HEAT TRANSFER FROM FLAMES

 $\frac{h_cD}{k} = 0.023 \times (7.46 \times 10^4)^{0.8} \times 0.70^{0.3}$ Nu=0.023 Re 0.8 Pr 0.3 $= 0.023 \times 7.91 \times 10^3 \times 0.889 \times 1.29$ hc=209 x 6.65 x 10⁻² 13.9 x 10⁻³ x 800 S Shinom Dt

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Heat Transfer from Flames

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© Paul Elek (Scientific Books) Ltd., 1976 First published in Great Britain in 1976 by Paul Elek (Scientific Books) Ltd., 54–58 Caledonian Road, London N1 9RN

and in USA by Paul Elek Inc., 10 South Broadway, Salem, New Hampshire 03079

ISBN 0 236 40044 4

Printed in Great Britain by Unwin Brothers Limited The Gresham Press, Old Woking, Surrey, England. A member of the Staples Printing Group.

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Acknowledgement

We are very grateful for the help given to us during the preparation of this text by Mr. Alec Taylor.

W.A.G. J.K.K. R.M.



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1 Introduction

Calculations of the heat transfer from flames and prediction of the thermal performance of combustion systems are of great importance, particularly with regard to fuel economy. The results of these calculations can be used either to improve the thermal efficiency of existing plant or to design new plant.

Flames and combustion products are defined in this introductory chapter together with a discussion of those components of flames and products which are involved in the processes of heat transfer. Subsequent chapters are concerned with basic convective and radiative heat transfer, convective and radiative heat transfer from flames and, finally, heat transfer from flames in practice.

It is difficult to define a flame precisely but, with some exceptions, a flame can be said to possess four main attributes. Flames are associated with (1) oxidation processes, (2) highly exothermic reactions between gases, (3) rapid temperature rise, and (4) emission of light. The reactants and products of the oxidation processes are present both in the flame and beyond the flame itself as defined by the outer envelope which emits light. Oxidation may, however, be complete at this envelope and virtually no reactants appear beyond it. In any case, heat transfer is important, not only from the flame, but also from the products of the oxidation or combustion reactions. In the text which follows, the term 'flame' will be used to include the products

which arise from it, unless it is obvious that only processes taking place within the flame envelope are being considered.

The most familiar, and the most industrially significant, flames are those arising from the combustion of a hydrocarbon fuel whether it be solid like coal, liquid like many of the petroleum fuels or gaseous like natural gas. As far as heat transfer is concerned, it is appropriate to consider the gaseous and particulate components of the products of combustion separately.

1.1 GASES

A simple hydrocarbon fuel burns to produce carbon dioxide and water, if combustion is complete. In oxygen:

$$C_n H_m + (n + m/4)O_2 \rightarrow n CO_2 + m/2 H_2O$$

In air:

$${\rm C}_n{\rm H}_m + (n+m/4)({\rm O}_2 + 3.76{\rm N}_2) \ \, \rightarrow \ \, n{\rm CO}_2 + m/2{\rm H}_2{\rm O} + 3.76(n+m/4){\rm N}_2$$

The concentration by volume of carbon dioxide and water vapour in the products of complete combustion for three fuels are given in Table 1.1.

Table 1.1 shows that the concentration of water vapour in the case of methane is twice that of the carbon dioxide, whereas, for the petroleum fuel oils, the concentration of water vapour is approximately equal to that of the carbon dioxide. These simple ratios are convenient to use in some calculations of radiative heat transfer from flames (Section 5.1). The carbon-hydrogen ratios of coals vary considerably and it is not possible to adopt this technique for coals in general.

If the temperature of the products is high enough, various dissociated species will also be present in significant amounts. For example, the combustion products of the fuel in air may contain CO, $\rm H_2$, $\rm O_2$, $\rm H$, O, OH, N, $\rm NO_2$ and NO in significant concentrations if the temperature is high enough, whilst the flame

Table 1.1. Volumetric concentration of carbon

dioxide and water vapour in the combustion products of three fuels.

Fuel	Excess air	°CO ₂	H ₂ O %
<pre>Coal (carbon, 74.0 % wt; hydrogen, 5.5 % wt;</pre>	0	16.8	8.2
oxygen, 8.6 % wt; sulphur, 1.2 % wt;	20	14.1	6.9
nitrogen, 1.0 % wt and water, 5.0 % wt)	30	13.1	6.4
Medium fuel oil (carbon,	0	14.1	11.1
85.3 % wt and hydrogen,	20	11.8	9.3
11.2 % wt)	30	11.0	8.6
Methane	0	9.5 8.1	19.0 16.1
	30	7.5	15.0

may contain in addition, various species such as CH or CH_2 which arise during combustion. The equilibrium composition of the products may be calculated by the kind of technique described in Appendix 1.

1.2 PARTICLES IN COMBUSTION PRODUCTS

In addition to the gaseous species, both liquid and solid particulate material may be present in flames, although in those flames derived from gaseous fuels, the only solid material which can be present is finely divided carbon. In flames derived from liquid and solid fuels, larger particles are formed from the droplets or particles of fuel. These may persist in the combustion products.

1.2.1 Finely Divided Carbon or Soot

The finely divided carbon particles formed in the flame cause the flame to be luminous. If combustion of these particles is not completed within the flame, they will emerge from the flame as soot. Soot emanating from, and the carbon within, the flame may be sampled and studied under the electron microscope. The particles are roughly spherical, of 0.005 μm to 0.25 μm (50 to 2500 Å) in diameter, and clustered together in chains as shown in Figure 1.1. Diffusion flames and slow-burning premixed flames produce larger particles, whilst smaller particles are produced by fast-burning premixed flames.

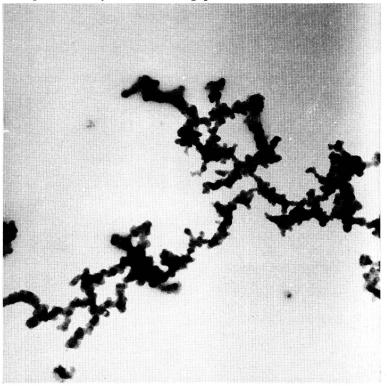


Figure 1.1 Electromicrograph of soot

The structure of the soot particles is important in that it influences their optical properties which control the radiative transfer to and from the soot. The particles in most soots have a basically graphitic structure with each particle consisting of a number ($^{2}10^{3}$) of small crystallites of around 2 nm in size, although there is a variation in soots from different sources. Thomas (1962) quotes sizes up to 4.8 nm for acetylene black and compares these with crystallites of a polybenzenoid hydrocarbon such as circumanthracene (C_{40} H_{16}). The ratio of hydrogen to carbon atoms in circumanthracene is 1:2.5 but the ratio for some other soots has been shown by chemical analysis to be 1:8.

The production of soot depends on two factors, formation of carbon particles and their combustion in the flame, and they may very well be different in different types of flames, including the broad classification of diffusion and premixed flames.

Diffusion flames

A simple diffusion flame usually has a pale bluish base and is luminous over the remainder of its length. Sometimes, soot is formed at the tip of the flame. Some combustible gases do not form carbon in their flames; they include carbon monoxide, methyl alcohol, formaldehyde, formic acid, carbon disulphide and cyanogen.

Very small diffusion flames are not luminous and carbon is only produced when the height of the flame is increased above a critical value. This critical height varies with the diameter of the burner or type of wick (for vapours) and the type of fuel, even for different members of an homologous series. The tendency to produce carbon increases with molecular weight for paraffins and alcohols but decreases for olefins, di-olefins, aromatics and cycloparaffins. The carbon to hydrogen ratio is obviously significant, but so too is the structure of the molecule; for example, the more highly branched paraffins have a greater tendency to produce carbon.

The luminosity of the flame depends on the amount of carbon formed and its temperature. If flame

temperatures are the same, as they are for many hydrocarbons, the onset of luminosity is a convenient index of carbon formed. In fact, the index used in the early experiments was the height at which soot appeared at the tip of the flame, or the tendency to smoke, as it was called. The onset of luminosity is, of course, a better index because the tendency to smoke depends on the passage of carbon through the flame.

The luminosity of the carbon in the flame and its liberation as soot or consumption by oxygen, depends on the position at which it is formed. Two examples illustrate this point. Methane requires a high temperature for decomposition, so carbon is formed in a region of relatively high temperature and late in the flame where oxygen is present. The particles will be hot and luminous but should also be quickly consumed so that little soot is produced. other hand, acetylene decomposes at lower temperatures and carbon is formed in a relatively cool region of the flame in the presence of lower quantities of oxygen. Soot is more likely to be produced. tendency for carbon and soot formation increases with gas flow but, if the flame becomes turbulent, this tendency is offset by entrainment of more air into the flame.

Premixed flames

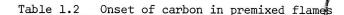
If the ratio of oxygen atoms to carbon atoms in a premixed flame is greater than 1 (0/C > 1) it seems reasonable to assume that all the carbon goes to form carbon monoxide and no solid carbon will be present. If 0/C < 1, solid carbon must be expected.

In practice, premixed acetylene-air flames become luminous when O/C is reduced to 1.2, but for many fuels the ratio is even higher - 1.5 to 2.5 - as shown by the data of Street and Thomas (1955) in Table 1.2.

Effects of pressure and temperature on soot formation

By and large, soot formation is greater at higher pressures but, in many cases, the effect is small for premixed flames.

Higher flame temperatures tend to shift the



(Street and Thomas, 1955)

Fuel	Oxygen/carbon ratio at the point of carbon formation
Ethane	2.1
Propane	2.1
<i>n</i> -pentane	2.2
<i>n</i> -octane	2.2
Ethylene	1.67
Acetylene	1.2
Benzene	1.75
Ethyl alcohol	2.5
Acetaldehyde	1.9
Diethyl ether	2.0

critical ratio to slightly richer mixtures because a greater effect is produced on the oxidation reactions rather than on the reactions producing carbon. The reverse is true for very rich mixtures and greater quantities of soot are produced at high temperatures.

Effects of additives on soot formation

The majority of substances, when added to premixed flames in small quantity, have little effect on soot formation (Gaydon and Wolfhardt, 1970). One exception is sulphur trioxide which, even in small quantities, increases the luminosity of premixed towns' gas/air and isobutane/air flames, in spite of the fact that the oxygen/carbon ratio is increased by the addition. Sulphur trioxide has little effect on diffusion flames.

The addition of 45% CO₂ stops carbon formation in a methane/air diffusion flame (Arthur, 1950).

in accordance with the Boudouard reaction, which is

$$CO \stackrel{1}{\leftarrow} \frac{1}{2} CO_2 + \frac{1}{2} C_{\text{solid}} + 20 \text{ kcal mol}^{-1}$$

Carbon formation is also reduced by some metal salts and barium salts are used to reduce smoke from diesel engines.

Electrical effects

Soot formation may be changed significantly by the application of electrical fields. Weinberg (1968) has shown considerable reductions in the amount of carbon formed and in the size of particle produced when a strong field, in the region of 10 kV, is applied. In this case, the structure of the soot was amorphous.

Production of soot

It is not possible to predict the amount of solid carbon present in a flame from equilibrium compositions. The rates of the reactions leading to the formation and removal of carbon determine whether carbon will be present. The formation of soot can be stated simply to begin with a small organic molecule and to end with a relatively large solid particle containing many thousands of atoms and a much higher carbon/hydrogen ratio than the original molecule. Such a transition must involve dehydrogenation and growth or condensation. A number of possible routes involving these processes have been suggested (Table 1.3) but no single one has been accepted in preference to the others.

1.2.2 Large Particles

(a) Char or carbonaceous residues

Coal particles decompose, when heated to a sufficiently high temperature, to produce volatile matter which is a mixture of combustible gases, carbon dioxode and water vapour. The residue, after evolution of the volatile matter, is a char particle which is comparable in size to the original coal particle. The physical form of this char is often

Route

Comments

Dehydrogenation and polymerisation via acetylene

Acetylene is a stable intermediate in rich premixed flames of other hydrocarbons. It gives soot readily under appropriate conditions, presumably because of its unsaturated character; but on the basis of O/C ratio, acetylene has a very low tendency to form soot.

Polymerisation via aromatics and polycyclic hydrocarbons

The evidence for this route lies in the similarity of the benzene ring to that of graphite and the ease with which benzene and naphthalene produce soot, both in premixed and diffusion flames. The drawback to this hypothesis is the lack of direct evidence of the presence of aromatics as intermediaries found in the flame.

Condensation and graphitisation

The formation of a mist has been observed in the pyrolysis of methane and other hydrocarbons (Parker and Wolfhard, 1950). If the products of the pyrolysis are burned as a diffusion flame, it is possible for the mist droplets (polymers) to graphitise as they pass through the flame. This route, however, is not compatible with the effect of electric fields on diffusion flames, which indicates that some growth of carbon particles must occur.

Nucleation, particle growth and coagulation

The growth of carbon particles held in a furnace through which hydrocarbon vapour is passed has been demonstrated by Tesner (1959) and it has been suggested that similar growth on appropriate nuclei, such as ions or C2, may take place in flames. The clustering of the spherical particles in soot, as shown by electron micrographs, seems to be evidence for a coagulation process.

that of a hollow sphere called a cenosphere. In these cases, where the mass is concentrated in the shell, it is suggested that the char burns effectively at constant 'diameter' until a very late stage in the combustion process.

Coals fed to power station furnaces in the UK are ground so that approximately 80% is less than 75 μ m (200 B.S. mesh). The size distribution is often expressed in terms of the mass fraction of material (dm) within an infinitesimally small interval of size (dd) by the Rosin-Rammler law:

$$\frac{\mathrm{d}m}{\mathrm{d}d} = n \ b \ d^{n-1} \ \exp(-b \cdot d^n) \tag{1.1}$$

where d is the particle size and b and n are constants. Integration of this expression gives the weight percentage (R) of material of particle size greater than d:

$$R = 100 \exp(-b.d^n)$$
 (1.2)

It is convenient to express this function in the form:

$$R = 100 \exp[-(d/d')^n]$$
 (1.3)

because d! is approximately equal to the mean particle size on a weight basis for the values of n found with ground coals (Field, Gill, Morgan and Hawksley, 1967). Values of n=1.2 and d!=50 μm may be used as reasonable estimates for pulverised coal (pulverised fuel or p.f.) in the UK.

Combustion of heavy residual fuel oils produces coked particles which result from the heavy bituminous material present. Again, it is usually assumed that these carbonaceous residues are approximately the same size as the original droplets in the spray and that the major part of the time taken for the combustion of the fuel is due to the combustion of these residues.

The droplet size distribution of a spray may be represented by the Nukiyama-Tanasawa equation (Equation 1.4), which is similar to that of the Rosin-Rammler expression (Equation 1.1). The Nukiyama-Tanasawa expression is usually stated in