THE TOTAL EMISSIVITIES OF LUMINOUS AND NON-LUMINOUS FLAMES

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Abstract - Total emissivities of CO₂-H₂O and CO₂-H₂O-soot mixtures arising in oil and gas combustion, $p_w/p_c = 1$ and 2 respectively, have been computed from the statistical band model and experimental spectral data for the gases and from the optical constants of soot using the Mie theory. For CO₂-H₂O mixtures the emissivity has been fitted by a one-clear three-gray gas model, suitable for use in the zone method of calculating radiative heat transfer, in the temperature range 1200-2400°K, accuracy 0.5 per cent for a 1000-fold range of $p_c L$, whereby

$$\varepsilon_g = \sum_{n=1}^{4} (b_{1,n} + b_{2,n} \cdot T) [1 - e^{-k_{g,n}(p_c + p_w)L}]$$

It is shown that the total emissivity of luminous CO₂-H₂O-soot mixtures can also be represented by a three-gray gas model with constant absorption coefficients $K_{m,n}$ where,

$$\varepsilon_m = \sum_{n=1}^3 a_{m,n} [1 - \mathrm{e}^{-K_{m,n}L}]$$

and the weighting coefficients $a_{m,n}$ are again linearly temperature dependent. At constant gas composition the $K_{m,n}$ are related to the soot concentration, c, by

$$K_{m,n} = \exp[q_{1,n} + q_{2,n} \cdot c]$$

so that the remaining coefficients, $a_{m,n}$, for luminous flame gases may be determined without recourse to trial and error.

NOMENCLATURE

	NOMENCLATURE		particle cloud $[(kg/m^3)^{-1}m^{-1}];$
$a_{g,n}$,	gray gas weighting coefficient	k_{λ} ,	specific absorption coefficient of a soot
	(gas mixture);		particle cloud $[(kg/m^3)^{-1}m^{-1}];$
$a_{g,m}$,	gray gas weighting coefficient	$K_{m,n}$,	gray gas fitting coefficient (gas-soot
	(gas-soot mixture);		mixture) $[m^{-1}];$
a_j ,	fine structure parameter of a spectral	<i>L</i> ,	path length [m];
	interval;	Р,	partial pressure [atm];
<i>A</i> ,	constant;	p_c ,	partial pressure of carbon dioxide [atm];
$b_{1,n}, b_{2,n},$	constants;	p_w ,	partial pressure of water vapour [atm];
b_c ,	mean spectral line half width for a gas	P_0 ,	reference pressure [1 atm];
	[cm];	P_T ,	total pressure [atm];
с,	soot concentration [kg/m ³];	$q_{1,n}, q_{2,n},$	constants;
$C_1, C_2,$	first and second Planck constants;	Τ,	temperature [°K];
d_j ,	mean line spacing in a spectral interval	T_{g} ,	gas temperature [°K];
	[cm];	T_0 ,	reference temperature [273°K];
$E_{\lambda,T}$ or E	ω, T , Planck distribution of the emissive	Х,	reduced optical path length (pLT_0/T_q)
	power of a black body;		[atm cm].
f(n, k),	function of soot real refractive index n		
	and absorption index k ;	Greek symb	ols
k _{g,n} ,	gray gas fitting coefficient $[atm^{-1}m^{-1}];$	α,	constant;
k_j ,	mean value of absorption coefficient in a	ε,	emissivity;
	spectral interval $[cm^{-1}atm^{-1}];$	ε_{g} ,	total emissivity of a real gas;
k _{s, n} ,	gray gas fitting coefficient for a soot	$\varepsilon_{g,n}$,	emissivity of gray gas n;

$\varepsilon(\omega)_i$,	average emissivity of the <i>i</i> th i.r. active
	component in the wavenumber interval
	$\Delta \omega$;
Е _т ,	total emissivity of a gas-soot mixture;
$\varepsilon_{m,n}$,	emissivity of gray gas n used in
	representing a gas-soot mixture;
$\varepsilon(\omega)_m,$	average emissivity of the gas-soot
	mixture in the wavenumber interval $\Delta \omega$;
ε_i ,	measured total emissivity of a real gas or
	gas-soot mixture;
λ,	radiation wavelength [µm];
ω,	wavenumber $[cm^{-1}];$
ρ ,	soot bulk density $[kg/m^3]$;
τ,	transmissivity.

1. INTRODUCTION

NOWADAYS industrial combustion chambers are developing in the direction of increased capacity and heat loading and their design requires well established means of predicting heat transfer and furnace performance. At the high temperatures of normal operation, radiation from the flame is usually the prevailing mode of heat transfer and much effort has been applied to developing methods of predicting radiative heat exchange.

The radiation from the flame and fully burnt combustion products of most conventional gas and oil fuels is mainly due to the vibration rotation spectra of carbon dioxide and water vapour and to the continuous spectra of suspended soot particles. Both gaseous components emit in significant bands of the i.r. as follows [1]:

 H_2O centred at 2.7 µm, 6.3 µm, 20 µm CO_2 centred at 2.7 µm, 4.3 µm, 15 µm.

In practical flames, the complexity of the radiative transfer problem is increased by the fact that banded and continuous emission from gaseous and particulate media are superimposed and gaseous emission bands can overlap. The object of this study is to provide convenient methods for specifying the emissivity of such composite media, to be presented either in the form of graphs of gas-soot mixture total emissivities or preferably in the form of the absorption and weighting coefficients for multiple gray gas models of the $\varepsilon_T - pL$ relationships of real gas and gas-soot mixtures. These are needed for engineering calculations by the zone method.

2. AIDS TO THE PREDICTION OF THERMAL EMISSION FROM FLAMES

Hottel and coworkers [2, 3] reduced and correlated much data and prepared total emissivity charts for H₂O and CO₂. Total emissivities derived from these charts have been found to be satisfactory [4] for engineering predictions of heat transfer from gases at conditions near to those of the measurements. However, the charts also show estimates of the total emissivities based on the extrapolation of the data to other conditions – primarily long path lengths, high temperatures, and pressures other than atmospheric, and in these situations the values derived from the charts are less accurate [5].

When mixtures of the gases exist, overlapping of the spectral bands, within which the radiant emission by respective gases occurs, requires that a correction be made to the individual gas emissivities. This correction was estimated by Eckert [6] from low temperature–low resolution spectra by multiplying together the respective spectral transmissivities, and these estimates were used by Hottel and Egbert [6] to form a graphical correction procedure.

Hadvig, see [7], has presented combined emissivity data on CO₂-H₂O mixtures in a form which greatly simplifies furnace calculations. Based on the assumption that the gas mixture emissivity, ε_q , is approximately inversely proportional to the gas temperature, T_g , it was found that over a restricted temperature range which generally covers furnace operating conditions the term ε_q . T_q is a function of $(p_w + p_c)$. L only. In addition, variation in the value of the ratio p_w/p_c has only a slight effect on the value of ε_a . T_a and the partial pressure ratio p_w/p_c is approximately equal to 2 for a gas mixture which is a product of the combustion of town gas or natural gas and is nearly equal to 1 for the products of combustion of fuel oil [8]. Using these two fixed ratios and the total emissivity charts of Hottel for water vapour and carbon dioxide, Hadvig developed charts of the combined mixture emissivities for various gas temperatures and carbon dioxide partial pressure-path length values, which are generally used in engineering calculations.

3. SEMI-EMPIRICAL DETERMINATION OF GAS EMISSIVITY

Penner [9] and Edwards [10] have performed a number of investigations in which they interpreted Hottel's charts and band absorption data from various sources, in terms of fundamental spectroscopic theory, which could be used to extrapolate the total emissivities to conditions different from those measured. An important result of these studies is the demonstration that the Statistical Band Model [11] describes the emissivity of hot water vapour and carbon dioxide to a good degree of accuracy.

The emissivity of the spectral region j (the "spectral" emissivity) is given by [11]

$$\varepsilon_j = 1 - \exp\left[\frac{-k_j X}{(1 + k_j X/4a_j)^{\frac{1}{2}}}\right]$$
(1)

where the fine structure parameter $a_j = b_c/d_j$ describes the line density.

The most extensive data on the spectral emissivity of water vapour and carbon dioxide has been presented by General Dynamics (Convair Division), Ludwig *et al.* [12], who provide data for determining the mean line half widths under various line broadening conditions.

The data for carbon dioxide, tabulated in the form of mean values over wavenumber intervals $\Delta \omega = 5$ or 10 cm^{-1} , result from an approximate theoretical calculation, based on measured integrated intensities made by Malkmus [13, 14]. Leckner [15] describes the use of this data and has shown that the weaker bands in the carbon dioxide i.r. spectrum centred at $10 \mu m$, $2 \mu m$, $1.4 \mu m$ and $1.25 \mu m$ do not contribute significantly to the total emissivity in the temperature and optical path length ranges used in this work. Therefore, these bands have not been considered here.

Measurements of the absorption coefficients and fine structure parameters for water vapour have been performed by General Dynamics under N.A.S.A. contracts [16, 17]. Emission and absorption measurements were made with path length of 0.6 m to 6 mthrough a uniform volume of high temperature (600– 3000°K) water vapour, produced above the combustion zone of a flat burner at wavelengths $1-10 \,\mu\text{m}$. The values are presented in the form of values averaged over $25 \,\text{cm}^{-1}$ intervals.

Earlier calculations and experimental results [18] complete the set of absorption coefficients and inverse values of line spacing in the spectral region $50-9300 \text{ cm}^{-1}$ and the temperature range $300-3000^{\circ}\text{K}$. The relative importance of the various water vapour spectral regions at various temperatures and path lengths are given by Leckner [19].

4. EMISSIVITY OF SOOT

In addition to the non-luminous emission from gas in a flame it is necessary to predict the luminous emission from soot. The spectral emissivity of soot can be described by

$$\varepsilon_{\lambda} = 1 - \exp(-k_{\lambda}cL), \qquad (2)$$

and the spectral absorption coefficient of a cloud of soot particles may be evaluated from the Mie theory [21, 22] by which, for $\pi d/\lambda \ll 1$,

$$k_{\lambda} = \frac{36\pi f(n,k)}{\rho\lambda}.$$
 (3)

Theory and experiment both show that the wavelength dependence of k_{λ} can be fitted by an equation of the type

$$k_{\lambda} = A \lambda^{-\alpha}.$$
 (4)

Values of the specific absorption coefficient, k_{λ} , have been calculated for the various optical properties of soot measured by Foster and Howarth [23] using equation (3), and compared with measurements by Hammond [20] on a small distillate oil flame. It was found that the wavelength dependence of each plot was very similar and that the essential difference is the magnitude of the constant A, for example the average of the results of Foster and Howarth [23] give,

$$k_{\lambda} = 2.72 \times 10^3 \lambda^{-1.090}, \tag{5}$$

and Hammond [20] gives

$$k_{\lambda} = 5.60 \times 10^3 \lambda^{-1.086}. \tag{6}$$

For the present work, values of the specific absorption coefficient were determined for the average soot optical properties, equation (5), of Foster and Howarth [23] between 1 and $10\,\mu\text{m}$ wavelength with a soot density of $1.65 \times 10^3 \text{ kg/m}^3$ which is the lowest of the measured values and gives predictions closest to Hammonds measurements. At the flame temperatures usually encountered in industrial practice approximately 96 per cent of the thermal energy is distributed [7] between 1 and 10 μm .

The total emissivity of a soot particle cloud may be obtained from equation (2) by integrating over all wavelengths

$$\varepsilon_T = \frac{1}{\sigma T^4} \int_0^\infty E_{\lambda, T} \varepsilon_\lambda \,\mathrm{d}\lambda \tag{7}$$

where $E_{\lambda,T}$ is the Planck distribution of the emissive power of a black body. Values of total soot emissivity computed from equation (7) using the various values of k_{λ} compare well with experimental values obtained from the literature [24] over a wide range of temperature and concentration conditions.

5. PREDICTION OF LUMINOUS FLAME EMISSIVITY

In obtaining total spectral emissivities for a luminous flame (essentially a gas-soot mixture) allowance must be made for the spectral overlap of both the gaseous and soot components.

As mentioned previously, Eckert [6] obtained a correction for the band absorption of mixtures of carbon dioxide and water vapour by multiplying the low resolution spectral transmissivities of components to obtain the transmissivity of a mixture. This procedure is not necessarily accurate because low resolution spectra, when re-examined under very high resolution, are found to be composed of a number of lines over which the true spectral absorptivity varies greatly.

For a CO_2 -H₂O-soot mixture the monochromatic transmissivity is given by

$$\tau_{\omega} = \exp(-k_{\omega, \text{CO}_2} p_c - k_{\omega, \text{H}_2\text{O}} p_w - k_{\omega, s} c)L \qquad (8)$$

and the average transmissivity over a small wavenumber region, $\Delta \omega$, embracing many lines is

$${}^{\tau_{\text{CO}_2,\text{H}_2\text{O},s}}_{=\frac{1}{\Delta\omega}\int_{\Delta\omega}}e^{-k_{\omega,\text{CO}_2}p_{\omega}L}\cdot e^{-k_{\omega,\text{H}_2\text{O}}p_{w}L}\cdot e^{-k_{\omega,\text{B}}cL}\cdot d\omega. \quad (9)$$

The soot spectrum is smooth and continuous and for small $\Delta\omega$ the soot term may be approximated by its average value and removed outside the integral. Similarly the spectral lines of hot carbon dioxide are heavily overlapped and in effect form a continuum so that the carbon dioxide term may also be removed outside the integral for small values of $\Delta\omega$. This effect is illustrated in the separate emission spectra of CO₂ and H₂O in hot gas cells and the emission spectrum of CO₂+H₂O in a propane flame with the same path length reported by Tourin [26] where it can be seen that in the 2.7 µm region where there is an important overlap of the CO₂ and H₂O bands only the H₂O band retains a distinguishable line structure. Consequently,

$$\bar{t}_{\text{CO}_2,\text{H}_2\text{O},s} = \frac{\bar{\tau}_{\text{CO}_2} \cdot \bar{\tau}_s}{\Delta \omega} \int_{\Delta \omega} \exp(-k_{\omega,\text{H}_2\text{O}} p_w L) \,\mathrm{d}\omega$$
$$= \bar{\tau}_{\text{CO}_2} \cdot \bar{\tau}_s \cdot \bar{\tau}_{\text{H}_2\text{O}}. \tag{10}$$

This analysis of the overlap of CO_2 and H_2O bands has been verified by Hines and Edwards [25] with a comparison of theory and experiment.

The average emissivity $\varepsilon(\omega)_m$ of a gas-soot mixture over a small wavenumber range $\Delta \omega$ is then given by

$$\varepsilon(\omega)_m = 1 - \prod_{i=1}^N (1 - \varepsilon(\omega)_i), \qquad (11)$$

with the restriction that no more than one of the N i.r. active components possesses an effective line structure. The total emissivity of the gas-soot mixture may then be obtained by summation over all the wavenumber intervals.

$$\varepsilon_{m,T} = \frac{1}{\sigma T^4} \sum_{\text{all } j} E(\omega_j) \varepsilon(\omega_j)_m \Delta \omega_j.$$
(12)

Hence by means of equations (1), (5), (11) and (12) it is possible to evaluate the total emissivity of a luminous flame for a wide variety of conditions as the Convair Gas Dynamics data allow sufficiently small $\Delta \omega_j$, $5-25 \text{ cm}^{-1}$ intervals, to satisfy the condition for accuracy.

A computer program has been written employing the analysis outlined above for the semi-empirical determination of the total i.r. emissivities of luminous flames. A wide range of temperatures, pressures, concentrations and path lengths, representative of those likely to be encountered in practice, were employed in the program. Throughout the computation the partial pressure of carbon dioxide, p_c , was 0.1 atm and the total pressure, P_T , equalled 1 atm.

6. DISCUSSION OF RESULTS

Initially the program was run without the soot model in order that charts of total emissivities of H_2O-CO_2 mixtures could be obtained. The form of these charts is very similar to those of Hadvig [8] as shown in Fig. 1.

Boynton and Ludwig [27] compared the General Dynamics data with that of Hottel for the total emissivity of hot water vapour. It was found that below 1500° K, where Hottel's charts [7] are closely related to



FIG. 1. The variation with temperature of the total emissivity of a CO_2-H_2O mixture from fuel-oil combustion based on gas dynamics data showing expected deviations from Hadvig's [8] chart at high temperature and low p_cL .



FIG. 2. The total emissivity of gas-soot mixtures from the combustion of fuel-oil vs soot concentration, c, times path length, L, for various gas concentrations at 1200°K.



FIG. 3. A total emissivity chart for gas-soot mixtures from fuel-oil combustion at 1800°K.

measured data, the values agree to within the combined estimated errors. At higher temperatures, however, it was found that the total emissivities lie considerably above Hottel's values, which are extrapolated. Leckner [19] also determined total emissivities of water vapour and carbon dioxide using the General Dynamics data. In the case of water vapour, the discrepancy with the Hottel charts was similar to that reported by Boynton [27]. Comparing the original measurements, on which the Hottel charts for water vapour were based, with the corresponding calculated emissivities it was found that a discrepancy of less than 10 per cent exists at optical path lengths greater than 5 atm. cm. This discrepancy increases towards shorter path lengths where it becomes about 30 per cent. In addition, total emissivities determined by Boynton were compared with the long path length data of Hottel and Mangelsdorf [2] and the Schmidt [28] data for pure water vapour at a total pressure of 1 atm. In each case the agreement was found to be within 10 per cent.

Similar discrepancies between measured and total emissivities were found for carbon dioxide. In the small optical path length region of Hottel's measurements and at temperatures in the range $600-1200^{\circ}$ K the error was as much as 30 per cent. Leckner [19] suggests that this is partly due, at low temperatures, to the neglect of the contribution of a weak vibration-rotation band situated in the 4·3 µm region. In addition, a second source of possible error is the measurements, which are more susceptible to errors at small path lengths than at long ones. The various discrepancies between the Hottel measurements and General Dynamics data computed emissivities are evident in Fig. 1.

Figure 2 demonstrates the introduction of the soot



FIG. 4. A total emissivity chart for gas-soot mixtures from gas combustion at 1800° K.



FIG. 5. The effect of temperature on the total emissivity of CO_2-H_2O -soot mixtures. The values of p_cL increase in steps of 0.001, 0.01, 0.1 and 1.0 atm. m from the bottom of the figure for each set of curves of constant cL.

model into the program. Of particular interest is the effect of increasing the gas partial pressure and soot concentration on the total emissivity. It is seen that at soot concentration-path length values greater than 0.001 (kg/m³)m the soot particle cloud emission predominates for the particular temperature at which the data is computed.

Figures 3 and 4 are typical luminous flame total emissivity charts for the partial pressure ratios $p_w/p_c = 1$ (oil combustion) and $p_w/p_c = 2$ (gas combustion) at temperature T = 1800°K. The charts are plotted in this form so as to facilitate clarity for use in radiative heat-transfer calculations.

Figure 5 summarises the variation of total emissivity with temperature for various fixed values of soot concentration-path length and partial pressure CO_{2^-} path length. It is seen that at low soot concentrations the total emissivity temperature dependence is typical of that shown by gases; that is the emissivity decreases with increase in temperature. The influence of temperature on the emissivity of a real gas is essentially due to two factors; the change in distribution of energy in the spectrum with changing temperature, and the change in shape of the spectral absorption bands. At high soot concentrations it is seen that the soot emission predominates and the emissivity increases with increasing temperature.

7. MODELLING REAL GASES FOR ENGINEERING CALCULATIONS

In the evaluation of heat transfer by thermal radiation in systems containing absorbing media it is often assumed that the medium is gray, that is the absorption is independent of the frequency of the radiation. This assumption is not satisfied for real gases such as water vapour and carbon dioxide as they emit and absorb only in discrete bands in the spectrum.

The form of the relations for calculating radiative heat transfer in an enclosure is generally greatly simplified if the gray gas assumption is made. Therefore, it is advantageous that the mathematical formulation which characterises a gray-gas system is retained in the representation of real gas emission. This is achieved by representing the emissivity of a real gas as the sum of the weighted emissivities of a number of gray gases [7]. The total emissivity of a gray gas is given by the equation

$$\varepsilon_g = 1 - \exp(-k_g pL) \tag{13}$$

where k_g is the absorption coefficient. The total emissivity of a real gas can be written as

$$\varepsilon_g = \sum_{n=1}^{N} a_{g,n} \left[1 - \exp(-k_{g,n} pL) \right]$$
(14)

with each weighting coefficient $a_{g,n} > 0$. The subscript g indicates that a gas is under consideration and the subscript, n = 1, 2, ..., N denotes the particularly gray gas component. A further restriction is that the emissivity cannot be greater than unity at large values of pL so that,

$$\sum_{n=1}^{N} a_{g,n} = 1.$$
(15)

If the number of terms in the summation is very large, $a_{a,n}$ may be considered as the fraction of energy in a blackbody spectral region in which the effective absorption coefficient is $k_{g,n}$. However, $a_{g,n}$ and $k_{g,n}$ may be more correctly considered as the numbers which make the series in equation (14) fit the given function of ε_a vs pL. Although in theory the emissivity of a gas approaches one as the value of pL becomes very large, because of the contribution by the wings of the lines in the principal bands and by the very weak lines between the bands, at all practically attainable values of pL the emissivity is considerably less than one. Therefore in fitting the emissivities of real gases with a finite number of terms, it is common to have one term with $k_{q,n} = 0$, physically corresponding to the windows in the spectrum between strong emission bands and sometimes referred to as the clear gas component.

The important advantage to be gained by representing a real gas by the weighted sum of gray gases is that in practical calculations the absorption coefficients, $k_{g,n}$, may be held constant and independent of temperature, and the temperature dependence of the emissivity carried by a variation of the weighting coefficients, $a_{g,n}$. The effect of this, for example, in the zone method of calculating radiative heat transfer, is that the total exchange areas become independent of the temperature field in the enclosure being considered and need be evaluated only once in the calculation.

8. FITTING GRAY GAS MODELS TO EMISSIVITY-pL DATA

Methods of fitting exponential series to data may be found in the literature. Hottel and Sarofim [7] describe a trial and error graphical method which tends to be rather time consuming when more than a two term fit is carried out. For this reason a technique for determining $a_{g,n}$ based on the method of least squares was developed for the purpose of this study. From equation (14)

$$\varepsilon_{g} = \sum_{n=1}^{N} a_{g,n} - \sum_{n=1}^{N} a_{g,n} e^{-k_{g,n}pL}$$
(16)

assuming a clear gas component, $k_{g,1} = 0$, and using the sum rule of equation (15), equation (16) becomes

$$\varepsilon_g = 1 - a_{g,1} - a_{g,2} e^{-k_{g,2}pL} - a_{g,3} e^{-k_{g,3}pL} - \dots$$
(17)

Now, if we have M tabulated values of emissivity vs optical path length (\tilde{e}_i, pL_i) we require to find the values of $a_{g,n}$ and $k_{g,n}$ which minimise the sum of the squares of the differences between the tabular values and the values given by equation (17), that is, to minimise the function $F(a_{g,n}, k_{g,n})$ where,

$$F = \sum_{i=1}^{M} (\varepsilon_{g,i} - \tilde{\varepsilon}_i)^2$$

= $\sum_{i=1}^{M} (1 - a_{g,1} - a_{g,2} \cdot \exp(-k_{g,2} \cdot pL_i) - \dots - \tilde{\varepsilon}_i)^2$ (18)

by solving the following simultaneous equations for $a_{g,n}$ and $k_{g,n}$

$$\frac{\partial F}{\partial a_{g,n}} = 0; \qquad n = 1, 2, \dots, N$$
$$\frac{\partial F}{\partial k_{g,n}} = 0; \qquad n = 2, \dots, N$$
(19)

with the condition, equation (15), that,

$$\sum_{n=1}^{N} a_{g,n} = 1.$$

Because the full set of equations in $a_{g,n}$ and $k_{g,n}$ are non-linear a hybrid solution was employed whereby the following linear equations were solved for $a_{g,n}$ with preset values of $k_{g,n}$,

$$U_j + V_j = \sum_{h=1}^{N} a_{g,h} \cdot W_{h,j} \qquad j = 1, 2, \dots, N-1$$
$$1 \Rightarrow \sum_{h=1}^{N} a_{g,h}$$

where

$$U_j = -\sum_{i=1}^{M} \tilde{\varepsilon}_i \cdot \exp(-k_{g,i} \cdot pL_i)$$
$$V_j = \sum_{i=1}^{M} \exp(-k_{g,j} \cdot pL_i)$$

and

$$W_{h,j} = \sum_{i=1}^{M} \exp(-k_{g,h} \cdot pL_i) \exp(-k_{g,j} \cdot pL_i) \quad (20)$$

and a search was made for the optimum values of $k_{g,n}$ using an interactive computer program with an on line conversational language.

9. GRAY GAS PARAMETERS FOR CO2-H2O MIXTURES

Using the above technique equation (14) has been fitted to total emissivity values for H_2O-CO_2 mixtures determined from the General Dynamics Data above. Partial pressure ratios of $p_w/p_c = 1$ and 2 were used, representing the cases of a mixture of the products of oil and gas combustion respectively. The partial pressures of water vapour and carbon dioxide are denoted p_w and p_c respectively. This is illustrated in Fig. 6 for the emissivity of an H_2O-CO_2 mixture the optimum $k_{g,n}$ values demonstrate an almost linear variation with temperature as shown in Fig. 8. This is in agreement with Johnson [30] who found a linear variation for a three term fit. Hottel and Sarofim [7, 29, 31] use a polynomial to describe the variation of weighting factors with temperature, but their higher order terms were of little importance.

As explained above it is better if the values of $k_{g,n}$ can be held constant and independent of temperature, and all the temperature dependence be carried by the weighting factors $a_{g,n}$. To explore this possibility fixed values of $k_{g,n}$ at a temperature representative of furnace conditions were used to fit the data at other temperatures. This is shown in Fig. 9 over the temperature



FIG. 6. A comparison of various gray gas equations fitted to the total emissivity of a CO_2 -H₂O mixture.

having a partial pressure ratio of $p_w/p_c = 1$, and a temperature of 1500°K, where different fits to the total emissivity-*pL* relationship using from one term to four terms are shown. As would be expected the fit improves progressively with the increasing number of terms used in equation (14).

It was found that for a four term (1 clear + 3 gray gas) representation of the emissivity, the deviation of the fitted values was never greater than 0.5 per cent over a 1000-fold range in variation of p_cL for temperatures between 600 and 2400°K. It is therefore seen that an adequate representation of a real gas for engineering purposes can be obtained using far fewer constants to fit the data than are required to describe the spectral parameters of the gas.

It was also found that for a four term (1 clear + 3 gray gas) representation of the real gas emissivity, the variation of the optimum $k_{g,n}$ with temperature is almost linear as shown in Fig. 7. In addition, the weighting coefficients $a_{g,n}$ which result from the use of range $1200-2400^{\circ}$ K where the $k_{g,n}$ values for the 1800° K $\varepsilon_g - p_c L$ relationship are used. Values of the coefficients $a_{g,n}$ may be obtained directly by solving equations (20). They were again found to vary linearly with temperature and are given by.

$$a_{q,n} = b_{1,n} + b_{2,n} \cdot T \tag{21}$$

where T is the gas temperature and the constants $b_{1,n}$ and $b_{2,n}$ are given in Table 1. Equation (21) has been obtained by fitting a least squares straight line to the $a_{g,n}$ values resulting from the use of the fixed $k_{g,n}$ values at 1800°K, Table 1.

It is seen therefore that by using the technique outlined previously, the representation of a real gas by the weighted emissivities of a number of gray gases may be carried out accurately and rapidly using a 1 clear + 3gray fit and is given by

$$e_g = \sum_{n=1}^{n=4} (b_{1,n} + b_{2,n}, T)(1 - e^{-k_{g,n}(p_c + p_m)L})$$
(22)



FIG. 7. The temperature dependence of the coefficients, $k_{g,n}$, for CO₂-H₂O mixtures.

where all the constants are provided in Table 1 for carbon dioxide-water vapour mixtures occurring in oil and gas combustion at atmospheric pressure.



FIG. 8. The temperature dependence of the gray gas weighting coefficients, $a_{g,n}$, for CO₂-H₂O mixtures.

Table 1. Values of the coefficients $k_{g,n}$ and $a_{g,n}$ in the gas emissivity equations for a CO₂-H₂O mixture applicable to the temperature range 1200-2400°K

$p_w/p_c = 1$						
n	$k_{g,n}$	$b_{1,n}$	b _{2.n}			
1	0	0.410	0.0000743			
2	0.91	0.284	0.0000258			
3	9.4	0.211	-0.0000654			
4	130.0	0.0958	-0.0000357			
		$p_w/p_c = 2$				
1	0	0.364	0.0000473			
2	0.69	0.266	0.0000719			
3	7-4	0.252	-0.0000741			
4	80.0	0.118	-0.0000452			

Units of $k_{g,n}$ are m⁻¹ atm⁻¹.



FIG. 9. The goodness of fit of gray gas equations to the total emissivity of a CO_2-H_2O mixture.

10. GRAY GAS PARAMETERS FOR CO₂-H₂O-SOOT MIXTURES

In order that the zone method of analysis may be extended to take account of luminous radiation from flames it would be convenient if the emissivity of a gas-soot mixture could also be expressed as the sum of a number of weighted gray gases. Rewriting equation (13) to represent a gray gas-soot mixture

$$\varepsilon_m = 1 - \exp(-K_m L) \tag{23}$$

then the emissivity of a real gas-soot mixture can be fitted directly by the weighted series of gray gases,

$$\varepsilon_{m} = \sum_{n=1}^{N} a_{m,n} [1 - \exp(-K_{m,n}L)]$$
(24)

bearing in mind that the coefficients $K_{m,n}$ are now a function of both soot concentration, c, and gas composition,

$$K_{m,n} = \phi(c, p_w/p_c, p_c).$$
 (25)

However, as furnaces are generally operated with a given fuel at a particular air-fuel ratio, it is the variation of the $K_{m,n}$ with soot concentration that is of practical interest. Equation (24) provides a means of representing the emissivity of a gas-soot mixture in a form suitable for use in the zone method of analysis.

At this point it is useful to examine previous representations of luminous emissivity. Johnson [30, 32] presented a model for luminous radiation based on the sum of a number of weighted gray gases. He showed that the emissivity of soot particles alone could be represented in this way using a three gray gas fit. To ensure compatability between the gray gas models fitted separately to the real gas and the soot respectively, he introduced the restriction that the $a_{g,n}$ weighting coefficients in the equations fitted to the gas alone were equal to the $a_{s,n}$ coefficients in the equations fitted to the soot alone. This implies a considerable degree of approximation in the fitted absorption coefficients of either the gas or the soot. His coefficients $a_{q,n}$, $k_{q,n}$ and $k_{s,n}$ were determined for the case of a mixture of the products of oil and gas combustion $(p_w/p_c = 1 \text{ and } 2 \text{ respectively})$ and various soots. The procedure adopted was to obtain a good representation of the gas emissivity thus fixing the $a_{g,n}$ (= $a_{s,n}$) and to determine a set of soot absorption coefficients $k_{s,n}$ which gave an acceptable representation of soot emissivity. Because of the approximate nature of the representation of the soot emissivity, the method was found to be slow, requiring trial and error to obtain a suitable fit. Moreover, with the linear temperature dependence of the gas weighting factors imposed on the soot equations, it was not possible to obtain an exact fit for the soot emissivity, except at one temperature. The errors incurred by this approximate procedure were in the order of 10-15 per cent falling to an insignificant amount at emissivities close to 1.

Wall [33] used a three term fit for a gas-soot-ash mixture; this consisted of a black ($K = \infty$), gray and clear gas model. He found that the clear component had no effect on emissivity as would be expected since soot radiation is continuous and there are no "windows" in the spectrum. Hence all the $K_{m,n}$ coefficients had non-zero values. The accuracy of fit was satisfactory except at relatively low temperatures ($\simeq 1200^{\circ}$ K) and small path lengths (less than 1 m) where the error was up to 30 per cent.

In the present investigation equation (24) has been fitted directly, using three gray gas terms, to the gassoot mixture data evaluated from the general dynamics gas data and the soot emissivity model above. The least squares technique for fitting an exponential series to data outlined above has been adapted for this purpose. It should be noted that in this case there is no clear term and equation (17) becomes

$$\varepsilon_m = 1 - a_{m,1} e^{-K_{m,1}L} - a_{m,2} e^{-K_{m,2}L} - \dots$$
(26)

and the simultaneous equations (20) become,

$$X_{j} + Y_{j} = \sum_{h=1}^{N} a_{m,h} \cdot Z_{h,j} \qquad j = 1, 2, \dots, N-1$$
$$1 = \sum_{h=1}^{N} a_{m,h} \qquad (27)$$

where

$$X_j = -\sum_{i=1}^{M} \tilde{\varepsilon}_{i,m} \cdot \exp(-K_{m,j} \cdot L_i)$$
$$Y_j = \sum_{i=1}^{M} \exp(-K_{m,j} \cdot L_i)$$

and

$$Z_{h,j} = \sum_{i=1}^{M} \exp(-K_{m,h} \cdot L_i) \exp(-K_{m,j} \cdot L_i).$$
(28)

As in the case of gas mixtures, it was found that the variation of the coefficients $K_{m,n}$ and $a_{m,n}$ with temperature was almost linear. As discussed previously it is desirable that the $K_{m,n}$ are made independent of temperature and Fig. 10 shows a three term fit of mixture emissivity-path length values at 1200°K, 1500°K and 2400°K with a constant soot concentration of 0.001 kg/m³ using the values of $K_{m,n}$ computed at 1800°K. It is seen that the fit is good, the error being not greater than 2 per cent at small path lengths ≈ 0.01 m.

In addition, the three term weighted gray gas equation has been fitted to gas-soot emissivity vs path length data for the soot concentration range $0.001-0.005 \text{ kg/m}^3$, this is considered to cover that range



FIG. 10. The three gray gas representation of the total emissivity of a gas-soot mixture.

most likely to be encountered in practice. It is found that the coefficients $K_{m,n}$ for $p_w/p_c = 1$ and $p_w/p_c = 2$, temperature $T = 1800^{\circ}$ K, when plotted on a logarithmic axis vs soot concentration on a linear axis give an almost linear relationship, except at small soot concentrations ($\approx 0.0001 \text{ kg/m}^3$). This may be accounted for by the fact that at very small soot concentrations the 3 gray gas approximation is not strictly valid and a 1 clear plus 3 gray gas fit provides a slightly more accurate fit. If it is assumed that the values of $K_{m,n}$ are



FIG. 11. Variation of the coefficients $K_{m,n}$, with soot concentration for a three gray gas fit to gassoot mixture data at 1800°K.

independent of temperature and 1800°K is representative of furnace conditions we may express $K_{m,n}$ as a function of soot concentration. Fitting least squares straight lines to the $K_{m,n}$ vs soot concentration values, shown in Fig. 6, we obtain

$$K_{m,n} = \exp[q_{1,n} + q_{2,n}c]$$
(29)

where c is soot concentration and $q_{1,n}$ and $q_{2,n}$ are constants given in Table 2.

Table 2. Values of the constants for the determination of the coefficients $K_{m,n}$ applicable in the temperature range $1200-2400^{\circ}$ K

н	$p_w/p_c = 1$		$p_w/p_c = 2$	
"	$q_{1,n}$	q _{2,n}	<i>q</i> _{1,n}	q _{2,n}
1	-1.252	558·55	-1.274	590.82
2	-0.221	665.38	-0.233	672.04
3	2.608	839.62	2.452	692·61

The resulting three term fits to the gas-soot mixture at various soot concentrations are shown in Figs. 12 and 13 for $p_w/p_c = 1$ and 2. It is seen that over the entire soot concentration range the fit is good, the deviation being not greater than 4 per cent at small values of L (<0.05 m). The choice of 1800°K as a characteristic temperature at which to freeze the values of $K_{m,n}$ is not critical because small deviations from the optimum absorption coefficients are accommodated by corresponding changes in the fitted values of $a_{m,n}$.

Use of equation (29) enables the representation of the gas-soot mixture emissivity-path length relationship without having to resort to trial and error methods. Two approaches are available for obtaining the coefficients $a_{m,n}$ for a gas-soot mixture. The equations (27) are solved for a three term fit using a value of $K_{m,n}$ from equation (29) and (i) the user's own mixture



FIG. 12. Representation of gas-soot mixture total emissivity by three gray gases with various soot concentrations, for oil combustion, $p_w/p_c = 1$, at $T = 1800^{\circ}$ K.



FIG. 13. Representation of gas-soot mixture total emissivity by three gray gases with various soot concentrations, for gas combustion $p_w/p_c = 2$, at $T = 1800^{\circ}$ K.

emissivity vs path length data or (ii) the emissivity vs path length data evaluated from the general dynamics gas data and the soot model. In practice it is found that approximately thirteen data points over the path length range 0.01-10.0 m provide a good indication of the emissivity-path length relationship with the minimum of calculation.

CONCLUSION

The gas, $CO_2 + H_2O$, and gas-soot emissivity vs path length data obtained from the general dynamics gas data and the soot model have been represented by the weighted emissivities of a number of gray gases. This simplified representation of the total emissivity of flame media is essential to the economy of the zone method of calculating radiative heat transfer which can now be extended to the case of luminous radiation for both gas and oil combustion.

The technique of freezing the gray gas absorption coefficients and allowing the temperature dependence of emissivity to be carried by the weighting factors was found to be both accurate and flexible over very wide ranges of temperature and path length.

For mixtures of CO₂ and H₂O only, values of all the multiple gray gas parameters $a_{g,n}$ and $k_{g,n}$ are presented for a four term fit at partial pressure ratios applicable to oil and gas combustion in the temperature range 1200–2400°K.

For gas-soot mixtures three term gray gas fits have been carried out at various temperatures and soot concentrations in the range $T = 1200-2400^{\circ}$ K and c = 0.0001-0.005 kg/m³. Equations for the coefficients $K_{m,n}$ are presented for practical soot concentrations and H_2O-CO_2 partial pressure ratios corresponding to oil and gas combustion.

The weighting coefficients $a_{m,n}$ may now be obtained by the solution of three linear simultaneous equations thus avoiding the necessity to resort to trial and error methods as used previously.

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REFERENCES

- R. H. Tourin, Spectroscopic Gas Temperature Measurement. Elsevier, New York (1966).
- H. C. Hottel and H. G. Mangelsdorf, Heat transmission from non-luminous gases—II. Experimental study of water vapour, *Trans. Am. Inst. Chem. Engrs* 31, 517-549 (1935).
- H. C. Hottel and V. C. Smith, Radiation from nonluminous flames, *Trans. Am. Soc. Mech. Engrs* 57, 463– 470 (1935).
- D. K. Edwards and A. Balakrishnan, Thermal radiation by combustion gases, *Int. J. Heat Mass Transfer* 16, 25-40 (1973).
- C. L. Tien, Thermal radiation properties of gases, in Advances in Heat Transfer, Vol. 5, edited by T. F. Irvine and J. P. Hartnett. Academic Press, New York (1968).
- H. C. Hottel and R. B. Egbert, Radiant heat transmission from water vapour, *Trans. Am. Inst. Chem. Engrs* 38, 531-568 (1942).
- 7. H. C. Hottel and A. F. Sarofim, *Radiative Transfer*. McGraw-Hill, New York (1967).
- S. A. P. Hadvig, Gas emissivity and absorptivity: a thermodynamic study, J. Inst. Fuel 43, 129–135 (1970).
- S. S. Penner and P. Varanasi, Approximate band absorption and total emissivity calculations for H₂O, *JnlQuantve Spectros. & Radiat. Transf.* 5, 215-227 (1965).
- D. K. Edwards, B. J. Flornes, L. K. Glassen and W. Sun, Correlation of absorption by water vapour at temperatures from 300 to 1100°K, *Appl. Optics* 4, 715–721 (1965).
- 11. R. M. Goody, Atmospheric Radiation, Part 1. Theoretical Basis. Oxford University Press, Oxford (1964).
- 12. C. B. Ludwig *et al.*, Study on exhaust plume radiation predictions, Interim Progress Reports, Parts I and II, General Dynamics/Convair GD/C-DBE-66-001 and GD/C-DBE-66-001a (1966).
- W. Malkmus. Infrared emissivity of carbon dioxide (2·7 μm band), J. Opt. Soc. Am. 54, 751-758 (1964).
- W. Malkmus, Infrared emissivity of carbon dioxide (4·3 μm band), J. Opt. Soc. Am. 53, 951-961 (1963).
- 15. B. Leckner, The spectral and total emissivity of carbon dioxide, *Combust. Flame* 17, 37-44 (1971).
- C. B. Ludwig *et al.*, Study on exhaust plume radiation predictions, General Dynamics/Convair, GD/C-DBE-66-017 (1966).

- C. B. Ludwig *et al.*, Study on exhaust plume radiation predictions, General Dynamics/Convair, NASA-CR-61233 (1968).
- C. C. Ferriso, C. B. Ludwig and A. L. Thomson, Empirically determined infrared absorption coefficients of H₂O from zero to 3000°K, *Jnl Quantve Spectros. & Radiat. Transf.* 6, 241–274 (1966).
- B. Leckner, Spectral and total emissivity of water vapour and carbon dioxide, Combust. Flame 19, 33-48 (1972).
- E. G. Hammond, Luminous radiation from within a small pressure jet oil flame, Ph.D. Thesis, Univ. Sheffield (1971).
- G. Mie, Beiträge zur Optik Trüber Medien, Speziall Kolloidaler Metallösungen, Ann. Phys. 25, 377-445 (1908).
- P. G. W. Hawksley, The physics of particle size measurement: Part 2 optical methods and light scattering, Mon. Bull. Br. Coal. Util. Res. Ass. 16, 181-209 (1952).
- P. J. Foster and C. R. Howarth, Optical constants of carbons and coals in the infrared, *Carbon* 6, 719–729 (1968).
- T. Sato, T. Kunitomo, F. Nakashima and H. Fujii, Study on radiation from luminous flames, (2nd Report, Experimental study in the case of combustion of liquid fuels), *Bull. J.S.M.E.* 9, 768-777 (1966).
- W. S. Hines and D. K. Edwards, Infrared absorptivities of mixtures of carbon dioxide and water vapour, *Chem. Engng Prog. Symp. Ser.* 64, 173–180 (1968).
- R. H. Tourin, Spectral emissivities of hot CO₂-H₂O mixtures in the 2.7 μm region, J. Opt. Soc. Am. 51, 799-800 (1961).
- F. P. Boynton and C. B. Ludwig, Total emissivity of hot water vapour—II. Semi-empirical charts deduced from long path spectral data, *Int. J. Heat Mass Transfer* 14, 963-972 (1971).
- E. Schmidt, Messung der Gesamtstrahlung der Wasserdampfes bei Temperaturen bis 1000°C, Forsch. Geb. IngWes. 3, 57-70 (1932).
- H. C. Hottel and A. F. Sarofim, The effect of gas flow patterns on radiative transfer in cylindrical furnaces, *Int.* J. Heat Mass Transfer 8, 1153-1169 (1965).
- T. R. Johnson, Application of the zone method of analysis to the calculation of heat transfer from luminous flames, Ph.D. Thesis, Univ. Sheffield (1971).
- 31. H. C. Hottel and A. F. Sarofim, Gaseous Radiation with Temperature Gradients; Allowance for Isotropic Scatter, Theory and Fundamental Research in Heat Transfer, edited by J. A. Clark, pp. 139–160. Pergamon Press, New York (1963).
- 32. T. R. Johnson and J. M. Beér, Paper 4: The zone method analysis of radiant heat transfer: a model for luminous radiation. In *Fourth Symp. on Flames and Industry*. The Institute of Fuel, London (1972).
- 33. T. F. Wall, The development of a mathematical model of an industrial P.F. furnace, Univ. Newcastle, New South Wales, Australia, Report Chem. Engng 72.1 (1972).

FACTEUR D'EMISSION TOTALE DES FLAMMES LUMINEUSES OU CLAIRES

Résumé—Les facteurs d'émission des mélanges CO_2-H_2O et CO_2-H_2O -suie correspondants à la combustion d'huile et de gaz, avec respectivement $p_w/p_c = 1$ et 2, ont été calculés à partir du modèle statistique de bande et des données spectrales expérimentales pour les gaz et à partir des constantes optiques de la suie déterminées à l'aide de la théorie de Mie.

Pour les mélanges CO_2-H_2O , le facteur d'émission a été estimé par un modèle à un gaz transparent et trois gaz gris, convenable pour le calcul du transfert thermique par la méthode de zonage, dans le domaine de témperature 1200-2400 K, avec une précision de 0,5 pour cent et 1000 valeurs de p_cL :

$$\varepsilon_g = \sum_{n=1}^{4} (b_{1,n} + b_{2,n}, T) [1 - e^{-k_{g,n}(p_c + p_w)L}].$$

On montre que le facteur total d'émission des mélanges CO_2-H_2O -suie peut être représenté aussi par un modèle à trois gaz gris avec des coefficients d'absorption constants $K_{m,n}$:

$$\varepsilon_m = \sum_{n=1}^{3} a_{m,n} [1 - e^{-K_{m,n}L}]$$

et les coefficients $a_{m,n}$ sont linéairement dépendants de la température. A composition constante du gaz, $K_{m,n}$ est relié à la concentration de suie c, par

$$K_{m,n} = \exp[q_{1,n} + q_{2,n} \cdot c]$$

de telle sorte que les coefficients $a_{m,n}$ pour les flammes lumineuses peuvent être déterminés sans recours à un ajustement empirique.

DIE GESAMTEMISSION LEUCHTENDER UND NICHTLEUCHTENDER FLAMMEN

Zusammenfassung—Die Gesamtemission der bei Öl- und Gasverbrennung auftretenden Gemische aus CO_2 und H_2O bzw. CO_2 , H_2O und Ruß wurde für $p_w/p_c = 1$ bzw. 2 aus dem statistischen Bandmodell und experimentell ermittelten Spektraldaten für die Gase sowie aus den optischen Konstanten für Ruß unter Verwendung der Mie-Theorie berechnet.

Für Gemische aus CO_2 und H_2O konnte die Gesamtemission durch ein bestimmtes Gasmodell (one-clear three-gray) im Tempereturbereich von 1 200 bis 2 400 K mit einer Genauigkeit von 0,5% in einem 1000 fachen Bereich von p_cL dargestellt werden, wobei

$$\varepsilon_g = \sum_{n=1}^{\infty} (b_{1,n} + b_{2,n} \cdot T) [1 - e^{-k_{g,n}(p_c + p_w)L}].$$

Die Gesamtemission strahlender Gemische aus CO_2 , H_2O und Ruß kann mit einem anderen Gasmodell (three-gray) mit konstanten Absorptionskoeffizienten $K_{m,n}$ dargestellt werden, wobei

$$\varepsilon_m = \sum_{n=1}^{3} a_{m,n} [1 - \mathrm{e}^{-K_{m,n}L}]$$

ist. Die Koeffizienten $a_{m,n}$ sind linear von der Temperatur abhängig.

Bei gleichbleibender Gaszusammensetzung besteht zwischen $K_{m,n}$ und der Rußkonzentration c die Beziehung

$$K_{m,n} = \exp[q_{1,n} + q_{2,n} \cdot c].$$

In diesem Fall können die verbleibenden Koeffizienten $a_{m,n}$ für leuchtende Flammengase ohne Iteration ermittelt werden.

ИНТЕГРАЛЬНАЯ ЛУЧЕПОГЛОЩАТЕЛЬНАЯ СПОСОБНОСТЬ СВЕТЯЩИХСЯ И НЕСВЕТЯЩИХСЯ ПЛАМЕН

Аннотация — В данной работе интегральная лучепоглощательная способность смесей CO_2-H_2O и CO_2-H_2O — сажа, возникающих при горении нефти и газа, с отношением $P_w/P_c = 1$ и 2, соответственно, рассчитана на основании статистической зональной теории и экспериментальных данных спектрального анализа для газов, а также на основании оптических постоянных сажи, рассчитанных с помощью теории Ми. Для лучепоглощательной способности смесей CO_2-H_2O использовалась модель газа, состоящего из одной части прозрачного газа и трех частей серого. Эта модель пригодна для зонального расчета лучистого тенлообмена в диапазона изменения p_cL , откуда

$$\varepsilon_q = \sum_{n=1}^{4} (b_{1,n} \pm b_{2,n} \cdot T) [1 - e^{-K_{g,n}(P_c + P_w)L}].$$

В статье показано, что интегральная лучепоглощательная способность светящихся смесей CO_2-H_2O — сажа может быть представлена моделью, состоящей из трех частей серого газа с постоянными коэффициентами поглощения $K_{m,n}$, где

$$\varepsilon_m = \sum_{n=1}^{3} a_{m,n} [1 - e^{-K_m, nL}],$$

а весовые коэффициенты $a_{m,n}$ также линейно зависят от температуры. При постоянном составе газа коэффициенты $K_{m,n}$ связаны с концентрацией сажи с соотношением:

$$K_{m,n} = \exp[q_{1,n} + q_{2,n} \cdot C].$$

Отсюда коэффициенты *а_{м. и}* для других газов со светящимся пламенем могут быть определены, не прибегая к методу последовательных приближений.