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RADIATIVE PROPERTIES OF CHAR, FLY-ASH, AND SOOT PARTICLES IN COAL FLAMES

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Preface

This is the Annual Report for the project titled "Radiative Properties of Char, Fly-Ash, Soot Particles in Coal Flames", which has been funded by the Department of Energy, Pittsburgh Energy Technology Center through a grant #DE-FG22-92PC92533. The period covered here is the first twelve months of the project, that is from September 15, 1992 to September 15, 1993.

Four students have been involved in the project during the first year. Mr. Sivakumar Manickavasagam joined the project as a Research Associate after completing his Ph.D. Dissertation at the University of Kentucky. Mr. Wu Zhang and Mr. Ramaswamy Govindan are the graduate students who started working on the project in Fall 1992 and 1993, respectively. Mr. Zhang was paid by the Mechanical Engineering Department in Fall 1992 and Fall 1993. The Department will continue to support these graduate students on part time base in Spring 1993, in order to satisfy the matching funds requirements set in the initial contract. During the Summer of 1993, Ms. Erin Rapela, an undergraduate student in Mathematics at the Clarion University in Pennsylvania joined our group and worked on multilayer sphere model. Ms. Rapela was temporarily involved in the project, and Mr. Govindan's contribution has not been significant so far. Because of these reasons, their names did not appear in the author list shown on the cover page of this report.

In the first year, the majority of experimental systems were designed, completed, and installed. Unfortunately, we needed to move in a new laboratory facility, which delayed our progress significantly. In order to compensate the lost time, we put more emphasis on the theoretical models and *ex situ* experiments. The second year will be used more effectively for the laser experiments. Note that, the University of Kentucky has contributed more than $8,000 to cover the cost of renovation of the new laboratory.

During the first year, we have completed three papers, which are listed below:

1: S. Manickavasagam and M. P. Mengüç, "Effective Radiative Properties of Coal/Char Particles at λ=10.6 μm", in *Heat Transfer in Fire and Combustion Systems-1993*, ASME-HTD. Vol. 250, pp. 145-154; Presented at the ASME National Heat Transfer Conference, Atlanta, GA, August 1993.

2: S. Manickavasagam and M. P. Mengüç, "Effective Optical Properties of Pulverized Coal Particles Determined from FT-IR Spectrometer Experiments, *Energy and Fuel*, 1993 (in press). (Also presented at the BYU NSF Advanced Combustion Engineering Research Center Annual Meeting, Park City, Utah, March 1993.)

3: M. P. Mengüç and S. Manickavasagam, "Effective Optical Properties of Pulverized Coal/Char Particles". Presented at the NSF Workshop titled *Radiative Transfer in*

Highly Coupled Physical Systems. University of Texas. Austin. Texas. October. 1993. (Joint Workshop between the U.S., Russia and Belorussia researchers.

The third paper is now being extended for publication in archival literature.

Contents

1 INTRODUCTION

A detailed understanding of pulverized-coal combustion process is crucial to developing more efficient and cost-effective combustion chambers and furnaces that use coal as the primary source of energy. Several complicated phenomena occur simultaneously in pulverized-coal flames. and radiation heat transfer is only one of them. However. the contribution of radiation to total heat transfer can be as high as 90% at large-scale pulverized-coal fired furnaces. Because of this. modeling of radiation heat transfer requires special consideration.

In predicting the radiative heat flux distribution in combustion systems, three important problems must be considered simultaneously: (i) mathematical formulation and solution of the radiative transfer equation (RTE). (ii) modeling of spectrally banded radiation from the combustion gases. and (iii) modeling of continuum radiation from the particles such as pulverized coal. char. fly-ash. and soot in the combustion products. The accuracy of the solution to the RTE depends on the accuracy of the radiative properties of the medium used in the analysis.

Mathematical models for the radiative properties of combustion gases, such as water vapor and carbon dioxide, are well established. Particle radiative properties, i.e. for pulverized coal. fly-ash. and soot. are more critical than those of combustion gases, because particles absorb. emit and scatter radiation within the entire wavelength spectrum, while gases contribute only in certain spectral bands. State-of-the-art reviews of the radiative property data of particles have been given by Viskanta and Mengüç (1987), Sarofim (1988), Blokh (1988). and Mengüç and Webb (1993). It is sufficient to say that there is no agreement between different researchers on the complex index of refraction of coal/char and soot particles; although. for fly-ash particles the available data is quite reliable (Goodwin. 1986).

Even if there were agreement on the complex index of refraction data of coals, it does not necessarily mean that their radiative properties can be determined accurately from the theory. In a combustion environment, it is very difficult to identify the coal/char particles with a single. unique shape, as they devolatilize and pyrolyze. These particles are inhomogeneous because of varying material properties and their porous nature. Also, their properties are functions of temperature and wavelength. Nevertheless. the assumption of spherical shape for combustion generated particles is widely employed. because the theory for spherical particles, i.e. the Lorenz-Mie theory, is readily available. This oversimplification, however, may yield large errors if the interaction of radiative heat transfer and combustion is to be treated in detail. As pointed out by Wiscombe and Mugnai (1986), there are significant differences in the radiative properties of irregular shaped particles when compared to the Lorenz-Mie theory calculations.

Probably the most important parameter which significantly affects the radiative transfer predictions is the particle concentration distribution. It has been shown first by Mengüç and Viskanta (1987) that if particle concentration distributions in a flame or combustion chamber are not known accurately, one cannot model the physics of the problem correctly. This is the case even if the radiative transfer equation is solved exactly and most accurate and up-to-date optical properties of particles are used. This means that, without having this information, one cannot study radiation-chemical kinetics interactions and determine the influence of radiation on heat loss from the flames. This information is critical in many practical systems, including the flames in large scale pulverized-coal fired furnaces and in fires.

Ideally, we should be able to predict these volume fractions from theory if we have a good grasp of the coal combustion mechanism. Only if we can determine the contribution of char, fly-ash and soot particles on local radiative balance, we can study micro-scale interactions, such as the effect of radiation on coal combustion. The experiments performed to obtain global flame properties, such as emission and absorption, would not help us to achieve these objectives. In the past, limited number of studies have been conducted to determine the effective global properties of coal flames. Although these studies are useful for immediate practical applications, they cannot be used for more detailed understanding of the interaction of radiation transfer and coal combustion.

Realize that the nature and the amount of contribution of char, fly-ash and soot particles to the radiative heat losses in flames are quite different. This is mainly because of differences in particle (*i*) size and shape; (*ii*) optical properties; and (*iii*) volume fraction distributions. In order to account for radiative heat transfer accurately, we need to know these particle properties accurately. On the other hand, the volume fractions of char, fly-ash and soot are not independent, but related to each other as well as to the combustion characteristics of the system.

The objective of our research effort can be summarized as: a) obtain the effective radiative properties of pulverized coal/char, and soot particles, and b) determine the concentration distribution of char, fly-ash and soot particles in coal laden flames as a function of different flame conditions.

To this extent, during the first year several sub-problems have been studied, which are briefly discussed in the next section.

2 RESEARCH ACCOMPLISHMENTS

In this section, we will briefly discuss different research tasks accomplished. The details of these studies, as discussed in our recent papers or in the form of preliminary internal reports are appended to the end of this report.

2.1 Effective Properties of Coal and Char Particles

In order to separate the coal-char concentration distribution from that of soot and fly-ash, and to investigate the evaluation of size distribution of these particles, we should identify these particles in flames using light absorption/scattering techniques. This requires that we should have an accurate knowledge of absorption/scattering characteristics of them. These properties are functions of particle size, shape, and complex index of refraction. Coal/char particles are quite irregular in shape and inhomogeneous in nature. Their refractive index is a function of particle material properties, which may not be standardized even for a specific coal.

Given this, the most reasonable approach is to determine the absorption and scattering characteristics of coal/char particles directly from experiments. Such an approach will give us all the required engineering properties, without being overwhelmed due to particle shape and material inhomogeneities. This task can be accomplished by exposing a cloud of coal and char particles to incident light, measuring the attenuation and angular scattering patterns, and after that reducing the data following an inverse radiation analysis to fundamental absorption and scattering cross-sections. This information can be obtained as a function of particle size, coal type, medium temperature, etc., and later can be used to interpret the actual flame data.

These effective radiative properties can be reported more conveniently in the form of effective complex index of refraction data. Here, it is assumed that irregular-shaped and inhomogeneous cloud of particles absorb and scatter in a same manner as a cloud of "equivalent" homogeneous spheres (see Figure 1). For this purpose, we use an inverse optimization scheme based on the Lorenz-Mie theory and find a set of refractive index data which yield the absorption and scattering efficiency factors determined from the experiments. The only other parameter required for this procedure is the effective surface areas of particles, which are measured independently using, e.g., electron microscope pictures of the particles.

We have attempted to determine the effective properties of different coal and char particles using *in situ* and *ex situ* diagnostic techniques. In the former approach, a CO_2-laser nephelometer was employed, and effective refractive index data were obtained at the wavelength of λ=10.6 μm. The experiments were performed using a laboratory-scale ethylene flame with suspended coal particles. The measurements were carried out at different flame heights, and the data reduction scheme was primarily based on scattering phase function coefficients of the particles, as shown in Figure 2. The details of this procedure are discussed in a recent paper, which is given in Appendix A.

The approach discussed above is very effective; however, because of the limited laser wavelengths which can be used in the experiments, it cannot be carried out over the entire wavelength spectrum. We also carried out a series of *ex situ* FT-IR spectrometer

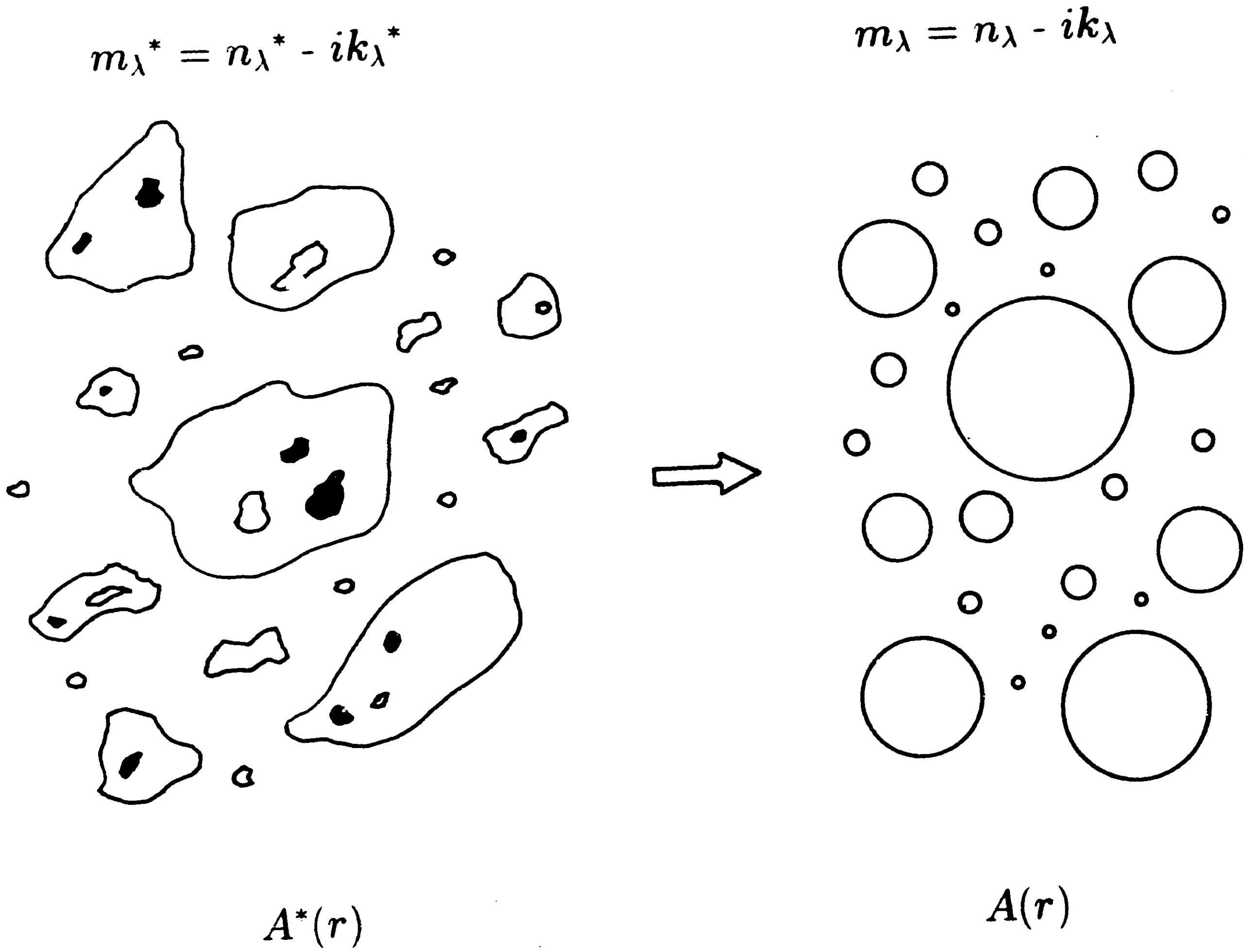

Figure 1: "Equivalent sphere" model used in determining the effective complex index of refraction ($m = n - ik$) data for coal and char particles.

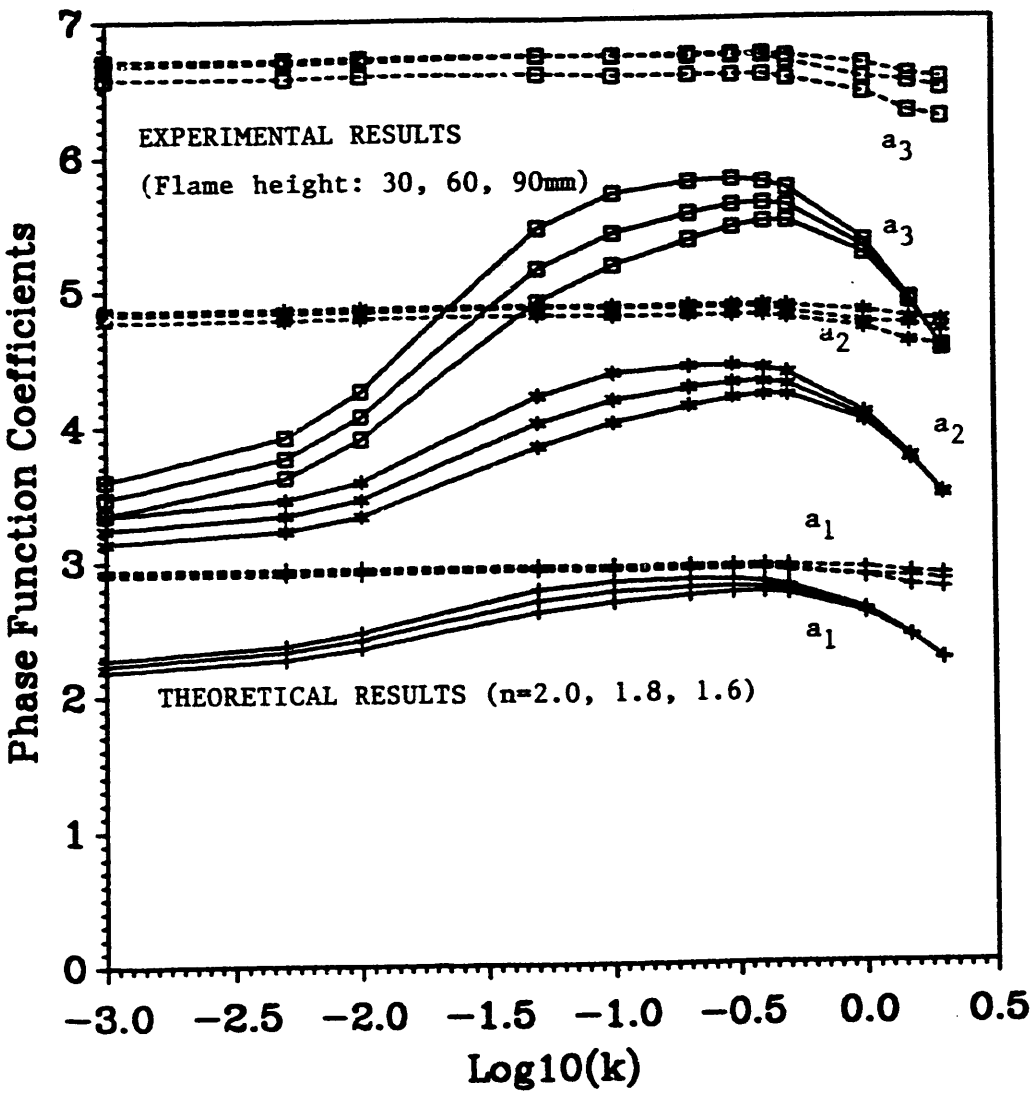

Figure 2: Effective phase function coefficient of coal particles vs. the imaginary part of the complex index of refraction $m = n - ik$. The experimental results (dashed lines) are for different flame heights of 30, 60, 90 mm, in descending order. The theoretical results (solid lines) are for n of 1.6, 1.8, and 2.0 (in ascending order).

experiments. In these studies, the particles were suspended in a KBr matrix, and their transmission and near forward scattering characteristics were measured over the wavelength spectrum of 2 to 22 μm. Following a detailed inverse radiation analysis including anisotropic scattering by polydisperse particles, effective refractive index data for "equivalent" spherical coal particles were obtained.

In Figure 3, the Blind Canyon spectral refractive index data obtained from FT-IR spectrometer experiments were compared against the data determined using CO_2-laser nephelometer at $\lambda=10.6$ μm. The range of FT-IR data show all possible uncertainties related to particle properties as well as experimental parameters. Once these parameters are established, the scatter of data is much less, even for the experiments conducted six month apart. The agreement between these two sets of results is very encouraging.

The procedure for the FT-IR spectrometer experiments is outlined in a recent paper, which will appear in *Energy and Fuels*. A copy of this work is given in Appendix B.

More recently, we have expanded this study to char particles. After preparing char at 400 and 600°C within an inert atmosphere of Argon gas, we followed the same procedure discussed above to determine char refractive index. The preliminary results of this worked were presented at a recent NSF workshop, and the paper was given in Appendix C. We continue this study and determine char radiative properties as a function of several different coal types and temperatures.

2.2 Multilayer Sphere Model

The radiative properties of particles can be calculated rigorously from the Lorenz-Mie theory if they are spherical in shape and homogeneous in nature (Bohren and Huffman, 1983). The theory, which was developed independently by Lorenz and Mie, gives a closed-form solution to the Maxwell equations for a planar electromagnetic wave incident on a spherical homogeneous particle if the complex index of refraction and the diameter of the particle are known.

The assumption of a spherical, homogeneous shape for combustion generated particles is widely used even for particles and droplets neither spherical nor homogeneous. This approximation is preferred because determining the radiative properties of a cloud of arbitrary-shaped or inhomogeneous particles is computationally difficult. However, in order to investigate the physics of coal combustion, it is important to study more than just the average properties.

To this extent, a computer program has been developed to study absorption and scattering by radially nonhomogeneous spherical particles. This algorithm is based on the formulation given by Mackowski, Altenkirch, and Mengüç (1990) and models the interaction

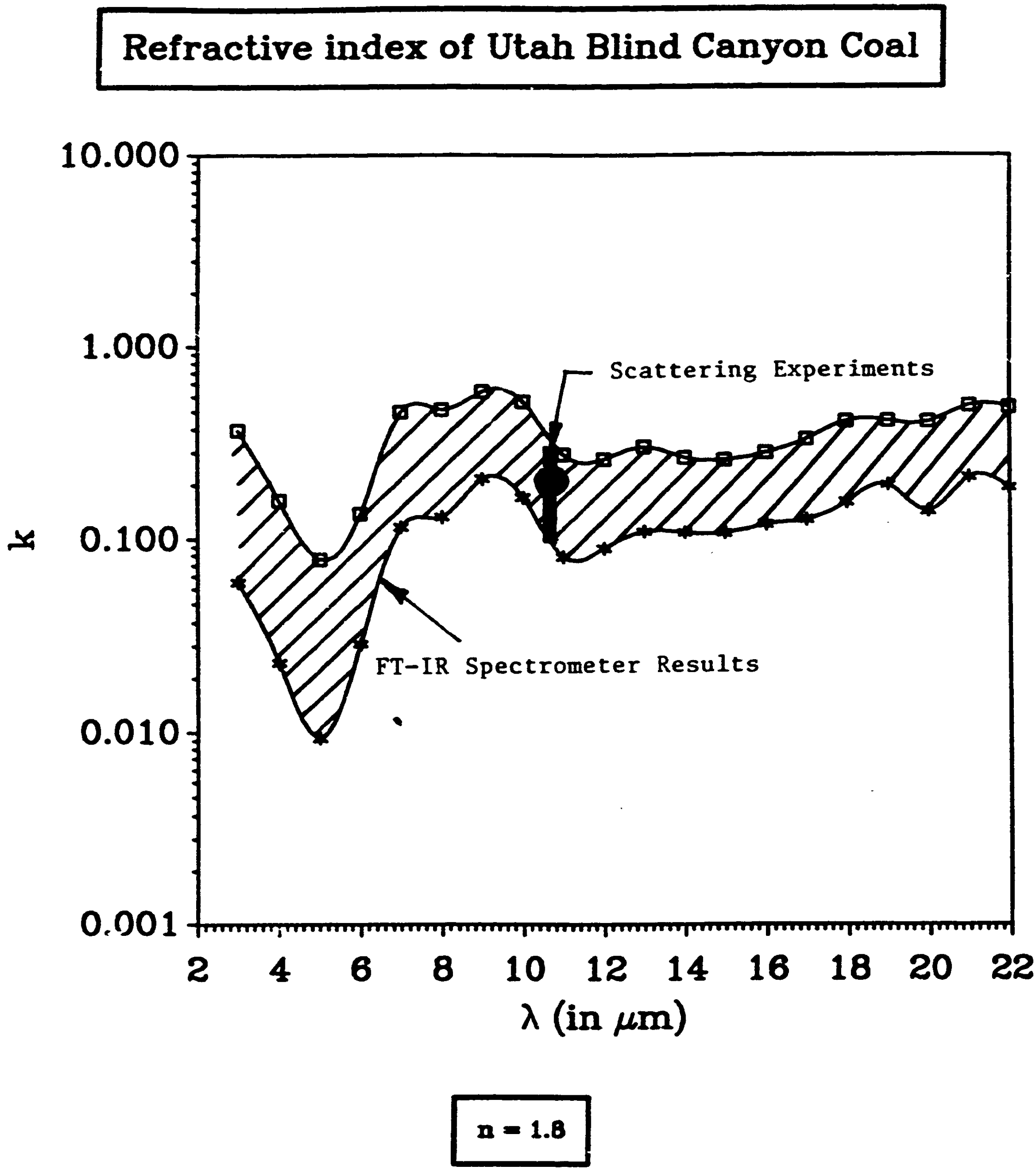

Figure 3: The spectral variation of the imaginary part of the complex index of refraction of Blind Canyon coal, as determined from FT-IR spectrometer experiments. The results obtained from scattering experiments at $\lambda = 10.6\ \mu m$. are also depicted

of a planar electromagnetic wave with a stratified spherical particle. [1]

Char and coal particles are inhomogeneous. Therefore, when we determine their effe radiativ and optical properties, the results correspond to that of a mixture of porous and ash particulates. Ash optical properties are relatively well known (Goodwin, 1 Given that, a more precise information about char properties can be determined usin inhomogeneous sphere model in the data reduction scheme discussed above.

Note that if we have a better knowledge of char optical properties, we can separate and ash concentration distributions from each other after char fragmentation. Also d the pyrolysis, coal/char particles are surrounded by a soot cloud. Such a multilayer m will allow us to determine these complex systems more accurately in the experiments.

The details of the model developed and some preliminary results are outlined in pendix D.

2.3 Soot Formation Model

Without knowing exactly how much soot is produced during the combustion of coal part it is not possible to separate the coal, ash, char or soot attenuation and their rel participation to the radiative transfer. Surprisingly, there is virtually no study in literature which concentrates on soot formation in coal combustion. Given the compl of this problem, we attempted to develop a simple, but physically acceptable mod predict soot formation. This model is applicable to diffusion flames, and the prelimi results are given in Appendix E.

2.4 Soot Radiative Properties

Initial soot particles are small (20-40 *nm* in diameter) and homogeneous spheres. I ever, after their formation they coagulate and eventually form large clusters (or, agglomerates). The radiative properties of these clusters are distinctively different than that of small spheres, and unless their shapes are modeled accurately, their participation to radiative transfer will not be accurate.

So far, we have been using a discrete dipole approximation to determine soot agglom radiative properties. Although this approach yields accurate results, it is computatio very time consuming. Instead, we have developed a new computer code, which is very satile and fast. This computer code is based on the Volume Integral Equation Formul (VIEF) and the method of moments developed by Iskander et al. (1989).

[1] Note that the computer program for this algorithm was written in modified form by another st Ms. Deepti Bhanti, and later used by Ms. Erin Rapela, a University Coal Research Intern, durir Summer of 1993. Neither of these students were financially supported by this project.

In the discrete dipole approximation, the particle is assumed to be composed of a number of small cubical cells and the dipoles are placed at the center and the corner of the cubes. Once the location of dipoles are determined, their interaction with external electromagnetic field as well as with the neighbouring dipoles are formulated. This formulation results in a set of linear algebraic equations, which are solved using standard procedures available in the literature to obtain the resultant field at each dipole. The scattering, absorption and extinction efficiencies are then determined using these fields. The VIEF is also similar in nature. The agglomerate is divided into a number of cubical cells and inside each cell the field is assumed uniform. Then the control volume approach is employed to reduce the governing equations to a set of linear algebraic equations. While deriving these equations the interaction between different cubes are also considered.

In a recent review reported by Ku and Shim (1992), the VIEF model is shown to be the best of different models available, in terms of accuracy and computing efficiency,although it is less rigorous than the discrete dipole approximation. However, given the uncertainity about soot agglomerate shape and optical properties, the error involved in the calculations (in the order of 20%) would not have a significant affect on the results.

This work is still in progress. We expect to finish a paper on this study within the next six months.

3 EXPERIMENTS

In this section, we will briefly list the experimental milestones. The details of the experimental systems and procedures will be detailed in forecoming papers. During the first year:

- The Nd:YAG laser was installed and optically aligned to yield a circular beam of diameter 3 *mm*. As it is, it can be used at four different wavelengths of 266, 355, 532, and 1064 nm. Also, it has a double-pulse option, which will allow us to perform detailed velocity measurements.

- A Raman shifter was designed and manufactured, which is the product of a collobation with Dr. V. Majidi of the Chemistry Department at the University of Kentucky. Hydrogen gas used in the Raman shifter is excited with the Nd:Yag laser at the wavelength of 532 nm. This addition provides the capability of several additional wavelengths beyond the four principal wavelengths of the Nd:Yag-laser. Using the Raman shifter, we will be making transmission measurements of the flame at near-infrared wavelengths (up to about 1600 nm).

- The burner was set up to produce diffusion flame using either methane or ethylene as fuel and air as the oxidizer.

- In order to reduce the experimental errors while recording scattering tomography measurements. the fuel tube was modified to yield a larger diameter flame.

- A new fluidized bed was designed and manufactured. It is going to be installed and tested within a month.

- A plexiglass shield was designed and manufactured to reduce any external draft which may affect the flame and the combustion conditions.

- A new version of LABTECH was installed on the lab computers for more efficient and faster data acquisition.

- A furnace was set up to prepare samples of char at different temperatures under an inert atmosphere. The difference in transmission characteristics of these samples would then be studied by obtaining transmission spectra using an FT-IR spectrometer.

4 FUTURE WORK

During the next year, we will perform transmission and scattering experiments at different harmonics of the Nd:YAG laser as well as at different wavelengths from the "Raman shifter". Experiments will be conducted using first ethylene diffusion flame and soot radiative and optical properties will be studied. After that the coal experiments will be performed. In all these experiments, the objective will be to identify the different particle concentration distributions along the flame for different operating conditions. On the other hand, we will continue using char particles in *ex situ* experiments to determine their complex index of refraction.

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