the emerging flux at the current value of m and the same quantity at a reference value of the optical thickness ($m_0 = 0.3964$). A comparison between the measured values and the simulation results show good agreement for a value of $C = 0.5$, which is less than the theoretical upper limit of 0.689, calculated by the procedure outlined in Appendix C.

Although the variable used in the comparison (the local radiative flux, \dot{e}_λ'') is not the same one discussed in the first part of this section, and whose distribution affects the PCO process (the local rate of radiant energy absorption, \dot{e}_λ'''), the two variables are strictly related and both significant in determining the resulting radiation field. It is therefore plausible to conclude that the comparison gives confidence in the reliability of the model.

Conclusions

The radiation field inside a photocatalytic reactor has been examined as a specific case of radiative transfer in absorbing-scattering media.

The assumptions made both in the derivation and in the solution of the radiative transfer equation have been presented and discussed on the basis of the particular physical features of the system under investigation.

The solution of the radiative transfer equation using a Monte Carlo simulation has demonstrated the relative importance of the different optical parameters and has produced useful criteria for the design and rating of photoreactors. It turned out that in order to exploit the reaction volume effectively, the order of magnitude of the optical thickness should be close to unity and that, for a given value of the absorption coefficient, the catalyst with the lowest albedo should be selected, while a precise evaluation of the phase function is not crucial to a reliable representation of the radiation field.

Finally, a preliminary experimental test has shown that there is good agreement between the values of those variables calculated by the model and those measured experimentally.

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Notation

- \dot{n} = reaction rate
- r = radial distance
- R_{ext} = external radius of the reactor
- s = linear distance
- \mathbf{x} = position vector
- κ = imaginary refractive index
- η = real refractive index

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Appendix A

- The assumptions under which Eq. 4 strictly holds true are
- (a) A homogeneous medium
 - (b) No emission by the medium, and
 - (c) Elastic (coherent) and independent scattering.

The first assumption can be made safely in almost all situations of practical interest, since the condition $D_{\text{cat}}/l_0 \ll 1$ is generally satisfied, and furthermore the particle concentration used in photocatalytic reactors is usually low: it therefore follows that the participating medium, actually heterogeneous, can be considered as a pseudohomogeneous one. Only if big particles ($D_{\text{cat}} \cong 0.5 \div 2$ mm) are used in thin reactors ($l_0 \cong 50 \div 100$ mm) does this assumption become questionable and the absorption at the surface of the particles must then be considered as a surface phenomenon. In this respect, the penetration of radiation into the catalyst particle and the mobility of the electron-hole pairs can become important once the characteristic dimension of the particle becomes considerable.

The second assumption can be justified easily since PCO processes usually occur at low temperatures (10 to 40°C).

The final assumption of elastic and independent scattering implies that (i) a scattering event changes only the direction of a photon's flight, not its energy, and (ii) each particle scatters radiation as if isolated. For the dimensions and the concentration of catalyst particles currently used, condition (ii) is widely verified in PCO processes. Regarding condition (i), some inelastic scattering may actually occur as a result of re-emission by the catalyst, which should result in photoluminescence. Since little visible photoluminescence was observed during the series of experiments, elastic scattering can be reasonably assumed.

It is worth noting that the assumption of elastic scattering allows substantial simplification of the modeling, since Eq. 4 can be written and solved separately for each wavelength. Should inelastic scattering be present, however, only minimal approximation would be required to enable each wavelength to still be considered separately.

Appendix B

Participation of the medium is assumed to be due only to the catalyst particles. This assumption suffers no limitation if the particles are suspended in pure water. In the case of PCO, where organics are dissolved in water, the assumption is still valid if the concentration of the organic material is sufficiently low (typically less than 50 ppm) so that their absorption is negligible compared to that of the catalyst. This requirement is not a severe limitation since the concentration of the pollutants degraded by PCO usually falls within the range of 10 to 100 ppm and the catalyst concentrations used are typically 1 to 2 kg/m³. It must also be noted that participation of most the organic pollutants considered for this type of process occurs in a wavelength range that is external to the one of catalytic activity of TiO₂ particles.

This assumption is very important with respect to the solution of the model equations since it allows the radiative transfer equation to be decoupled from the mass balance equation for the reacting species, and therefore makes sequential solution of these equations possible.

Table 1. Dependence of Optical Parameters on Various Characteristics of the System

	Wavelength	Particle Conc.	Particle Size	Cat. Comp.	Surface Status
m	N*	Y	Y	N	N
C	Y	N	N*	Y	Y
$p(\omega' \rightarrow \omega)$	N*	N	N*	Y	Y

*If particles are large compared to the wavelength of the incident radiation, that is, $\pi D/\lambda > 5$.

The fluidodynamic problem need not be examined when the reactor is a CSTR or a high-flow PFR, because the catalyst concentration can be considered uniform in these cases. In general, the catalyst concentration distribution should be obtained in advance through the solution of the momentum balance equation, which is decoupled from the radiative transfer and reaction problems.

Under the previous assumptions, the modeling of a reactor where a PCO process occurs can be undertaken through the sequential solution of the radiative transfer equation and the mass balance equations for the reacting species. With respect to the mass balances, $\dot{e}_\lambda''(\mathbf{x})$ can be regarded as a known point-valued function.

With regard to the values of those optical properties entering the radiative transfer equation— $k_\lambda \sigma_\lambda$ (or m_λ, C_λ) and $p_\lambda(\omega' \rightarrow \omega)$ —the first two can be measured using a UV-spectrophotometer and integrating spheres, respectively, while the evaluation of $p_\lambda(\omega' \rightarrow \omega)$ is not easy theoretically or experimentally.

A summary of the factors affecting a particle's optical properties is provided in Table 1.

Appendix C

Kerker (1969) provides a correlation to determine an upper limit for the albedo of "large" diameter particles:

$$C = \frac{(1 + W)}{2},$$

where W , the contribution of specular reflection to scattering efficiency, can be calculated from a knowledge of the material's complex refractive index. Using the measurements provided by Palik (1985) for rutile titanium dioxide—at $\lambda = 360$ nm, $\lambda = 3.87$, and $\lambda = 0.251$ —and a second correlation provided by Kerker, a value of 0.3785 is obtained for W . Thus an upper limit for the albedo of rutile titanium dioxide is 0.689.

The crystal structure of the TiONA VC titanium dioxide used was confirmed to be greater than 70% rutile by X-ray diffraction.

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