Attenuation of Infrared Radiation by Diesel Fuel Generated Particle and Droplet Aerosols

1985

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ATTENUATION OF INFRARED RADIATION BY DIESEL FUEL GENERATED PARTICLE AND DROPLET AEROSOLS

BY

SOODABEH KARIMI
B.S., University of Central Florida, 1983

RESEARCH REPORT

Submitted in partial fulfillment of the requirements for the Master of Science degree in Industrial Chemistry in the Graduate Studies Program of the College of Arts and Sciences University of Central Florida
Orlando, Florida

Summer Term
1985
ABSTRACT

The object of this project was to explore the absorbance and scattering properties of carbon particle smoke in the infrared and visible regions of the spectrum. Laboratory scale apparatus were developed to produce smoke in the form of carbon particles, droplet aerosols and combinations of the two. These smokes were made from diesel fuel and fog oil.
ACKNOWLEDGEMENTS

I would like to thank the faculty, staff, and my friends at the Department of Chemistry, University of Central Florida, for giving me the support I needed to complete my graduate work. I am greatly indebted to Dr. Chris Clausen for all the understanding, patience, and support he has given me. Without his extra time and dedication, and encouragement, I would not have been able to achieve my goals.

I am also grateful to Dr. Graeme Baker, Dr. George Hertel, Dr. Guy Mattson, and Mrs. Claire McClure for their time and effort. I would also like to extend my gratitude to Mr. Paul Morgan of the Engineering Technology Incorporated for his support which enabled me to complete this work.

I would especially like to express my deepest appreciation to my husband Tim, my parents, and my family for their love and patience.
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INTRODUCTION

BACKGROUND

Light can be scattered if a particle of the right size, that is, of a diameter that approximates the wavelength of the light, is placed in its path.

The fact that a material absorbs radiation strongly in one spectral region does not require it to absorb strongly or to absorb at all in another region. Consequently, although most carbons are "black" in the visible region, i.e. absorb and/or scatter radiation so strongly that the thinnest practical layers are opaque, it may be possible that such a black material has some transparency in the IR region. Thus, if the degree of transparency of a sample is not great enough, (the absorption of a thin layer is still too high) the transparency can be increased by decreasing the thickness of the layer so that IR transmission/absorption (T/A) spectroscopy becomes feasible. T/A measurements have proved to be useful only for materials such as coals and chars, i.e. materials which have not been too strongly heated. Materials which have been subjected to high temperatures so that the carbonization process has progressed to a substantial extent are "blacker" in the IR and present greater obscuration of the IR beam. The reason why the T/A characteristics of the coal and char samples change is because they contain molecular solids.¹

Molecular solids having condensed aromatic structures are semiconductors whose energy gap decreases with increasing molecular size.
When a molecular crystal is heated to progressively higher temperatures, decomposition occurs and aromatic domains develop and grow; short range order increases and the energy gap decreases progressively. After heating at relatively low temperatures, partially decomposed organic materials visually appear black, i.e. there is a complete band of absorption (due to absorption and/or scattering) through the visible region, terminating in the near-IR. As the carbonization temperature is increased, the limit of this band moves progressively into the IR region; this progressive "blackening" is shown in Fig. 1.2

The curves schematically represent the low-frequency portions of the absorption bands formed after carbonization. The data points are the midpoints of transparency taken from Kmetko's data for the carbonization of a cellophane film about 20 microns thick.2 Carbonization temperatures and estimates of the band gap are shown above the data points. From these and similar data it is apparent that the absorption, which is electronic in origin, moves rapidly into the IR range. The narrowing band gap results in extensive IR absorption for the chars or raw cokes heated in the 500-700°C range. At the higher temperatures required to form calcined cokes or "carbons," the IR absorption is even more extensive.

For IR radiation of 1000 cm⁻¹, which is 10 µm equal to 0.12 eV absorption is strong for chars and total for carbons. Effectively, even very thin layers of carbons will be opaque to IR radiation of energies greater than about 0.2 eV.1 Fig. II3 shows the range for
Figure I. Schematic representation of absorption by carbons.

Figure II. Light spectrum.
infrared and visible light. The absorbance increase with increasing wave number is attributed to the variation of the intrinsic absorptivity of the carbon black with the wavelength. Extinction due to scattering is expected to be small because the aggregate size of the carbon black is small compared to the wavelength of infrared radiation.  

MECHANISM OF CARBONIZATION OF HYDROCARBONS

It is clear that carbonization is an aromatic growth and polymerization process. In a general sense, one can envision carbonization by the scheme shown in Fig. III in which a small aromatic structure is polymerized to an aromatic polymer, which ultimately achieves the three-dimensional order of graphite.

Aromatics are the key building blocks for carbon, so that non-aromatic structures are first aromatized before undergoing the carbonization process. For example, the aliphatic polymer polyvinyl chloride thermally converts to a pitch containing polycyclic aromatic structures, prior to the formation of carbon. The overall process of carbonization is exceedingly complex. However, the following processes which represent some of the major reactions involved in the pyrolysis of aromatic hydrocarbons can be considered individually.

1. C–H, C–C bond cleavage to form reactive free radicals.
2. Molecular rearrangement.
3. Thermal polymerization.
4. Aromatic condensation.
5. Elimination of side chains.
Figure III. General reaction scheme for carbonization.
Although all of these processes can occur in parallel during carbonization, they can be considered separately from a mechanistic viewpoint.

The initial thermal reaction in the carbonization of an aromatic hydrocarbon is only poorly understood. It is believed to involve the formation of a free radical intermediate. There are two types of radicals that can be formed by bond cleavage in the aromatic molecule. The first is a $\sigma$ radical produced by breaking an aromatic carbon-hydrogen bond. This reaction is a high energy process since the bond dissociation energy is on the order of 100 Kcal/mole. The $\sigma$ radical intermediate is very unstable and the free electron is localized. For example, the naphthyl radical has been detected by ESR only when frozen in a solid matrix at 77 K. The second type of radical is an aromatic $\pi$ radical which is considerably more stable. Much less energy (approximately 77 Kcal/mole) is needed to break the methyl carbon-hydrogen bond in toluene. The unpaired electron is resonance stabilized and simple $\pi$ radicals such as the benzyl radical can be detected by ESR at room temperature.

Stein has recently used principles of thermochemical analysis to predict the initial reaction pathways in the pyrolysis of polynuclear aromatic hydrocarbons. The addition polymerization of anthracene was proposed to proceed by the reaction shown in Fig. IV. The $\pi$ radical could be generated by a small amount of the unstable anthryl $\sigma$ radical. Theoretical studies such as these coupled with recent experimental breakthroughs in observing unstable radicals could greatly clarify the initial reactions of carbonization.
Figure IV. Initial reactions in the pyrolysis of anthracene.

Figure V. Thermal polymerization of naphthalene.
The reacting intermediate, once formed, can undergo direct polymerization as in the formation of naphthalene polymer from naphthalene shown in Fig. V. These initial polymerization reactions involve the loss of hydrogen which can often be accomplished through internal hydrogen transfer. The importance of H-transfer in pyrolysis is apparent as shown in Fig. VI which lists the major condensable volatile materials identified during the pyrolysis of several polynuclear aromatic hydrocarbons. These products all consist of hydrogenated derivatives of the original compound with hydrogen added at the most reactive position in the molecule.

A very important step in the early stages of carbonization is that of thermal rearrangement. It is this reaction that often makes it difficult to relate the starting structure to the subsequent course of graphitization. Fig. VII presents several instances of thermal rearrangement which have been documented in our studies. As shown in the examples for acenaphthylene and bifluorene, this reaction can transform unstable five-membered rings into more stable six-membered ring systems without the loss of carbon atoms. The last example, methylene-phenanthrene illustrates a similar type rearrangement which involves the loss of carbon atoms.

Either the starting molecule or a rearranged entity serves as the building block in carbonization. One of the factors that makes carbonization so complex is the presence of so many polymerization sites in an aromatic molecule. For example, 11 reaction products are possible from the simple dimerization of anthracene. As the reaction progresses, the number of possible isomeric structures increases rapidly.
Starting Material

Reaction Product

Volatile

\[ \text{Figure VI. Hydrogenated reaction products from the pyrolysis of aromatic hydrocarbons.} \]

\[ \text{Figure VII. Thermal rearrangement reactions in pyrolysis.} \]
The site in the aromatic ring at which polymerization should predominantly occur can usually be predicted. Various reactivity parameters can be used for this purpose including free valences, unpaired spin densities, localization energies, and thermochemical kinetic analysis. Steric effects are also important in the polymerization process and can override reactivity factors.

As shown in Fig. VIII the polymerization process for aromatic hydrocarbons can occur in two stages giving rise to either noncondensed polymers, or condensed polymers. For naphthalene, the loss of two hydrogen atoms between two reacting molecules leads to polymers in which the units are linked by single bonds. An additional loss of two hydrogen atoms produces a fully condensed polymer. Although the condensed and noncondensed polymers have virtually the same molecular weights, they vary considerably in structure and properties. The noncondensed polymers are nonplanar and their reactivities and ionization potentials change very slowly with increasing polymerization. The condensed polymers are fully planar and show marked changes in reactivity and ionization potential for increasing size. The relative role of these two processes is critical in carbonization.

The thermal polymerization pathways were determined for a number of aromatic hydrocarbons. Fig. IX illustrates the initial reaction products that have been identified in the pyrolysis of anthracene. A number of noncondensed dimers are formed. However, only certain of these structures have the right steric conformation to undergo an addition dehydrogenation reaction to give a fully condensed molecule.
Figure VIII. Polymerization-condensation process in carbonization.
Figure IX. Reaction products from the pyrolysis of anthracene.
containing only six-membered rings. Polymerization involving the most reactive 9-position in the anthracene ring does achieve this result.

Similar data for the pyrolysis of naphthalene are shown in Fig. X. Polymerization at the most reactive 1-position leads to naphthalene polymers which can form fully condensed polymers composed of only six-membered rings, while polymerization utilizing the less reactive 2-position can inhibit condensation.

It has been shown that naphthalene and anthracene-derived pitches are complex mixtures of polymers containing from 2 to 10 units of the starting materials. These polymers are only partially condensed and structures representing the average composition of the pitches are shown in Fig. XI.

Lewis and Singer have used the reaction scheme in Fig. XII to show how odd-alternate radicals are involved in the polymerization condensation processes in carbonization. As illustrated for naphthalene a noncondensed polymer (III) is formed by rapid polymerization. This polymer contains 3 noncondensed naphthalene units and a total of 30 carbon atoms. The loss of a single hydrogen atom from the polymer leads to a free radical (IV) which contains 30 carbon atoms with a single sp3 tetrahedral carbon. The total aromatic \( \Pi \) system contains 29 carbon atoms and the unpaired electron is stabilized by a resonance delocalization as shown. The loss of an additional hydrogen would create a fully condensed molecule, but would not result in a substantial increase in resonance stabilization.

A further complication of the carbonization process is that the eventual polymerization to carbon occurs in two dimensions. The key
Figure X. Reaction products from the pyrolysis of naphthalene.

Figure XI. Average structures of naphthalene and anthracene-derived pitches.
Figure XII. Formation of stable odd-alternate free radical structures in carbonization.
to this process is how well the aromatic building blocks polymerize
to develop a perfect graphitic network. Fig. XIII\textsuperscript{5} demonstrates how
the molecule zethrene, identified from pyrolysis of acenaphthylene
has the perfect shape and reactivity to polymerize in two dimensions
to a planar graphitic-like structure without vacancies. In contrast,
Fig. XIV\textsuperscript{5} shows that the poorly graphitizing compound tetrabenzoz-
naphthalene, which has a nonplanar structure, cannot polymerize without
creating vacancies.\textsuperscript{5}

COMPONENTS OF CARBON BLACK AND SOOT

1. Particulate carbon and carbonaceous material.

The solid carbon and carbonaceous material in carbon blacks and
soots are generally particulate in nature; i.e. consisting of separable
etities ranging from about 10 \textmu m to 1 mm in size. This is because
as they were formed by deposition from the gaseous phase, or by
carbonization, they had to form entities small enough to be swept
along by a stream of gas. Particulate carbon formed in the gaseous
phase, whether by incomplete combustion or by thermal decomposition
of hydrocarbons is of colloidal size (less than about 1 \mu m) and of
unique microstructure and morphology.\textsuperscript{8}

2. Inorganic matter.

This includes inorganic oxides and salts, fragments of metal, and
adsorbed liquids and gases, especially water, sulfuric acid, and
nitrogen oxides.

3. Insoluble carbonaceous matter.

Resins may be present as a coating, binder, or as separate entities.
Figure XIII. Two-dimensional polymerization scheme for zethrene.

Figure XIV. Two-dimensional polymerization scheme for tetrabenzo-naphthalene.
Incompletely carbonized fragments of solid fuel, or macroscopic dimensions, may also be present.

4. Soluble organic fraction (SOF).

This includes several classes of compounds, especially polynuclear aromatics (PNA). SOF removed by extraction with a particular solvent such as toluene is referred to as (toluene) extract.  

PRESENT STUDY

At present studies have been done on the ability of condensate of a vaporized hydrocarbon to obscure (i.e. strongly absorb) in the visible spectrum. The possibility exists, however, that by using a product that contains carbon particles one may be able to produce obscuration in the infrared (IR) spectrum as well.

It is possible that the desired carbon particles might be obtained as the product of a combustion process. The task then is to create a combustion process that produces carbon particles or chains with the desired diameters ratios. The task implies a mechanism that strips hydrogen from the hydrocarbon fuel by a modified or partially completed combustion process. Variables available for control of the combustion process are many and some include the choice of fuel, pretreatment of fuel, fuel/oxygen ratio, oxygen/"air" ratio, residence time, and process temperature.

The intent of this research was to develop and test a laboratory scale apparatus for carbon particle generation, and to conduct laboratory experiments aimed at obtaining concentration measurements, transmittance measurements, and extinction coefficient determinations.
In order to produce carbon particle smoke suited to infrared obscuration, two generators were assembled - one a static model, the other a continuous one. The developmental efforts resulted in an experimental apparatus from which the extinction spectra of carbon particle smoke can be obtained while allowing selection of fuel, fuel/oxygen ratio, oxygen/"air" ratio, residence time, and process temperature. The efforts described herein proceed through initial data generation but include no parametric or optimization efforts. These data, however, did provide a base for initialization of apparatus for future studies. Data obtained included qualitative observations, transmittance, and concentration measurements; from those, extinction coefficients were derived. Cursory examinations were also made of yield, settling rates and figures of merit.
APPARATUS

Static Smoke Generator

A simple cell with a variable temperature element (Fig. XV), was designed and built to allow the generation and study of infrared obscuring atmospheres. It was used to:

1) assess the suitability of available instrumentation for the studies of interest;
2) accumulate background experience;
3) determine the IR absorption characteristics of No. 2 diesel fuel, and
4) generate preliminary data.

The cell was capable of generating a "smoke" from different fuels and fuel blends while varying the metal surfaces, temperatures, and gas atmospheres. Fig. XVI provides typical infrared spectra obtained with this cell and a Perkin-Elmer Model 1420 spectrometer and data station. The spectra shown are for the cell empty, the cell with a No. 2 diesel fuel droplet smoke, and for unheated diesel fuel. This set of data illustrates the inability of a simple diesel aerosol to provide significant obscuration in the infrared region. After some experience was obtained with the static cell a continuously operating laboratory system was built.

Dynamic Smoke Generator

The objective in developing the dynamic smoke generator (DSG) was to allow study of the infrared spectral characteristics of continuously
Figure XV. Static smoke generator.

Figure XVI. Typical infrared absorption obtained with the static cell.
generated smoke. The intent was to obtain a relative assessment of the IR absorption characteristics of aerosol/particle products produced under various generator conditions.

**Small Cell Version**

The laboratory system shown in Fig. XVII was the original configuration of the DSG. The apparatus employed a variable temperature reaction chamber that could produce vapor or that could be used in conjunction with oil, air, and diluent gas ratios to produce products of combustion processes. The apparatus generated a continuous "smoke" while the IR absorption characteristics were monitored under real time conditions. Initial tests proved the continuous generation concept valid but other considerations made modifications necessary. The small size of the cell and the closeness of the windows to the smoke stream resulted in condensation and particle settling on the windows, thus necessitating changes in the cell arrangement.

**Figure XVII.** The dynamic smoke generator.
Modified Cell Version

The modified cell DSG is shown in Figure XVIII. Modifications included enlarging the smoke chamber to a volume of 6.7 liters and adding a mechanical stirrer. A Nicolet Mx-S fourier transform infrared spectrometer (FTIR) replaced the Perkin-Elmer instrument used on the static cell. The substitution increased the beam path length to 18 cm and allowed a complete IR spectrum to be obtained in 10 seconds instead of several minutes as with the Perkin-Elmer spectrometer. IR transmission characteristics were used to determine occurrence of steady-state conditions in the cell. A typical spectrum is shown in Fig. XIX for a carbon particle smoke, and in Fig. XX for a fog oil droplet aerosol.

Figure XVIII. The modified cell dynamic smoke generator.
Figure XIX. Determination of steady-state conditions for a droplet aerosol.

Figure XX. Determination of steady-state conditions for a carbon particle smoke.
In addition to obtaining infrared absorption spectra, data were collected on smoke concentrations. Concentration samples were taken from two ports located in the sides of the cell at the same height as the FTIR beam. Samples were drawn from the chamber by a digital air sampler and concentrations measured gravimetrically by collecting the smoke particles on weighed mm MSA 77332 absolute fiber filter discs. Concentrations determined during steady-state conditions were used in combination with absorption data to calculate mass extinction coefficients.

**Large Chamber Version**

Two additional features were added to the DSG following the experimental program with modified cell. One feature allowed simultaneous production, then mixing, of droplet aerosols and particle smokes. The other addition replaced the modified cell with a one cubic meter chamber.

The DSG was designed, as shown in Fig. XXI, to produce an aerosol composed of both droplets and carbon particles. The impetus behind this configuration was to allow investigation of the degradation or synergistic effect on absorption that may develop between droplets and particles. It was further desired to define effects related to settling and/or evaporation rates of the droplet aerosols compared to the droplet/particle mixes. In preparation for these studies a larger collection chamber was desired to minimize wall effects that might be present in the 6.7 liter chamber.

A one cubic meter chamber was designed and built to be compatible with the FTIR instrumentation and the DSG smoke and aerosol generators.
Figure XXI. The dynamic smoke generator-droplet and particle mixing.
A 17.4 cm wide side port was extended from the main chamber and the FTIR beam was directed through windows in the side port.

**PROCEDURES**

The following steps were taken in experimentally determining the extinction coefficient for diesel fuel. The smoke chamber was cleaned using a vacuum cleaner. The windows were prepared for FTIR scanning using cardboard and Saran Wrap. The spectrum of the Saran Wrap window was stored in the BACKGROUND file of the FTIR. The effect of the Saran Wrap was thus cancelled during the scanning run. The discharge tubes of both systems were connected providing a single discharge to the chamber. Depending on the study, either system 1 (droplet producer) or system 2 (particulate producer) or both systems (for both droplet and particulate production) were used.

**Particulate Studies**

The nitrogen, air, and fuel needles were positioned inside the tube which was located in the oven. The thermocouple was put under the quartz tube at the same location as the fuel needle. The 20 cc syringe was filled with diesel fuel and placed on the syringe pump, which was then connected to the fuel needle. The nitrogen was turned on at this point to provide a flow of 0.775 l/min. An exhaust fan which was connected to the chamber to maintain steady state was then turned on. After the BACKGROUND scanning, a piece of cardboard was placed between the chamber and the window so that the window was not affected by the smoke between samplings. The oven and thermocouple were then turned on. After the temperature reached 960°C, the oxygen was turned on to provide
a flow of 2.05 l/min. The syringe pump was turned on and adjusted to a flow of 0.434 l/min. As soon as fuel ignition was observed a timer was turned on. (A CO₂ connection was placed in the chamber in case of any flames). The sampling proceeded as described under Sampling Procedure in this section.

Droplet Studies

The steps taken for the droplet system were as described above with the following exceptions. There was air flow in system 1; the nitrogen flow was 1.3 l/min; oven temperature was brought to 500°C; and the timer was turned on when the aerosol flow was observed exiting the tube. A heating coil was used to keep the discharge tube of system 1 at 150°C. In addition to nitrogen flow in system 1, the nitrogen flow in system 2 was also turned on, with a flow of 0.775 l/min. Air, oven, and fuel were all turned off in system 2.

Combined Particulate and Droplet Studies

The combined studies were done in the manner described above with both systems working together for the production of the mixture. The fuel flow in each system was reduced by half to get a flow of 0.22 ml/min for each system. The air flow in system 2 was also cut in half to give a flow of 1.1 l/min. The oven temperatures were 500°C for system 1 and 960°C for system 2.

Sampling Procedure

Two inline float samplers, each containing a Fixt-Flo air sampler filter were weighed before and after each sampling. One sampler was placed near the IR beam and samples were collected at a rate of 1.7
liters/min, using the vacuum line and a rotometer. The other sampler was placed near the main part of the chamber and samples were collected using another vacuum line, and the volume of the air samples was measured using a wet test meter.

Table 1

<table>
<thead>
<tr>
<th>Time (second)</th>
<th>Procedure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2900</td>
<td>Cardboards behind the windows were removed for scanning.</td>
</tr>
<tr>
<td>3010</td>
<td>Sampling was started.</td>
</tr>
<tr>
<td>3310</td>
<td>Scan.</td>
</tr>
<tr>
<td>3335</td>
<td>Cardboards were replaced.</td>
</tr>
<tr>
<td>3610</td>
<td>Sampling was stopped. Volume on the wet test meter was recorded.</td>
</tr>
<tr>
<td>3630</td>
<td>Everything was turned off except N₂ flow and the exhaust fan.</td>
</tr>
<tr>
<td>6800</td>
<td>Cardboards behind the windows were removed for scanning.</td>
</tr>
<tr>
<td>6910</td>
<td>Sampling was started using a new filter paper.</td>
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<tr>
<td>7210</td>
<td>Scan.</td>
</tr>
<tr>
<td>7235</td>
<td>Cardboards were replaced.</td>
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<tr>
<td>7510</td>
<td>Sampling was stopped. Volume on the wet test meter was recorded.</td>
</tr>
<tr>
<td>10700</td>
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</tr>
<tr>
<td>10810</td>
<td>Sampling was started using a new filter paper.</td>
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<tr>
<td>11110</td>
<td>Scan.</td>
</tr>
<tr>
<td>11135</td>
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<tr>
<td>11410</td>
<td>Sampling was stopped. Volume on the wet test meter was recorded.</td>
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<tr>
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</tr>
<tr>
<td>14710</td>
<td>Sampling was started using a new filter paper.</td>
</tr>
<tr>
<td>15010</td>
<td>Scan.</td>
</tr>
<tr>
<td>15035</td>
<td>Cardboards were replaced.</td>
</tr>
<tr>
<td>15310</td>
<td>Sampling was stopped. Volume on the wet test meter was recorded.</td>
</tr>
<tr>
<td>15330</td>
<td>Exhaust fan and N₂ flow(s) were turned off.</td>
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RESULTS AND DISCUSSION

The experimental program with the modified cell DSG was initially oriented toward establishing preliminary operational settings. Following these tests, the apparatus was used to generate droplet aerosols and particle smokes from both diesel fuel and fog oil. Extinction spectra were obtained on droplet, particles, and mixtures of the two.

Similar data were obtained on diesel fuel products in the one cubic meter chamber. Preliminary experiments were also conducted in that chamber to provide a cursory look at settling times and figures of merit.

Keep in mind that these data were acquired without any attempt at optimization. Initial settings for the carbon particle generator were maintained throughout.

Preliminary Tests

The modified cell DSG was used to establish settings for temperature, fog oil flow rate, and gas flow rates. These initial runs produced transmittance and extinction coefficient values as a function of carbon particle generator temperature. In addition, as the parameters were varied, the contents of the cell were observed in terms of color, density, and particle/filament presence. Results of experiments at a generator temperature of 715°C are shown in Table 2. Ranges of the independent variables that gave favorable results were identified and thus initial settings for the DSG were
Table 2
Initial experiments with the carbon particle generator at 715°C using fog oil.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Visual Observations ¹</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Oil ml/min</td>
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<tr>
<td>.090</td>
<td>.54</td>
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<tr>
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¹Observations: particle (carbon)-0 to 4, none to large number; smoke color-w=white, y=yellow, b=black; smoke density-l=low, m=medium, h=high; carbon fiber-n=none, s=some, m=many.
defined. Worthy of note was that fact that the gas used (air) did not require oxygen dilution with an inert gas ($N_2$).

Tests with the DSG established that stable carbon particle generation could be obtained from fog oil with a combustion zone temperature of $960^\circ C$ using a fuel to air ratio (mass basis) of 1:6.7. It was also found that digital air samplers did not provide sufficient sampling rates and they were replaced with a vacuum manifold. The volume of air sampled was measured with a wet test meter and the sample rate was monitored with a rotometer.

**Fog Oil Particle Smoke**

Extinction coefficients for a fog oil droplet aerosol were obtained using the modified cell DSG. The vaporization of the fog oil was conducted at $500^\circ C$ for comparison to a similar set of data contained in reference 9. A typical set of data obtained from these experiments is compared with that of the reference source in Fig. XXII. These experiments demonstrated that extinction coefficients from the DSG agree favorably with data obtained from larger static systems.

Extinction coefficient measurements were also performed on carbon particle smokes obtained from the partial combustion of fog oil. The carbon particle generator was operated at $960^\circ C$ and the fuel to air spectra are shown in Fig. XXIII. Comparison of the extinction spectra between DSG generated droplet aerosols and carbon particles is shown in Fig. XXIV. The superiority of carbon particle smoke over the aerosol formed by vapor condensation is readily apparent in the 8 to 20 micrometer region.
Figure XXII. Extinction spectra of fog oil droplet aerosol formed at 500°C.

Figure XXIII. Extinction spectra of fog oil carbon particles formed at 960°C.
Figure XXIV. Comparison of extinction spectra of fog oil droplets and particles.
Samples of carbon particles generated from fog oil at 960°C were examined by SEM. Micrographs of the particles are shown at magnifications of X3000 and X54000 in Fig. XXV. The micrographs show that the particles consist of small carbon spheres that have agglomerated to form fibers. The average diameter of the particles is approximately 0.15 micrometers with the agglomerated filaments reaching lengths of 10 micrometers.

**Diesel Fuel Particle Smoke**

After successfully demonstrating the feasibility of generating carbon particle smokes from fog oil, the feasibility of using No. 2 diesel fuel in the DSG was investigated.

Extinction spectra were obtained for diesel fuel droplet aerosols produced with the vapor generator operating at 500°C. Typical extinction spectra for several runs are shown in Fig. XXVI. Extinction spectra of diesel fuel carbon particle smokes generated under the same conditions as used for fog oil are shown in Fig. XXVII. The results obtained for these experiments showed carbon particle smokes from No. 2 diesel fuel as good or better than those obtained from fog oil. As a consequence, diesel fuel was used in all subsequent experiments.

A comparison of the extinction spectra of the diesel fuel carbon particle smoke and droplet aerosol is shown in Fig XXVIII. The comparison is similar to that obtained for fog oil and again demonstrates the increased obscuration capability of the particle smoke compared to the droplet aerosol in the far IR region.
Figure XXV. Micrographs of carbon particles formed from fog oil at 960°C.
Figure XXVI. Extinction spectra of diesel fuel aerosol formed at 500°C.

Figure XXVII. Extinction spectra of diesel fuel carbon particles formed at 960°C.
Estimates of the degree of conversion of diesel fuel to carbon particles were made. With the carbon particle generator at 960°C and the fuel to air ratio at 1:6.7, all of the generator efflux was passed through an absolute filter. From the measured mass of particles generated, the average yield of particles from the diesel feedstock was calculated to be approximately 10 percent. It is expected that higher yields would be obtained by optimizing generator conditions. Samples of particles generated from No. 2 diesel fuel at 960°C were examined by SEM. Micrographs of the particles are shown at X4000 and X60000 in Fig. XXIX. The micrographs show that the particles consist of small carbon spheres that have agglomerated to form fibers.
Figure XXIX. Micrographs of carbon particles formed from No. 2 diesel fuel at 960°C.
The average diameter of the particles is approximately 0.13 to 0.21 micrometers with the agglomerated filaments reaching lengths of 7.5 to 10 micrometers.

**Diesel fuel droplet/particle smoke**

The effect of mixing a droplet aerosol and a particle smoke was investigated in an attempt to determine synergistic interaction. For example, the droplets may coat the particles and diminish their effectiveness while on the other hand, the mixture could act to retard the evaporation of the droplets and slow the settling process.

For these initial experiments the vapor generator was maintained at 500°C and the carbon particle generator at 930°C. Condensation of the vapor into droplets occurred prior to mixing with the particle stream.

Preliminary extinction spectra are provided for three tests on a diesel fuel droplet/particle mixture in Fig. XXX. For these tests the diesel fuel flow to the particle generator was equal to that to the droplet generator. Extinction spectra for the droplet/particle mixture is compared to that for the droplet aerosol in Fig. XXXI and to the carbon particle smoke in Fig. XXXII. Samples of No. 2 diesel fuel droplet/particle mixture generated at 500°C and 960°C respectively were examined by SEM. Micrographs of this mixture are shown at X78000 and X20000 in Fig. XXXIII. The micrographs show that the mixture consists of small carbon spheres that have agglomerated to form fibers. The average diameter of the particles is approximately 0.15 micrometers with the agglomerated filaments reaching lengths of 7.5 to 10 micrometers.
Figure XXX. Extinction spectra of diesel fuel droplet/particle smoke.
3.0
2.0
1.0

Droplet/particle

0 4 8 12 16 20

WAVELENGTH, \(\mu m\)

Figure XXXI. Comparison of extinction spectra of diesel fuel droplet and droplet/particle smokes.

3.0
2.0
1.0

Droplet/particle

0 4 8 12 16 20

WAVELENGTH, \(\mu m\)

Figure XXXII. Comparison of extinction spectra of diesel fuel particle and droplet/particle smokes.
Figure XXXIII. Micrographs of diesel fuel droplet/particle smoke formed at 500°C and 960°C.
Studies in the one meter chamber

Following integration of the one cubic meter chamber with the DSG, a series of tests were conducted to validate measurements and to compare results with those from the modified cell.

Comparison with modified cell

A comparison of the extinction spectra obtained for droplet, particle and droplet/particle smokes in the one meter chamber and the smaller 6.7 liter cell is given in Figs. XXXIV, XXXV, and XXXVI. Agreement between the two was generally good.

Figure XXXIV. Comparison of test chambers for diesel fuel droplet aerosol formed at 500°C.
Figure XXXV. Comparison of test chambers for diesel fuel particle smoke formed at 960° C.

Figure XXXVI. Comparison of test chambers for mixed droplet/particle smokes.
Sampling probe locations

To determine whether uniform smoke and aerosol concentrations were present in the main chamber and near the FTIR beam (side port), concentration samples were obtained from each location. Extinction spectra for three smoke types are compared for the center chamber and the side port sample locations in Fig. XXXVII. The data show that good uniformity is obtained in the chamber.

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Figure XXXVII. Effect of concentration sampling probe location on extinction spectra.
Settling rate

A cursory look at the settling rate of carbon particulate smoke by comparison to the settling of diesel droplet aerosols and droplet/particle mixes is shown in Fig. XXXVIII. The smokes were generated by using a constant diesel fuel mass flow of 0.3645 grams per minute. In each test the one cubic meter chamber was charged until it reached a steady state (3000 seconds) at which time density measurements were begun. The test chamber was allowed to vent by natural convection during the buildup period prior to achieving steady-state conditions. Thus, the densities are not representative of the maximum yield of airborne particles, but rather represent steady-state yields. The maximum yields could be significantly higher because some of the airborne material exits the chamber during the 3000 second buildup period. The data point at 3000 seconds represents an average steady-state density for several samples. After this point was recorded, smoke production ceased and the system was allowed to settle without stirring.

Figure XXXVIII. Relative settling time for diesel fuel carbon particle and droplet smokes.
Another criteria used to judge the effectiveness of an obscuration system is the figure of merit. The figure of merit is equal to the product of the yield factor times the extinction coefficient. The yield factor itself is equal to the ratio of airborne mass to the total mass of material disseminated. Figures of merit for the three smoke systems at four different wavelengths are shown in Fig. XXXIX. The data exhibited that the particle and droplet/particle smokes are more effective obscuration systems and for longer periods of time than the droplet aerosol.

![Figure XXXIX. Relative figure of merit for diesel fuel carbon particle and droplet aerosols.](image-url)
Figure XXXIX. (continued) Relative figure of merit for diesel fuel carbon particle and droplet aerosols.
Figure XXXIX. (continued) Relative figure of merit for diesel fuel carbon particle and droplet aerosols.
CONCLUSIONS AND RECOMMENDATIONS

The object of this project was to explore the feasibility of carbon particle smoke that could provide obscuration in the infrared as well as the visible spectrum. Laboratory scale apparatus was developed to produce smoke from carbon particles, droplet aerosols, and combinations of the two. These smokes were made from No. 2 diesel fuel and fog oil.

Experimental results show that by the partial combustion of diesel fuel or fog oil, carbon particle smokes can be generated that outperform diesel fuel or fog oil vaporization/condensation droplet aerosols in the infrared spectral region. Figure XL shows extinction spectra in the 2 to 20 micrometer region for a diesel droplet aerosol, a carbon particle smoke and a combined droplet/carbon particle smoke. Each of the obscuration systems was produced in a one cubic meter chamber using equal amounts of diesel fuel.

Relative settling rates for carbon particle smokes and diesel droplet aerosols are shown for a densely loaded chamber in Fig. XLI. In these tests, the chamber was charged with identical amounts of diesel fuel product and was vented by natural convection during the buildup period. While the yield of airborne material is greater for the droplet aerosol, its rate of settling is also greater and eventually, the density of airborne material becomes the same for each of the systems. These studies suggest that carbon particle smokes,
Figure XL. Extinction spectra for diesel fuel carbon particle and droplet aerosols.
Figure XLI. Relative settling time for diesel fuel carbon particle and droplet smokes.
when used in combination with a droplet aerosol, might have a beneficial effect by slowing the settling and/or evaporation of the droplet aerosol. These data were obtained in a densely loaded, unvented chamber, and those effects on evaporation rate are not presently known.

Another criteria used to judge the effectiveness of these obscuration systems was the figure of merit. The figure of merit is defined as the product of the extinction coefficient and the yield factor where the yield factor is the ratio of airborne mass to the total mass of material disseminated. Comparison of the figures of merit at a wavelength of 12.5 micrometers is shown in Fig. XLII. These data and other presented herein show that the carbon particle and carbon particle-aerosol mixtures are more effective in the long infrared spectrum than the droplet aerosol alone.

At this point of study, optimization of the production of carbon particles with respect to either size (length to diameter ratio) or yield has not been attempted. Consequently, the infrared obscuration properties of diesel fuel carbon particles shown should be considered an embarkation point for further study, rather than an end result. However, it is reasonable to assume that such an effort would produce significant increase in overall effectiveness, and should be undertaken.
Figure XLVII. Relative figure of merit for diesel fuel carbon particle and droplet aerosols at 12.5 micrometers.
REFERENCES