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A.J. Hunt, J. Ayer, P. Hull, F. Miller,
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Solar Radiant Processing of Gas-Particle Systems for Producing Useful Fuels and Chemicals

A.J. Hunt, J. Ayer, P. Hull, F. Miller, R. Russo, and W. Yuen

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

This paper reviews the research program at LBL studying direct radiant heating for the production of fuels and chemicals. The research is investigating the use of gas-particle suspensions to absorb concentrated sunlight to supply energy for endothermic chemical reactions. The goal of the research is to understand the optical, thermodynamic, and chemical processes in solar heated particle suspensions through a balanced program of analytical and experimental investigations. The use of small particles as solar absorbers is discussed and spectral extinction efficiencies are calculated from Mie theory for various particle sizes. An equation for calculating the heat transfer from a particle to the surrounding gas at arbitrary Knudsen number is developed. The experimental section outlines the current laboratory studies of direct radiant heating that utilizes a high intensity radiant source to simulate concentrated sunlight. Some preliminary experimental results are presented.

INTRODUCTION

LBL has been involved for the past seven years in the development of solar thermal receivers that utilize suspended particles as solar absorbers and heat exchangers to heat gases for power and industrial process heat applications (1). This program resulted in the design, construction (2), and successful solar demonstration (3,4) of the Mark I, Small Particle Heat Exchange Receiver (SPHER) at the solar test facility at Georgia Institute of Technology in 1982.

Our present research extends the earlier work to new methods of initiating chemical reactions. The unique combination of high direct solar flux density and high temperatures in a gas-particle suspension offers a new and unexplored environment for chemical processes. Direct radiant heating of gas-particle mixtures may be used for heating a working gas, processing chemical feedstocks or inducing chemical reactions in the suspending gas. However, before efficient and effective receiver/reactor designs can be developed it is imperative to understand the underlying physical processes. The particles must be absorbing in order to convert the radiant solar energy to thermal or chemical energy. The complex index of refraction, size, and shape of the particles have profound effects on the optical and thermal properties of gas-particle mixtures. The choice of particle size and mass loading (mass of particles per unit volume) have important effects on the size and shape of the receiver, reaction time and process conditions. Particle entrainment methods and the particle suspension flow path are also critical to the successful operation of a direct absorption receiver.

ANALYTICAL STUDIES

To initiate the study of chemistry in radiantly heated gas-particle suspensions, a survey of chemical reactions in or between gases and absorbing solids was performed. A number of suitable reactions were identified and optical, physical, and chemical data were obtained the for the solids involved. Using this data, the optical properties of the particle suspensions were calculated to determine the energy absorbed by the particles. Having determined the heat input to the particles, the heat transfer between the particles and the surrounding gas was calculated to determine the temperatures and heating rates of the particles. To do this, a heat

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transfer model was developed that was suitable for all particle sizes treated in this work.

The phenomena involved in the direct radiant heating of small particle suspensions are basically similar for a wide range of particle sizes. However, the importance of some effects can vary widely with particle size and mass loading. This study is concerned with particles small enough to be entrained in flowing gases, e.g., having diameters of a few hundred micrometers down to submicron sizes. The optimum particle loading per volume of gas depends on the application being considered. Very low particle densities are sufficient for gas phase reactions in which the particles act as the radiant heat exchanger or catalyst for gas phase reactions. On the other hand, if thermal processing of a particulate feed stock is desired, wherein the gas basically provides the transport system, much higher loading densities are appropriate. A case involving intermediate particle loading densities is encountered when it is desired to initiate reactions between the gas and particles. One of the goals of this research is to define the range of mass loading for various applications and its effect on receiver design.

Optical Calculations

The absorption and scattering of sunlight by spherical particles can be calculated once the wavelength-dependent complex refractive index and the particle size distribution are determined. Tabulations of the refractive index were obtained from a literature search, and incorporated in a computer data base for several materials identified in the chemical survey. Mie calculations were used to determine the absorption and scattering efficiencies (cross sectional area for absorption or scattering divided by the geometric cross section of the particle). A computer program using a Mie subroutine was written to calculate the attenuation of monochromatic radiation by a suspension of particles with a known size distribution. The calculation was limited to single scattering. A second computer program was written to calculate the attenuation of energy from radiant sources possessing a broad spectral distribution. In this program the spectral distribution of an arc lamp or sunlight was convolved with the spectral attenuation of the particle distribution from the Mie calculation.

In Figure 1a, the calculated extinction efficiency (sum of the absorption and scattering efficiencies) is plotted versus wavelength for various particle sizes. Because of multiple scattering in particle suspensions, the effective attenuation in a reactor falls between values predicted by extinction and absorption. In figure 1b the attenuation of polychromatic radiation (in this case the solar simulator) is plotted versus the product of particle mass loading and path length for three particle size distributions. This figure permits the rough determination of the size of the receiver required to absorb a desired fraction of light within the particle suspension when the particle mass loading is specified or vice versa. The information in this figure must be combined with the spatial dependence of the radiant flux pattern to determine the heat input to the particles. All graphs were calculated using the optical properties of magnetite.

Heat Transfer Calculations

As the particles absorb radiant energy they begin to heat and transfer energy to their surroundings by conduction, convection, radiation, and possibly through chemical reactions. Both the initial particle heating rate and the final steady state temperature will be determined by the heat transfer rates. If the particle is small, natural convection is negligible in most cases because the Grashof number is also small ($Gr \sim d^3$,

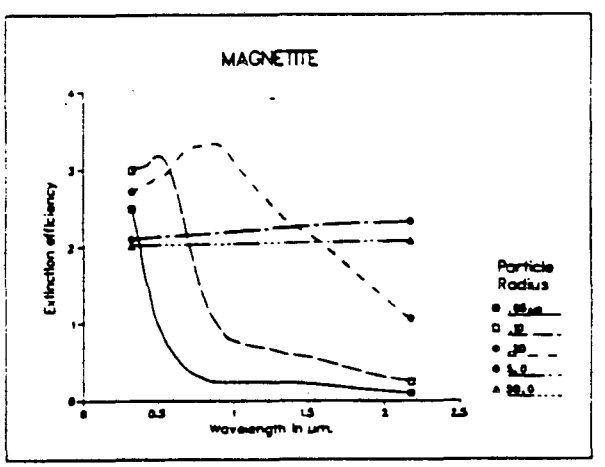

Figure 1a. Graphs of the extinction efficiency of a magnetite particle as a function of the wavelength of radiant flux. Graphs for several different particle sizes are shown.

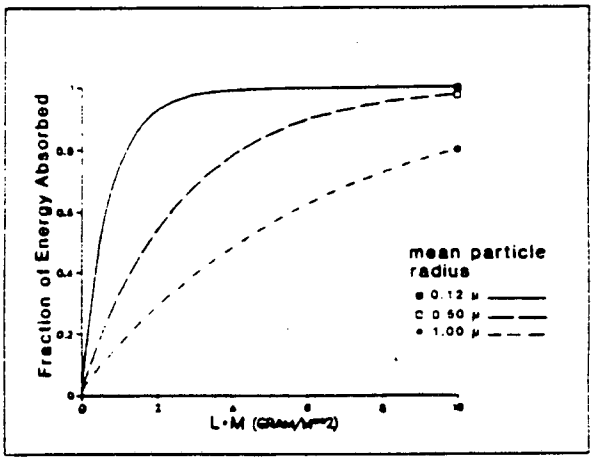

Figure 1b. Fraction of the energy absorbed from a Xenon arc-lamp as it passes through a suspension of magnetite particles as a function of the optical depth (product of the mass of particles per unit volume and the path length of the light). Graphs for three different gaussian distributions of particle sizes are shown to illustrate the effects of particle size on the ability of the gas-particle suspension to absorb light.

where d is the particle diameter). Forced convection is not important as long as there is no relative motion between the particle and gas, which is usually the case for micron sized particles. Assuming the particle is not reacting, conduction is thus the only mechanism by which energy is transferred to the gas. (The gas is taken to be transparent; only the particles interact radiantly.) To complete an energy balance on the particle it is necessary to know this conductive term; we propose a model for it that is applicable regardless of the Knudsen number (5).

The characteristics of conductive heat transfer from a particle to the surrounding gas may be broken into three regimes depending on the value of the Knudsen number (Kn), defined as λ/d, where λ is the gas molecule mean free path and d is the characteristic dimension of the particle. For $Kn < 10^{-3}$ the continuum approximation for heat transfer applies. For $Kn > 10$ free molecular flow conditions prevail and expressions for the heat transfer based on molecular collisions apply. In the transition region, $10^{-3} < Kn < 10$, analytical modeling of heat transfer is difficult because neither the continuum nor the kinetic theory approach is strictly correct.

The model we used for the conductive heat transfer is the following: a spherical particle with radius a is stationary in an infinite gaseous medium with temperature T_∞ as $r \to \infty$ (r is the radial coordinate with origin at the particle center). The region outside the particle is divided into two zones. Beyond a spherical boundary of radius $\lambda + a$, continuum conduction is assumed to hold, where λ is the mean free path of the gas molecules. Within one mean free path of the surface it is assumed that the gas molecules collide only with the particle and not with one another. The molecules striking the particle are assumed to have a Maxwellian velocity distribution at temperature T_B, the zone boundary temperature. The particle is maintained at a fixed temperature T_p; the required energy is supplied or removed by radiation or chemical reaction.

To obtain the steady state heat flow, the Laplace equation is solved in spherical coordinates for the temperature field outside the boundary of radius $a+\lambda$. The solution, $T = A/r + T_\infty$ contains a constant A, determined by the zone boundary condition. Next, the energy carried to and from the particle is calculated from kinetic theory assuming a boundary temperature T_B. A is then determined by equating energy flows at the boundary. With A known, the continuum temperature distribution may be used to solve for T_B and the resulting expression for the heat transfer Q is:

$$Q = \frac{4\alpha a k \Phi (T_p - T_\infty)}{Kn + \frac{\Phi\alpha}{(2Kn + 1)}} \qquad (1)$$

where α is the accommodation coefficient (a measure of how well the molecules thermally accommodate to particle temperature), k is the thermal conductivity of the gas, and Φ is a numerical constant which depends of the internal energy of the gas molecule (Φ = 34/75 for monatomic gas and 48/95 for a diatomic gas).

A nondimensionalized boundary temperature may be defined as:

$$\frac{T_B - T_\infty}{T_p - T_\infty} = \theta; \qquad (2)$$

which results in a quantity that varies between 0 and 1. θ vs. Kn is plotted in Fig. 2. As Kn approaches 0, T_B approaches T_p and the continuum temperature gradient (with no temperature jump) results. For air at STP this corresponds to a particle diameter of $\geq$ 15 μm. As Kn increases toward infinity T_B goes to T_∞ and a temperature jump at the surface appears. This happens for particles of diameter less than .075 μm in air at STP. By calculating Kn for a particle of interest, reference to this plot reveals to what extent there is an effective temperature gradient around it.

The Nusselt number as a function of Kn can also be calculated for the general case from the heat transfer equation and the result is plotted in Fig. 3. Again by finding the appropriate Kn, Nu can easily be determined from the graph. It is important to note that Nu decreases as Kn increases, and the heat flux per area from a particle is $q = (Nuk/2a)(T_p - T_\infty)$. Therefore, as the particle becomes smaller, q increases since Nu does not decrease faster than a. This means that it is increasingly difficult for a small particle to be at a temperature which is different from the surrounding gas as the particle size decreases.

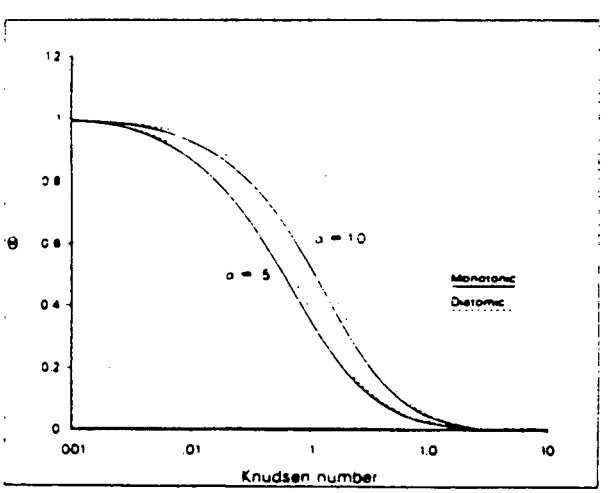

Figure 2. The non-dimensionalized boundary temperature as a function of the Knudsen number for both a monatomic and a diatomic gas. Graphs for values of the accommodation coefficient of 0.5 and 1.0 are shown for each gas.

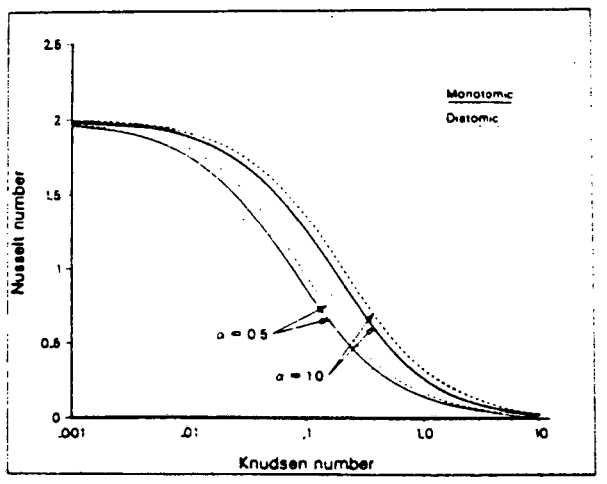

Figure 3. The Nusselt number as a function of the Knudsen number for a monatomic and a diatomic gas, respectively. Graph for values of the accommodation coefficient of 0.5 and 1.0 are shown for each gas.

Shown in Fig. 4 is a comparison of our result with those of two other workers (6 , 7). The experimental points were taken by Takao using a sphere in a rarefied gas to achieve a mean free path on the order of sphere radius (Kn $\sim$ 1). (In order for a particle to have an equivalent Knudsen number at STP, its diameter would be about 0.07 μm.) Our treatment matches his data at least as well as his analytic expression does, and ours is far simpler to apply outside regions not shown on the graph. Also plotted for comparison is Sherman's empirical formula.

Because Equation 1 can be used in an energy balance to calculate the particle temperature for arbitrary Knudsen numbers, it is now possible to calculate particle temperatures for any radiant heating condition (8). The equation is limited to cases in which the particle size is not large enough to cause gravitational settling which would induce an additional forced convection term. However, the present treatment provides an upper bound to radiatively heated particle temperatures for falling particles because the forced convection will tend to reduce the temperature difference between particles and gas. The primary value of the equation lies in its ability to predict the heat transfer at values of Kn $\sim$ 1 where a useful expression with an analytic basis was not previously in

use. The expression should find use in other areas where particle temperature is important, such as combustion or particle-gas heat transfer in the atmosphere.

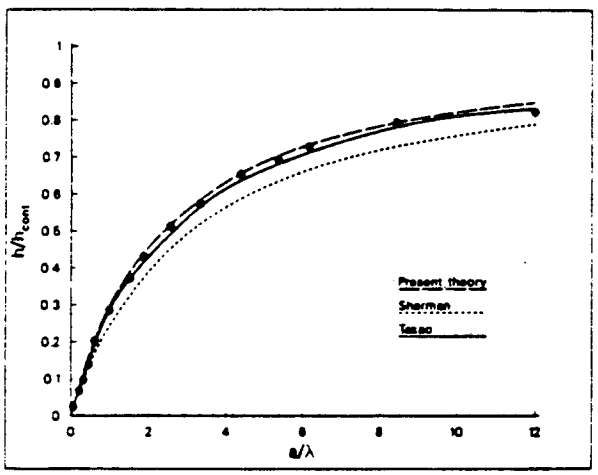

Figure 4. The non-dimensionalized heat transfer coefficient as a function of the ratio of particle radius to mean free path of a gas molecule. The points shown are experimental data from Takao. (7)

EXPERIMENTAL STUDIES

In order to simulate concentrated solar radiation in the laboratory, an arc-image furnace was constructed. A high intensity xenon arc lamp was mounted at one focus of a deep ellipsoid that reflects light coming from the arc to the other focus of the ellipsoid. A two-dimensional translational stage was constructed to provide stable mounting for the ellipsoidal reflector insuring reproducible flux profiles. A similar, but three-dimensional translation stage was constructed to allow precise positioning of the reactor vessel at the focus of the reflector. It also serves as the mount for a scanning calorimeter used to make spatial measurements of the radiant flux. A spatial integration of these measurements was made to determine total power available in the reactor zone. These measurements indicate a peak flux density on the order of 4000 kW/m^2 and a total input power to the reactor of 490 Watts, assuming an 8% reflection due to the vessel window.

The detailed three-dimensional map of the flux density was a critical factor in the design of the receiver/reactor. In the reactor in current use, the gas-particle mixture enters the reactor vessel at the top, is swirled in a cyclone fashion toward the bottom and is exhausted through a central tube. Light from the solar simulator passes through the bottom of a flat quartz window and is focussed just below the exhaust tube to ensure that all particles pass through the high intensity portion of the beam (see Figure 5). A number of experiments were conducted to observe the heating of particle-gas mixtures in the reactor. When the reactor was wrapped with insulation, temperatures in excess of 1200°K were reached with particle mass loadings less than 10 grams per cubic meter of carrier gas. Temperatures were measured with a Chromel-Alumel thermocouple placed in the exhaust tube of the reactor chamber.

Work was completed on a mechanical shaker and cyclone chamber for entraining small particles in a gas stream. Commercially available powders of carbon, hematite, and magnetite were successfully entrained in a gas stream and optical extinction measurements were performed on the particle suspensions. These particle materials were chosen

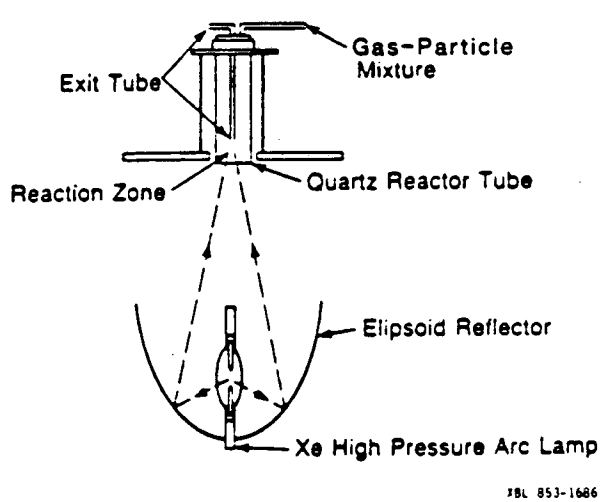

Figure 5. Diagram of the reactor vessel placed at the focus of the arc- image solar simulator.

for initial experimentation because of their possible roles in various reactions of interest for the production of useful fuels and chemicals The mass loading of the particles in the suspension was determined by drawing a known volume of the gas-particle mixture through a filter and weighing the filter. Samples were cut from the filter and scanning electron micrographs were made to determine particle size distributions.

As another application of absorbing suspensions we have undertaken preliminary studies of solar detoxification of hazardous chemical waste using the solar simulator. The toxic wastes most resistant to destruction by incineration are the polychlorobiphenyls (PCB's). Dichlorobenzene was chosen as a surrogate for PCB because it is considerably less toxic but has chemically similar properties. An injection system for introducing the hazardous waste material into the particle-gas stream was installed and tested. In tests using carbon particles as the absorbing material and air as the carrier gas, temperatures near 1200°K were reached and the carbon particles were oxidized during passage through the reactor. Although the carbon particle suspension was sufficiently dense to absorb enough of the radiation passing through the quartz window to reach this temperature, the mass of carbon oxidized was a small fraction of the fuel that would have been needed to achieve the detoxification by direct combustion. After leaving the reactor, the gases were passed through a water bubbler for chemical analysis. Equipment with the accuracy to determine if 99.999% destruction or removal efficiency (DRE) had been achieved was not available, so an ion selective electrode was used to monitor the HCl content of the water from the bubbler. The measurement indicated that 108% of the dichlorobenzene has been destroyed with an instrument error of ±10%.

CONCLUSION

The use of a gas-particle mixture as a solar absorption medium for heating gas has already been demonstrated. In this paper we have discussed research directed towards extending the small particle absorption concept to other applications, including the solar production of fuels and chemicals, and the destruction of toxic wastes. The field is entirely new and many issues still need to be addressed. We have broken ground by identifying and gathering data on possible reactions, calculating absorption characteristics of particle suspensions, developing a satisfactory particle to gas heat transfer model, and constructing a laboratory system that will allow these reactions to be studied experimentally.

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