# Limiting values of the thermal power and flame temperature from hydrocarbon pool fires

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As well known, risk is a combination of probability and consequences of an accident. Different concepts were developed in evaluating accident consequences. First, the worst-case concept, meaning that the most negative consequences imaginable are described. A more applied approach is the reference to the maximum credible accident scenario. In analyzing the consequence of accidental hydrocarbon fires and the potential for domino effects, the evaluation of the flame extent and temperature are of the utmost importance. The primary effects of pool fires are due to thermal radiation and issues of interplant/tank spacing employees' safety zones, fire wall specifications are to be addressed on the basis of a proper consequence analysis. In order to avoid too conservative results, imposing anti-economic geometric constraints, for example in term of spacing, a realistic scenario evaluation is therefore needed. By means of real scale experimental tests it was verified that both the thermal power and the flame temperature T increase as the pool area increases, up to reach maximum values in connection with a "critical pool dimension". Dealing with pool areas higher than the critical one, experimental results, performed by different researchers at different scales, show a decrease of T. An in-depth analysis of the different concurring phenomena connected to a pool fire development allowed identifying the limiting step controlling the flame temperature. In fact, the trend of T is mainly determined by the increasing difficulty of oxygen diffusion within the internal bulk of gaseous hydrocarbons.

In this paper, we propose a pool fire model suitable:

- to provide a theoretical insight into the above-mentioned experimental trends;
- to obtain the maximum values of the flame temperature and of the thermal power, considering the pool size and the chemico-physical characteristics of the hydrocarbon.

#### 1. Introduction

Usually, the development of a pool fire requires:

- a release of some liquid flammable material (LNG, LPG, gasoline and so on), forming a pool on the soil;
- the rapid vaporization and mixing with air of the substance, up to generate a flammable cloud;
- an effective ignition source.

Once initiated, the fire can behave in different ways, according to the characteristics (size, shape, temperature and composition) of the liquid pool and the possible interactions with the surroundings (confinement, windy or calm environment, nature of the soil, etc.).

In particular, very high wind speeds could even extinguish the flame arising from relatively small pools.

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In all the other situations, the behaviour of the fire after the ignition is qualitatively similar, since it invariably involves:

- an increase of the vaporization rate, due to the radiating heat absorbed from the pool;
- the formation and rise of a column of hot gases, which favours the entrainment and mixing with the flammable vapours of increasing quantity of fresh air, and after all the fire power;
- The increase of the temperature up to a level determined from the balance between the aforesaid power and the heat transferred to the environment, particularly as sensible heat of the fumes and by radiation.

When this temperature is reached, the fire goes on in pseudo steady-state conditions, up to the exhausting of the pool. Even if pool fires have been studied for many years, at present no best approach to fire modelling is available in the scientific and technical literature.

The specific analysis of rather complicated situations (partial confinement, irregular shapes, complex kinetics, unsteady-state) usually requires the use of sophisticated integral models and/or CFD calculations.

On the contrary, when entire classes of similar phenomena can be described by means of few, important variables, and only approximate, conservative results are enough, relatively simple analytical models can be more useful. The simplified approach of this study aims to correlate the maximum radiating power of the fire with the characteristics of the flammable material and the pool size.

In order to treat these situations, following simplifying assumption can be made:

- pseudo steady-state conditions;
- simple geometry (circular pools) and still air conditions;
- global rate of combustion controlled by stoichiometry (provided that the gas phase lies within the flammability limits, practically instantaneous reaction occurs, owing to the high temperatures).

Then, the radiating heat from the unit surface,  $q_r$ , can be calculated by means of few parameters, such as:

the pool diameter,  $D_0$ ; the height, h, the mean temperature, T, of the flame and the properties of the involved substances.

Moreover, the experimental results obtained by various researchers, summarized by Crawley (1982), show that h and T varies with the pool size according to typical behaviours summarized in Table 1 and Figure 1. In the following, we develop a relatively simple pool fire model justifying these behaviours and suitable to calculate with good approximation the maximum thermal power emitted from a pool fire.

*Table 1- Aspect ratio*  $(h/D_0)$  *of the pool, as a function of the pool size.* 

Diameter of the pool D <sub>0</sub> [m]	h/D <sub>0</sub>
~ 0,10	3÷4
1	2÷2,5
10÷15	1,5÷2

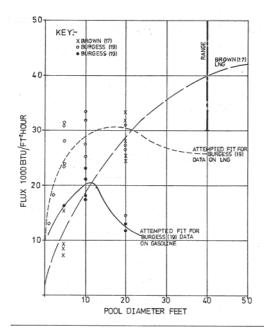


Fig. 1 Experimental data for LNG and gasoline pool fires (Crawley, 1982).

### 2. Model description

#### 2.1 Essential features of the model

Parameters used to model pool and flame shape are as follows. Let P be a circular pool of diameter  $D_0$ , containing a liquid hydrocarbon  $C_mH_n$ , and F the flame zone, characterized by cylindrical symmetry [radius R(z), height h] and mean temperature T, where the hydrocarbon vapours mix with the surrounding air, A, and burn. In the following, the attention will be focused on the interconnected phenomena involved in the behaviour of the hot gases in the flame region F.

### 2.2 Combustion stoichiometry

Let  $n_v$  and  $n_{ah}$ , be respectively, the molar flow rates of hydrocarbon vaporizing from the pool and of air entrained into the hot column. Taking into account the stoichiometry and assuming the complete combustion of the hydrocarbon:

$$C_mH_n+(m+n/4)O_2=mCO_2+n/2H_2O$$
 (1)

the molar flow rates of the gaseous components entering and leaving the system are easily calculated as summarized in Table 2.

As the flame burns out above the height h, we assume than the composition of the gas mixture reaches the low flammability limit, LFL, at the end of the region F. Nevertheless, the LFL varies with the content of the inert gases in the mixture. In particular, according to Lewis et al. (1961), increasing the diluents concentration, the oxygen one decreases down to a minimum value, while the hydrocarbon concentration only slightly increases, as shown in Table 3.

Table 2- Molar flow rates of the i- component involved in the pool fire ( $n_{ie}$  and  $n_{iu}$  are the molar inflows and outflows, respectively; the ratios  $V_{ih}$  are used in equation (12) for calculating  $\Delta H$ .

Component	n <sub>ie</sub> [kmol s <sup>-1</sup> ]	n <sub>iu</sub> =n <sub>ih</sub> [kmol s <sup>-1</sup> ]	$v_{ih} = n_{ih}/n_v$
$C_mH_n$	$n_{\rm v}$	-	-
$O_2$	$0,21n_{ah}$	$0,21n_{ah}$ - $(m+n/4)n_v$	0,21 <i>f</i> -m-n/4
$N_2$	$0,79n_{ah}$	$0,79 n_{ah}$	0,79 f
$CO_2$	-	$mn_v$	m
$H_2O$	-	$(n/2)n_v$	n/2
Total	$n_{\rm v} + n_{\rm ah}$	$n_{ah}+(n/4)n_v$	<i>f</i> +n/4

Table 3- Compositions of some mixtures at low flammability limit  $(y_L, and y_{LO_2})$  are the molar fractions of hydrocarbon and oxygen, respectively): m=mixture with the minimum oxygen concentration;  $s=stoichiometric\ mixture$ .

Combustive		Metl	Methane		Propane		Hexane	
		$\mathbf{y}_{L}$	$y_{\text{LO}_2}$	$\mathbf{y}_{\mathrm{L}}$	$y_{\text{LO}_2}$	$\mathbf{y}_{\mathrm{L}}$	$y_{LO_2}$	
air		0,053	0,199	0,022	0,205	0,012	0,207	
air diluted with $N_2$	(m)	0,060	0,120	0,029	0,117	0,018	0,119	
air diluted with H <sub>2</sub> O	(m)	0,068	0,138	-	-	0,021	0,134	
air diluted with CO <sub>2</sub>	(m)	0,071	0,147	0,037	0,142	0,022	0,145	
air diluted with $N_2$	(s)	0,060	0,120	0,027	0,126	0,014	0,140	
air diluted with H <sub>2</sub> O	(s)	0,067	0,138	-	-	0,015	0,149	
air diluted with CO <sub>2</sub>	(s)	0,070	0,147	0,030	0,153	0,016	0,158	

Since nitrogen represents nearly 90% of the inert gases in the fumes, in the following we assume that the molar fraction of the oxygen at height h,  $y_{O_2h}$ , corresponds to that of the stoichiometric mixture where the diluent is pure nitrogen, reported as  $y_{LO_2}$  in the fifth row of Table 3.

On the other hand, from Table 2 it results  $y_{O_2h} = [0.21n_{ah} - (m+n/4)n_v]/[n_{ah} + (n/4)n_v]$ . Then:

$$n_{ah} = n_v \left[ m + (1 + y_{O_2h}) n/4 \right] / (0,21 - y_{O_2h})$$
(2)

Since steady-state conditions are assumed, the mass flow rate of the fumes leaving the system is simply the sum of the entering ones:  $m_h=m_v+m_{ah}=M_vn_v+M_an_{ah}$  or else, by virtue of equation (2):

$$m_h = M_a f_s n_v \tag{3}$$

where  $f_s$  is a stoichiometric coefficient given by:

$$f_s = [m + (1 + y_{O_2 h})n/4]/(0,21 - y_{O_2 h}) + (12m + n)/29$$
(4)

on assuming  $M_v=12m+n$  and  $M_a=29$  as hydrocarbon and air molar mass [kg kmol<sup>-1</sup>], respectively. As one can verify, it practically results:  $M_f\cong M_a=29$  kg kmol<sup>-1</sup>, and  $m_h\cong m_{ah}$ , independently of the considered hydrocarbon

#### 2.3 Buoyancy and entrainment

According to Palazzi et al. (2005), the velocity of the fumes leaving the system is:

$$v_h = [(r-1)gh]^{1/2}$$
 (5)

where:

$$r = \rho_a / \rho_f \cong T / T_a \tag{6}$$

The global mass flow rate at the height h can be expressed as:

$$m_h \cong m_{ah} = 2\pi R_h v_h f_e \rho_f h \tag{7}$$

where  $f_e$  is an entrainment constant. On the other hand, by definition, it also results:

$$m_h = \pi R_h^2 V_h \rho_f \tag{8}$$

## 2.4 Heat exchanges and energy balance

Since  $T \gg T_a$  and  $T \gg T_1$  some simplifications are allowed, as:

$$T^4 - T_a^4 \cong T^4 - T_1^4 \cong T^4$$
;  $T - T_1 \cong T - T_a$ .

The heat radiating from the unit surface of the hot region, q<sub>r</sub>[kW m<sup>-2</sup>], is:

$$q_r = \varepsilon \sigma T^4 \tag{9}$$

being  $\epsilon$  the flame emissivity and  $\sigma$ =5,67·10<sup>-11</sup>kWm<sup>-2</sup>K<sup>-4</sup> the Stephan-Boltzman constant. Let  $\Delta H_v$  the heat of vaporization of the hydrocarbon at its normal boiling point, the vapour molar flow rate is determined from equation:

$$n_{v} = \pi R_0^2 \epsilon \sigma T^4 / \Delta H_{v}. \tag{10}$$

The energy balance of the system can be written:

$$\Delta H n_v = -2\pi R_h h \varepsilon \sigma T^4. \tag{11}$$

In the last equation,  $\Delta H$  is the enthalpy difference for unit mol of vapourized hydrocarbon, calculated as:

$$\Delta H = \Delta H_c + \Sigma v_{ih} c_{pmi} (T - T_a) + (n/2) \Delta H_{vH_{\gamma}0}$$
(12)

where  $\Delta H_c$  is the enthalpy of combustion of the hydrocarbon,  $c_{pmi}$  the mean specific heat of the component i,  $\Delta H_{vH_2O}$  the heat of vaporization of the water at temperature  $T_a$  and the values of the ratio  $v_{ih}$ = $n_{ih}/n_v$  are reported in Table 2.

### 2.5 Model development

On combining equations (3), (5), (7), (8), (10) and (11), the variables T, h,  $R_h$ ,  $m_h$ ,  $n_v$  and  $v_h$  can be correlated to the pool size,  $R_0$ .

To the end of this study, the following equations are particularly useful:

$$R_0 = \left[2M_a^2 f_s^2 \epsilon^2 \sigma^2 T^8 \Delta H_v^{1/2}\right] / \left[f_e^{3/2} \rho_f^2 (r-1) g(-\Delta H^{5/2})\right]$$
(13)

$$h/D_0 = (1/4)[-\Delta H/(f_e \Delta H_v)]^{1/2}$$
(14)

since they allow calculating, once given  $R_0$ , the values of the other source parameters, h and T, usually required to estimate the risk of exposition to thermal radiation.

### 3. Results and discussion

In Table 4 are reported the values of the most significant parameters involved in pool fires of different size and the corresponding thermal radiation, obtained by means of the equations (13), (14) and (9), with reference to some representative hydrocarbons. The calculations were accomplished by putting  $\varepsilon$ =1 and  $f_e$  =0,06. Owing to the conservative assumption on the emissivity, both the hydrocarbon vaporization and the energy transferred to the environment are overestimated. These observations evidence that the cautious assumption  $\varepsilon$ =1 exerts opposite effects on the fire strength and determines only a slight underestimation of the temperature, while  $q_r$  is anyhow overestimated.

The value of  $f_e$ , corresponding to the maximum fit of the calculated results with the experimental data, is reasonably interposed between the ones  $(0,01\div0,04)$  characterizing the development of fires into a confined environment (Palazzi et al., 2005) and those  $(0,32\div1,2)$  related to turbulent free jets (Palazzi, 2001). By assimilating methane, propane and hexane to LNG, LPG and gasoline respectively, the results in Table 4 agrees fairly well with the set of experimental data reported by Crawley (1982), in particular as regards the trend of T,  $q_r$ , and  $h/D_0$  in pools of intermediate size ( $D_0$  up to  $5\div6$  m). Although the calculated values of  $q_r$  can be considered conservative, one should remember that the model gives only the mean level of the specific heat radiation. Since the temperature is not uniformly distributed in real fires, some of the experimental values of  $q_r$  can exceed those reported in Table 4, in limited portions of the flame surface. In any case, the mean value of  $q_r$  seems more useful than the maximum one, to obtain more realistic estimates of the global heat radiation of the flame.

At last, a brief discussion is developed in the following on the physical significance and on the limitations of the trends in Table 4, also in comparison with the experimental results reported in Figure 1. The behavior of a real fire due to the combustion of a given hydrocarbon generally depends not only on the pool size, but also on various constraints, arising from fluid-dynamics, energy balance, stoichiometry, kinetics and

diffusive limitations. The last two items have no effect on the results in Table 4, since our model is based on the hypothesis of an instantaneous, complete combustion, so that the hydrocarbon immediately burns as it mixes with air. The increasing trends of T,  $h/D_0$  and  $q_r$  versus the pool diameter then reflect the combined effects of the other constraints.

In particular, T increases when  $R_0$  increases, as the rate of heat generation is proportional to the rate of vaporization of the hydrocarbon, and then to  $R_0^2$ , whereas the rate of the heat transfer to the environment is proportional to  $R_0$ h, and h increases more slowly than  $R_0$ . The sensible heat of the fumes also rises with T, so that  $\Delta H$  continuously shrinks, according to equation (12). The condition  $\Delta H$ =0 then determines the asymptotic value of T, as, from equation T,  $R_0$  tends to infinity.

Hence, according to our model, the behavior of T,  $q_r$ , and  $h/D_0$  as a function of  $R_0$  is essentially determined by the energy balance. Practically speaking, this consideration is rigorous only in the range of the pool sizes where the kinetics and diffusive limitations are effectively negligible. Indeed, decreasing  $R_0$ , the temperature continuously decreases, so that the hypothesis of instantaneous reaction no longer holds, owing to the reduction of the kinetic constant. Since the rate of vaporization also diminishes, below a certain critical size the combustion rate becomes even too low to sustain the fire. Therefore, the behavior of the small flames is largely dominated by the kinetics. On the other hand, the rate of mixing of air with the hydrocarbon vapours in also limited, being determined by intensity of turbulence and pool size. Then, increasing  $R_0$ , the hypothesis of uniform concentration at the height h becomes much less realistic, since increasing quantities of mixture lie below the LFL in the inner part of the ascending hot gases, leaving the system unburned. This empirical evidence modifies the heat balance, so that the temperature increases more and more slowly, up to reach a maximum value,  $T^*$ , in correspondence of a particular pool size,  $R_0^*$ .

Table 4- Dependence of the most significant properties of pool fires on the size.

Hydrocarbon	y <sub>LO<sub>2</sub></sub>	D <sub>0</sub> [m]	h [m]	T [K]	h/D <sub>0</sub>	q <sub>r</sub> [kW m <sup>-2</sup> ]
Methane	0,120	0,1	0,31	899	3,1	37
		1	2,5	1028	2,5	63
		6	12	1108	2,0	86
		15	26	1140	1,7	96
		$\infty$		1243		
Propane	0,126	0,1	0,32	886	3,2	35
		1	2,6	1011	2,6	59
		6	12	1086	2,0	79
		15	27	1116	1,8	88
		œ		1210		
Hexane	0,140	0,1	0,34	830	3,4	27
		1	2,6	932	2,6	43
		6	12	990	2,0	55
		15	27	1012	1,8	60
		œ		1076		

The above-mentioned behaviour is depicted in the already-mentioned Figure 1, showing experimental results obtained from LNG (Brown et al., 1974) and gasoline pool fires (Crawley, 1984). The trends show a small reduction of the temperature beyond the critical pool size  $R_0^*$ , due to the increasing of the mass of the hydrocarbon heated by the flame, without burn. These effects are more pronounced for the higher hydrocarbons, whose reaction initially involves some endothermic steps, subtracting even more energy to the system, if a complete combustion does not take place. Although the existence of a maximum temperature of the flame connected to diffusive limitations, the precise values of  $R_0^*$  and  $T^*$  depend as well on the properties of the fuel.

Notwithstanding the aforesaid restrictions, the proposed model can be used without modifications to estimate the radiating heat of a pool fire. Indeed, it allows obtaining suitable results for pools of diameters up to 5÷6 m, and conservative estimates in case of greater pools.

### 4. Conclusions

The analytical pool fire model here presented appears relatively straightforward to use, allowing a cautious estimate of the thermal power and of flame geometric parameters.

The model matches fairly well experimental data reported in literature for different kinds of hydrocarbons. Moreover, it explains on a physical basis the trends of the flame temperature, height and heat radiation versus the pool size.

The model can be applied to calculate in a simple way the radiating heat, obtaining suitable results for pools of diameters up to 5÷6 m and conservative estimates in case of greater pools.

The geometry of the pool is dictated by the surroundings (i.e. diking) and even if the model was successfully applied to the most common situation of circular pool, it must be remarked that it can be easily adapted to investigate similar scenarios (e.g. road and rail tunnel fires wind effect, and so on).

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