

VOL. 26, 2012

Guest Editors: Valerio Cozzani, Eddy De Rademaeker Copyright © 2012, AIDIC Servizi S.r.I., ISBN 978-88-95608-17-4; ISSN 1974-9791



DOI: 10.3303/CET1226061

# Flame Heights of Di-tert-butyl Peroxide Pool Fires -Experimental Study and Modelling

Stefan Schälike\*<sup>a,b</sup>, Klaus-Dieter Wehrstedt<sup>a</sup>, Axel Schönbucher<sup>b</sup>

<sup>a</sup>Federal Institute for Material Research and Testing (BAM), Unter den Eichen 87, 12205 Berlin, Germany <sup>b</sup>University Duisburg-Essen, Institute for Chemical Engineering I, Universitätsstr. 7, 45141 Essen, Germany \*stefan.schaelike@bam.de

The flame heights of di-tert-butyl peroxide (DTBP) pool fires with diameters between 0.03 m < d < 3 m are determined by means of visible images obtained by a VHS video recorder. The time-averaged  $H_{av}$  and maximum flame height  $H_{max}$  were evaluated according to the intermittency criterion. For the relative time-averaged flame heights values in a range of  $3.1 < H_{av}/d < 14.8$  are obtained while the relative maximum flame heights are in a range of  $3.5 < H_{max}/d < 17.6$ . The experimental measurements were used to establish a new Froude number correlation.

# 1. Introduction

Case histories have shown that pool fires belong to the most frequent accidents when combustible substances are released in the process industry e.g. during transport or storage (Persson and Lönnermark, 2004; Mannan, 2005). A key quantity for hazard calculations based on pool fires is the flame height due to its influence on the view factor calculation for determining the critical thermal distances. A wide set of experimental data and empirical correlations are available e.g. for wood crib fires (Thomas, 1963), LNG fires (Moorhouse, 1982) and gasoline or JP-4 fires (Heskestad, 1983; Mangialavori and Rubino, 1992, Pritchard and Binding, 1992; Muños et al., 2004) depending on the fuel and pool diameter *d*. The flame heights of other hazardous substances like organic peroxides are less understood and only a few sets of flame height data are available (Wehrstedt and Wandrey, 1993; Chun, 2007; Mishra, 2010). Organic peroxides are known to be highly reactive, combustible and more or less thermally unstable compounds, due to their energy-rich -O-O- peroxy bond. Di-tert-butyl peroxide (DTBP) is a compound of wide industrial use as an initiator for radical reactions, a resin hardener or a crosslinking agent. To close the lack of missing data on the flame height of organic peroxides laboratory- and large-scale pool fire tests with di-tert-butyl peroxide are conducted.

# 2. Materials and Methods

## 2.1 Locality

The laboratory tests were carried out in a special test bunker (10 m x 5 m x 5 m). Air ventilation was used to get ambient conditions after each fire test. The ventilation was stopped during the tests to achieve wind still conditions.

The field experiments were conducted on a circular test area enclosed by a three-sided earth wall. Wind still conditions were awaited and low thermal lift was achieved by starting the tests at still air.

Please cite this article as: Schaelike S., Wehrstedt K.D. and Schoenbucher A., 2012, Flame heights of di-tert-butyl peroxide pool fires – experimental study and modeling, Chemical Engineering Transactions, 26, 363-368 DOI: 10.3303/CET1226061

#### 2.2 Flame height measurements

The flame heights during the burning of circular steel pans of different diameters (0.03 m, 0.06 m, 0.5 m, 1 m and 3 m) completely filled with fuel were determined by means of the visible images obtained from a VHS video recording. The sequences of the stationary burning time were digitalized and divided into images at 25 frames per second. A MATLAB algorithm was then used to evaluate the maximum height of the visible luminous flame on basis of a temperature criterion for each image defined by the RGB colour model (R 255, G 242, B 199) (Heskestad, 2002). In this study the time-averaged  $H_{av}$  as well as maximum flame height  $H_{max}$  were evaluated according to the intermittency criterion (Zukoski et al., 1985). The intermittency I(H) is defined as the fraction of time in which the flame height is at least higher than H. The time-averaged flame height is defined as the height at which the intermittency reaches a value of 0.5 and the maximum flame height is determined by the height the intermittency reaches a value of 0.05 (Zukoski, 1995).

## 3. Theory

Pool fires are referred to as buoyancy driven diffusion flames. The combustion is a result of the evaporation of the liquid fuel caused by the heat feedback from the combustion zone. Volatiles driven off from the pool surface mixed with the surrounding air raises up and form a turbulent fire plume. Morton et al. (1958) developed an integral formulation for a fire plume with the assumptions of a point source of buoyancy, small density variations compared to the ambient density, an air entrainment velocity being proportional to the local vertical plume velocity, similar profiles for vertical velocity and the buoyancy force in horizontal section and a "top hat" temperature and axial velocity profile (Morton, 1959; Morton, 1965). This theory is supported by experimental measurements on hydrocarbon pool fires. Heskestad (1983) correlated the flame height of laboratory scale fires in the absence of wind against the non-dimensional parameter N:

$$N = \left[\frac{c_{\rho,air} T_{a}}{g \rho_{a}^{2} \left(-\Delta h_{c} / r\right)^{3}}\right] \frac{\dot{Q}_{c}^{2}}{d^{5}} = \frac{\pi^{2} c_{\rho,air} T_{a} r^{3}}{16 \left(-\Delta h_{c}\right)} Fr_{f}^{2}$$
(1)

where  $\dot{Q}_c$  is the total heat release rate,  $c_{p,air}$  is the specific heat of air at constant volume,  $\rho_a$  and  $T_a$  are the ambient density and temperature, g is the acceleration of gravity,  $\neg \Delta h_c$  is the heat of combustion and r is the actual stoichiometric mass ratio of air to fuel. For many fuels and different diameters this correlation is:

$$H/d = -1.02 + \frac{A}{d}Q_c^{2/5} = -1.02 + 15.6 N^{1/5}$$
<sup>(2)</sup>

with 
$$A = 15.6 \left[ \frac{c_{\rho,air} T_a}{g \rho_a^2 (-\Delta h_c / r)^3} \right]$$

A typical value is  $A = 0.235 m / W^{2/5}$  which is valid over a wide range of hydrocarbon fuels, besides gasoline with  $A = 0.200 m / W^{2/5}$  and acetylene with  $A = 0.211 m / W^{2/5}$ . For a wide engineering use the flame heights are correlated against the fuel Froude number  $Fr_f$  defined as:

$$Fr_{f} = \frac{m_{f}}{\rho_{a}\sqrt{g\,d}} \tag{3}$$

where  $\dot{m}_{r}''$  is the mass burning rate of the fuel. By using Eqs.(1,2) these correlations typically have the form:

$$H/d = a Fr_f^b u^{*c} \tag{4}$$

where a, b, c are empirical coefficients and  $u^{c}$  is a scaled wind velocity which can be neglected in the absence of wind. The empirical coefficients a, b, c for hydrocarbon pool fires obtained from many experiments are listed in Table 1:

Correlation name	a [-]	b [-]	c [-]	Notes	Reference		
Thomas 1	42	0.61		wooden crib fires; <i>H</i> <sub>av</sub> /d	[Thomas, 1963]		
Thomas 2	55	0.67	-0.21	wooden crib fire; <i>H<sub>max</sub>/d</i>	[Thomas, 1963]		
Moorhouse 1	6.2	0.254	-0.044	44 LNG pool fires; cylindrical flame shape;[Moorhouse, 1982] H <sub>max</sub> /d; d = 12.2 x 15.4 m			
Moorhouse 2	4.7	0.21	-0.114	4 LNG pool fires; conical flame shape;[Moorhouse, 19			
				<i>H<sub>max</sub>/d; d</i> = 12.2 x 15.4 m			
Mangialavori	31.6	0.58		heptanes, hexane and isobutene	[Mangialavori and		
and Rubino				pool fire; <i>H<sub>max</sub>/d</i>	Rubino, 1992]		
Pritchard and	10.615	0.305	-0.03	mostly LNG pool fires;	[Pritchard and		
Binding				d = 6 – 22 m; <i>H<sub>max</sub>/d</i>	Binding, 1992]		
Muños 1	7.74	0.375	-0.096	gasoline and diesel pool fires;	[Muños et al.,		
				d = 1 – 6 m; <i>H<sub>av</sub> /d</i>	2004]		
Muños 2	8.44	0.298	-0.126	gasoline and diesel pool fires;	[Muños et al.,		
				d = 1 – 6 m; <i>H<sub>max</sub>/d</i>	2004]		
Fay	15.5	0.4		$H_{av}\!/d$ calculations and LNG pool fires	[Fay, 2006]		

 Table 1: Parameters used to evaluate the relative flame heights of hydrocarbon pool fires by Eq.(4)

To check the quality of the obtained estimates evaluated from the different correlations the normalized mean square error (NMSE) and the fractional bias (FB) used by Rew and Deaves (1995) is applied. Given observed values  $x_e$  and the corresponding predicted values  $x_p$ , NMSE and FB can be calculated from:

$$NMSE = \frac{1}{n} \sum_{1}^{n} \frac{(x_{e} - x_{p})^{2}}{x_{e} x_{p}}$$
(5)

and

$$FB = \frac{1}{n} \sum_{1}^{n} 2 \frac{x_e - x_p}{x_e + x_p}$$
(6)

NMSE measures the degree of correlation while FB indicates the degree of deviance.

## 4. Results and discussion

The flame heights of DTBP pool fires depending on the pool diameter corresponding to the intermittency criterion (Figure 1, d = 3 m) are shown in Table 2 together with the mass burning rates (Chun, 2007) and fuel Froude numbers used in Eq.(3):

Table 2: Measured flame heights of DTBP pool fires

d	[m]	0.03	0.06	0.5	1	3
H <sub>av</sub> /d	[-]	14.80	12.83	7.52	5.45	3.10
H <sub>max</sub> /0	d [-]	17.50	16.92	11.54	8.90	3.89
ṁ″ <sub>f</sub>	[kg/(m²s)]	0.18	0.20	0.26	0.28	0.30
Fr <sub>f</sub>	[-]	0.24	0.20	0.09	0.07	0.04

It is found that  $H_{av}$  of DTBP pool fires is two times higher than that of hydrocarbon (Muños, 2004) pool fires. From Eq.(2) with r = 0.075 and  $-\Delta h_c = 36600$  kJ/kg (Chun, 2007) for DTBP follow



Figure 1: Intermittency of H/d for a DTBP pool fire d = 3 m

The data for both  $H_{av}$  and  $H_{max}$  (Table 2) are correlated with Eq.(4) with c = 0 (without wind):

$$H_{av} / d = 46.65 F r_f^{0.80} \tag{8}$$

$$H_{\rm max} / d = 56.96 \, Fr_{\rm f}^{0.76} \tag{9}$$

In Figure 2 the results of Eq.(8) are shown in comparison with the experimental results and with the correlations for  $H_{av}/d$  from Table 1. In Figure 2 and Table 3 it can be seen that the Heskestad, the Fay and the Muños 1 correlation underestimate the measured  $H_{av}$  of DTBP pool fires especially for smaller diameters while for larger diameters (d = 3 m)  $H_{av}$  is better estimated. The Thomas 1 correlation gives a relatively good estimate of  $H_{av}$  over the whole investigated diameters. The *best* estimate is given by the new Eq.(8) since the NMSE and FB in Table 3 show the smallest deviances.

In Figure 3 and Table 4 the results of Eq.(9) are shown in comparison with the experimental results and with the correlations for  $H_{max}/d$  from Table 1. It can be seen that the Moorhouse 1, Moorhouse 2 and Muños 2 correlations underestimate  $H_{max}$ . The Mangialavori and Thomas 2 correlation lead to a better estimate. The best estimate is given by the new Eq.(9) since the NMSE and FB in Table 3 show the smallest deviances.

Table 3: NMSE and FE of different correlations for  $H_{av}/d$ 

	Heskestad	Muños 1	Thomas 1	BAM		
NMSE [-]	0.780	0.794	0.031	0.007		
FB [-]	0.319	0.474	-0.083	-0.018		



Figure 2: Experimental and correlated  $H_{av}/d$  against the pool diameter

It is remarkable, that the coefficients a  $\approx$  50 and b  $\approx$  0.8 used in Eqs. (8, 9) are considerably higher than those previously used with hydrocarbon pool fires.



Figure 3: Experimental and correlated H<sub>max</sub>/d against the pool diameter

	Moorhouse 1	Moorhouse 2 Muños 2		Pritchard and Mangialavori		Thomas 2	BAM
				Binding	and Rubino		
NMSE [-]	0.885	1.288	0.537	0.311	0.068	0.027	0.010
FB [-]	0.689	0.795	0.469	0.323	-0.115	-0.547	0.007

Table 4: Comparison NMSE and FE of different correlations for H<sub>max</sub>/d

#### 5. Conclusions

1. The time-averaged flame height  $H_{av}/d$  of DTBP pool fires is two times higher compared to hydrocarbon pool fires, which leads consequently to larger critical distances to be observed to the vicinity.

2. Common flame height correlations derived from hydrocarbon pool fires fail to estimate the  $H_{av}/d$  and  $H_{max}/d$  of DTBP pool fires.

3. New Froude number correlations are proposed and applied specifically for DTBP.

#### References

Chun, H., 2007, Experimental investigation and CFD simulation of DTBP pool fires. PhD Thesis, BAM Dissertation Series, Volume 23, Berlin, ISBN 978-3-981655-0-0.

Fay, J., 2006, Pool fire models. Hazard. Mater. B 136, 219.

Heskestad, G., 1983, Luminous flame heights of turbulent diffusion flames. Fire Saf. J., 5, 103.

Heskestad, G., 2002, in DiNenno, P.J (Ed.) SPFE Handbook of Fire Protection, 3<sup>rd</sup> ed., National Fire Protection, Quincy, 2-1.

Mangialavori, G., Rubino, F., 1992, Experimental tests on large-scale hydrocarbon pool fires. 7<sup>th</sup> International Symposium on Loss Prevention and Safety Promotion in Process Ind., Taormina, Italy, 83-1.

Mannan, S., 2005, Fire. In Lee's Loss Prevention in the Process Industries, Elsevier Butterworth-Heinemann, Oxford, 16/1.

Mishra, K. B., 2010, Experimental investigation and CFD simulation of organic peroxide pool fires. PhD Thesis, BAM Dissertation Series, Volume 63, Berlin, ISBN 978-3-9813550-6-2.

Moorhouse, J., 1982, Scaling criteria for pool fires derived from large-scale experiments. I. Chem. Sym., 71, 165.

Morton, B.R., 1959, Forced plumes. J. Fluid Mech., 5, 151.

Morton, B.R., 1965, Modeling fire plumes, Proc. Combust. Inst., 10, 973.

Morton, B.R., Taylor, G.I., Turner, J.S., 1965, Turbulent gravitational convection from maintained and instantaneous sources. Proc. Roy. Soc., A234, 1.

Muñoz, M., Arnaldos, J., Casal, J., Planas, E., 2004, Analysis of the geometric and radiative characteristics of hydrocarbon pool fires. Combust. Flame, 139, 263.

Persson, H., Lönnermark, A., 2004, Tank fire review of fire incidents 1951-2003, Brandforsk Project 513-021, Swedish National Testing and Research Institute, Boras, Sweden.

Pritchard, M.J., Binding, T.M., 1992, A new approach for predicting thermal radiation levels from hydrocarbon pool fires. Symp. on Major Hazards Onshore and Offshore, Manchester, 491.

Rew, P.J., Deaves, D.M., 1995, The validation and application of pool fire models, SERA 4.

Thomas, P.H. 1963, The size of flames from natural fires. Proc. Combust. Inst., 9, 844.

Wehrstedt, K.-D., Wandrey, P.A., 1993, Burning behavoir of liquid and explosive compounds in dependence of the pool diameter. PTB-Bericht W-54, ISBN 0341-6739, 97.

Zukoski, E.E., Cetegen, B.M., Kubota, T., 1985, Visible structure of buoyant diffusion flames. Proc. Combust. Inst., 20, 361.

Zukoski, E.E., 1995, in Cox, G. (ed.): Combustion Fundamentals of Fire, Academic Press, San Diego, 101.