Determination of The Thermal Lethality Distances Generated by The Radiative Flux Emitted by The Di-Tert-Butyl Peroxide (DTBP, C8H18O2) Fireball: Use of Characteristic Curves

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Abstract. Di-tert-butyl peroxide or DTBP is a very dangerous organic peroxide, widely used as a modifier, cross-linking agent and polymerization initiator in the industry. Its widespread use pushes us to set up studies assessing the dangers of this product, since it has been at the origin of Bleve explosions producing fireballs with a very devastating power and thermal effects. The hazard studies of this product remain very minimal. Our work consists in determining the thermal effect distances of a resulting fireball during the rupture of a DTBP storage tank, based on the characteristic curves of the thermal doses deduced from the specific model of P. Blankenhagel modeling a fireball of an organic peroxide. The authors propose a new graphical method that allows to efficiently determine the hazard zones of the effects of thermal doses, and consequently, the delimitation of the safety distances in case of an accident Bleve. The adequate utilization of this method can improve the response time of first responders in disaster areas to set up safety zones and evacuate people, and at the same time improve the safety of a large number of facilities.

1. Introduction
Organic peroxides are very dangerous flammable products, used widely in industry, as modifying agents to promote aridity in many oils, or as cross-linking agents in rubber production and as polymerization initiators in polystyrene and polypropylene production processes. Uncontrolled initiation of decomposition during transport or storage can lead to dangerous scenarios. The increased pressure in closed containers, the capacity for self-ignition and vigorous combustion and the physical-chemical properties can cause great damage during the production process, which can often be the cause of Bleve explosions producing fireballs.

The development of these fireballs differs generally, from that of liquid hydrocarbon fuels (LPG and LNG) [1]. Thus, based on several experiments and studies, a new model is proposed for organic peroxide fireballs by modifying the constants of the known empirical and semi-analytical equations [1–3].

Our work focuses on the evaluation of the thermal effect distances related to the intensity of the thermal radiation and the thermal dose felt from a fireball generated by a Bleve of an organic peroxide, based on the semi-analytical and empirical model proposed by P. Blankenhagel [1], which determines the characteristics of the fireball and the duration of the phenomenon.
In this paper, we first present the radiative flux model of DTBP. Then, the steps of realization of the graphical abacus and the characteristic curves of the main thermal doses of lethality and damage. And finally, the methodological approach developed to link the characteristic curves of thermal doses to the distances of effects on people and goods, as well as a comparison between analytically calculated values and those deduced graphically.

2. Methods
The objective of this manuscript is to provide a safe, efficient and fast (almost instantaneous) way to provide the results and deductions of a classical predictive and anticipatory study of the hazard and safety distances, related to the thermal effects of fireballs generated during a blue explosion of a storage or transport tank of organic peroxide, i.e., Di-tert-butyl peroxide (DTBP). For this purpose, we based ourselves on the solid flame model, applied to the specific model of P. Blankenhagel for a Bleve explosion of DTBP. As well as the formulation of the thermal dose as a function of the duration of exposure to radiation [4].

We proceeded to several manipulations and mathematical transformation to pass from the model of the solid flame applied to the organic peroxide (DTBP) and the analytical formulation of the thermal dose, to make the variable corresponding to the distance as the first term of a parametric function whose parameter is the value of the thermal dose. For each thermal dose, it is possible to obtain the analytical formulation distance-radiative fraction-heat of combustion-weight of DTBP involved in the explosion and the formation of the fireball \(X_{vs}(H_{r}, f_{h}, M)\), called here characteristic curves. These characteristic curves are grouped in the same graphical abacus with the addition of the characteristic curve of the fireball radius. Figures 1 represent the graphical chart containing the characteristic curves plotted as a function of the profiles DTBP-rupture pressure-weight of the product involved in the Bleve-thermal dose effect distance. The determination of the conditions and the domains of definition is carried out with the application of the graphic calculator GeoGebra, while the final plotting is carried out by means of the software Matlab.

The graphical abacus for the thermal effect distances of organic peroxide (DTBP) is a powerful tool for the delimitation of danger and safety zones. The properties of the solid flame model, on which its design and formulation is based, allow it to be used for the location of the various industrial units adjacent to the DTBP storage, transport or processing tanks in the near and far field. The exploitation of the abacus is done by reading the projection of the intersection segment between the vertical line corresponding to the mass of the fuel contained in the tank \(X=value, \text{ in kg}\), with the characteristic curves of the thermal doses pre-established on the Y axis, which correspond to the intervals of the distances of effects, as well as to the radius of the fireball. The plots below the curve representing the radius of the fireball are not to be taken into consideration, since they are inside the fireball, since in these cases the receiver of the thermal dose is inside the fireball which is aberrant.

3. Results

3.1. Modeling the radiative flux intensity for an organic peroxide:
The modeling of the intensity of the radiative flux is done on the basis of the solid flame models, with which we associate the characteristic model of the fireball proposed by P. Blankenhagel [1].

The solid flame model is a more realistic model than the point source model, since it takes into account the geometric shape of the radiation source [5–7]. And assuming that the heat is radiated from the surface of the flame [7]. The system of the following equations defines the solid flame model [1,5,8–10]:

\[
X_{vs}(H_{r}, f_{h}, M)\]
We adopt the assumptions for the DTBP parameters:

- The radiative fraction ranges from 0.23 to 0.36 ($f_h \approx 0.3$) [1,3];
- The atmospheric transmissivity ranges from 0.9-1 ($\tau_a \approx 1$) [1,3];
- The heat of Combustion ($\Delta H_c \approx 36000kJ/kg$);
- The view factor has the following formulation [5,11,12]:

\[
X = \left( \frac{1}{4\pi} \cdot (f_h \cdot \Delta H_c \cdot \tau_a) \cdot (c \cdot a^3)^{1/4} \cdot M^{1-k/4} - (0.75 \cdot b_1 \cdot M^{b_2}) \right)^{1/2}
\]

(4)

The duration of exposure to thermal radiation coincides with the life of the fireball [9,10,13]. It is expressed as follows:

\[
I_{dose} = t_{eff} \cdot (I_{th})^{4/3} = t_d \cdot (I_{th})^{4/3}
\]

(3)

3.2. Realization of the graphical abacus of the thermal doses:

The transformation of the system of equation n°1 provides the analytical formulation n°4:

\[
X = \left( \frac{1}{4\pi} \cdot (f_h \cdot \Delta H_c \cdot \tau_a) \cdot (c \cdot a^3)^{1/4} \cdot M^{1-k/4} - (0.75 \cdot b_1 \cdot M^{b_2}) \right)^{1/2}
\]

(4)

The P. Blankenhagel model for organic peroxide (DTBP) is given by the analytical formulation [1]:

\[
D_{DTBP} = 5.10 \cdot M^{0.325}
\]

(5)

By substituting the parameters of the system of equation n°5 in equation n°4 and adopting the considered assumptions, we find the following analytical formulation:

\[
X = \left( 902.880 \cdot a^{-3/4} \cdot M^{0.915} - 14.631 \cdot M^{0.65} \right)^{1/2}
\]

(6)

The mandatory mathematical conditions for the validation of the potential solutions of equation n°6, namely: the analytical term under the square root is positive and the value of X is strictly greater than the radius of the fireball. These conditions are grouped in the table 1, with the most quoted thermal doses of lethality [14,15]:

| Thermal dose (kW/m²)³·s | Effects on people | Effects on equipment | Math. Condition (M > -- kg) |
|-------------------------|-------------------|----------------------|---------------------------|
| 85                      | Pain threshold    |                      | 0.203                     |
| 200                     | 1st degree burns  |                      | 2.289                     |
| 600                     | Irreversible effects |                    | 51.423                    |
3.3. *Comparison between analytical results and graphical deduction of effect distances*

In order to be able to determine the level of possible gain from the use of the graphical abacus realized, it is essential to measure the variation and the difference with the results obtained by the direct analytical formulation of equation n°6 (table 2), this will determine the degree of precision that this abacus can provide us. For this purpose, we will simulate the thermal effects following the loss of containment of several hydrocarbon storage tanks, containing different masses, from 100 kg to 10000 kg.

From our reading of the data summarized in Table 2, we see that the variation between the values measured analytically by means of equation n°6, and those deduced from the characteristic curves of the graphical abacus (Figure n°1), for the five simulated cases, does not exceed 5%. Regarding the impact of this variation on the determination of the distances of effects of the thermal doses, the absolute difference did not exceed the 04 meters.

We conclude that the values deduced from the graphical abacuses present an accuracy close to 95%, and consequently their use will be very beneficial in terms of accuracy and speed of obtaining results.

![Figure 1. Abacus graph of thermal doses calculated from P. Blankenhagel model](image1)

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1 The projection of the intersection segment between the vertical line corresponding to the mass of the fuel contained in the tank, with the thermal dose curves, we determine the intervals of the effect distances, as well as the radius of the fireball.
Table 2: Comparison between values read on the chart and those measured analytically.

| P. Blankhagel model (weight in kg) | Abacus exploitation (weight in kg) |
|-----------------------------------|-----------------------------------|
| Fireball radius                   |                                   |
| 100                               | 500                               |
| 1000                              | 5000                              |
| 10000                             | 50000                             |
| TDU 2600                          | 47.96                             |
| TDU 2000-2200                     | 60.05                             |
| TDU 1800                          | 64.87                             |
| TDU 1200                          | 21.78                             |
| TDU 1000                          | 25.80                             |
| TDU 700                           | 12.51                             |
| TDU 600                           | 14.55                             |
| TDU 200                           | 29.26                             |
| TDU 85                            | 43.46                             |

| Variation                        | Difference                       |
|----------------------------------|-----------------------------------|
| Fireball radius                  |                                   |
| -5.08%                           | 0.61                             |
| -3.91%                           | 0.78                             |
| -3.71%                           | 0.93                             |
| 1.54%                            | 0.62                             |
| 1.76%                            | 0.88                             |
| TDU 2600                         |                                   |
| -4.09%                           | 2.04                             |
| TDU 2000-2200                    |                                   |
| 0.09%                            | 0.05                             |
| -0.78%                           | 0.70                             |
| TDU 1800                         |                                   |
| -0.21%                           | 0.13                             |
| 0.46%                            | 0.44                             |
| TDU 1200                         |                                   |
| -5.30%                           | 3.80                             |
| -2.79%                           | 0.05                             |
| 4.75%                            | 0.06                             |
| TDU 1000                         |                                   |
| -4.43%                           | 1.20                             |
| -2.59%                           | 1.03                             |
| 3.01%                            | 2.71                             |
| 1.42%                            | 1.84                             |
| TDU 700                          |                                   |
| -3.74%                           | 0.46                             |
| -1.36%                           | 1.18                             |
| -2.35%                           | 3.78                             |
| -3.29%                           | 3.48                             |
| -2.17%                           |                                 |
| TDU 600                          |                                   |
| -3.02%                           | 0.45                             |
| -0.15%                           | 0.06                             |
| 0.49%                            | 0.26                             |
| -0.20%                           | 0.24                             |
| -1.18%                           | 2.01                             |
| TDU 200                          |                                   |
| -2.48%                           | 0.74                             |
| -0.60%                           | 0.39                             |
| 0.21%                            | 0.19                             |
| -0.77%                           | 1.50                             |
| -0.77%                           | 2.09                             |
| TDU 85                           |                                   |
| 1.07%                            | 0.46                             |
| -1.94%                           | 1.85                             |
| -0.82%                           | 1.06                             |
| 1.07%                            | 2.90                             |
| -0.97%                           | 3.70                             |

4. Discussion:
The graphical abacus obtained by grouping the characteristic curves made on the basis of the analytical formulation of the thermal model of the solid flame, applied to the model of P. Blankenhagel [1], specific to fireballs from organic peroxides (DTBP), constitutes a quick way to determine the lethality zones and the deduction of the associated safety distances.
A more or less thorough look at the transformations carried out and the methodology followed, sheds light on the following points:
- The distance of effects of a thermal dose depends closely on the mass of the stored product;
- The characteristic curve of a thermal dose is a graphical representation of an increasing function with respect to the mass;
- The greater the mass of the stored product, the greater the intensity of the radiant flux emanating from the surface of the fireball, which increases the number of thermal effects felt;
- The slope of the characteristic curves in the graphical charts of the thermal doses at the log-log axes is not constant, this indicates that the curves are non-parallel lines and that a vertical line at the horizontal X axis will not necessarily intersect all the characteristic curves, hence the validity of the definition domains and the initial conditions assumed at the beginning of the analytical formulation.
5. Conclusion:
The Di-tert-butyl peroxide (DTBP, C8H18O2) is one of the most widely used organic peroxides in the industry for its multiple industrial applications. For example, as radical initiators in the plastic industry (polymerizations), rubber industry (vulcanizations) or to crosslink (cure) resins. Nevertheless, their use is not without danger. It can be the cause of Bleve explosions with the most devastating effects. This explains the importance of risk studies related to its handling, in order to accurately predict the safety distances of its effects.

The utilization of characteristic curves simplifies the study, prediction and modeling of thermal effects, since the effect distance of a thermal dose can be determined in a single step, avoiding intermediate calculations, since the characteristic curves show the relationship between the actual quantities (distance, thermal dose, weight of organic peroxide). Furthermore, the determination of the effect distances will depend on the choice of the characteristic curve included in the graphical abacus. In addition, the graphical thermal dose abacus based on the analytical formulation of P. Blankenhagel is a fast, safe and accurate means of determining the safety distances of thermal effects with precision, which can be a considerable asset in the hands of the first responders, during the occurrence of a major incident of the Bleve type and whose DTBP is at its origin.

6. Nomenclature

\( I_{th} \) is the incident radiation received by target, in W/m²;
\( I_{dose} \) is the thermal dose received by target, in \((W/m²)^{3/4}/s\);
\( f_h \) is the fraction of heat radiated, (-);
\( M \) is the mass of fuel in fireball, in kg;
\( t_d \) is the fireball duration, in s;
\( \Delta H_c \) is the heat of Combustion, in kJ/kg;
\( \tau_a \) is the Atmospheric transmissivity, (-);

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