

3

THE COMBUSTION BEHAVIOUR OF HYDROCARBONS

3.1 Introduction

In order to be capable of displaying burning, a chemically reacting system needs to be able to release heat to the extent of MJ or tens of MJ per kg of substance reacted. If this pre-requisite is fulfilled, the precise type of combustion behaviour which occurs, e.g., explosive or steady, depends upon other factors including the effectiveness of mixing of fuel and oxidant and, very importantly, heat transfer from reacting system to surroundings.

3.2 Heats of combustion

Table 3.1 gives some heats of combustion (calorific values) for common substances including petroleum fractions.

The calorific values of petroleum products are therefore high, twice that for dried wood. The value for natural gas is higher still. Note that the calorific values are heat released per kg of fuel; a full mass balance on the combustion would require that the weight of oxidant – almost always air in practical applications – was also accounted for. Heats of combustion of alkanes (methane, ethane, propane, butane, pentane etc.) on a molar basis obviously increase with carbon number. On a kg basis, methane is about 55 MJ kg^{-1} (as we have seen), and this drops gradually to about 45 MJ kg^{-1} for octane and higher. 45 MJ kg^{-1} is of course the heat value of petroleum distillates, and this also applies to pure alkanes beyond about C_8 . The reason why the lower hydrocarbons have higher values is their greater proportion of C—H as opposed to C—C bonds. Biodiesels have been included in the table because of their increasing importance in the moves towards carbon-neutral fuels.

A mass balance on the burning of a petroleum fuel in air, which also predicts emissions, follows. Octane C_8H_{18} (molar mass 0.114 kg) is used as a representative compound.

Table 3.1 *Heats of combustion of common materials*

Material	Heat of combustion/MJ kg ⁻¹
Wood	≈17 if 'seasoned', ≈20 if dry
Natural rubber	≈44
Bituminous coal	In the approximate range 20–35, depending on the moisture and mineral contents
Lignite	≈8 in the bed-moist state, rising to ≈20 when air dried, depending on the mineral content
Paper and cardboard	15–17
All liquid petroleum fractions (gasoline, naphtha, kerosine, diesel and residual fuel oil)	43–46
Natural gas	≈55*, depending on the precise composition
Biodiesels	≈37

* It is more conventional to express calorific values of gases in MJ m⁻³, the volume being referred to 1 bar pressure and 288 K. The calorific value of natural gas so expressed is 37 MJ m⁻³.

Element	kg per mol fuel	mol per mol fuel	Stoichiometry	Product
C	0.096	0.096/0.012 = 8	C + O ₂ ↓ CO ₂	CO ₂ 8 mol
H	0.018	0.018/0.002 = 9 (expressed as H ₂)	H ₂ + 0.5O ₂ ↓ H ₂ O	H ₂ O 9 mol

From the third and fourth columns of the table:

$$\text{O}_2 \text{ requirement} = (8 + 4.5) \text{ mol} = 12.5 \text{ mol}$$

For every mole of oxygen in the combustion, 79/21 = 3.76 moles of nitrogen involved

$$\text{Accompanying nitrogen} = (3.76 \times 12.5) \text{ mol} = 47 \text{ mol}$$

Composition of the post-combustion gas per kg of the fuel burnt.

N ₂	47 mol
CO ₂	8 mol
H ₂ O	9 mol

Allowing for condensation of the H_2O , the composition of the gas is 14.5% carbon dioxide and 85.5% nitrogen.

The calculation is for stoichiometric conditions. If, as will often be the case, there is excess air there will be some excess oxygen and correspondingly more nitrogen in the post-combustion gas.

Even if the water condenses it will not, under equilibrium conditions, be fully free of vapour. There will be the pressure of water vapour corresponding to whatever temperature the liquid water is at. If there is condensation to that degree, then to within about 20% a barrel of petroleum fuel burnt results in a barrel of water in the environment.

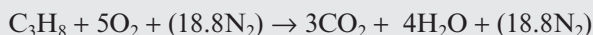
3.2.1 *Adiabatic flame temperatures*

Once a hydrocarbon/air mixture has ignited, the flame temperature attained depends upon the extent of heat transfer from flame to surroundings. Clearly the maximum temperature a flame can reach is that in the limit where burning is adiabatic, there being no heat transfer to the outside so that all of the heat of combustion is retained as sensible heat in the reaction products. To estimate adiabatic flame temperatures for hydrocarbon compound combustion is not difficult, and an example is given below.

We attempt to estimate the adiabatic flame temperature of propane, given the following data [1, 2]:

$$\begin{aligned} \text{net heat of combustion of propane} &= 2045 \text{ kJ mol}^{-1} \\ \text{specific heat of water vapour} &= 43 \text{ J }^\circ\text{C}^{-1}\text{mol}^{-1} \\ \text{specific heat of carbon dioxide} &= 57 \text{ J }^\circ\text{C}^{-1}\text{mol}^{-1} \\ \text{specific heat of nitrogen} &= 32 \text{ J }^\circ\text{C}^{-1}\text{mol}^{-1} \end{aligned}$$

Propane burns according to:



and the net heat of combustion applies where the water remains in the vapour phase: the gross value applies if the water condenses to liquid and in so doing releases its heat of vaporisation. When a mole of propane is burnt, the reaction products clearly have a heat capacity:

$$[(3 \times 57) + (4 \times 43) + (18.8 \times 32)] \text{ J }^\circ\text{C}^{-1} = 945 \text{ J }^\circ\text{C}^{-1}$$

If conditions are adiabatic, the temperature rise is:

$$(2045000/945)^\circ\text{C} = 2165^\circ\text{C}$$

This gives a final temperature, for a starting temperature of 25°C , of 2140°C .

The above calculation could be refined in a number of ways. For example, the specific heats used are those at 1200°C, whereas a more accurate treatment would incorporate these as a function of temperature. Nevertheless, the value obtained above is in fair agreement with the literature value of 2250 K (1977°C) [3] and the important point which a reader should appreciate is that adiabatic flame temperatures for hydrocarbon reactions in air are always in the neighbourhood of 2000°C. Of course, excess fuel or excess air will have the effect of lowering this temperature because of their effect on the heat capacity of the post-combustion gas, to which they add. If the working above is repeated for conditions of 20% excess fuel, the calculated adiabatic flame temperature lowers to about 2100K. As has already been pointed out, this is an upper limit on actual flame temperatures, but a useful one in that it is often approached quite closely. This will become clearer in later sections of this chapter.

3.3 Flash points

3.3.1 Introduction

If it is desired to store or transport a hydrocarbon liquid – a single compound such as benzene or a complex blend such as a petroleum fraction – judgement as to the safety is made on the basis of the flash point. This is the minimum temperature of bulk liquid at which there will be a flash if a flame is brought into contact with the equilibrium vapour, and can be determined by the open- or closed-cup methods according to national standards. As described in Chapter 1, flash points have been in use for a very long time [4] and continue, in the twenty-first century, to be the criterion by which particular liquids are assessed for fire safety. Table 3.2 gives the flash points of some liquids.

The table contains values for hydrocarbon compounds and oxygenated hydrocarbon compounds as well as ranges for diesel and coal tar.

3.3.2 Correlation of flash points of pure organic compounds with flammability limits

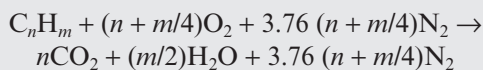
The flash point was developed as an empirical means of classifying liquids according to their ignition hazards: the higher the flash point the better. Griffiths and Barnard [6] have pointed out that at least for pure hydrocarbon compounds the flash point can be calculated on the basis that it is the temperature at which the equilibrium vapour pressure of the subject liquid (calculable from the Clausius–Clapeyron equation) is such that the vapour concentration in the air contacting the liquid corresponds to the lower flammability limit. By this means they obtained a good calculated value – in close agreement with experiment – for the flash point of toluene, and this

Table 3.2 Flash points of selected organic liquids. Taken from [5], all closed-cup values

Liquid	Flash point/°C
Benzene, C ₆ H ₆	-11
Toluene, C ₆ H ₅ CH ₃	4
<i>n</i> -octane	13
Methanol, CH ₃ OH	12
Ethanol, C ₂ H ₅ OH	13
Acetone, CH ₃ COCH ₃	-18
North American diesel fuels	82–166
Coal tars, by-product of coking	90–135

was followed by an equally satisfactory calculation of the flash point of benzene [7]. For the purposes of these calculations, the flammability limit can be taken to correspond to the proportion of fuel in the fuel–air mixture at half-stoichiometric. The method is outlined below.

Consider a hydrocarbon of ‘generalised’ molecular formula C_{*n*}H_{*m*}:



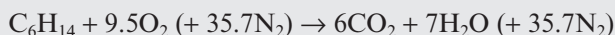
The stoichiometric proportion ϕ of the hydrocarbon vapour is given by:

$$\phi = 1/\{1 + 4.76(n + m/4)\}$$

The proportion ϕ^* at half-stoichiometric is given by:

$$\phi^* = \phi/2 = 0.5/\{1 + 4.76(n + m/4)\}$$

and this is an estimate of the proportion at the flash point. Let us apply this to one or two simple hydrocarbons, starting with hexane (boiling point 69°C) which burns according to:

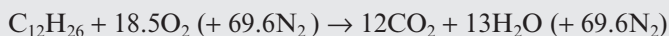


The proportion ϕ^* required for there to be a hazard when the vapour mixes with air is therefore:

$$\phi^* = 0.5/\{1 + 4.76(6 + 14/4)\} = 0.0108$$

In a total pressure of 1 atmosphere (10⁵ Pa) there will therefore be a hazard if the pressure of hexane is 1080 Pa or greater. The equilibrium vapour

pressure of hexane at 15°C is several times this, hence hexane vapour is an ignition hazard at ordinary storage temperatures. Consider now dodecane, $C_{12}H_{26}$, boiling point 216°C, which burns according to:



The proportion ϕ^* required for there to be a hazard when the dodecane vapour mixes with air is therefore:

$$\phi^* = 0.5 / \{1 + 4.76(12 + 26/4)\} = 0.0056 \text{ (0.56\%)}$$

In a total pressure of 1 atmosphere this would require a vapour pressure of the hydrocarbon of 560 Pa. Dodecane would have such a vapour pressure at about 70°C, so its vapour is not a hazard at ordinary storage temperatures.

3.3.3 Calculated flash points of petroleum fractions

3.3.3.1 Correlation with vapour pressures

It has been pointed out that the above approach can, with a few very moderate approximations, be extended to any petroleum fraction for which the Reid vapour pressure (RVP) is known [8]. In extending the calculation of flash points for pure organic compounds to petroleum fractions, the difficulties are twofold: the fact that such a fraction does not have a single boiling point, only a boiling range, and the fact that the Clausius–Clapeyron equation only applies to pure compounds. These difficulties are addressed in recent work [8]. Instead of a boiling point the RVP is used to obtain the constant of integration. There can arguably be no single value for the vapour pressure of a petroleum fraction at any one temperature, since evaporation from liquid to vapour phase causes composition changes to the liquid and the extent of this will depend on the extent of evaporation and, therefore, on the volume of the space into which the vapour is evaporating. However, the RVP is determined under standardised conditions and is viewed in the industry as ‘the vapour pressure’ of the fraction. As for the second difficulty – the non-applicability of the Clausius–Clapeyron equation – over a limited temperature range an equation of that form can be taken to apply on an empirical basis. This requires very thoughtful choice of a value for the latent heat of vaporisation at temperatures well below the boiling point, and such are available in thermodynamic tables. In this way, good values for the flash points of petroleum fractions have been calculated [8].

The difficulty of non-applicability of the Clausius–Clapeyron equation to petroleum fractions also applies to biodiesels, composed of fatty acids of

typically C₁₈. These, because of their carbon neutrality, are becoming increasingly prevalent and knowledge of their flash points is important. Attempt to calculate the flash points from the Clausius–Clapeyron equation have however been strongly deprecated [9]. With biodiesels there is no ‘operational’ quantity corresponding to the RVP for petroleum fractions which can be used in flash point estimations on the basis of flammability limits and stoichiometry.

3.3.3.2 The Factory Mutual equation

An equation originally proposed by fire researchers at Factory Mutual is:

$$t_F = 0.683t_B - 71.7 \quad \text{Eq. 3.1}$$

where t_F is the closed-cup flash point (°C) and t_B the initial boiling point (°C). The concept of ‘initial boiling point’ relates to a blend of hydrocarbon compounds such as would constitute a petroleum fraction. If the equation is to be applied to pure compounds, t_B is the normal boiling point. Investigations by the present author [10] suggest that this equation gives good agreement with experimental values for all classes of hydrocarbon compounds: alkane, alkene, alkyne and aromatic. There are corresponding correlations for families of hydrocarbon derivatives, e.g., alcohols and ethers. A calculation of the flash point of cyclohexane from the Factory Mutual equation is given below.

For cyclohexane:

$$t_B = 81^\circ\text{C} \Rightarrow t_F = -16^\circ\text{C}$$

Experimental closed-cup flash point of cyclohexane [5] = -18°C

3.3.4 Recent developments in the understanding of flash points

Flash points are expected to continue to be the basis of assessing particular liquids for fire safety in storage and transportation. The hydrocarbon specialist in the twenty-first century needs to be aware that the advances in understanding of the flash point according to the principles of ignition limits and stoichiometry [11–16] have revealed uncertainties in the widely accepted experimentally deduced flash points for some substances. For example, it has been shown by calculations based only on vapour pressures and stoichiometry [11] that the flash point of dimethyl ether given in several authoritative sources⁹ cannot possibly be correct. That for benzoic acid is also very uncertain [12, 13]. The reader is encouraged to have not a sceptical but a mildly critical attitude towards published flash point data.



Figure 3.1 *Closed-cup flash point apparatus. Reproduced courtesy of Sanyo-Gallenkamp, Loughborough, UK.*

The *fire point* of a liquid fuel is a few degrees higher than the flash point and is the temperature of the bulk liquid at which a flame is sustained when a pilot flame contacts the vapour. It can, of course, only be determined in an open-cup arrangement. It often occurs in the range 1.2–1.5 times the stoichiometric proportion of vapour. Flash points and fire points are often quite challenging to determine accurately in spite of the apparent simplicity. This is particularly so with the more basic designs of flash point apparatus. A modern and quite advanced flash point apparatus is shown in Figure 3.1. This has the features of programmability of the temperature and a sensor to detect the flash instead of reliance on visual observation.

3.3.5 Flash points in law

If a flash point is invoked in litigation it is not usually sufficient to declare that a flash point was ‘determined by the ASTM (or whatever) standard’. A formal report needs to bear the signature of an official authorised by the standards body who will have undergone training (see following section). Additionally to ASTM (USA, HQ in Philadelphia PA) there are British, European and Japanese standards’ bodies for flash points. ASTM accreditation of a UK organisation is possible via United Kingdom Accreditation Services (UKAS). As an appendix to this chapter a hypothetical but totally realistic litigation case study relating to flash points is analysed.

3.3.6 Standards for flash points

We first note the role of the standards body ISO, which was founded in 1946–7 by representatives of 25 countries. Its HQ is in Geneva. It is the world’s largest organisation for the development of standards but, as will be noted later, by no means the oldest. Its standards appertain to products, services and practices and exceed in number 19000. In fact ISO functions as a

network of national standards bodies which include, amongst many others, American National Standards Institute (ANSI), Standards Australia (formerly Standards Association of Australia), European Standards (EN) and the British Standards Institution (BSI). There are over 100 countries which are full members of ISO, that is, there is a standards body within each of the countries which is part of the network referred to. Nominees of those bodies are eligible for membership of ISO technical committees. BSI is represented on 727 such committees, ANSI on 619, Standards Australia on 439.

Sometimes a standard issued by ISO and that by the standards body representing a member country are one and the same standard, for example:

**BS EN ISO 13736:2008 Determination of flash point,
Abel closed-cup method**

This provides a method for the determination of the closed-cup flash point of liquids. It is for those with a flash point between 30.0°C and 70.0°C. There is also:

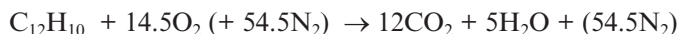
**ISO 2592 IP 36 Determination of flash and fire points,
Cleveland open cup method**

IP denotes Institute of Petroleum, a US body which is not the representative of the US at ISO. However such bodies can unite their standards with those of ISO via (in this case) ANSI. It is by no means essential that a standard issued by a standards body also have an ISO equivalent. ASTM – American Society of Testing and Materials – long predates ISO and has been involved in standards appertaining to petroleum for over a century. ASTM standards for flash points are seen as being authoritative. Calibration liquids available for particular standards, e.g. a liquid with flash point of ‘certified value 115°C’ can be purchased for use with:

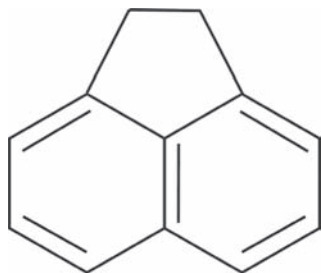
**UKAS /BS EN ISO /IEC 17025 Flash Point Reference Standard,
Cleveland Open Cup**

where IEC denotes International Electrotechnical Commission, founded in 1906 jointly by UK and US representatives, therefore well predating ISO. There will be a return in the discussion to this particular standard calibration liquid. Flash point standards are available for particular types of flammable liquid, e.g. ISO 3679:2004, the scope of which includes paints and varnishes. Its upper limit is 110°C. There is also ISO 10156:1996 for paint and lacquer thinners.

Returning to the matter of the 115°C liquid flash point standard, we examine acenaphthalene a.k.a. acenaphthene, C₁₂H₁₀ which burns according to:



Its structural formula is shown below.



Structure of acenaphthalene

According to the half-stoichiometric rule previously studied, its flash point would be at whatever temperature corresponded to the equilibrium vapour pressure:

$$[10^5 \times 0.5 / (1 + 14.5 + 54.5)] \text{ Pa} = 714 \text{ Pa. (5.4 mmHg)}$$

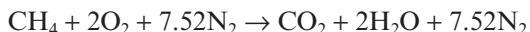
From Perry's, vapour pressure of acenaphthalene at 114.8°C is 5 mm Hg! This means that this compound matches the specifications of the standard calibration liquid referred to earlier. No claim that it is the standard can of course be made: that is proprietary information.

Examples of case studies where flash points have been invoked are provided in Table 3.3. The examples are all taken from reports published online by the US Chemicals Safety Board (CSB), HQ in Washington.

3.4 Thermal radiation and its relevance to flames

This section will not comprise an introductory sketch of radiation heat transfer *per se* – obtainable from numerous sources elsewhere – but a summary of how quite simple radiation calculations can give good predictions of flame temperatures. In later sections this will be applied to various sorts of combustion behaviour encountered in hydrocarbon accidents, including the jet fire.

Whereas radiation from a solid, e.g., a heating element, is a surface effect that from a gas is a volumetric effect. Consider the combustion of methane:



The post-combustion gas is 2:1 water vapour. Carbon dioxide and water are 'participating gases', whereas N₂ and O₂ are transparent to thermal radiation. Hydrocarbons are also strongly participating. Post-combustion products alone at say 1500 K will have an emissivity of only about 0.05–0.07. In a turbulent flame such as a jet fire unburnt fuel is mixed with the combustion products and this has the effect of dramatically increasing the emissivity, and this might be aided by the formation of carbon particles as intermediates. The flame is then said to be 'optically thick'. In fact, an estimate of radiative emission from a flame can be obtained by assuming it to be a black body at a single 'flame temperature' in the following way.

Table 3.3 *Case studies involving flash points*

Location and date	Nature of the accident	Details and reference
Houston TX, 2004	Explosion in a polyethylene wax processing facility	Flash point of the wax determined by ASTM D93-02a which is entitled: 'Standard Test Methods for Flash-Point by Pensky-Martens Closed Cup Tester' http://www.csb.gov/assets/document/Marcus_Report.pdf
Wichita KS, 2007	Explosion in a tank of solvent, initiated by static	Flash point of the solvent reported as being 14°C http://www.csb.gov/assets/document/CSB_Study_Barton_Final.pdf
de Moines IA, 2008	Fire originating in a 300 gallon tank of ethyl acetate	Flash point of ethyl acetate noted as being -4°C http://www.csb.gov/assets/document/Barton_Case_Study_-_9_18_2008.pdf
Paterson NJ, 1998	Explosion during dye manufacture. One reactant 2-ethylhexylamine	Flash point of 2-ethylhexylamine noted as being 52°C http://www.csb.gov/assets/document/Morton_Report.pdf
Georgetown CO, 2007	Cleaning at a hydroelectric plant with methyl ethyl ketone	Flash point of methyl ethyl ketone at the scene not expected to comply with the literature value because the fire began in a space measurably below atmospheric pressure http://www.csb.gov/assets/document/Xcel_Energy_Report_Final.pdf

The form of the Stefan–Boltzmann law which applies is:

$$q/A = \varepsilon \sigma \{T^4 - T_o^4\} \quad \text{Eq. 3.2}$$

where q/A = radiative flux (W m^{-2})

σ = Stefan–Boltzmann constant = $5.7 \times 10^{-8} \text{W m}^{-2} \text{K}^{-4}$

ε = emissivity = 1 for a black body

T_o = temperature of the surroundings

e.g., a methane jet fire (see section 3.6.3.) at 1300 K, surroundings at 298 K:

$$q/A = 162 \text{ k W m}^{-2}$$

This is the heat transferred by radiation which is, of course, less than the total heat released since radiation is not the only mode of heat transfer: there is convection and also loss of heat on dispersion of the burnt gas. The

proportion of heat transferred by radiation is typically about 0.2. Treatment of the flame as a black body at a single temperature is sometimes referred to as the 'solid flame model'.

3.5 Hydrocarbon combustion phenomenology

3.5.1 Preamble

We shall be concerned with types of combustion behaviour observed in hydrocarbon accidents: the jet fire, the pool fire, the fireball, the vapour cloud explosion and the flash fire. These will be given coverage adequate to equip a reader to perform basic calculations, such as might be required in an accident follow-up or for risk assessment, in respect of each.

A hydrocarbon safety professional, particularly one with a background in chemistry or chemical engineering rather than say mechanical engineering or physics, needs to be aware that there are certain features of hydrocarbon oxidation which do not normally come within the province of process safety but which are of great intrinsic interest and have been the subject of laboratory investigations from the nineteenth century to the present time. An outline of these follows.

3.5.2 Low-temperature oxidation

In all combustion phenomena of interest in process safety there is ignition, attainment of temperatures in excess of 1000°C and virtually complete conversion of the hydrocarbon to carbon dioxide and water. In laboratory reactors, batch or continuous, hydrocarbon oxidation under certain conditions of reactor temperature, total pressure and fuel:oxygen ratio enters a regime where there is no ignition, but instead 'low-temperature oxidation'. There is incomplete reaction, therefore there is unburnt fuel in the post-reaction gas, and two principal types of phenomenology. One is 'slow combustion', where the mixture of fuel and oxidant develops (and, in a continuous reactor, maintains) a temperature excess up to a few tens of degrees due to the chemical reaction. The other is 'cool flame' behaviour, where multiple flames each with an amplitude of about 100 K occur, and again conversion to products is incomplete. Cool flames are oscillatory and can, in a continuous reactor, be sustained indefinitely. Cool flames were known to Sir Humphry Davy.

Very many hydrocarbons and oxygenated hydrocarbons have, over the last 60 or so years, been examined for cool flame behaviour. In the 1970s and 1980s, acetaldehyde and propane were studied particularly closely. Modelling of such behaviour requires two coupled differential equations: one for heat balance and hence temperature (T), and one for the concentration of a chain-branching intermediate (x), which is often a peroxide. Neither a thermal nor

a kinetic model singly can represent cool flame behaviour, hence the importance of the ‘Unified Theory’, which brings the two things together and enables oscillatory behaviour to be represented as a limit cycle in the x - T phase plane. Many interesting variants on simple oscillatory behaviour have been reported experimentally, including temperature histories such that cool flames and full ignitions alternate [17] and abrupt changes in both the oscillation amplitude and frequency in response to a very small adjustment in the reacting conditions [18].

Apart from recognition of their possible role in engine knock [3], cool flames have received relatively little attention in the context of *applied* combustion science. This is undoubtedly at least partly because, as already pointed out, the types of combustion behaviour with which fuel technologists and fire protection experts are concerned are not in the low-temperature oxidation regime, but in the ‘full ignition’ regime. Over the last 25–30 years huge amounts of reliable experimental data on cool flames for various organic compounds, and related modelling, have found their way into the research literature. There is scope for further thought as to how all of this might profitably be incorporated into hydrocarbon safety practice. For example, is the thermal behaviour leading to any of the ‘full ignition’ phenomena of interest preceded by cool flame behaviour, as has certainly been observed in laboratory experiments? If so, is there scope for enhanced safety by suppression of cool flames using a suitable chemical additive? Here is possibly a fruitful area of future R&D.

3.5.3 Jet fires

A jet fire is the combustion behaviour expected when a gas or two-phase hydrocarbon leaks from a small orifice and ignites. In the previous chapter it was shown how to calculate the rate of discharge from the upstream pressure, and this in turn can be used to make simple estimations of jet fire length.

A jet fire is ‘non-premixed’: fuel exits the orifice as pure fuel and all contact with oxidant (air) is subsequent to this. It is not a diffusion flame. In such, fuel–air contacting is purely by diffusion, whereas in a jet fire flame there is also mixing due to the momentum with which the fuel exits the orifice. There are, in the literature, many correlations for jet fire length, including:

$$L(\text{m}) = 18.5 (Q/\text{kg s}^{-1})^{0.41} \quad \text{Eq. 3.3}$$

where L is the length and Q is the discharge rate. An application is in the following shaded area.

Consider a 1 cm² hole in a gas-bearing pipe or vessel containing methane at 30 bar. The ambient temperature is 15°C. Using equations 2.1 and 3.3, and

taking the coefficient of discharge to have value unity, calculate the length of the resulting jet flame if there is ignition.

Solution

$$Q = C_d AP \sqrt{(M\gamma/RT)[2/(\gamma+1)]^{(\gamma+1)/(\gamma-1)}}$$

↓

$$Q = 0.52 \text{ kg s}^{-1}$$

↓

$$L = 14.1 \text{ m}$$

In principle there has to be an orientation dependence of the jet flame length, but in ORA a single equation such as the above is often taken to apply to all orientations. The orientation influences the flame properties via convection coefficients, diffusion (with its gravity dependence) and radiation view factors. Horizontal flames might tend to become ‘banana shaped’ through buoyancy effects, whilst not differing markedly in length from a vertical one receiving the same influx of fuel gas. In two-phase flow, it is possible for the liquid to ‘rain out’ at the orifice exit, and burn separately as a pool fire.

In modelling of the radiation field around a turbulent jet flame, the flame can be represented as a point source of energy half way along the axis. In our previous numerical example, therefore, it would be 7 m from the leak orifice and 7 m from the flame tip. Incident flux q' (W m^{-2}) a distance D from this point source given by:

$$q' = FQ/4\pi D^2 \tag{Eq. 3.4}$$

where F = proportion of the heat transferred by radiation (≈ 0.2 if the fuel is methane) and Q = total rate of energy release by the combustion (W).

At distances very close to the flame the model breaks down. Under such circumstances the ‘black body’ flux is taken to apply for the purposes of simple combustion calculations. Predictions of injuries to persons can be made, e.g., skin burns require 10 kW m^{-2} for about 10 s or 100 kW m^{-2} for 1 s. These ideas are illustrated in the following example.

A pipe bearing natural gas at an internal pressure of 70 bar, temperature 288 K, develops a leak of area 2 cm^2 . Calculate:

The leak rate, if the coefficient of discharge = 0.8

The length of the resulting jet flame

The total rate of release of energy by the flame
 How close to the flame a person would need to be to experience skin
 burns through 10 s of exposure
 Calorific value of methane = 55.6 MJ kg⁻¹

Solution

For methane, $\gamma = 1.3$, $M = 0.016 \text{ kg mol}^{-1}$
 also, $C_d = 0.8$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 288 \text{ K}$

↓

$$Q = 1.9 \text{ kg s}^{-1} \quad \text{flame length} = 24 \text{ m}$$

Total rate of heat release =

$$1.9 \text{ kg s}^{-1} \times 55.6 \times 10^6 \text{ J kg}^{-1} = 1.06 \times 10^8 \text{ W (106 MW)}$$

Now a distance D from the flame: $q' = FQ/4\pi D^2$ (equation 3.4)

For skin burns through 10 s of exposure

$$q' = 10 \text{ kW m}^{-2}$$

$$10 \text{ kW m}^{-2} = 106000 \text{ kW} \times 0.2 / [(4\pi D^2) \text{ m}^2]$$

↓

$$D = 13 \text{ m}$$

3.5.4 Pool fires

A pool fire occurs when flammable liquid is spilt and ignites. Pool fires are laminar only up to about 10 cm diameter; larger ones are turbulent. The flame front contains a high proportion of evaporated fuel vapour at a relatively high temperature, making the flame front emissive. Radiative heat transfer from the flame front to the pool surface promotes further evaporation. A pool fire displays a steady burning rate until fuel is close to being depleted, and there are two means of estimating the steady mass loss rate per unit pool area.

Assigning this the symbol m' :

$$m' = 0.1 \text{ kg m}^{-2} \text{ s}^{-1} \text{ for any pool fire}$$

This is used in ORA, where the only liquid fuel of interest is crude oil. Alternatively:

$$m' = 10^{-3} \frac{\text{heat of combustion}}{\text{heat of vaporisation}} \text{ kg m}^{-2} \text{ s}^{-1}$$

e.g., benzene: heat of combustion 41859 kJ kg^{-1}
 heat of vaporisation 436 kJ kg^{-1}

$$m' = 10^{-3} \times \{41859/436\} \text{ kg m}^{-2} \text{ s}^{-1} = 0.096 \text{ kg m}^{-2} \text{ s}^{-1}$$

There are also several experimentally based correlations in the literature for pool fire height, e.g.:

$$H/D = 42 \left\{ m' / \left[\sigma_a \sqrt{gD} \right] \right\}^{0.61} \quad \text{Eq. 3.5}$$

where $D(\text{m})$ = pool diameter and $H(\text{m})$ = pool height, σ_a = density of air at ambient temperature (kg m^{-3}), g = acceleration due to gravity (9.81 m s^{-2}). This applies to a pool fire in still air; a modification is required if there is wind.

Thermal radiation from a pool fire is represented similarly to that for a jet fire. The fire is treated as a point source, and:

$$q_{\text{rad}}(x) = Q_{\text{rad}}/4\pi x^2 \quad \text{Eq. 3.6}$$

where $q_{\text{rad}}(x)$ = radiative flux (W m^{-2}) a distance x from the source

Q_{rad} = total radiation rate (W)

$$Q_{\text{rad}} = \lambda m Q \quad \text{Eq. 3.7}$$

where Q = total heat-release rate (W)

m = mass burning rate (kg s^{-1})

λ = fraction of total combustion heat transferred as radiation

Example

A tank containing gasoline is surrounded by a circular dike of diameter 10 m. The gasoline leaks and occupies the area bounded by the dike. If there is ignition, calculate:

- the total radiative flux from the flame
- the flame temperature
- the radiative flux a person standing 15 m from the circumference will experience

Use a value of 0.4 for λ , a value of $0.1 \text{ kg m}^{-2} \text{ s}^{-1}$ for m' , a value of 1.17 kg m^{-3} for the density of air at ambient temperature and a value of 45 MJ kg^{-1} for the calorific value of the fuel.

Solution

$$m = m' \{ \pi r^2 \} = 7.9 \text{ kg s}^{-1}$$

$$\text{Total rate of radiation } (Q_{\text{rad}}) = 0.4 \times 7.9 \times 45 \times 10^6 \text{ W}$$

$$= 1.4 \times 10^8 \text{ W}$$

$$\text{Height given by equation 3.5: } H/D = 42 \left\{ m' / \left[\sigma_a \sqrt{gD} \right] \right\}^{0.61}$$

⇓

$$H/D = 2.3, H = 23 \text{ m}$$

The 'area' can be approximated by a cylinder of height H and diameter D , whereupon:

$$\begin{aligned} \text{radiative flux} &= [1.4 \times 10^8 / (2\pi \times 5 \times 23)] \times 10^{-3} \text{ kW m}^{-2} \\ &= 194 \text{ kW m}^{-2} \end{aligned}$$

$$\begin{aligned} \text{approximating to a black body, temperature} &= \\ \{ 194000 / \text{Stefan-Boltzmann constant} \}^{1/4} &= 1360 \text{ K} \end{aligned}$$

The flux at a distance of 15 m is clearly:

$$q_{\text{rad}}(x = 15 \text{ m}) = Q_{\text{rad}} / 4\pi x^2 = 1.4 \times 10^8 / (225 \times 4\pi) = 50 \text{ kW m}^{-2}$$

3.5.5 Fireballs and BLEVEs

'Fireball' means rapid combustion of a 'catastrophically leaked' quantity of fuel, with a duration usually of the order of seconds. A BLEVE (boiling liquid expanding vapour explosion) is a particular sort of fireball, involving a substance which is gas at room temperature but which is stored at such temperatures as a liquid under its own highly superatmospheric vapour pressure. The usual examples of substances displaying BLEVE behaviour are LPG (primary constituent propane) and vinyl chloride monomer (VCM). A BLEVE is actually a physical, not a chemical, explosion and can involve non-flammable substances. When a pressure cooker (in which the fluid is of course water) blows up, that is a BLEVE. If the substance having undergone such an explosion is flammable and ignition follows, a fireball is the result and the 'BLEVE-fireball' is the most precise description. This is often simply called a BLEVE.

Liquefied natural gas (LNG) is a cryogen and though it might burn as a fireball it does not BLEVE in the sense described in the final sentence of the previous paragraph. Physical explosions are possible with LNG, in which case BLEVE behaviour in that sense might be considered in a follow-up. BLEVEs are not expected at offshore installations; the susceptible materials are not to be found there. Fireballs are expected in the event of sudden release of gas or

two-phase inventory. Generic equations and correlations for 'fireballs' are often applied to BLEVEs.

An experimental correlation for maximum fireball diameter is:

$$D(\text{m}) = 5.25[M(\text{kg})]^{0.314} \quad \text{Eq. 3.8}$$

where M = quantity released.

There are several variants on this, some used in ORA. A correlation for duration of a fireball is:

$$t_p(\text{s}) = 2.8(V/\text{m}^3)^{1/6}$$

where t_p = duration and V = vapour volume leaked, referred to ambient conditions (1 bar, 288 K).

e.g., for 100 tonne (10^5 kg) methane, using equation 3.8:

$$D(\text{m}) = 5.25[10^5]^{0.314} \text{ m} = 195 \text{ m}$$

$$V = \{1 \times 10^5 / 0.016\} / (P/RT) \text{ m}^3 = 149652 \text{ m}^3$$

$$t_p = 20 \text{ s}$$

Fireballs pose a significant radiation hazard. The proportion of the combustion heat radiated from the fireball is about 0.2. Calculations are complicated by the fact that a fireball, unlike a jet fire or pool fire, cannot be treated as being steady. A recent [19] simplified thermal treatment of fireballs uses a previously reported experimental plot of radiation flux against a suitably defined dimensionless time [20] as a 'template', in order to calculate peak fireball temperature for particular amounts of propane so burnt. This will be explained in the following outline.

The dimensionless time is:

$$t' = g^{0.5}t/V^{1/6}$$

where t = time since ignition (s), g and V are as previously defined. The *maximum* heat release occurs at about $t' = 6$. Now the plot of radiative flux against dimensionless time for a propane fireball [20] can, to a fair approximation, be drawn as an isosceles triangle with its apex at the time corresponding to $t' = 6$ and the baseline spanning t' values of 0 and 12. The plot so re-drawn is reproduced as Figure 3.2. The dashed line is the triangle and the solid line shows approximately where and how the true plot deviates from it. The maximum is shown as a cusp, whereas of course it is a smooth maximum in the original. The calculation in the shaded area below builds upon these ideas. It is based on information given in [20].