Multiple Fires of Organic Peroxides and Hydrocarbons

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- ➢ Mass burning rates of peroxide pool fires

- ➢ Mass burning rates of multiple peroxide and HC pool fires
- ➢ Flame heights of multiple peroxide and HC pool fires
- ➢ Thermal radiation of peroxide pool fires

- ➢ Conclusions

Mass burning rates according to Hottel (1959):

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

n-pentane, d = 25 m

$$\dot{m}''_f \approx 0.06\,\text{kg/(m}^2\,\text{s)}$$

$\dot{m}''_f$	[kg/(m² s)]	mass burning rate
$\dot{Q}_{ba,tot}$	[kW]	total
A_P	[m²]	pool surface area
Δh_v	[kJ/kg]	enthalpy of vaporization
$c_{p,v}$	[kJ/(kg K)]	heat capacity of fuel vapor
$c_{p,f}$	[kJ/(kg K)]	heat capcity of the liquid fuel
$T_{f,bp}$	[K]	boiling temperature
$T_{f,a}$	[K]	ambient temperature

Model for the mass burning rate of HC pool fires according to Burgess und Hertzberg (1962):

$$\dot{m}''_f = \beta \frac{-\Delta h_c}{\Delta h_v} \approx 10^{-3}\,\text{kg/(m}^2\,\text{s)} \frac{-\Delta h_c}{\Delta h_v}$$

$-\Delta h_c$	[kJ/kg]	enthalpy of combustion

$$\beta = f_{rad} \frac{\varepsilon_{F,f}}{\varepsilon_F} \varphi_{F,f}\, S_u\, c_f = 5.8 \cdot 10^{-4}\,\text{kg/(m}^2\,\text{s)}$$

$f_{rad} = 0.5$: Fraction of heat radiated

$\varphi_{F,f} = 0.4$: View factor between flame and pool

$\frac{\varepsilon_{F,f}}{\varepsilon_F} = 0.5$: Emissivity ratio

$S_u = 0.06\,\text{m/s}$: Limit burning velocity for natural convection

$c_f = \rho_v \cdot \text{UEL} = 3.1\,\text{kg/m}^3 \cdot 0.031 = 0.096\,\text{kg/m}^3$: Maximum fuel concentration for flame propagation

Di-tert-butyl peroxide,
(DTBP), d = 3.4 m

$\dot{m}_f'' \approx 0.30\,\mathrm{kg/(m^2 s)}$

Tert-butyl peroxybenzoate
(TBPB), d = 3.4 m

$\dot{m}_f'' \approx 0.37\,\mathrm{kg/(m^2 s)}$

Tert-butyl peroxy-2-ethyl
hexanoate (TBPEH),
d = 3.4 m

$\dot{m}_f'' \approx 0.53\,\mathrm{kg/(m^2 s)}$

Microcalorimetric measurements for DTBP, TBPB show a 1st order kinetic:

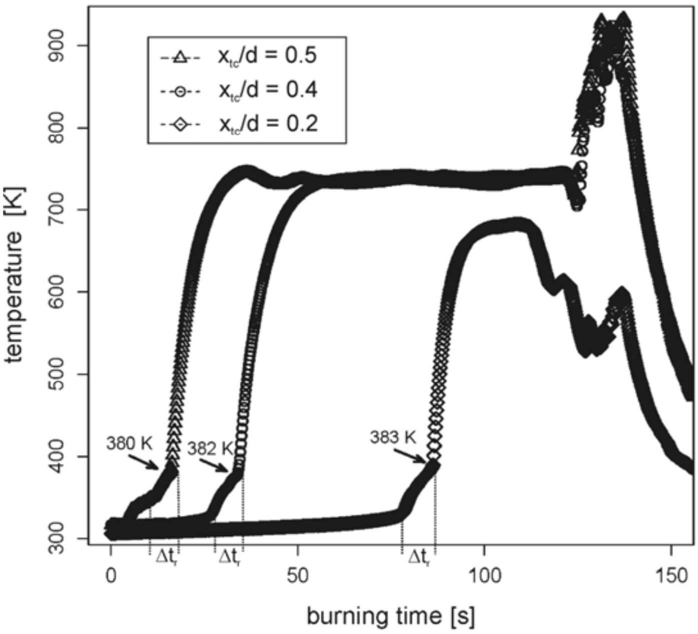
$$T_{onset} \approx 365\,\mathrm{K} \quad ,$$

$$T_{SADT} \approx 358\,\mathrm{K} \quad , \quad T_{SADT} \approx 338\,\mathrm{K}$$

DTBP
(aliphatic)

TBPB
(aromatic)

Reason: Aromatic compounds show a lower heat capacity and consequently



Liquid phase decomposition during the burning (reaction time $\Delta t_r \approx 5 - 10$ s) has to be taken into account.

Thermocouple measurements at different heights of the liquid (left side of the arrows) und gas phase (right side of the arrows) of a DTBP pool fire (d = 0.06 m)

An additional heat rate due to liquid phase decomposition $\dot{Q}_d$ has to be taken into the energy balacnce:

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

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

$-\Delta h_d$	[kJ/kg]	heat of decomposition
U	[–]	conversion

$\dot{Q}_d$ can be modeled as an ideal, isotherme, continuously stired tank reactor (CSTR):

$$\boxed{Da = \tau\, k(T) = \Delta t_r\, k(T)}$$

Da	[–]	first order Damköhler number
τ	[s]	space time
k	[s^{-1}]	reaction rate constant

$k \approx 5 \cdot 10^{-3}\ s^{-1}$

$$\boxed{U = \frac{Da}{1 + Da} \approx 0.02 - 0.04}$$

Heat rates in peroxide pool fires

d = 3. 4 m		DTBP	TBPB
$\dot{Q}_d$	[kW]	150	364
$\dot{Q}_{ba,rad}$	[kW]	379	366
$\dot{Q}_d / \dot{Q}_{ba,rad}$	[–]	0.4	0.99
$\dot{Q}_d / A_P$	[kW/m²]	21	51
$\dot{Q}_{ba,rad,P} / \dot{Q}_{ba,rad,HC}$	[–]	2	1.9

The observed higher mass burning rates of peroxide pool fires can be explained by the additional heat rate due to liquid phase decomposition $\dot{Q}_d$.

Model for the mass burning rates of peroxide pool fires based on energy balance according to Burgess und Hertzberg:

$$\boxed{\dot{m}''_{f,th} = \frac{\beta(-\Delta h_c) + \left(1 + \frac{\beta}{S_u\, c_f}\right)\dot{Q}_d / A_P}{\Delta h_v + c_{p,v} T_{f,b} - c_{p,f} T_{f,a}}}$$

$\dot{m}''_{f,exp} = 0.30\,\mathrm{kg/(m^2 s)}$	$\dot{m}''_{f,th} = 0.31\,\mathrm{kg/(m^2 s)}$	DTBP
$\dot{m}''_{f,exp} = 0.37\,\mathrm{kg/(m^2 s)}$	$\dot{m}''_{f,th} = 0.39\,\mathrm{kg/(m^2 s)}$	TBPB

Simplified model:

$$\boxed{\dot{m}''_{f,th} = \frac{1.1\alpha + \beta(-\Delta h_c)}{\gamma}}$$

Using linear regression for α against the tabulated T_{onset} according to Wehrstedt und Malow (2005):

$$\alpha = \dot{Q}_d / A_P = -1.27\, T_{onset} + 501.07\,\mathrm{K}$$

Calculating β using the particular decomposition products and heats of vaporization shows an average value of:

$$\beta = 1.5 \cdot 10^{-3}\,\mathrm{kg/(m^2 s)}$$

$$\gamma = \Delta h_v + c_{p,v} T_{f,b} - c_{p,f} T_{f,a} = 220\,\mathrm{kJ/kg}$$ aromatic compound

$$\gamma = \Delta h_v + c_{p,v} T_{f,b} - c_{p,f} T_{f,a} = 250\,\mathrm{kJ/kg}$$ aliphatic compound

Example TBPEH:

$$T_{onset} = 334\,K \quad , \quad -\Delta h_c = 34455\ kJ/kg$$

$$\alpha = \dot{Q}_d / A_P = -1.27 \cdot 334\,K + 501.07 = 77\,kW/m^2$$

$$\beta = 1.5 \cdot 10^{-3}\,kg/(m^2 s)$$

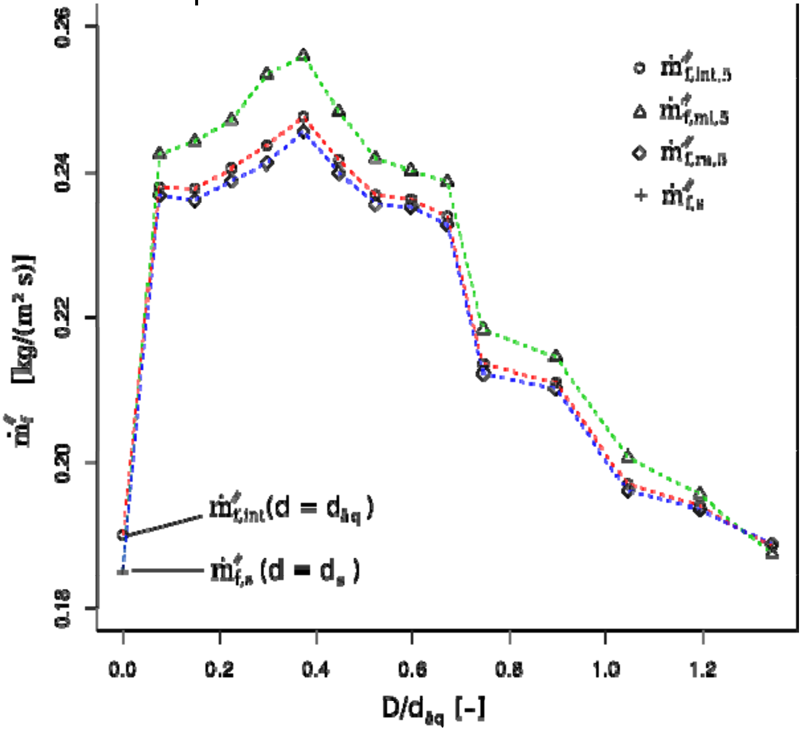
$$\gamma = \Delta h_v + c_{p,v} T_{f,b} - c_{p,f} T_{f,a} = 250\,kJ/kg$$

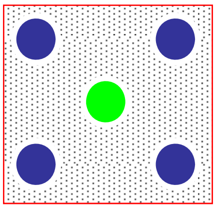
$$\dot{m}''_{f,th} = \frac{1.1 \cdot 77\,kW/m^2 + 1.5 \cdot 10^{-3}\,kg/(m^2 s) \cdot 34455\,kJ/kg}{250\,kJ/kg} = 0.55\,kg/(m^2 s)$$

$$\dot{m}''_{f,exp} = 0.53\,kg/(m^2 s)$$

Example for a multiple DTBP pool fire with N = 16

Mass burning rates of a multiple DTBP pool fire with N = 5





The mass burning rates $\dot{m}''_{f,mi}$ are up to 1.4 times higher in comparison to single fires.

$$\dot{m}''_{f,int}(D/d_{äq} = 0)$$

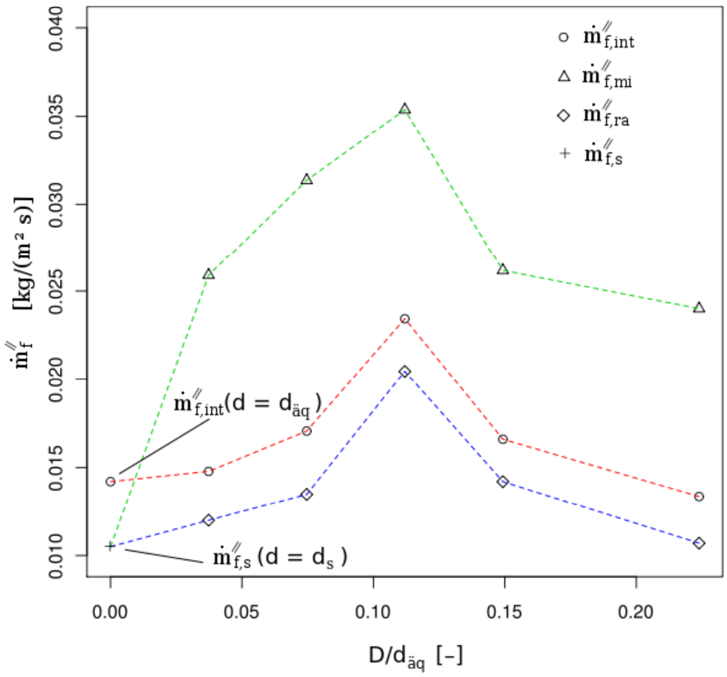
Only a small deviation of the mass burning rates between the inner and outer pools:

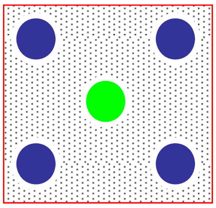
$$\dot{m}''_{f,mi} / \dot{m}''_{f,ra} \approx 1.05$$

A maximum at D/d$_{äq}$ ≈ 0.4 is observed.

The mass burning rates are influenced until a distance of D/d$_{äq}$ ≈ 1.35.

Mass burning rate of a multiple n-heptane pool fire with N = 5





The mass burning rates $\dot{m}''_{f,mi}$ are up to 1.8 times higher in comparison to single fires.

$$\dot{m}''_{f,int}(D/d_{äq} = 0)$$

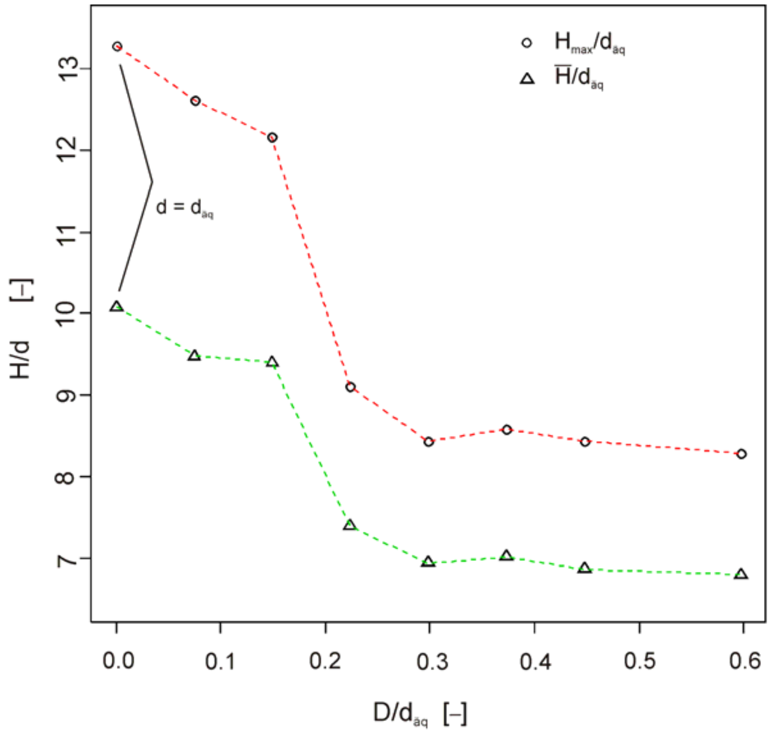
Only a small deviation of the mass burning rates between the inner and outer pools:

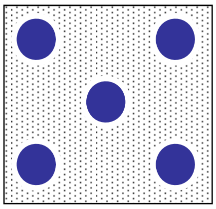
$$\dot{m}''_{f,mi} / \dot{m}''_{f,ra} \approx 1.8$$

A maximum at D/d$_{äq}$ ≈ 0.12 is observed.

The mass burning rates are influenced until a distance of D/d$_{äq}$ ≈ 0.23.

Flame heights of a multiple DTBP pool fire with N = 5

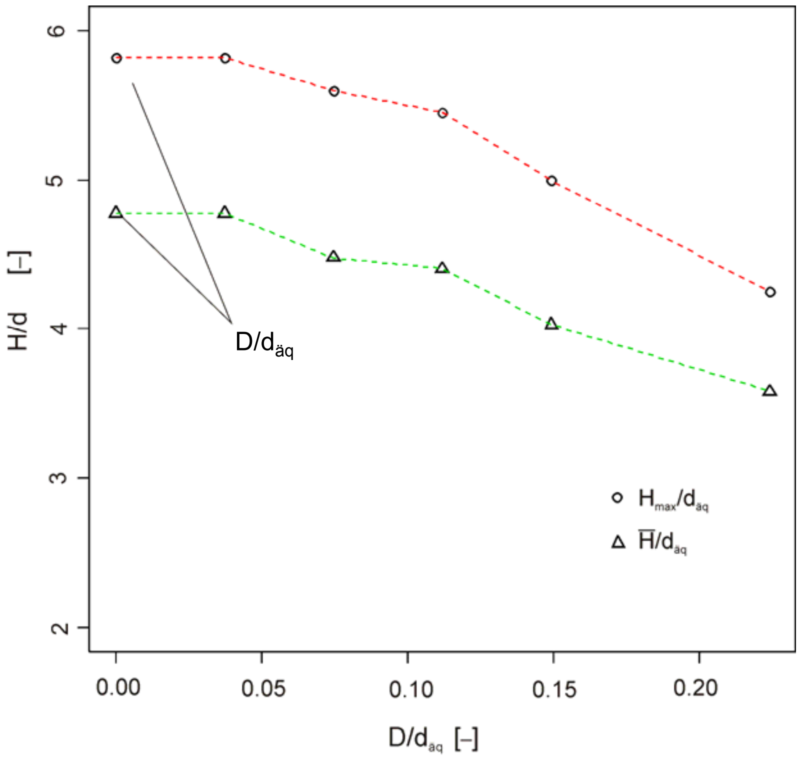


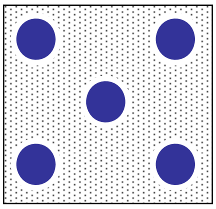


Single pool fires d = $d_{äq}$ have higher maximum and averaged flame heights in comparison to multiple fires.

For large D/$d_{äq}$ a constant flame height of a single pool fire with a diameter of d_s is observed.

Flame heights of a multiple n-heptane pool fire with N = 5

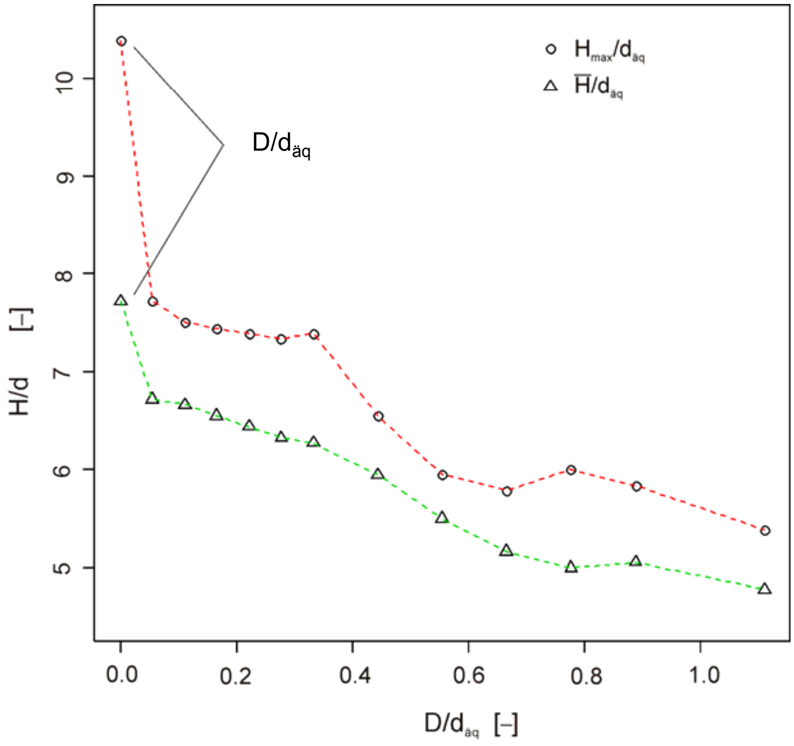


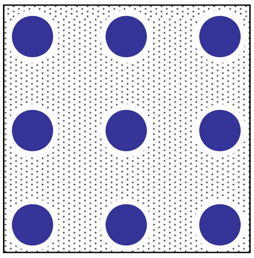


A single pool fires d = $d_{äq}$ have higher maximum and averaged flame heights in comparison to multiple fires.

The decrease of the maximum and averaged flame heights are more constant in comparison to DTBP pool fires.

Flame heights of a multiple DTBP pool fire with N = 9

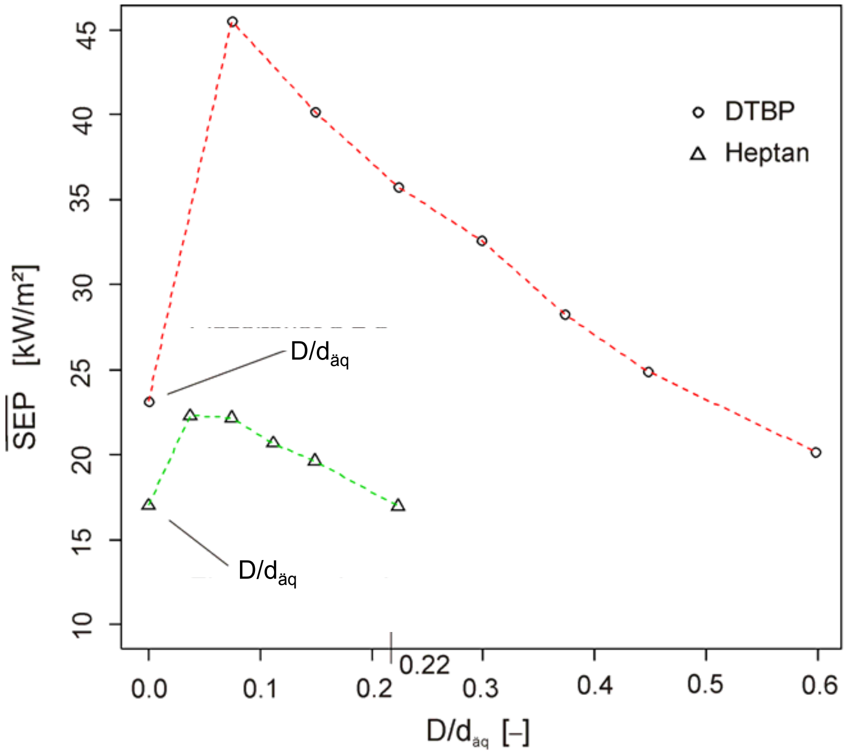


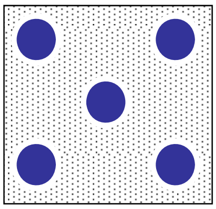


An increase of the array size leads to an stronger descrease of the maximum and averaged flame height.

An array improves the air entrainment leading to a more efficient combustion.
→ lower flame heights
→ higher thermal radiation

Surface emissive powert of multiple pool fires with N = 5



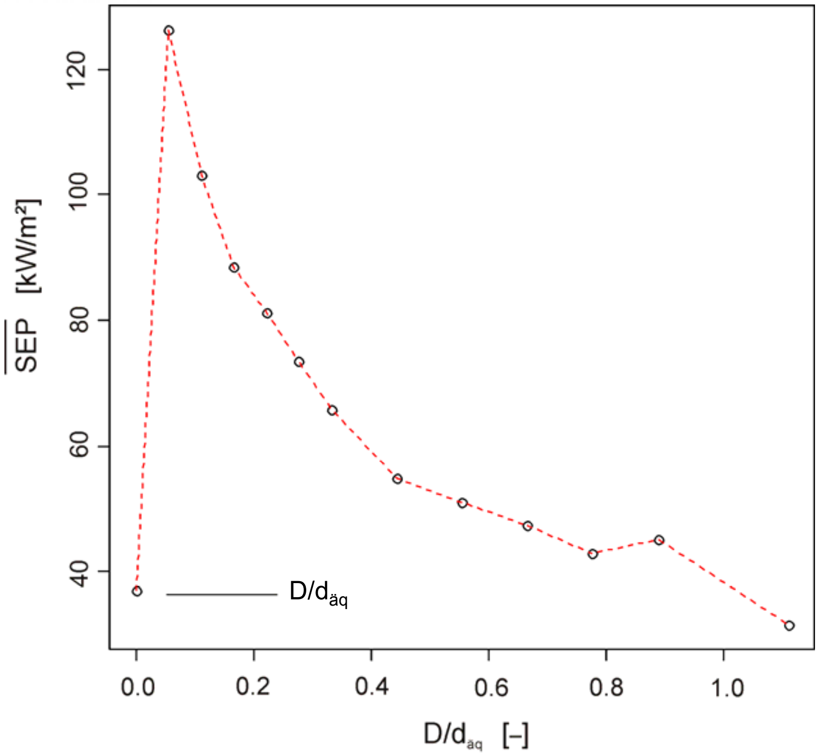


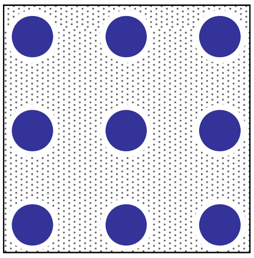
In the range of small $D/d_{äq}$ the $\overline{SEP}$ of mulitple DTBP pool fires shows an enhancement:

$$\frac{\overline{SEP}_{multi}}{\overline{SEP}_{single}} = 1.96$$

A similar behaviour can be observed for n-heptane at which the enhancement is smaller:

$$\frac{\overline{SEP}_{multi}}{\overline{SEP}_{single}} = 1.32$$





The enhancement of the $\overline{SEP}$ increases with the number of N for small $D/d_{äq}$:

$$\frac{\overline{SEP}_{multi}}{\overline{SEP}_{single}} = 3.37$$

For larger $D/d_{äq}$ the $\overline{SEP}$ curve descreases strongly.

Conclusions

A new model for the mass burning rate of peroxide pool fires including a liquid phase decomposition reaction has been developed.

The mass burning rates of multiple fires are by a factor of 1.4 (DTBP) und 1.8 (n-heptane) higher in comparison to single fires with the same surface area. A maximum at $D/d_{äq} \approx 0.4$ (DTBP) and $D/d_{äq} \approx 0.12$ (n-heptane) can be observed.

The maximum and averaged relative flame heights $H/d_{äq}$ of multiple fires are always smaller in comparison to the respective single fire of the same surface area and which further decrease with increasing $D/d_{äq}$.

The thermal radiation of mulitple fires is for small $D/d_{äq}$ explicitly higher (factor 3.37 for DTBP, factor 1.32 for n-heptane) in comparison to single fires. With increasing $D/d_{äq}$ the thermal radition decreases strongly.

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