Mass Burning Rate of a Large TBPB Pool Fire – Experimental Study and Modeling

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Data and prediction for the mass burning rate of a tert-butyl-peroxy-benzoat (TBPB) pool fire (pool diameter = 3 m) is presented. The mass burning rates of TBPB fires are up to six times higher and less dependent on pool diameter compared to hydrocarbon pool fires caused by an additional heat release rate due to exothermic decomposition reaction in the liquid phase. This heat release rate is calculated using a 1st order reaction kinetic obtained from micro calorimetric measurements. A new model is derived considering the heat release rate due to the decomposition reaction which is shown to be 100 % of the heat release rate radiated to the pool surface. With the presented model, including also physical quantities, especially the limiting fuel concentration for upward flame propagation, it is possible to predict the mass burning rates of large TBPB pool fires. The predicted values are in very good agreement with the experiments.

1. Introduction

Pool fires belong to the most frequent accidents when combustible substances are released in the process industries during transport, handling or storage (Person and Lönnermark, 2004; Mannan, 2005). A pool fire is defined as a buoyancy controlled non-premixed flame which burns above a liquid pool due to vaporization with a small initial momentum. A key quantity for hazard calculations relating to pool fires in fire safety science is the mass burning rate $\dot{m}_f''$. For hydrocarbon pool fires a wide set of experimental data e.g. (Blinov and Khudiakov, 1957; Burgess et al., 1961; Mudan, 1984) and theoretical studies e.g. (Hottel, 1959; Hertzberg, 1973; Burgess and Hertzberg, 1974) on the mass burning rates depending on the fuel and pool diameter d are available. The mass burning rates of other hazardous substances like organic peroxides are less understood and only a few sets of pool fire data are available (Wehrstedt and Wandrey, 1993; Chun, 2005; Mishra and Wehrstedt, 2012). Di-tert-butyl-peroxy-benzoate (TBPB) is a compound of wide industrial use as an initiator for radical reactions, a resin hardener or a cross linking agent. To close the lack of missing data on the mass burning rates of organic peroxides a large-scale pool fire experiment with TBPB is conducted. A new model to describe the mass burning rates of TBPB pool fires taking into account the heat release rate due to the liquid phase decomposition reaction is presented.

2. Experimental setup

The large-scale experiment with the TBPB fire (d = 3 m) has been carried out on the open air BAM Test-site Technical Safety (in Horstwalde, south of Berlin). Steel trays were used with a rim height of 0.08 m, the fuel layer had a thickness of 0.05 m. The mass loss during the burning of the fuel was measured with a load cell mounted under the tray as one point of a three-point construction. The mass loss records had a time resolution of $\Delta t = 0.1$ s and a precision of 0.25 %. The fuel temperatures during the burning of the peroxide were measured with NiCr-Ni thermocouples (1 mm in diameter, time resolution of $\Delta t = 0.01$ s with a precision of 0.1 K) connected to a multi data recorder. The thermocouples were placed in 1 cm steps on the radial coordinate r beginning at the flame axis (r = 0) and on three axial positions x_{tc}. The thermocouple

measurements are corrected for thermal conduction (Sears, 1954) against what heat losses due to thermal radiation are negligible. The heat of combustion is measured with an IKA-C5003 using DIN 51900-3 (DIN 51900-3, 2005).

3. Theory

The experimental studies of Blinov and Khudiakov (1957) on liquid hydrocarbon (HC) pool fires have shown two basic burning regimes are possible: convectively dominated burning for small diameter $d \leq 20$ cm and radiatively dominated burning for $d \geq 20$ cm, particularly for $d \geq 1$ m. In the convective regime the flow can be laminar or turbulent and is always turbulent for radiatively driven flames. Flames in the radiative regime can be optically thin or thick. These distinctions can be made on basis of the pool diameter (Babrauskas, 1984) shown in Table 1.

Table 1: Burning modes of pool fires depending d

pool diameter d [m]	burning mode
< 0.05	convective, laminar
0.05 to 0.2	convective, turbulent
0.2 to 1	radiative, optically thin
≤ 1	radiative, optically thick

For the mass burning rate Hottel (1959) has modelled:

$$\dot{m}_f''(d) = \frac{\dot{Q}_{ba,tot}(d)}{A_P(T_{f,bp}\,c_{p,v} - T_{f,a}\,c_{p,a} + \Delta h_v)} \tag{1}$$

where $\dot{Q}_{ba,tot}$ is the total heat release rate back to the fuel surface, A_P is the pool area, $T_{f,bp}$, $T_{f,a}$ are the fuel temperatures at the boiling point (bp) and at ambient temperature (a), $c_{p,v}$, $c_{p,a}$ are the heat capacities of the fuel vapor and the liquid fuel at ambient temperature and Δh_v is the enthalpy of evaporation. For safety engineering application the radiative, optically thick regime is of primarily interest, so Eq.(1) can be simplified to:

$$\dot{m}_f'' = \frac{\dot{Q}_{ba,rad}}{A_P(T_{f,bp}\,c_{p,v} - T_{f,a}\,c_{p,a} + \Delta h_v)} \tag{2}$$

where $\dot{Q}_{ba,rad}$ is the heat release rate due to radiation back to the fuel surface. For this radiation regime Burgess and Hertzberg (1974) developed a model based on the following physical quantities, where it is assumed that the term with the heat capacity difference in the denominator of Eq. (2) is much smaller then Δh_v:

$$\dot{m}_f'' \equiv \beta \frac{-\Delta h_c}{\Delta h_v} = f_{rad}\frac{\varepsilon_{F,f}}{\varepsilon_F}\varphi_{F,f}\,c_f\,S_u\,\frac{-\Delta h_c}{\Delta h_v} \approx 10^{-3}\frac{-\Delta h_c}{\Delta h_v} \tag{3}$$

where β is a composite factor, f_{rad} is the fraction energy radiated, ε_F is the flame emissivity, $\varepsilon_{F,f}$ is the flame emissivity as viewed by the absorbing liquid fuel reservoir, $\varphi_{F,f}$ is the view factor between the flame and the fuel surface, $c_f = UEL\,\rho_v$ is the limit fuel concentration for upper flame propagation, UEL is the upper explosion limit, ρ_F is the density of the fuel vapor and S_u is the limit burning velocity for natural convection. For hydrocarbon pool fires realistic values for the quantities in β are $f_{rad} = 0.5$, $\varepsilon_F / \varepsilon_{F,f} = 0.5$, $\varphi_{F,f} = 0.4$, $c_f = 0.032 \cdot 3\,\text{kg/m}^3 = 0.096\,\text{kg/m}^3$, S_u = 0.06 m/s.

4. Results and discussion

4.1 Fuel surface temperature and heat of combustion

A measurement of the fuel surface temperatures is shown in Figure 1. The arrow indicates the time where the fuel surface has the same height as the thermocouple. Hence, the fuel temperature of the liquid phase is given on the left side of the arrow while the right side of the arrow shows the gas phase temperature short above the fuel surface. An averaged value of the fuel surface temperature T_v = 403 K is constant over the surface area. The depth of penetration of the hot-zone a_{hz} into the liquid fuel indicated by a temperature increase to 310 K is much lower for TBPB pool fires ($a_{hz,TBPB} \approx$ 4.5 mm at t = 100 s) in comparison to hydrocarbon pool fires e.g. n-heptane pool fires ($a_{hz,HC} \approx$ 12 mm at t = 100 s) (Nakakuki, 1994; Cheng et al., 2011). The smaller $a_{hz,HC}$ is caused by the higher energy loss due to the high evaporation rates in TBPB pool fires which inhibits the heat being conducted deep into the fuel. The sharp temperature decrease at t = 130 s is due to the effect of a periodic flame oscillation which is not considered in this paper (Mishra, 2009).
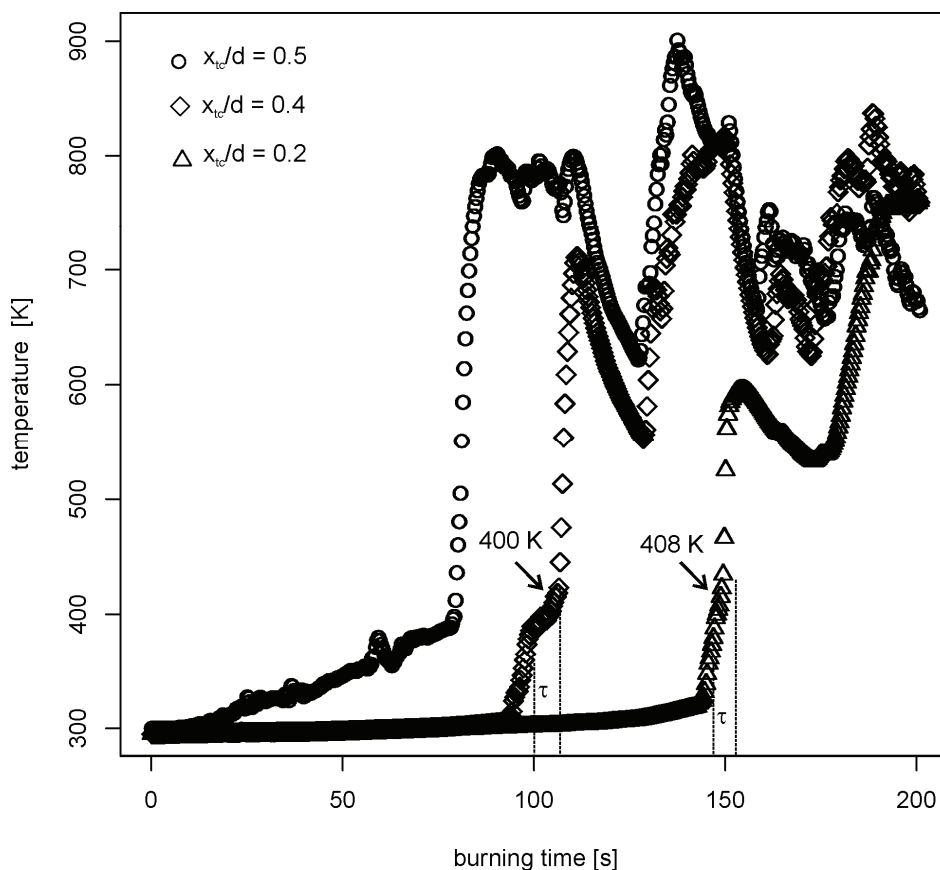

Figure 1: Fuel surface temperatures of a TBPB pool fire at the pool center, where x_{tc} is the height of the thermocouples over the pool surface

The measured heat of combustion is $-\Delta h_c$ = 30,113 kJ/kg.

4.2 Mass burning rate

The mass burning rate of the TBPB pool fire (d = 3 m) during the steady burning time is measured to be $\dot{m}''_f = 0.37$ kg/(m² s). It can be seen that the mass burning rate of the TBPB pool fire is up to six times higher than mass burning rates known from hydrocarbon pool fires $\dot{m}''_{f,TBPB}(d = 3\,m)/\dot{m}''_{f,HC}(d = 3\,m) \approx 6$.

In the following it can be shown that Eqs.(1-3) are not applicable for TBPB pool fires without modifications. This is caused by a heat release rate $\dot{Q}_d$ due to the decomposition reaction of the liquid TBPB which has

to be introduced into Eqs. (1-3). Using the energy balance of Burgess and Hertzberg (1974) modified by including the additional heat release rate $\dot{Q}_d$, leads to:

$$\dot{m}_f'' = \frac{\dot{Q}_{ba,rad} + \dot{Q}_d}{A_p (T_v c_{p,v} - T_{f,a} c_{p,a} + \Delta h_v)} \qquad (4)$$

Eq. (4) is valid for radiatively controlled pool fires (d ≥ 1 m) which occur during an accident and show a little variation of the mass burning rate with increasing diameter. Therefore it is only necessary to predict one critical value for the mass burning rate in a range d ≥ 1 m.

The heat release rate $\dot{Q}_d$ in Eq.(4) can be calculated using the model assumption of an ideal, isotherm, continuous stirred tank reactor (CSTR). This model can be used, because the decomposition reaction occurs only in a thin liquid layer. During the combustion process this layer sinks down, whereby the products formed in the liquid phase by the decomposition reaction are vaporized and fresh liquid TBPB enters into the reaction zone. The expected conversion is very small, so that the liquid is ideal mixed. The thickness δ_{rz} of the reaction zone for a TBPB pool fire d = 3 m can be calculated using Eq.(5):

$$\delta_{rz} = v_a(d)\, \tau(d) \approx 3.6 \cdot 10^{-4} \text{ m/s} \cdot 9 \text{ s} \approx 3 \cdot 10^{-3} \text{ m} \qquad (5)$$

where $v_a = \dot{m}_f'' / \rho_l$ is the burning velocity, τ is the residence time and equal that time the liquid phase has a temperature at which a significant conversion can occur (365 K < T < 403 K). A 1st order (n = 1) reaction kinetic with a reaction rate constant $k = 9.5 \cdot 10^{-3}$ s^{-1} at T_v = 403 K is taken from measurements of Chung-Ping et al. (2012). For the CSTR a residence time can be calculated by:

$$\tau(d) = \frac{V_{rz}}{\dot{V}_{in}} = \frac{\delta_{rz}}{v_a(d)} \qquad (6)$$

where $V_{rz} = \delta_{rz} A_P$ is the volume of the reaction zone, $\dot{V}_{in} = v_a(d) A_P$ is the volume flow rate entering the reaction zone. With known τ and with a stoichiometric coefficient $\nu = -1$ the Damköhler number Da can be calculated by:

$$Da = \tau k \qquad (7)$$

The Damköhler number is directly connected to the conversion U in a CSTR for n = 1:

$$U = \frac{Da}{1+Da} \qquad (8)$$

With the enthalpy of the exothermic decomposition $-\Delta h_d$ = 1,377 kJ/kg obtained from measurements of Malow and Wehrstedt (2005) the heat release rate $\dot{Q}_d$ can be calculated as:

$$\dot{Q}_d(\dot{m}_f'') = U(\dot{m}_f'')\, \dot{m}_f''\, A_P\, (-\Delta h_d) \qquad (9)$$

Using Eqs. (4-9) and the heat capacities for TBPB $c_{p,v}$ = 1.4 kJ/(kg K) (Goos and Burcat, 2010), $c_{p,a}$ = 1.7 kJ/(kg K) obtained from Gimzenski and Audley (1993), the enthalpy of vaporization Δh_v = 205 kJ/kg (Lide, 1996), the heat release rate $\dot{Q}_{ba,rad,TBPB}$ for the radiative optical thick regime and the heat release rate $\dot{Q}_d$ can be calculated for the TBPB pool fire (Table 2). It can be recognized that the heat release rate $\dot{Q}_d$ is ≈ 100 % of $\dot{Q}_{ba,rad,TBPB}$. The fire is controlled by two different mechanism given by the heat release rate $\dot{Q}_{ba,rad,TBPB}$ and the heat release rate $\dot{Q}_d$. The heat release rate $\dot{Q}_{ba,rad,TBPB}$ is about two times higher than those of hydrocarbon pool fires. The exothermic decomposition reaction plays a major role in peroxide pool fires directly affecting the fuel surface area.

Table 2: Heat fluxes of a radiatively controlled TBPB pool fire (d = 3 m)

$\dot{Q}_d$	$\dot{Q}_{ba,rad,TBPB}$	$\dot{Q}_d / \dot{Q}_{ba,rad,TBPB}$	$\dot{Q}_{ba,rad,HC}$	$\dot{Q}_{ba,rad,TBPB} / \dot{Q}_{ba,rad,HC}$	$\dot{Q}_d / A_P$
364 kW	366 kW	0.99	190 kW	1.93	51 kW/m²

Based on Eqs. (3),(4),(9) a new model for $\dot{m}_f''$ for TBPB pool fires is developed and leads in the radiatively controlled limit (d ≥ 1 m) to:

$$\dot{m}_f'' = \frac{\beta\,(-\Delta h_c) + \left(\dfrac{\beta}{S_u\, c_f} + 1\right)\dot{Q}_d / A_P}{c_{p,v}\, T_v - c_{p,a}\, T_a + \Delta h_v} \tag{10}$$

For the calculation of β from the quantities given in Eq.(3) the values of HC pool fires are used, but the fuel concentration c_f is calculated using specific data for TBPB. This peroxide is flammable over a wide range of mixtures up to < 100 % (Brandes and Möller, 2008). High concentrations of ignited TBPB do not yield in carbon dioxide and water as main products. New investigations (Schälike et al., 2012) show that organic peroxides have two different ignition steps in the fuel rich region. The first ignition step happens as a thermal decomposition of the TBPB which leads in the gas phase mainly to the products benzene, carbon dioxide, acetone and ethane (Tobolski and Mesrobian, 1954). The second ignition step is a high temperature ignition of the decomposition products leading to chain branching. Hence, for flame propagation not only the decomposition, but also the high temperature ignition has to be taking into account. Therefore, the benzene concentration at T_v = 403 K is chosen as the limiting species for a sustainable flame. Using the ideal gas law for density calculation ρ_v and the upper explosion limit UEL (8.6 vol.%, (Brandes and Thedeus, 2003)) of benzene leads to a limit benzene concentration of c_f = 0.086 ·2.4 kg/m³ = 0.21 kg/m³. With this value of c_f for TBPB pool fires the constant β is calculated as β = $1.32 \cdot 10^{-3}$ kg/(m² s). With the new model Eq. (10) it is for the first time possible to predict the mass burning rates for large pool fires of liquid peroxides, e.g. TBPB or DTBP. Substituting the discussed values for the influencing quantities into Eq.(10) a mass burning rate $\dot{m}_{f,pred}''$ = 0.39 kg/(m² s) for a TBPB pool fire (d = 3 m) in the radiatively controlled limit can be predicted in very good agreement with measurements $\dot{m}_{f,exp}''$ = 0.37 kg/(m² s). This model can be used to describe the mass burning rates of large TBPB pool fires which is very helpful in safety science applications. For safety science it is also important to have conservative values from the model which should not under predict the experimental results.

5. Conclusions

In this study the mass burning rate of a TBPB pool fire is studied and a new model is developed. The major results can be summarized:

1. The mass burning rate of a TBPB pool fire in the radiatively controlled optically thick regime is six times higher than those of hydrocarbon pool fires.

2. For a TBPB pool fire an additional heat release rate $\dot{Q}_d$ due to an exothermic decomposition reaction in the liquid phase of the fuel is introduced. The calculation of $\dot{Q}_d$ is based on a 1st order reaction kinetic which depends on the conversion, mass burning rate, pool cross section, and the heat of decomposition. It can be shown that $\dot{Q}_d$ is ≈ 100 % of the heat release rate $\dot{Q}_{ba,rad,TBPB}$ radiated back to the fuel surface.

With the heat release rate $\dot{Q}_d$ a new model is developed to predict the mass burning rates for large pool fires of liquid peroxides.

3. Further can be shown from the new model that the radiated heat release rate to the fuel surface of TBPB pool fires is two times larger than that heat release rate for hydrocarbon pool fires.

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