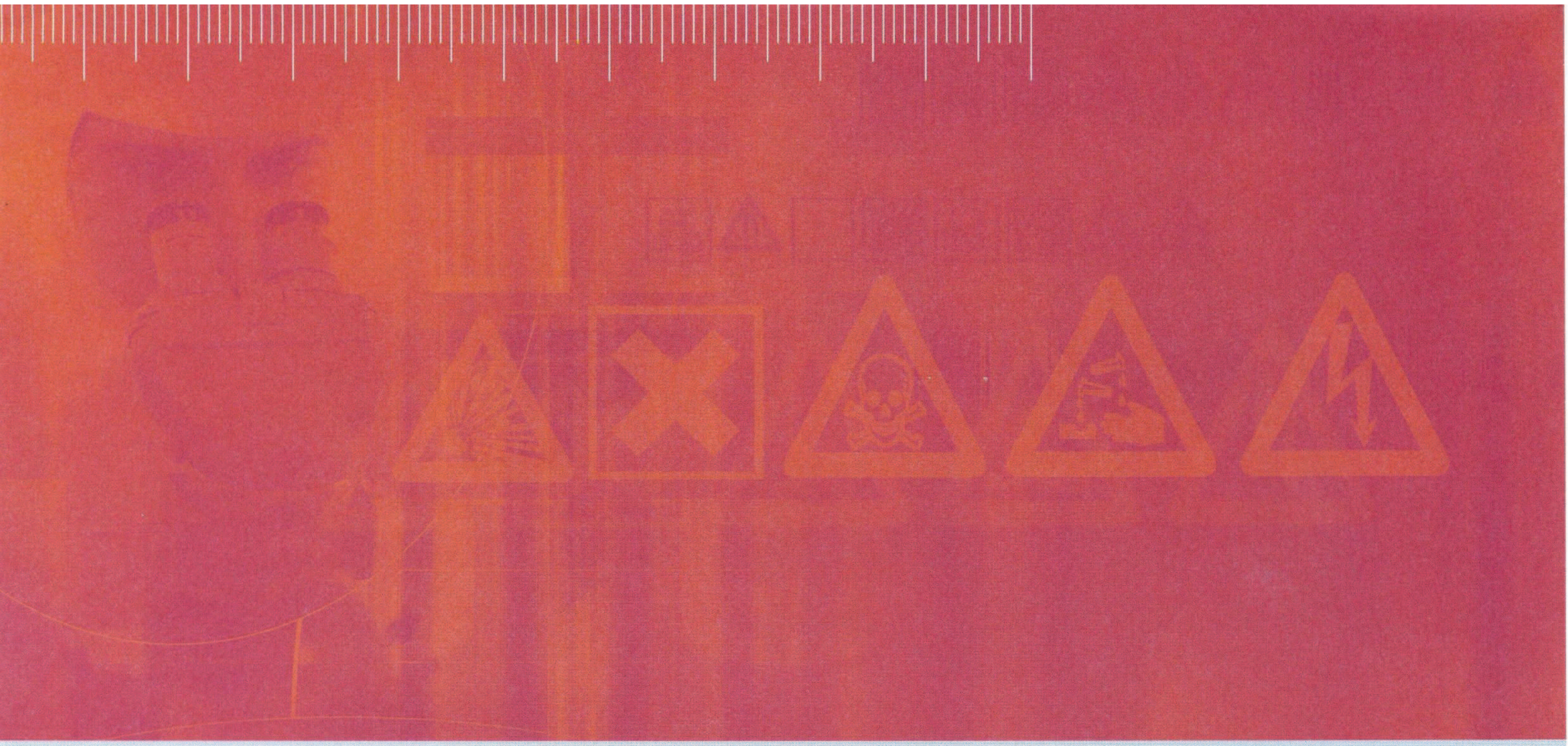

STUDY REPORT 22/01/2015
DRA-15-111777-00792A

Formalization of the knowledge and tools in the field of major risks (DRA-76)

Ω-13

Standard boil-over and thin layer boil-over

INERIS

maîtriser le risque
pour un développement durable

Omega 13 Report – Standard boil-over and thin layer boil-over

<u>List of participants in the study</u>: Stéphane Duplantier

PREAMBLE

The present report was established on the basis of information provided to INERIS, on available and objective (scientific or technical) data and regulations in force.

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The present study report written in English is for information only. The French version shall prevail over any translation that may be made.

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1. INTRODUCTION

1.1 PURPOSE AND CONTEXT

The OMEGA reports are a comprehensive collection formalizing the expertise of INERIS in the field of accidental risks. This collection covers the following topics:

- Risk analysis,
- Physical phenomena involved in chemical accidents (fire, explosions, BLEVE, etc.),
- Risk control of major accidents,
- Methodological aspects for achieving regulatory requirements (safety studies, critical review of safety studies, etc.).

These reports are intended to present the knowledge considered consolidated at the time of their publication. These reports are available to stakeholders in the control of major accidents, who will make proper use of them under their responsibility. Some of these reports are translated into English in order to facilitate their dissemination. The concepts presented in these reports are not intended to substitute for regulatory requirements.

1.2 AREA OF APPLICATION

Up to now, all flammable liquids with the characteristics of a significant viscosity and a certain boiling range were considered capable of giving rise to a boil-over. Recent work has shown that boil-over, as considered up to today, was not always representative of the phenomena observed on certain products.

Indeed, following work conducted in the GT DLI (National Working Group on the Flammable Liquids Tanks Farms), it appeared that certain products could not give rise to standard boil-over; they may, however, give rise to another hazardous phenomenon. This phenomenon was called « thin layer boil-over » because of the smaller amount of suspended liquid product.

The goal of this document is to recall the characteristics of each of these phenomena and to subsequently specify, when information is available, the phenomena which may be observed for products most currently stored in depots for flammable liquids.

Let us recall that these results led to a new addition of an excerpt of the omega 13 report then relating to standard boil-over which was transmitted electronically by the BRTICP on October 7th 2008.

1.3 STRUCTURE OF THE DOCUMENT

Therefore, the contents of this reference document consist of three parts:

- The first part deals with the experimental description of these phenomena,
- The second deals with thin layer boil-over modeling, allowing the calculation of the effect distances associated with this phenomenon,

- The third part deals with standard boil-over modeling in order to calculate the effect distances associated with this phenomenon.

Further, for each of the phenomena, the limits to using the models are specified before proposing work to be carried out in order to improve modeling of these dangerous phenomena.

1.4 NEW ITEMS RELATIVE TO THE PREVIOUS VERSION OF THE Ω13 REPORT

Taking into account the comments expressed earlier, in this version a new phenomenon is being considered: thin layer boil-over, which, like boil-over (henceforth designated standard boil-over), has an eruptive phenomenon, but of a limited extent. It is mainly distinguishable from standard boil-over by the absence of a heat wave in the liquid before the triggering of the boil-over. It is also essential to specify that this phenomenon, observable on a small scale, has never been observed on an industrial scale.

Thin layer boil-over was only observed within the scope of a study dealing with three products: jet fuel Jet-A1, gasoil and domestic fuel oil. In fact, these products were removed from the list of products capable of giving rise to standard boil-over. The two dangerous phenomena were also removed for petrol because its viscosity is too low to ensure sufficient cohesion of the liquid for sudden vaporization of the water to act on fuel as a piston.

The previous version of the Ω13 report established a criterion making it possible to determine whether boil-over was conceivable. Today we consider that there is no criterion on the thermodynamic properties of flammable liquids by which it is possible to know whether a product will give rise to one of the two phenomena: a standard boil-over or a thin layer boil-over, except for those points which are more a matter of common sense:

- the flammable liquid has to be lighter than water;
- the flammable liquid has to be more viscous than fuel in order to observe a piston effect;
- a pure liquid, containing only a single product and thus having a single boiling temperature, cannot be the centre of standard boil-over; however, it may give rise to thin layer boil-over;
- a product miscible with water can neither give rise to standard boil-over nor to thin layer boil-over.

For information only, the model described in this document for thin layer boil-over is the one described in the French regulation (circular of July 23rd 2007) and for which a computer version was developed in Excel format[1].

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[1] Downloadable tool at the following address: http://aida.ineris.fr/textes/circulaires/images/text4593_05.xls

2. PREAMBLE

2.1 REMINDER ABOUT THE COMBUSTION OF A HYDROCARBON IN THE LIQUID PHASE

This preamble is necessary in order to better understand the mechanism that lead to the suspension of flammable liquid. Indeed, the initial conditions depend on the response of the product to the heat flow emitted by the flame located above the tank.

Indeed, for both of the two dangerous phenomena, standard boil-over and thin layer boil-over, it is necessary to have both a tank on fire and water present at the bottom of the tank. It is the same mechanism which leads to the suspension of the flammable liquid, that is, sudden vaporization of the water.

Concerning the response of the liquid to the tank fire, it is helpful to recall the mechanism shown in the following diagram:

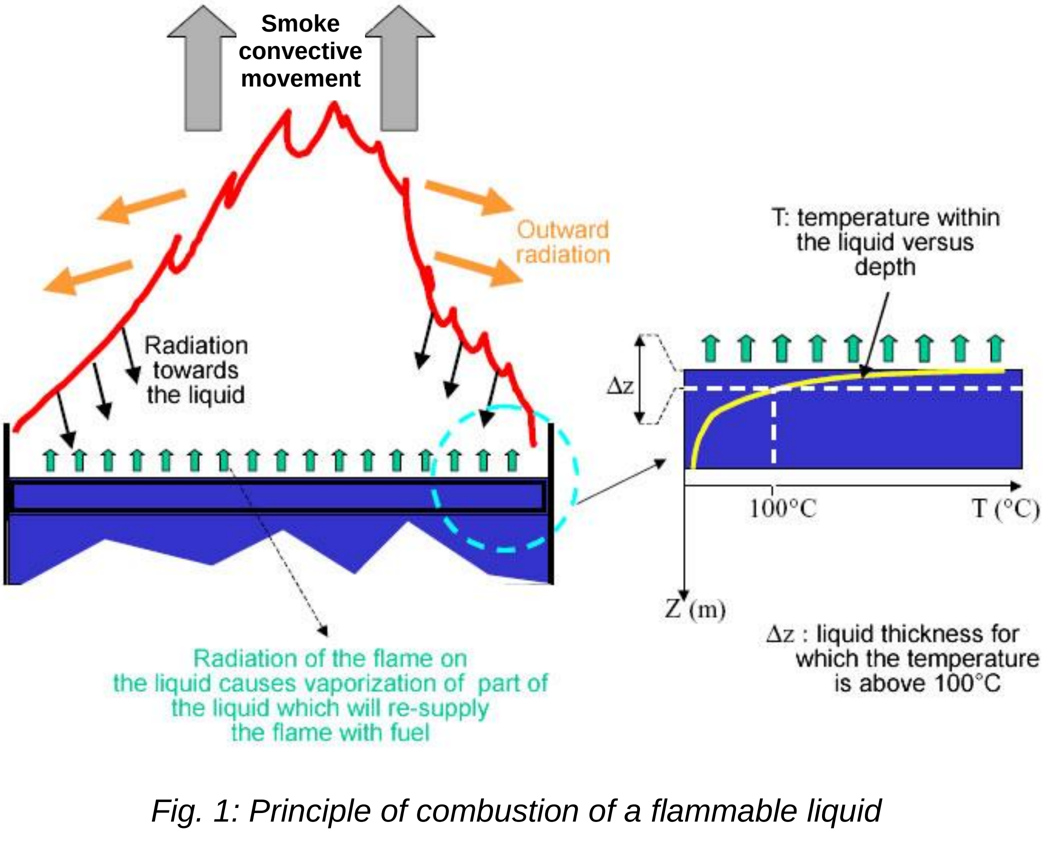


Fig. 1: Principle of combustion of a flammable liquid

Schematically, the flame will be positioned above the flammable liquid at a distance permitting conditions favorable to its stabilization.

This position of equilibrium is characterized by the fact that the energy fraction emitted by the flame towards the surface of the liquid is sufficient for ensuring its evaporation with an adequate flow rate so that, after mixture with the entrained air, the flame may remain steady.

This average position is relatively stable insofar that:

- if the evaporation rate is too great, the mixture will be close to the upper flammability limit and combustion will take place in a higher position, thereby moving the flame away from the surface of the liquid. This leads to a decrease in the radiative flux emitted on the surface of the liquid and thus to a reduction of the liquid’s evaporation. In the end, the flame is approximately re-positioned in its initial position.
- if the evaporation rate is too low, the mixture will be close to the lower flammability limit and the flame will therefore be positioned lower and therefore closer to the surface of the liquid. This will cause an increase in the evaporation rate and therefore a displacement of the flame upwards towards its initial position.

Understanding this mechanism is essential since it shows that the surface of the liquid is subject in an approximately constant way to a radiative flux which allows the constant fueling of the flame.

This radiative flux is at the origin of the process resulting in the dangerous phenomena studied in this document. Indeed, the radiative flux leads to a rise in the temperature of the liquid’s surface and this rise in temperature propagates within the liquid according to its thermodynamic properties and more particularly to the composition of the liquid (either homogeneous or a mixture).

Depending on the composition of the fuel, there will be simple propagation of the heat within the liquid by conduction and convection or there will also be a distillation of the liquid which may lead to its separation into several products of various densities. These two different mechanisms have been detected for each of the two hazardous phenomena studied here. This is described in the two following chapters for thin layer boil-over and standard boil-over.

2.2 DETECTING THE PRESENCE OF THE HEAT WAVE

This paragraph is dedicated to presenting an experimental campaign conducted by INERIS which has allowed the identification of the « signature » of a heat wave within the liquid for different fuels.

The procedure for evaluating whether or not a product has the propensity for being the centre of a standard boil-over or a thin layer boil-over is described in this paragraph. The steps in the decision-making process are shown in the following diagram. The experimental procedures to be applied for this determination are described subsequently.

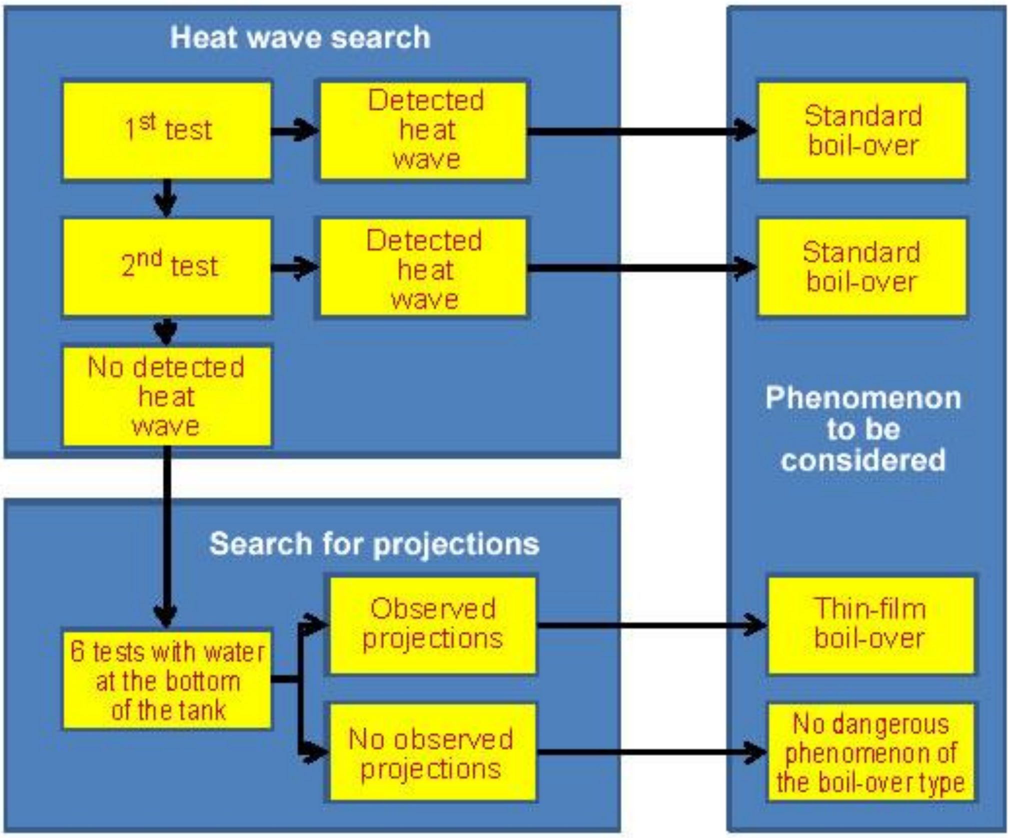


Fig. 2: Principle to know the dangerous phenomenon to be considered for a flammable liquid

Testing for the heat wave

In order to identify the presence of a heat wave, it is possible to measure the temperature profile in a tank on fire. The experimental device used will include, at the least, a thermocouple every centimeter in a tank with a minimum diameter of 80 cm so as to not have edge effects. It is schematically illustrated in Fig. 3.

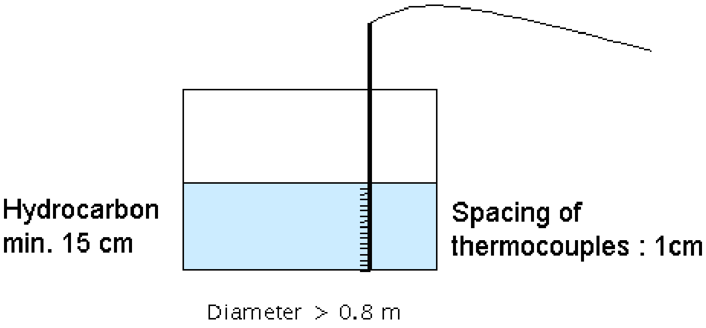


Fig. 3: Experimental device set up for measuring the temperature profile.

As the goal is to find out whether a heat wave is formed, only hydrocarbon is placed in the tank (thus no water at the bottom of the tank).

Under the assumption that hydrocarbon has a strong viscosity at room temperature, the product has to be heated in order to be put in place and setting it on fire must be carried out before the hydrocarbon returns to its storage temperature.

Testing for projections

Description of the phenomenon may be accomplished at a small scale in a tank with a diameter of 30 cm and a height of 20 cm. It is useful to retain a ratio between the height and diameter of less than or equal to 1 without it being less than 0.25.

For each test, the combustible liquid is poured into the tank first. Then, water is added at the bottom of the tank by means of a funnel. Before each test, a period for stabilizing the fluids is respected in order to make sure that all the water is actually located at the bottom of the tank.

The amounts used for the tests have generally shown that projections were observed for 3L of hydrocarbons initially present with a water base between 10 and 30 cL. This value has to be adjusted depending on the size of the tank. The goal is to put a sufficient amount of water in the bottom of the tank so that there is no formation of a water lens. This also assumes that the bottom is sufficiently flat.

The tests will have to be duplicated; they will be systematically filmed.

2.3 PRESENCE OF A HEAT WAVE

In order to illustrate the results which may be observed during the application of the procedure, the procedure as applied to the case of light crude oil is presented in the following paragraphs.

2.3.1 TESTING FOR THE HEAT WAVE

The graph Fig. 4 shows the change in the temperature profile for light crude oil: this is a hydrocarbon for which a heat wave has formed, characteristic of standard boil-over. Indeed, lighter fractions have burnt first leaving space for a significant thickness of heavy ends at a constant temperature of 200 °C.

These hot heavy ends, due to the effect of gravity, move down to the bottom of the tank and are replaced at the surface with lighter fractions. The hydrocarbon present under the heat wave is broken down, letting light fractions pass through the heat wave and retaining the heavy ends, thereby contributing to its gradual thickening.

Of course, in order to observe standard boil-over, the heat wave has to move down faster than the liquid level in the tank.

While the thermocouple located at 1 cm from the bottom reaches a temperature of 100°C, there is still 6 cm of fuel at a temperature of 200°C. It is this amount of fuel which would have been suspended if a water deposit had been present at the bottom of the tank.

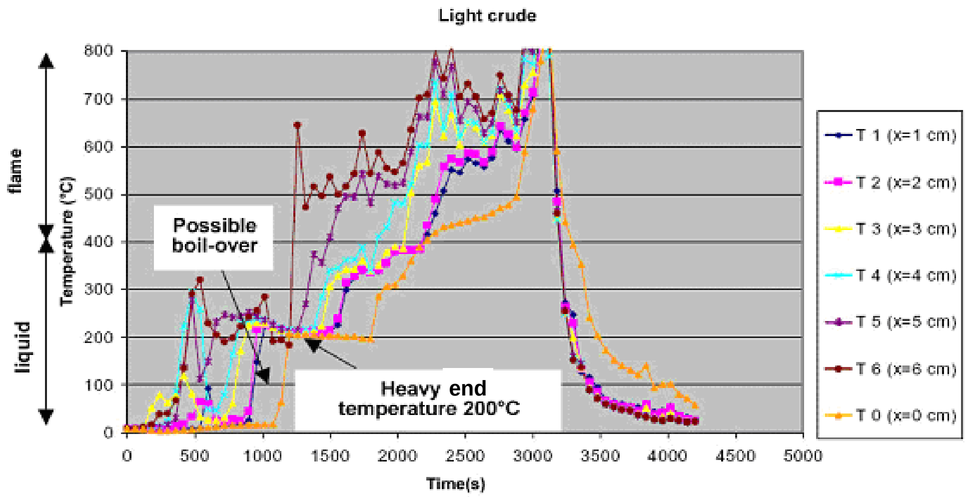
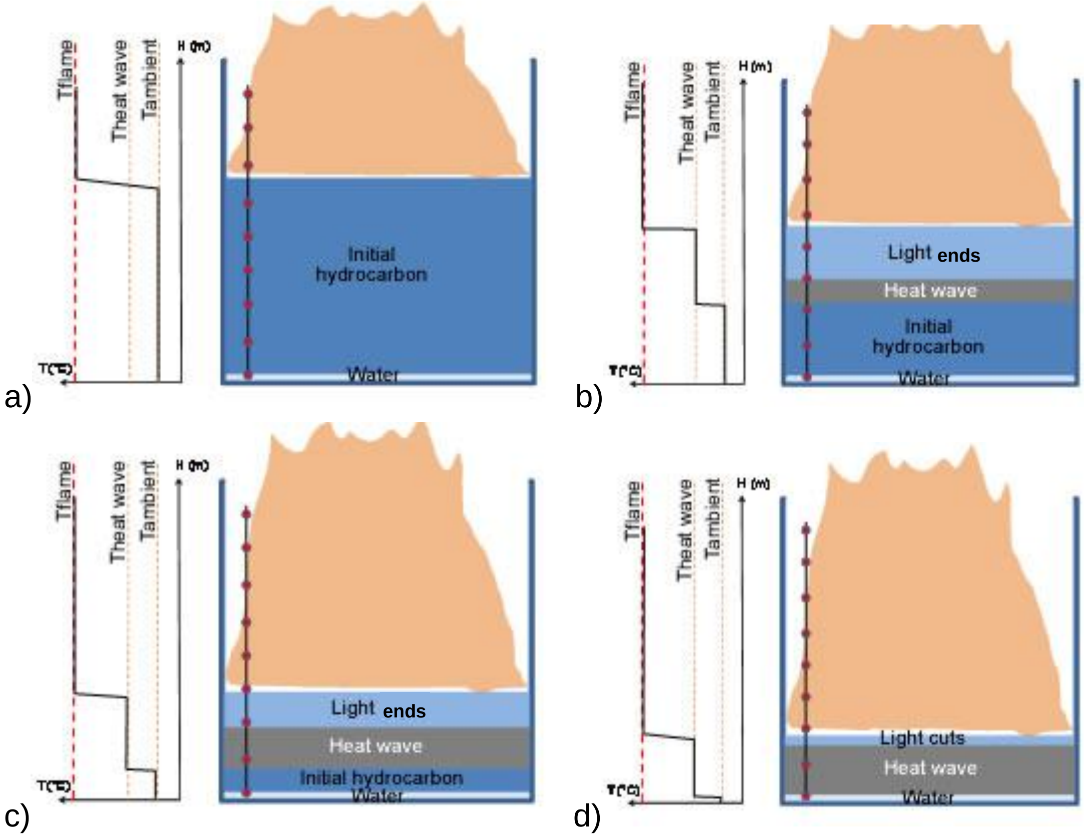


Fig. 4: Temperature gradient in the event of a fire of light crude

The following diagram shows the gradual change of the temperature in the liquid before a possible boil-over happens.



2.3.2 TESTING FOR PROJECTIONS

In the case of light crude oil, as the heat wave has been detected, it is no longer necessary to test for projections. For information only, the tests were conducted all the same, and it was observed that, under the applied experimental conditions, the eruptive phenomenon is relatively limited. It is more similar to an overflow of an inflamed liquid without any projection as shown by the following image sequence (cf. Fig. 5).

Fig. 5: Image sequence relating to the test with light crude.

2.4 ABSENCE OF A HEAT WAVE WITH PROJECTION

The procedure was then applied to other flammable liquids which up to now have been considered as being able to give rise to standard boil-over.

2.4.1 TESTING FOR THE HEAT WAVE

The following graphs show that for gasoil (GO), JET A-1 and domestic fuel oil, only a heat gradient over a few centimeters is visible. The case of domestic fuel oil is shown on a graph at a larger scale before those of GO and of the jet fuel JET-A1 which have similar aspects.

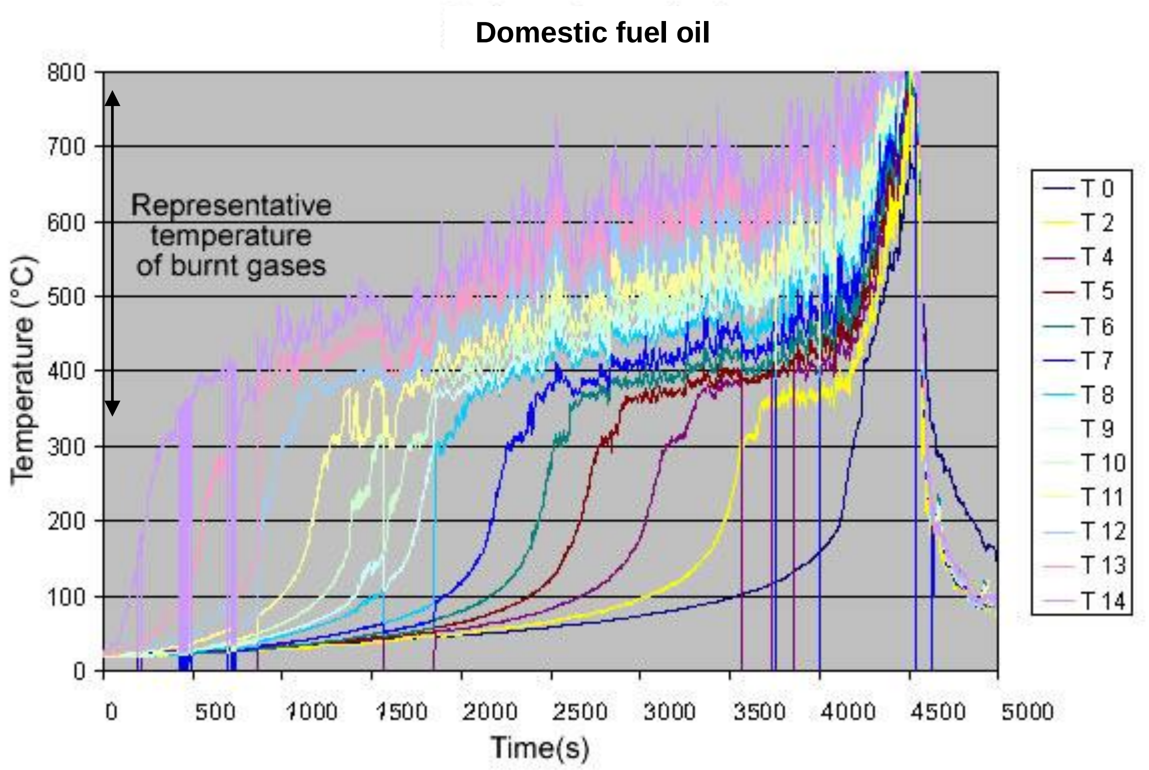
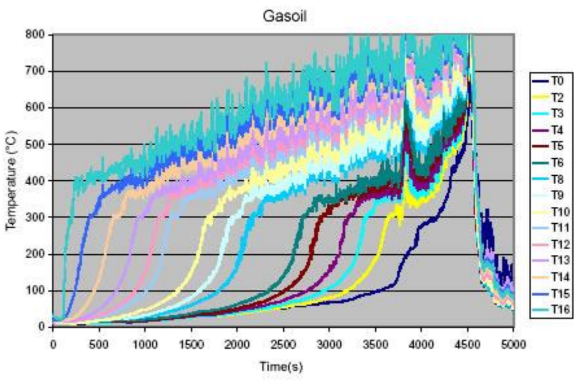
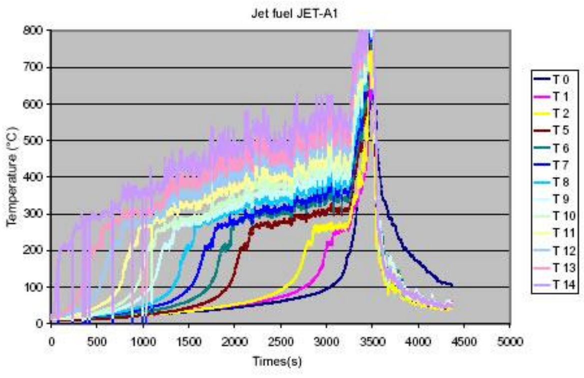


Fig. 6: Example of the change in temperature within the liquid.

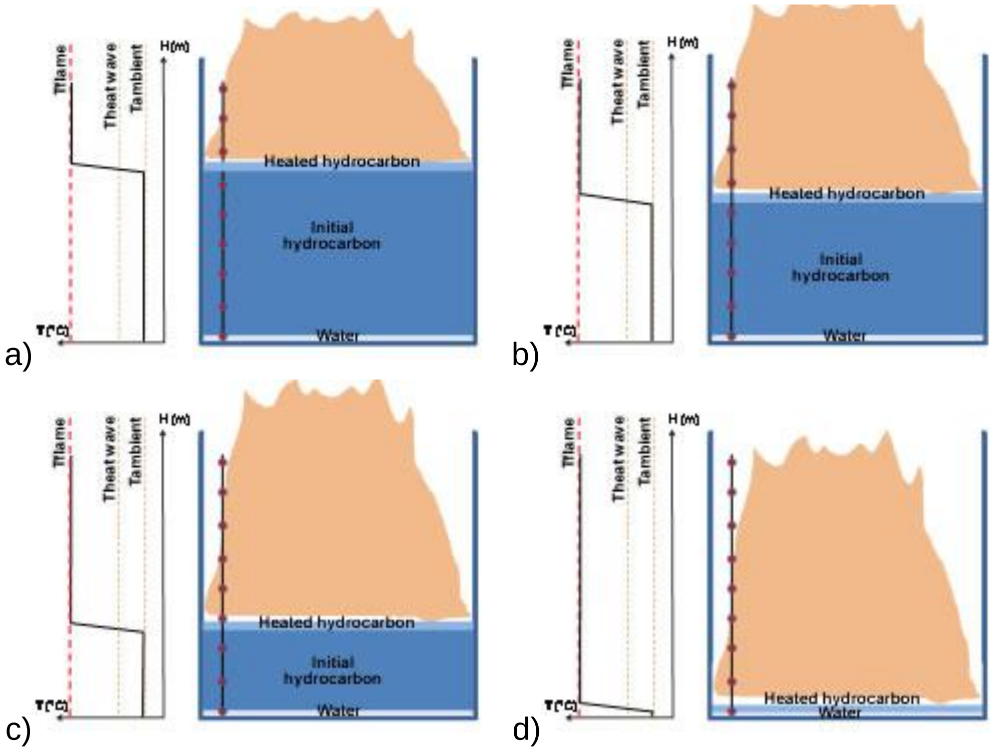
Examination of this figure shows that:

- There is no temperature plateau as is the case for light crude oil.
- At a given height, the temperature increases very slowly up to 100°C. The temperature then increases more radically as soon as the level of the liquid approaches this height.
- Finally, the temperatures reached are characteristic of those measured in the flames.

	
a) temperature gradient for gasoil	b) temperature gradient for Jet-A1

This observation demonstrates that these products cannot give rise to standard boil-over since there is no distillation of the product during its combustion. Therefore, it is possible that a phenomenon of « thin layer » boil-over would be able to occur with these fuels.

A schematic illustration of the temperature gradients is provided in the following figures:



Furthermore, It is important to note that the consequences associated with this new phenomenon would be less, given that only a few centimetres of product would be suspended.

2.4.2 TESTING FOR PROJECTIONS

Several amplitudes of this phenomenon have been observed during tests depending in particular on the different fuels.

The so-called « thin layer » boil-over is very well illustrated by the sequence of images proposed in Fig. 7, which break down the phenomenon. This test related to gasoil and a fireball was created. It should be noted that the latter is not the main source of radiation. The lower portion of the flame located under the fireball seems to have a greater radiation.

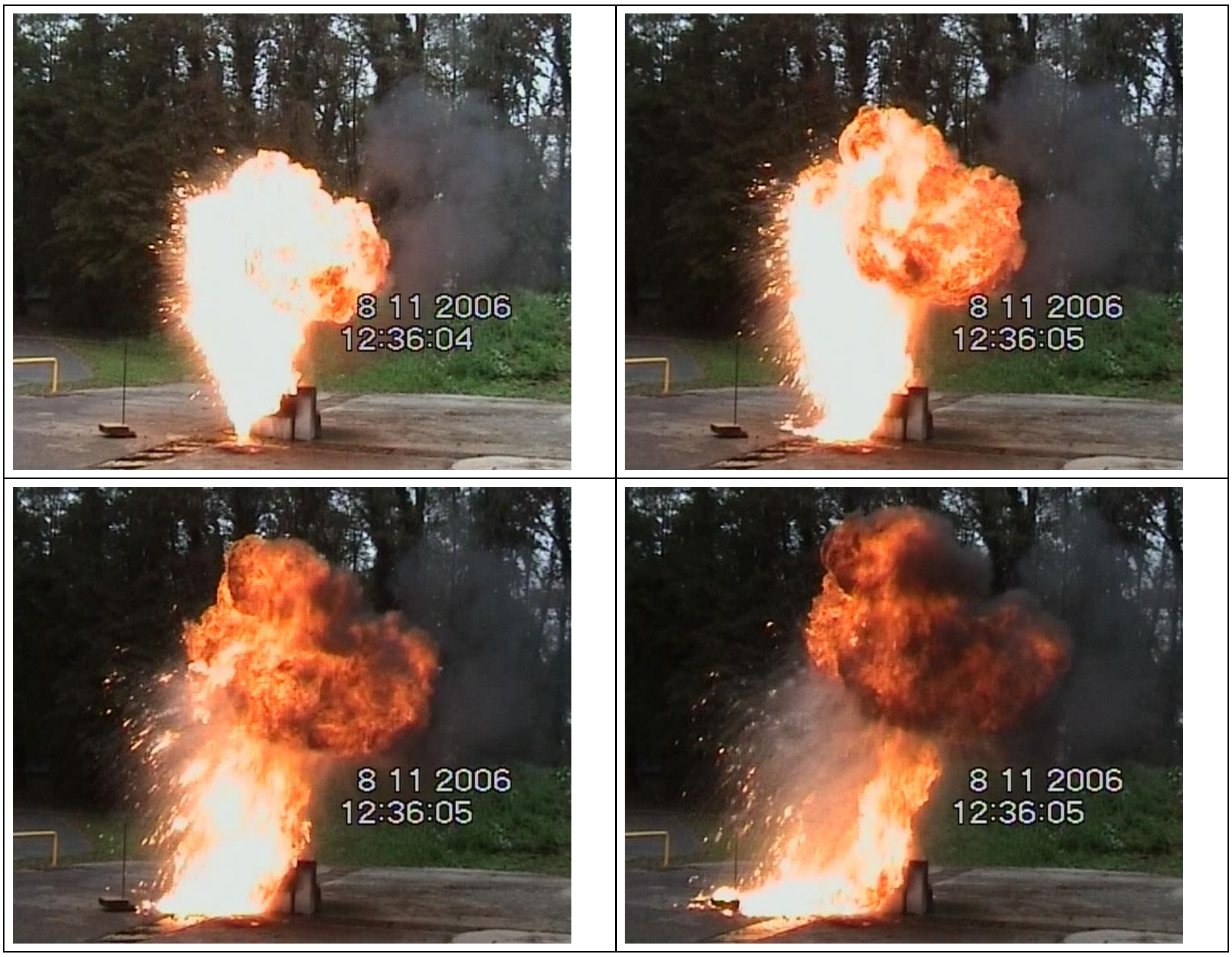


Fig. 7: Test with 3 L of gasoil and 20 cL of water.

This fireball phenomenon was observed during INERIS tests on gasoil and domestic fuel oil.

Moreover, the tests conducted on JET-A1 did not give rise to the formation of a fireball but to several successive projections of inflamed liquid of lesser amplitude as shown in the photographs in Fig. 8.

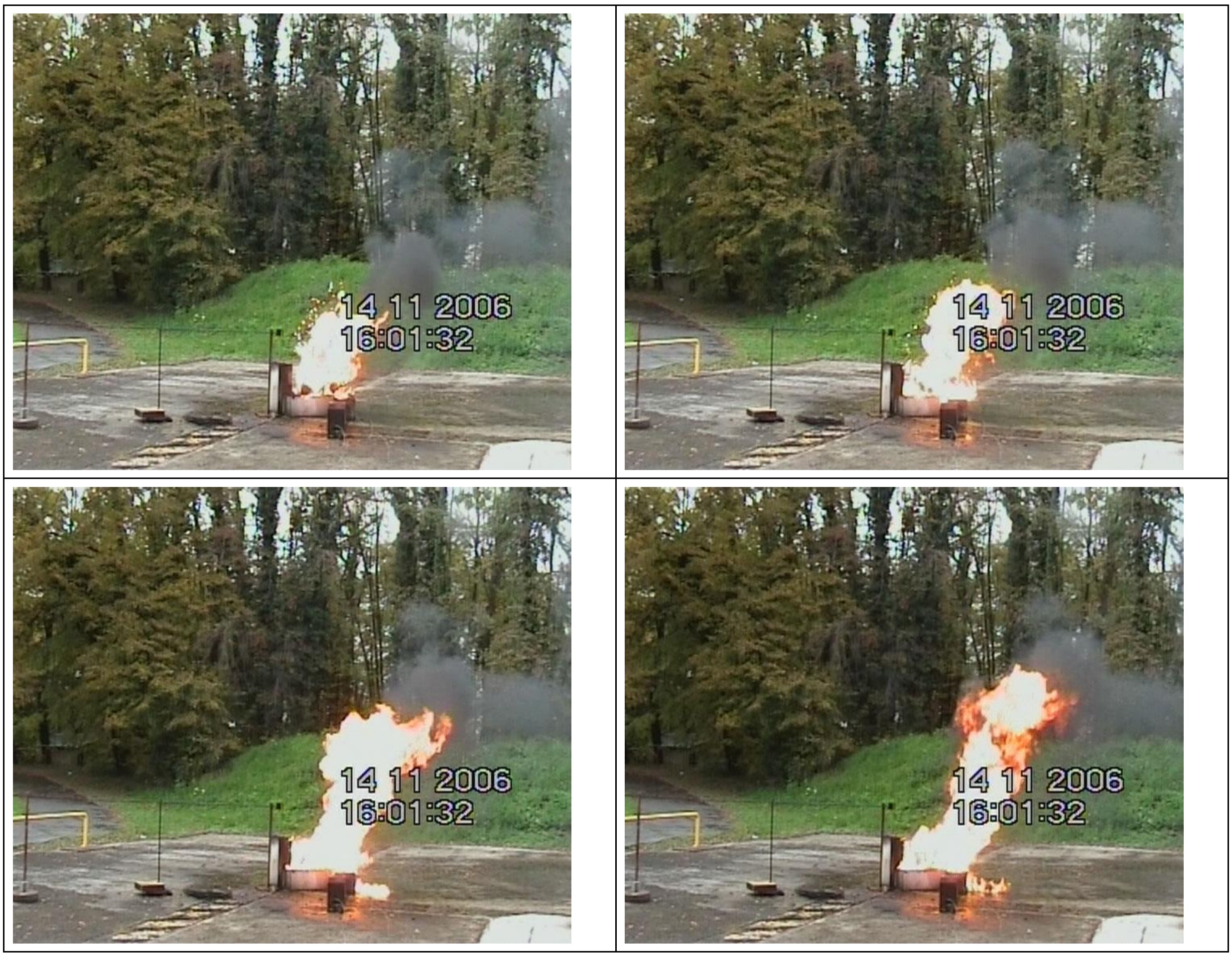


Fig. 8: Tests with 3 liters of JET-A1 and 25 cL of water

2.5 ABSENCE OF A HEAT WAVE WITHOUT PROJECTIONS

Other products were also tested according to the procedure described earlier, in particular fuel (gasoline/petrol).

2.5.1 TESTING FOR THE HEAT WAVE

It should be noted that if gasoil, domestic fuel oil and JET A-1 have an identical temperature profile shape, petrol differentiates itself from these other products by having a different thermal gradient change (cf. Fig. 9). This difference may be either related to an optical absorption coefficient of the radiation which might be better for petrol, or to the lower viscosity of petrol which facilitates convection movements within the liquid and thus promotes its temperature homogenization. This implies very rapid and more homogeneous heating-up of petrol.

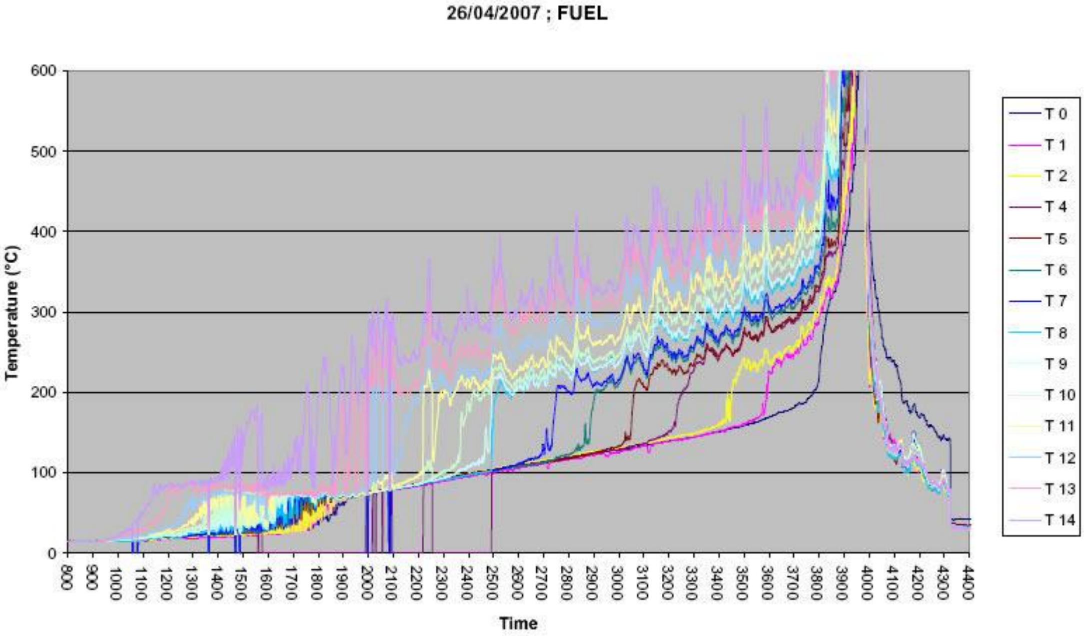


Fig. 9: Change in temperature within petrol

2.5.2 TESTING FOR PROJECTIONS

For petrol, no projection or fireball was observed. Water thus tends to pass through petrol by creating a cloud of vapour and therefore does not give rise to a piston effect which may propel the hydrocarbon.

The origin of this observation may be due to the viscosity of petrol which is of the order of 0.37 cSt at 100 °C and is thus insufficient for a piston effect. That of JET A-1 is higher (about 0.73 cSt), allowing the observation of inflamed projections but no fireball. Only a larger viscosity such as that of gas oil and/or domestic fuel oil (0.81 and 0.92 cSt respectively) allows a sufficient piston effect for suspending the totality of the remaining flammable liquid.

2.6 CONCLUSIONS

In order to determine the products susceptible to giving rise to standard boil-over, thin layer boil-over or none of these phenomena, an experimental procedure was proposed. This procedure includes two main steps which allow, respectively, identification of the presence or absence of a heat wave and the search for the presence of possible projections if there is no heat wave.

Finally, the following points are officially recorded today:

- the presence of a heat wave leads one to consider that standard boil-over is possible. Relevant fuels are ones for which the boiling range is sufficiently extended and for which the viscosity is sufficient for the piston effect to be observed;
- the absence of a heat wave and the presence of projections lead to retaining the possibility of thin layer boil-over. The products capable of

giving rise to thin layer boil-over are ordinary domestic oil, gasoil and jet fuel jet-A1;

- the absence of a heat wave and the absence of projections lead to not retaining any of the two boil-over type phenomena. Petrol is an example of a product which does not produce either standard boil-over or thin layer boil-over.

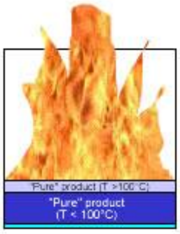
3. THIN LAYER BOIL-OVER

The object of this chapter is to describe the model developed for evaluating the consequences of thin layer boil-over. Subsequently, examples for comparison with the experimental results are given before specifying the limits of the use of the model.

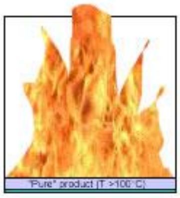
3.1 THIN LAYER BOIL-OVER

The different steps leading to thin layer boil-over are described below.

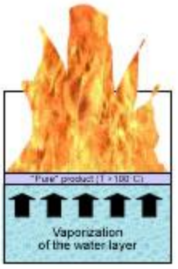
Initially upon setting fire to the tank, the product filling the volume of the tank has a homogenous composition which will remain so throughout the fire. However, a temperature gradient occurs and an area where the temperature is greater than 100°C with limited thickness may be identified.



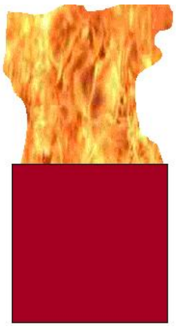
Due to the radiation of the flames on the surface of the liquid, the liquid is subject to a local increase in temperature without any modification of composition. There is no heat wave formation. The not very thick hot area (T>100°C) progresses towards the bottom of the tank as the product is gradually consumed at the same rate as the surface of the liquid.



Once the whole of the combustible fuel located below this temperature area of greater than 100°C has been consumed, there is contact between water and this area.



The contact between the combustible fuel heated to more than 100°C and the water causes evaporation of the fuel. This sudden vaporization leads to a significant increase in volume and plays the role of a piston by suspending the remaining flammable liquid in the tank.



A fraction of the liquid overflows from the tank and another fraction is suspended while being fragmented into drops and vaporizing upon crossing the flames forming a quick combustion area.

Fig. 10: Schematic illustration of the different phases of a thin layer boil-over

It is important to note from now on that the extent of this phenomenon will depend:

(1) on the viscosity of the product. If the product is not very viscous, the piston effect will be weaker because water vapour will fragment the liquid layer of hydrocarbons. It is even possible that no piston effect will occur if the viscosity of the product is too low.

(2) On the thickness of the liquid layer of hydrocarbons, for which the temperature is greater than 100°C, this depends on the intrinsic properties of the hydrocarbon.

3.2 DESCRIPTION OF THE THIN LAYER BOIL-OVER MODEL

The proposed model is based on successive calculations which allow one to describe the phenomenon at different characteristic instants (cf. paragraph 3.1). These different characteristic instants are presented below.

A first « standard » combustion phase of the flammable liquid which is located before the contact between the flammable liquid at a temperature above 100°C and water. During this phase, a fraction of the energy radiated by the flames is transmitted to the liquid. This fraction leads to evaporation of the liquid which will again feed the flames and also preheat the liquid over a few centimeters. The preheated thickness depends on the nature of the fuel. During this phase, no projections occur; the duration of this phase may be estimated by dividing the height of the liquid present at the moment when it is set on fire by the regression rate which is a characteristic of the product on fire as well as of the diameter of the tank. At the end of this phase, the important quantity is the thickness of flammable liquid for which the temperature is above100°C.

The second phase occurs when the liquid layer for which the temperature is above 100°C arrives in contact with the water present at the bottom of the tank. At this instant, water suddenly vaporizes and acts as a piston by suspending the layer of hydrocarbons located above the water. The output quantities of this phase are the ejection rate of the liquid, the latter depending on the amount of water present at the bottom of the tank – this value was set at 0.01 m, it is an order of magnitude of the amount of water likely to be present in a hydrocarbon tank during normal operation – as well as the composition of the mixture (water in a vapor phase, fuel in a vapor and liquid phase).

The third phase consists of the combustion of the suspended hydrocarbon. This phase is mainly driven by the air entrainment within the jet. Indeed, during the suspension of the liquid, the mixture rapidly becomes too rich in fuel and it is then necessary that air (oxygen) be introduced in order to observe the combustion of the liquid after its evaporation. Subsequently, a thermodynamic assessment is carried out taking into account the drawn air as well as the heat emission resulting from the combustion of the hydrocarbon in the vapor phase with the entrained air.

The last phase relates to the evaluation of the consequences in terms of thermal fluxes on the environment. Taking into account the duration of the phenomenon (less than a minute) a calculation of a thermal dose is performed.

The main hypotheses of each of these phases are specified in the following paragraphs in order to better understand how this model was built. More detailed calculations are not provided in order to facilitate the reading of the document.

3.2.1 DETERMINATION OF THE DELAY FOR THE OCCURRENCE OF THE PHENOMENON AND OF THE HEIGHT OF LIQUID LIKELY TO BE SUSPENDED.

The reader may refer to paragraph 3.1 in order to be reminded of the succession of phenomena observed in the case of a thin layer boil-over.

3.2.1.1 THICKNESS OF SUSPENDED LIQUID

In order to determine the amount of liquid capable of being suspended, which in fact corresponds to the amount for which the temperature is above 100°C, the relationship proposed by *Broeckmann* (92) was retained:

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(\alpha \frac{\partial T}{\partial z}\right) + V_a \frac{\partial T}{\partial z} + \frac{k}{\rho C_p} q_r \exp(-kz)$$

This relationship allows us to determine the depth at which a temperature of 100°C is observed and it involves the following physical data:

- thermophysical data of the fuel: density ρ (conductive heat transfer), absorption coefficient of the radiation k (radiative heat transfer with the flame), modified heat diffusivity α (conductive heat transfer),
- radiative flux received by the fuel q_r (radiative exchange, taking into account the diameter of the tank following the relationship proposed by Mudan and Croce (86)),
- combustion rate V_a which is linked with the regression rate; these values may be determined from databases or tests.

3.2.1.2 BOIL-OVER START TIME

In order to estimate the start time for the phenomenon, one just needs to know the height of liquid at the moment when the fire began. Indeed, nothing happens beyond a tank fire as long as there is a liquid height greater than a few centimeters. Therefore, the boil-over start time may be obtained from the initial height of the liquid, the thickness which is suspended and the specific regression rate of the product by means of the following relationship:

$$Time\ to\ the\ start\ of\ boilover = \frac{(Initial\ liquid\ height - Suspended\ thickness)}{\mathrm{Re}gression\ rate}$$

Note: unlike standard boil-over, for which the amplitude decreases with a reduction in the initial liquid level, the amplitude of thin layer boil-over is independent of this parameter. Only the amount of product having reached a temperature above 100°C is affected.

3.2.2 DETERMINATION OF THE EJECTION RATE AND OF THE COMPOSITION OF THE MIXTURE FOLLOWING VAPORIZATION OF THE WATER CONTAINED AT THE BOTTOM OF THE TANK

The water thickness at the bottom of the tank is one centimeter. This value was retained by the GT DLI (National Working Group on the Flammable Liquids Tanks Farms) based on discussions with the industrialists present.

3.2.2.1 ESTIMATION OF THE EJECTION RATE

The ejection rate was estimated based on the hypothesis of vaporization of a water height of 1 cm at the bottom of the tank.

$$V_{eject} = \left[\frac{2 \times P_{\mathrm{inter}\_water\_HC} \times H_{water}}{\rho \times H_{HC}} \right]^{0.5}$$

Comments: this value is comprised between 8 and 12 m/s.

3.2.2.2 ESTIMATION OF THE COMPOSITION OF THE INITIAL WATER AND HYDROCARBON MIXTURE

The composition of the mixture is then calculated on the basis of a « homogeneous » mixture at the highest point of the tank.

$$\rho_{mix(HC+water)} = \left[\frac{M_{water} + M_{HC\_liq} + M_{HC\_gas}}{Vol_{global\_gas} + Vol_{HC\_liq}} \right]$$

Note: The mixture is considered at pressure equilibrium between the liquid and gas phase.

3.2.3 DETERMINATION OF THE GEOMETRICAL CHARACTERISTICS OF THE RADIATING FLAME VOLUME

3.2.3.1 AIR ENTRAINMENT

The relationship retained to estimate the air entrainment is based on one of those used for the jets. Indeed, in a first approximation, the liquid projection is similar to a biphasic jet consisting of a mixture of water and hydrocarbons, with a duration of a few seconds.

However, the size of the jet and its short duration ensure that the relationship may not be applied without any modifications. This was done keeping in line with the small scale tests. An acceptable compromise consisted of multiplying the air draft flow rate by a corrective coefficient of 10.

$$M_{air} = 10 \times \left[0.32 \times M_{mix} \times \frac{V_{eject}}{1.2 \times D_{\tan k}} \times \left(\frac{\rho_{air}}{\rho_{mix}} \right)^{0.5} \right]$$

3.2.3.2 ESTIMATION OF THE VOLUME OF BURNT GASES PRODUCED AND DETERMINATION OF THE NEW COMPOSITION OF THE GASES

In order to then estimate the geometry of the flames, it is assumed that the combustion of the hydrocarbons present in the mixture is controlled by the availability of an oxidizer in the mixture, in this case oxygen from air. Indeed, at the top of the tank, the relevant mixture cannot be inflamed for lack of air. The jet is thus discretized and the air entrainment flow rate is calculated for each interval in order to determine the new composition of the mixture of water, air, burnt gases, hydrocarbon in the liquid and gas phase (cf. Fig. 11).

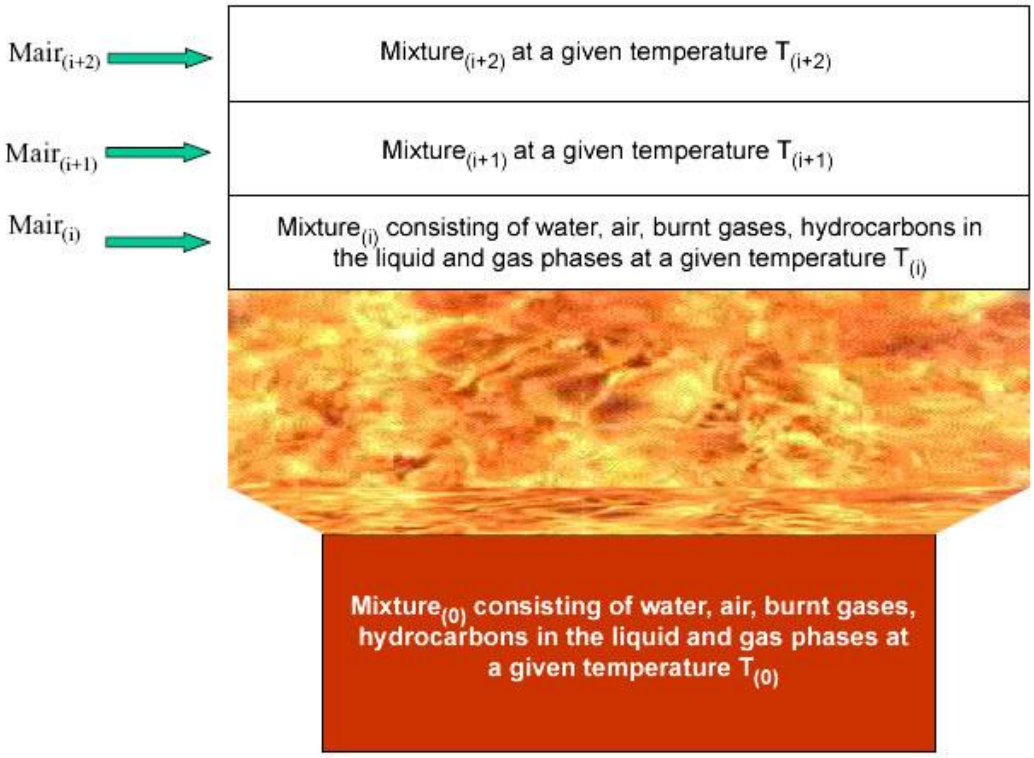


Fig. 11: Principle for the calculation of the combustion of the jet

As for the combustion, it presumably takes place under stoichiometric conditions and only the fuel in the gas phase should burn. Subsequently, the energy released by the combustion is assumed to contribute to both the rise in temperature of the mixture and the vaporization of the hydrocarbon, which is still in the liquid phase (as droplets). The global yield of the combustion is taken to be equal to 40%.

3.2.3.3 ESTIMATION OF THE VOLUME AND GEOMETRY OF THE FLAMES

To estimate the volume of the flames which will emit radiation, the hypothesis was made of cylindrical geometry of a diameter equal to 1.2 times the diameter of the tank. This value is a compromise between cases when small size fireballs and cylinders have been observed. It should be noted that when fireballs were observed at a small scale, they did not form the most radiative portion of the burning mass. For larger scales, it is difficult to make a better estimation of the geometry of the flames insofar as this phenomenon has never been observed. The geometry described earlier was therefore retained for lack of anything better.

The height of the fire cylinder is obtained from the calculation of the composition carried out in the previous step. The height of the flame cylinder is estimated to be reached as soon as the temperature of the jet passes below a temperature of 500°C. It should be noted that as soon as the combustion is finished, the temperature within the jet decreases relatively rapidly.

3.2.4 DETERMINATION OF THE ENVIRONMENTAL CONSEQUENCES

3.2.4.1 ESTIMATION OF THE SURFACE EMISSIVE POWER OF THE FLAMES

In order to estimate the effects on the environment, the surface emissive power of the flames has to be known, the latter is taken to be equal to 150 kW/m², which corresponds to a temperature of 1,000°C by using the Stefan-Boltzmann equation

$SEP = \sigma T_f^4$

This is a conservative hypothesis since this high temperature is considered over the height of the cylinder, while tests have shown that this value is smaller as soon as the altitude increases.

3.2.4.2 CALCULATION OF THE EFFECT DISTANCES

The effect distances are calculated based on the current hypothesis of a solid flame of cylindrical form, allowing the calculation of the flux received at a given point and considering an exposure time corresponding to the existence period of the phenomenon.

Φ is the flux received at a given point and t is the exposure time to this flux. The latter is calculated according to the following relationship:

$$\phi = F_{\max}\ \tau(x)\ SEP \qquad (kW/m^2) \qquad [1]$$

wherein F_{max}: view factor between the target and the fire cylinder,

$\tau(x)$: attenuation factor in air between the surface of the fire cylinder and the target.

The view factor is determined from the relationship hereafter.

In regards to a vertical elementary surface (perpendicular to the ground):

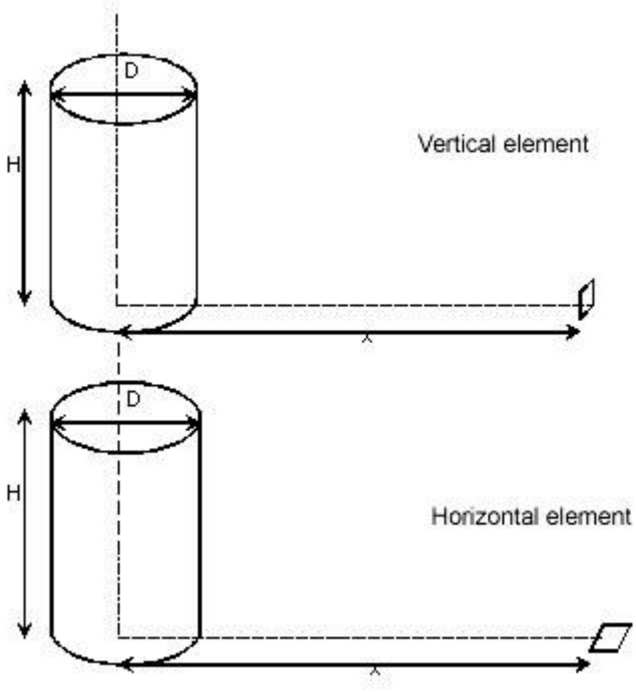


Fig. 12: Position of the targets relatively to the fire cylinder

For a vertical element:

$$F_v = \frac{1}{\pi X} Arc\tan\left(\frac{L}{\sqrt{X^2-1}}\right) + \frac{L}{\pi}\left[\frac{(A-2X)}{X\sqrt{AB}} Arc\tan\sqrt{\frac{A(X-1)}{B(X+1)}} - \frac{1}{X} Arc\tan\sqrt{\frac{X-1}{X+1}}\right]$$

wherein:

$R = D/2$
$L = H/R$
$X = x/R$

$A = (X+1)^2+L^2$
$B = (X-1)^2+L^2$
F_v: Form factor for a vertical target

For a horizontal target (parallel to the ground):

$$F_h = \frac{1}{\pi}\left[Arc\tan\left(\frac{\sqrt{X+1}}{\sqrt{X-1}}\right) - \left(\frac{X^2-1+L^2}{\sqrt{AB}}\right) Arc\tan\left(\sqrt{\frac{(X-1)A}{(X+1)B}}\right)\right]$$

wherein:

$R = D/2$
$L = H/R$
$X = x/R$

$A = (X+1)^2+L^2$
$B = (X-1)^2+L^2$
F_h: Form factor for a horizontal target

The maximum view factor, F_{max}, at a given distance is then given by the following formula:

$$F_{\max} = \sqrt{F_h^2 + F_v^2}$$

It should be noted that for a target at a height h from the ground, it is sufficient to divide the flame cylinder into two along a horizontal plane at altitude h in order to apply the previous formulae on each cylinder half.

Subsequently, a thermal dose calculation is carried out ($\phi^{4/3}t = thermal\ dose$) by which effects on persons may be estimated on the basis of the doses referenced in the French regulation (decree of 29.09.2005).

- **1 800 (kW/m²)$^{4/3}$ .s for significant lethal effects (SELS),**
- **1 000 (kW/m²)$^{4/3}$ .s for lethal effects (SEL),**
- **600 (kW/m²)$^{4/3}$ .s for irreversible effects (SEI).**

3.3 COMPARISON BETWEEN MODELING AND EXPERIMENTATION

The model was compared with the results observed in several tests. The comparison first dealt with the case of a tank of gasoil with a diameter of 30 cm with a residual height of 3 cm of hydrocarbons at the bottom of the tank at the moment when the hydrocarbon is in suspension. Fig. 13 shows the change in temperature and of the hydrocarbon mass in the flame along the vertical axis calculated with the model presented earlier. In this graph, a progressive decrease in the amount of unburnt hydrocarbons from 1.4 kg is seen at the output of the tank to 0kg at 1.3 m of altitude and in parallel, a progressive increase in the temperature from 400 K to 1300 K. These values are comparable with the observations carried out during the small scale tests.

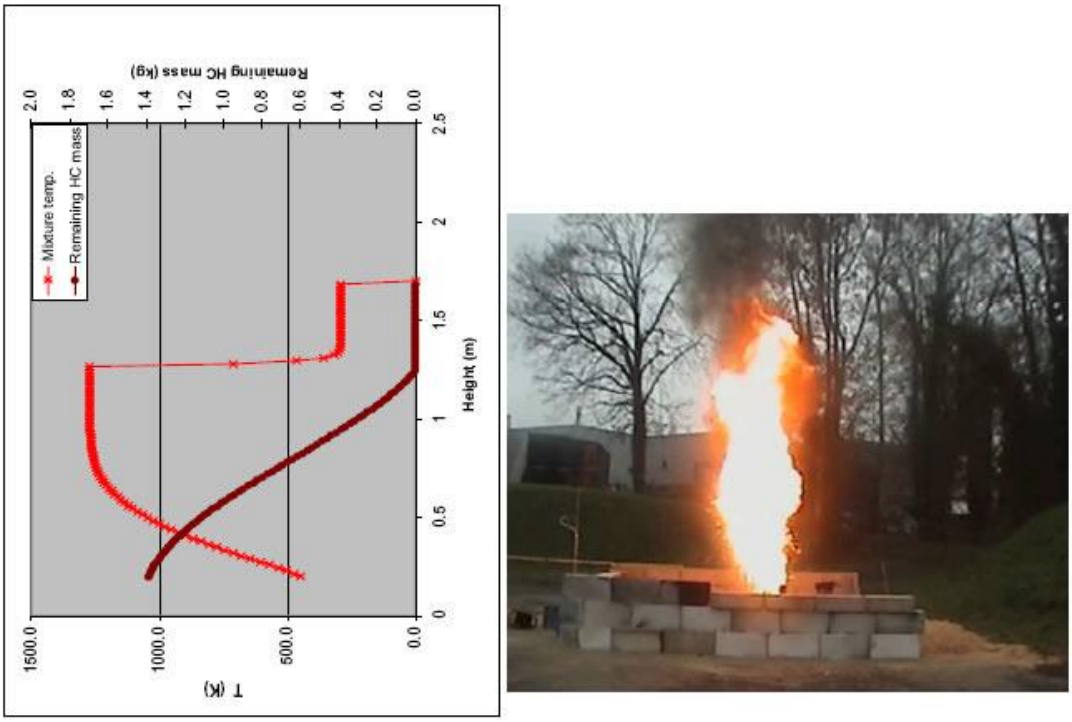


Fig. 13: Calculated change in temperature and in remaining hydrocarbon mass versus altitude

The influence of the diameter of the tank was studied by considering a tank with a diameter of 60 cm (twice the one of the previous case). The obtained results are shown in Fig. 14, they show that the height of the cylinder is 2.4 m for the 60 cm diameter compared to 1.3 m for the tank with a diameter of 30 cm.

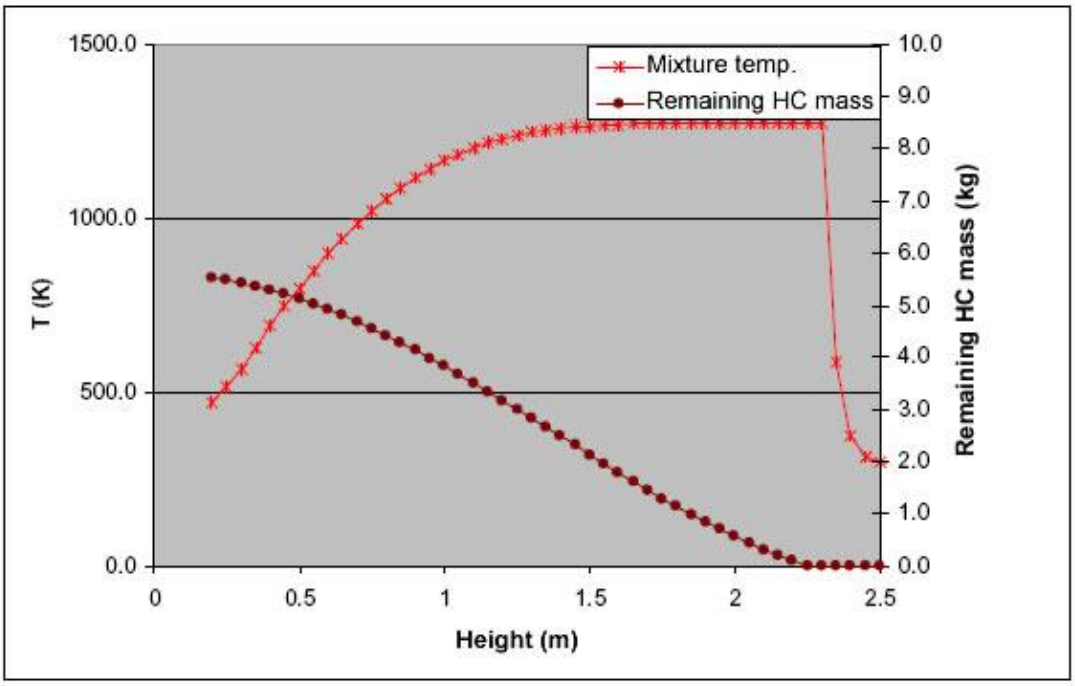


Fig. 14: Calculated change in the temperature and remaining hydrocarbon mass versus altitude for 3cm of hydrocarbon and a tank diameter of 60 cm

This comparative example shows that the tool gives orders of magnitudes comparable with those observed at a small scale and that the influence of the diameter has well been taken into account.

Moreover, it should be noted that the calculated duration of the phenomenon is comparable to the one observed to the order of one second, thereby confirming that the calculated ejection rates are realistic.

3.4 THE MODEL'S LIMITS

The model was developed from data collected from small scale tests only. Therefore, the provided results should thus be considered as probable orders of magnitude insofar as that they were obtained based on overestimating hypotheses. Further, it should also be kept in mind that, when extrapolating these phenomena to larger scales, care should be taken insofar that the tests were conducted under favorable conditions: a very flat tank bottom while most real tanks have a concave or convex bottom, the absence of obstacles at the bottom of the tank –no floating roof for example, …

A tool was developed on the basis of the model shown in the previous paragraphs. The model is not designed for standard boil-over, the tool should only be used for products identified in the tool (domestic fuel oil, gasoil and JET-A1). It is based on a water height of 1 cm at the bottom of the tank.

Finally, to our knowledge, today no thin layer boil-over of great extent has occurred on an industrial site.

3.5 CONCLUSIONS

In order to better understand the effects of a fire of a tank of hydrocarbons containing a water deposit, INERIS conducted an experimental campaign with several hydrocarbons representative of fuels stored in depots. This experimental campaign demonstrated that the phenomenon resulting from the presence of water strongly depended on the characteristics of the involved hydrocarbon and more particularly on its propensity for forming a heat wave during its combustion. Indeed, it is the heat wave which conditions the extent of the eruptive phenomenon: the thicker it is, the larger the amount of fuel participating in the fireball.

During this test campaign, for certain tested fuels (JET-A1, gasoil, domestic fuel oil), no heat wave was observed and in fact these products cannot develop a standard boil-over. However, at a small scale, eruptive phenomena were observed since the upper fraction of the liquid is heated by the radiation of the flame at a temperature above the boiling point of water. The contact between the heated hydrocarbon and the water leads to the formation of these eruptive phenomena.

The second part of this study was dedicated to the development of a model to evaluate the consequences in terms of thermal radiations on the environment. Indeed, to this day, this phenomenon has been the subject of very few studies, particularly from a modeling aspect. In fact, a first version of a tool for calculating the thermal effects associated with a thin layer boil-over was developed. This version of the tool was compared with results from small-scale tests. Taking into account the previous comments on the role of the scale factor, the results provided by this model should be considered as sensible values of effect distances.

As regards the extrapolation of these phenomena to larger scales, care should be taken insofar that the tests were conducted under conditions favorable for their occurrence (a very flat tank bottom while most tanks have a concave or convex bottom, absence of obstacles at the bottom of the tank – no floating roof for example,…).

Finally, these elements, experimental results and calculation tools were used within the framework of the French regulation (circular of July 23rd 2007). These references are found in part 6.

4. STANDARD BOIL-OVER

4.1 « STANDARD » BOIL-OVER

4.1.1 REMINDER

A boil-over is a sudden foaming phenomenon involving atmospheric tanks and resulting from the transformation of liquid water (water deposit, free water, emulsion) into vapour contained in a tank on fire. A schematic illustration of the different phases is shown in Fig. 16. This phenomenon is at the origin of violent projections of fuel, of the boiling of the contents of the tank, of extension of the flames and that formation of a fireball.

For that to occur, it was currently recognized that the hydrocarbon must meet two criteria:

1) a range of boiling temperatures 60°C beyond the boiling temperature of water at the hydrocarbon/water deposit interface pressure i.e. beyond 393°K,

2) a kinematic viscosity greater than that of JET-A1 at 393°K, i.e. $\nu HC > 0.73$ cSt.

A notable characteristic of this phenomenon is the presence of a heat wave, of which the formation process is described in the following figure.

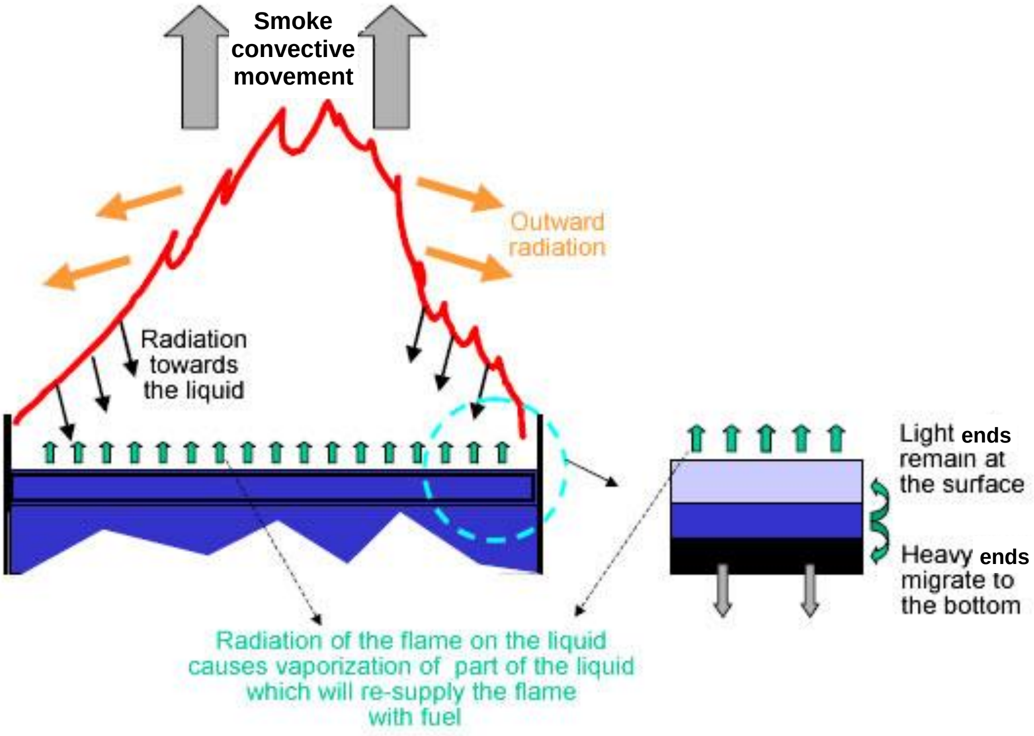
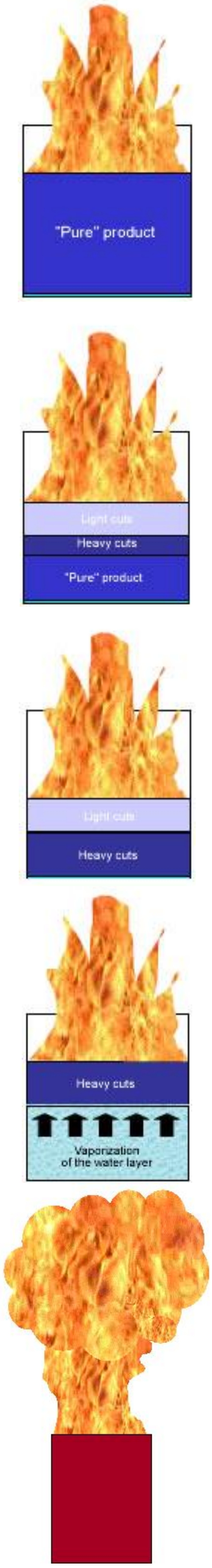


Fig. 15: Schematic process of formation of the heat wave in the case of standard boil-over



At the beginning of the tank fire, the fuel occupies the whole volume of the tank with a quasi-homogenous composition.

Due to the radiation of the flames on the surface of the liquid, the liquid undergoes distillation which leads to the separation of light ends from heavier ends. The latter gradually move down towards the bottom of the tank under the effect of gravity, this is the formation of the heat wave.

The phenomenon lasts until the heavier ends, called heat waves, reach the water located at the bottom of the tank. This heat wave has a temperature of the order of 200 °C.

The contact between the heat wave and the water causes evaporation of the latter. This sudden vaporization leads to a significant increase in volume and plays the role of a piston by suspending the remaining flammable liquid in the tank.

A fraction of the liquid overflows from the tank and another portion is suspended while fragmenting into drops and vaporizing while crossing the flames <u>to form a fireball during its combustion</u>.

Fig. 16: Schematic illustration of the different phases of a boil-over

4.1.2 PHENOMENA TO BE QUANTIFIED IN A BOIL-OVER

The phenomena induced by a boil-over are the following:

- Development of a volume of vapour by the piston effect,
- Formation of a fireball,
- Overflow and spreading of inflamed hydrocarbons outside the diked area.

These three phenomena are discussed briefly in the following paragraphs.

4.1.2.1 PISTON EFFECT

Under the pressure of the interface, the specific gravity of vapour is 1,700 to 2,000 times less than that of liquid water under normal temperature and pressure conditions. Consequently, in order that the generated vapour volume fill the tank, it is sufficient that the thickness of the water deposit, as an order of magnitude, be of one 1,700th to 2,000th of the height of the tank, i.e. of the order of one centimeter for most current tanks.

The vapour volume developed quasi instantaneously will act on the bulk of hydrocarbons overhanging it like a piston. Consequently, the volume increase ΔV consecutive to the vaporization of the water contributes to the movement of the hydrocarbon bulk by instantaneously imparting to it the kinetic energy $PVAP.\Delta V$, in which PVAP is the vapour pressure at the water/hydrocarbon interface at the moment when the water reaches the hot area.

4.1.2.2 CONSEQUENCES OF THE PISTON EFFECT: FIREBALL, OVERFLOW AND SPREADING OF BURNING HYDROCARBONS TO THE EXTERIOR

Following this piston effect, the thereby propelled hydrocarbon will give rise both to a fireball above the tank and to a pool fire around the tank due to the liquid jets which have fallen onto the ground. Indeed, the ejected fluids resulting from the piston effect may be driven with a significant kinetic energy and may fall on the ground while they are still in a state of combustion.

It should be noted that, in general, the fireball phenomenon appears to be the most dangerous event (or phenomenon) for persons (at a long distance) generated by the boil-over. Its characteristics and its thermal effects will thereby be described in chapter 4.2.

In order to quantify these effects, the following data relating to hydrocarbons should be known:

	Fuel oil No.2	Light crude oil	Heavy crude oil
Boiling temperature (K)	544	535	621
Initial boiling temperature corresponding to a 15 % vaporized fraction (K)	453	348	368
Final boiling temperature corresponding to a 85 % vaporized fraction (K)	653	823	1047
Critical temperature (K)	929.8	686	810
Critical pressure (Pa)	$1.53.10^6$	$1.86.10^6$	$1.525.10^6$
Density of the liquid phase at 288°K (kg/m^3)	990	802	905
Density of the gas phase at 300°K (kg/m^3)	11.65	6.686	9.7
Latent heat of Vaporization at the boiling temperature (J/kg)	$8.6.10^5$	$2.92.10^5$	$3.384.10^5$
heat of Combustion (J/kg)	$4.01.10^7$	$4.33.10^7$	$4.184.10^7$
Upper flammability limit (volume %)	0.055	0.055	0.055
Viscosity at 393°K (cSt)	10	2	5.2

Table 1: Properties of hydrocarbons capable of giving rise to boil-over

All the data listed in Table 1 are required for applying the model described hereafter.

4.2 MODELING THE PHENOMENON AND ITS CONSEQUENCES

The goal of this chapter is to present a calculation method to determine the characteristics of the boil-over and more specifically of the fireball generated by this phenomenon as well as associated thermal effects.

4.2.1 METHOD USED BY INERIS STEMMING FROM OMEGA 13 - VERSION 2003

As indicated in the previous chapter, the boil-over may generate both the formation of a fireball and projections of inflamed products, which may form a fire pool outside of the tank.

The following sections of this document consider only the modeling of the thermal effects on humans and on the environment due to the fireball.

The main steps for modeling the effects of the formed fireball during a boil-over are the following:

- determination of the amount of hydrocarbon involved in the formation of the fireball,
- estimation of the characteristics of the fireball,
- description of the heat radiation effects of the fireball on an exposed person and/or the environment.

4.2.1.1 AMOUNT OF HYDROCARBON PARTICIPATING IN THE FORMATION OF THE FIREBALL

It is clear that for a boil-over to occur, it is necessary that the downward velocity of the heat wave – in other words the thickening of the hot area – exceed the combustion rate of the hydrocarbon contained in the tank. In the opposite case, there would no longer be any hydrocarbon to create a possible fireball. This is the first verification to be carried out.

Subsequently, the amount of suspended liquid will depend on the difference between the two velocities.

The hydrocarbon's combustion rate v_1 is evaluated by a semi-empirical relationship (Burgess et al., 1961) taking into account particularly the heat of the hydrocarbon's combustion, its vaporization heat and its heat capacity:

$$v_1 = 10^{-3} \frac{\left(\dfrac{\Delta H_c}{\rho_l(TM)}\right)}{L_V + \displaystyle\int_{TSER}^{TBUL} C_p(T).dT} \qquad (m/s) \qquad [2]$$

with $TM = (TBUL \times TSER)^{0.5}$

wherein ΔH_c: heat of the hydrocarbon's combustion (J/kg),
$\rho_l(TM)$: density of the hydrocarbon at temperature TM (kg/m^3),
L_V: latent heat of vaporization of the hydrocarbon (J/kg)
C_p: heat capacity (J/kg K),
$TSER$: initial temperature of the hydrocarbon in the tank (K),
$TBUL$: boiling temperature of the hydrocarbon (K).

As for the propagation velocity v_2 of the heat wave, it is estimated by calculating the ratio between the height of liquid hydrocarbon $HLIQ$ contained in the tank at the moment when the fire breaks out and the start time of the boil-over t_{BO} at the same moment such that:

$$v_2 = \frac{HLIQ}{t_{BO}} \qquad (m/s) \qquad [3]$$

wherein $HLIQ$: height of liquid hydrocarbon contained in the tank at the moment when the fire breaks out (m),

t_{BO}: start time of the boil-over from the moment when the fire breaks out (s).

The boil-over start time t_{BO} is estimated from the energy transfer required for the amount of hydrocarbon to vaporize the water. Indeed, boil-over occurs when the heat wave reaches the water deposit, in other words, the totality of the hydrocarbon amount contained above the water deposit will have been raised from the service temperature *TSER* of the tank to the temperature of the heat wave *TWAV*. A simple expression of the boil-over start time is thereby defined, taking into account neither the change in the liquid's height nor that of the heat wave's temperature (upper bound expression):

$$t_{BO} = \frac{\rho_l(TSER)\, C_p(TSER)\, \big(TWAV - TSER\big) HLIQ}{\Phi} \qquad \textbf{(s)} \qquad \textbf{[4]}$$

wherein $\rho_l(TSER)$: the hydrocarbon's density at temperature *TSER* (kg/m^3),

$C_p(TSER)$: heat capacity at temperature *TSER* (J/kg K),

Φ: fraction of the radiated flux of the flame in the tank fire, which heats up the tank's contents from the upper layer down to the bottom, taken to be equal to 60 kW/m^2.

In order to calculate the temperature of the heat wave *TWAV* at the moment when the boil-over occurs, the adopted approach consists of considering the distillation curve of the relevant hydrocarbon and of noting that only the fractions for which the boiling temperature is equal to or greater than the temperature *TWAV* of the heat wave participate in the fireball.

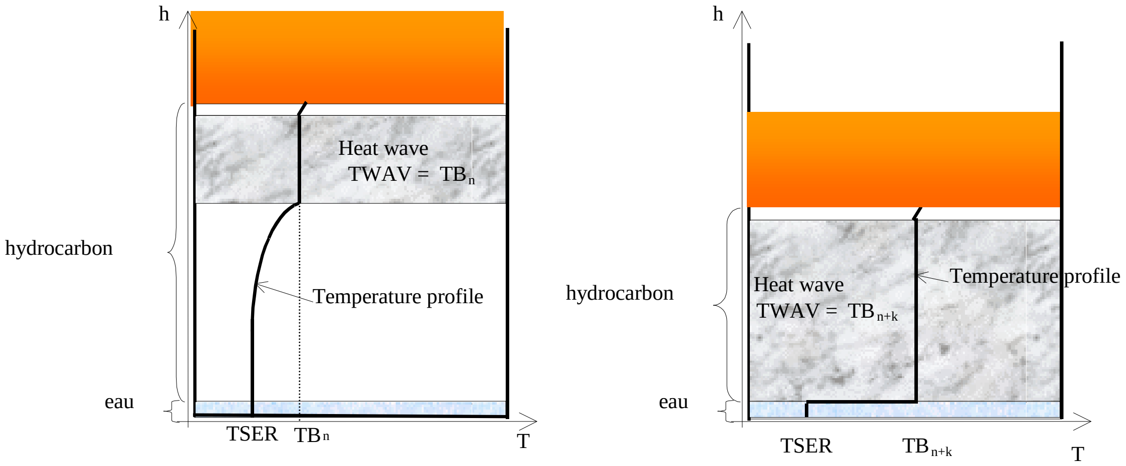


Fig. 17-a (time t) Fig. 17-b (time t_{BO})

Fig. 17: Heat wave propagation diagram

In referring to Fig. 17 and retaining the approach developed notably by Broeckmann (1992), at instant *t*, the heat wave's temperature *TWAV* corresponds approximately (to within ε) to the boiling temperature of the fraction of index *n*

(Fig. 17 – a). This weak difference ε is related to the interface film between the liquid and the combustion area.

When boil-over occurs, i.e. at instant $t = t_{BO}$, the boiling fraction bears the index $n+k$ and, accordingly $TWAV(t_{BO}) = TB_{n+k}-\varepsilon$ (Fig. 17 – b). In the following, and conservatively, the difference ε will be neglected.

Next, the distillation curve of the involved hydrocarbon should be described. This curve represents the cumulated volume percent of hydrocarbons distilled depending on the temperature, when the latter is in a range comprised between a so-called initial boiling temperature *TIN* (the lower boiling temperature) and a so-called final boiling temperature *TFIN* (the highest boiling temperature). In general, these two temperatures, *TIN* and *TFIN,* which are the limits to the range of boiling temperatures, correspond respectively to volume fractions of the distilled product *XIN = 15 %* et *XFIN = 85 %* (Fig. 18).

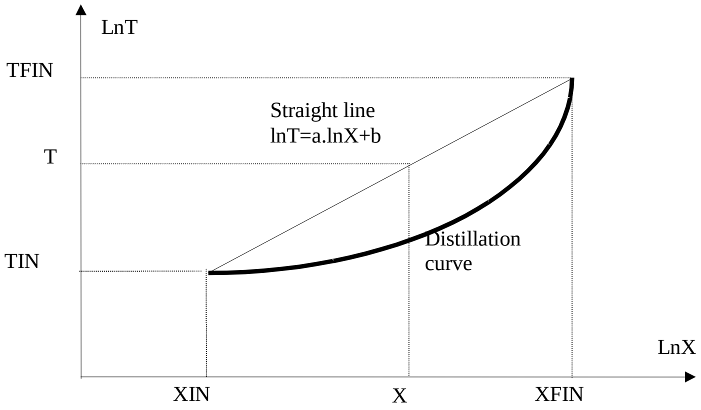


Fig. 18: Hydrocarbon distillation curve -
Approximation of the curve by a straight line

To simplify, and while still over-estimating, the option is taken to assimilate these curves to straight lines in logarithmic coordinates. Insofar that only the fractions for which the boiling temperature is greater than or equal to *TWAV* will participate in the fireball, this approach is wise in the sense that it leads to over-estimating the mass involved in the fireball.

Indeed, Fig. 18 shows that for a same temperature *TWAV*, the proportion of already vaporized volume is less and accordingly the mass involved in the fireball is then larger.

Thus, in logarithmic coordinates, the equation of the distillation curve is of the type:

$$\ln T = a \ln X + b \qquad [5]$$

wherein T: fuel temperature (K),
X: vaporized liquid fraction at this temperature (%).

Thus when boil-over occurs, the relationship between the heat wave's temperature at the hydrocarbon/water deposit interface, *TWAV*, and the vaporized hydrocarbon fraction at this instant, X_{BO}, will be the following:

$$\ln TWAV = a \ln X_{BO} + b \qquad [6]$$

Now, when boil-over occurs (at t_{BO}), the vaporized hydrocarbon fraction X_{BO} is none other than the one which has been already consumed at the combustion rate v_1, reduced to the total amount of fuel present in the tank when the fire broke out.

This is expressed by the following formula:

$$X_{BO} = \frac{v_1 . t_{BO}}{HLiq} + XIN \qquad (-) \qquad [7]$$

It is thus that *TWAV* is a function of t_{BO}. By combining the equations [4], [6] and [7], a system of equations is obtained which allow the calculation of t_{BO} and *TWAV*. An iterative calculation should therefore be carried out in order to determine values of *TWAV* and t_{BO} which simultaneously verify both of these equations.

The time required before the start of the boil-over allows an estimation of the mass susceptible to participate in the fireball.

The reasoning should be applied to the mass remaining in the tank when the boil-over occurs, i.e. the mass of hydrocarbons present in the tank when the fire breaks out, reduced by the amount of hydrocarbon having burnt before the boil-over occurred.

Next, the mass of hydrocarbon vapor participating in the fireball phenomenon should be estimated. In a prudent and simplified approach, it is considered that **the amount of hydrocarbon remaining in the tank at the moment of the boil-over is in its entirety in vapor form in the fireball.** This amounts to assuming that there is no fluid fallout on the ground, even if these fluid projections exist in the reality of the phenomenon (§ 4.1.2.2).

Thus, by referring to the distillation curve (assimilated to a straight line in logarithmic coordinates), when the temperature reaches *TWAV*, the product fraction already consumed by the combustion is known and has the value X_{BO}.

Accordingly, the mass of vapor *MVAP* capable of participating in the fireball will correspond to a volume fraction X_{VAP} equal to $(1 - X_{BO})$ and its expression will therefore be the following:

$$MVAP = X_{VAP}\ MLIQ = (1 - X_{BO})\ MLIQ \qquad (kg) \qquad [8]$$

Wherein *MLIQ*: Hydrocarbon mass contained in the tank at the beginning of the fire (kg).

4.2.1.2 CALCULATION OF THE FIREBALL'S CHARACTERISTICS

The fireball effect is a complex phenomenon which is not very easy to quantify.

At the start of a violent boil-over, a column rich in flammable vapors rises rapidly in the atmosphere up to an altitude where its mixing with an air supply will allow its combustion. A torus-shaped, mushroom-shaped or ball-shaped fire mass will develop and burn very rapidly, accompanied by a sudden increase in the radiation emitted by the enflamed mass.

The fireball's surface emissive power ϕ_0 is taken to be equal **to 150 kW/m²**[‖]**.** This value was corroborated by experimental work which, in worst case scenarios, led to the measurement of a value of ϕ_0 equal to123 kW/m^2 (Broeckmann, 1992).

From this fireball's emissive power, the flame temperature *TFLA* may be written in the following form:

$$TFLA = \left(\frac{\phi_0 + \varepsilon.\sigma.TAMB^4}{\varepsilon.\sigma} \right)^{1/4} \qquad (K) \qquad [9]$$

with ε: emissivity ($\varepsilon = 0.6$ for gas flames),

σ: BOLTZMANN constant, i.e. $5.677.10^{-8}$ W/m² K,

TAMB: ambient temperature (K).

Given a flame emissivity value ε equal to 0.6, equation **[8]** gives a flame temperature *TFLA* of 1,443K.

The combustion of the fireball takes place at the upper flammability limit.

The fireball may consequently be considered as representative of a homogeneous concentration of hydrocarbon vapor equal to the upper flammability limit *LSI*.

This means that in 1 m^3 of hydrocarbon-air mixture, a mass of hydrocarbon vapor is found equal to:

$$\boldsymbol{\rho_g(TFLA)\ LSI} \qquad [10]$$

wherein $\rho_g(TFLA)$: density of the hydrocarbon vapors present at *TFLA* (kg/m^3),

LSI: Upper flammability limit (% by vol.).

Consequently, the hydrocarbon concentration *C* present in the fireball is expressed as:

$$\mathbf{C = \rho_g(TFLA)\ LSI} \quad \textit{(kg of hydrocarbon / m}^3\textit{ of hydrocarbon-air mixture)} \quad [11]$$

By over-estimating the total mass of generated hydrocarbon vapor without taking into account the burnt fraction, the volume V_{FB} of the fireball is then defined as follows:

[‖] The radiation intensity is less than the values usually considered for a BLEVE (200 to 300 kW/m²), since in the case of liquid hydrocarbons, the fireball is confined to an environment of black fumes.

$$V_{FB} = \frac{MVAP}{C} \qquad (m^3) \qquad [12]$$

The radius of the fireball, r_{FB}, is thus expressed as:

$$r_{FB} = \left(\frac{3}{4\pi} V_{FB} \right)^{1/3} \qquad (m) \qquad [13]$$

The lifetime of the fireball t_{FB} is estimated by the empirical formula of HIGH (Bagster, 1989), i.e.:

$$\mathbf{t_{FB} = 0.295\ (MVAP)^{0.32}} \qquad (s) \qquad [14]$$

The height h_{FB} of the fireball's centre may be calculated by the following empirical relationships:

$$\bar{t} = \frac{t_{FB}\ TFLA^{10/3}}{MVAP^{1/3}\ 10^{10}} \qquad [15]$$

$$h_{FB} = \left(\frac{68.571\,\bar{t}}{2.857 + \bar{t}} \right) \left(\frac{MVAP}{TFLA} \right)^{1/3} + HEQU \qquad (m) \qquad [16]$$

4.2.1.3 CALCULATION OF THE FIREBALL'S THERMAL EFFECTS

4.2.1.3.1 CRITICAL THERMAL LOADS RETAINED BY HUMANS

The radiative thermal effects of a fireball on a given population depend on the intensity of the radiations as well as on the exposure time to these radiations. INERIS retains the thresholds of the French regulation (circular of September 29th 2005), i.e.:

- **1 800 $(kW/m^2)^{4/3}$ .s for significant lethal effects (SELS),**
- **1 000 $(kW/m^2)^{4/3}$ .s for lethal effects (SEL),**
- **600 $(kW/m^2)^{4/3}$ .s for irreversible effects (SEI).**

The flux densities $\phi_{threshold}$ (wherein threshold represents SELS, SEL and SEI) are expressed versus the exposure time to the source.

In an overestimated approach, the latter is taken to be equal to the lifetime of the fireball, t_{FB}:

$$\phi_{Seuil}^{4/3}\ t_{FB} = threshold \qquad (kW/m^2)^{4/3}\ .s \qquad [17]$$

4.2.1.3.2 CALCULATION OF THE DISTANCES OF THERMAL EFFECTS

The radiated flux $\phi(X)$ received at a distance X from the centre of the fireball is written as:

$$\phi(X) = F_{view}\ \tau(x)\ \phi_0 \qquad (kW/m^2) \qquad [18]$$

wherein F_{view}: view factor between the target and the fireball,

$\tau(x)$: attenuation factor in the air between the surface of the fireball and the target.

Fig. 19 illustrates the configuration retained for calculating the distances of effects generated by the fireball on a target.

For a fireball, the view factor F_{view} is calculated simply as a function of the distance X from the centre of the fireball to the target and of the radius r_{FB} of the fireball:

$$F_{view} = \left(\frac{r_{FB}}{X}\right)^2 \qquad (-) \qquad [19]$$

To take into account the radiation's atmospheric attenuation in the calculation of the heat flux, the transmissivity factor $\tau(x)$ depending on the distance x between the envelope of the fireball and the target $x = X\text{-}r_{FB}$ may be estimated, for example, by means of the empirical Bagster law (1989):

$$\tau(x) = 2.02\left(p_w\ x\right)^{-0.09} \qquad (-) \qquad [20]$$

with p_w: Partial vapour pressure of water in the air at a given relative humidity (N/m²),

x: Distance between the envelope flame and the target (m).

This equation is only valid when $10^4 < p_w\ x < 10^5$ N/m. This latter quantity depends on the air's relative humidity and on the temperature of the ambient air.

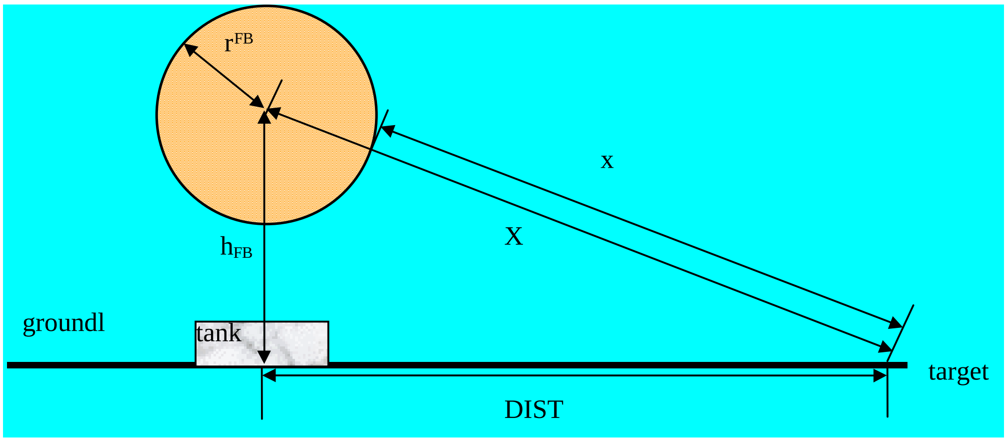


Fig. 19: Notations relating to the fireball

The fluxes $\phi_{threshold}$ corresponding to the thresholds of the significant lethal effects (SELS), lethal effects (SEL) or irreversible effects (SEI) are obtained respectively at distances $X_{threshold}$ from the centre of the fireball where it is verified that:

$$\phi_{threshold} = \phi(X_{threshold}) = \left(\frac{r_{FB}}{X_{threshold}}\right)^2 \tau(x_{threshold})\phi_0 \qquad (kW/m^2) \qquad [21]$$

Given that $\tau(x)$ is implicitly a function of the distance X from the fireball's centre and that the distance X is itself explicit in function to the transmissivity factor $\tau(x)$, the determination of the effect distances $X_{threshold.}$ automatically requires an iterative calculation.

Hence, the only remaining step is to determine the distances of thermal effects on the ground $DIST_{threshold}$ defined between the centre of the tank and the target:

$$DIST_{threshold} = \sqrt{X_{threshold}^{2} - h_{FB}^{2}} \qquad (m) \qquad [22]$$

4.2.2 ESTIMATION OF THE CONSEQUENCES BY MEANS OF SIMPLE CORRELATION

In order to avoid recoding the whole of the equations described earlier, in the following paragraphs, we present simple correlations based on the results provided by the equations above. They allow us to obtain the effect distances for the three most widespread products capable of giving rise to conventional boil-over: heavy crude oil, light crude oil and fuel oil No. 2.

The correlations for determining the effect distances depending on the mass of stored product may generally be written as follows:

$$DIST_{Threshold} = A_{Threshold}\, MLIQ^{B_{Threshold}} \qquad (m) \qquad [23]$$

wherein $DIST_{Threshold:}$ Distance associated with the threshold effect Threshold (m),

MLIQ: Hydrocarbon mass contained in the tank at the start of the fire (kg),

$(A_{Threshold}, B_{Threshold})$: Pairs of constants to be determined according to the stored product and according to the threshold.

The pairs of constants $(A_{Threshold}, B_{Threshold})$ were determined for different changes in safety distances and are shown in the following table:

	Constants associated with $DIST_{SELS}$		Constants associated with $DIST_{SEL}$		Constants associated with. $DIST_{SEI}$	
Stored product	A_{SELS}	B_{SELS}	A_{SEL}	B_{SEL}	A_{SEI}	B_{SEI}
Fuel oil No.2	0.264	0.467	0.42	0.455	0.573	0.449
Light crude	0.17	0.466	0.267	0.454	0.363	0.448
Heavy crude	0.14	0.478	0.249	0.46	0.345	0.452

Table 2: Pairs of constants $(A_{Threshold}, B_{Threshold})$ for stored products.

INERIS proposes the use of these three relationships for the products identified in Table 2 when the reader does not have the whole version of the tool.

For all other products capable of giving rise to standard boil-over, the model presented earlier may be used if the physico-chemical properties of the hydrocarbons are known.

4.3 THE MODEL'S LIMITS

The model's limits are:

- on the one hand, the determination of the heat wave's characteristics and more particularly its formation mechanism as well as the products which make it up. Indeed, the heat wave was clearly identified but no data exists as to the exact composition of this heat wave.
- on the other hand, the mode of suspending the liquid (fractionation of the liquid) and its combustion during this phase (diffusion flame at the periphery and gradual rise of the fireball under the effect of buoyancy which is not taken into account).
- determination of the amount of fuel which falls back on the ground: suspended fuel for which the characteristic size is too large for it to burn before falling back on the ground. For the moment, all the material is assumed to participate in the formation of the fireball.
- determination of the overflowing fraction that is not suspended. It is also recognized that a part of the liquid may overflow without being fractionated and thus not participate in the formation of the fireball.

All these points indicate that it is best to over-estimate the calculated effect distances.

4.4 CONCLUSIONS

Boil-over is a phenomenon which has been little observed during the last 2 decades. As a reminder, the main cases listed in the previous version of omega 13 prior to this period:

- **YOKKAICHI (JAPAN)**, October 15th 1955 (case No. 6051);
- **TACOA (VENEZUELA)**, December 19th 1982 (case No. 6052);
- **MILFORD HAVEN (GB)**, August 30th 1983 (case No. 6077);
- **THESSALONIKA (GREECE)**, February 24th 1986 (case No. 6076);

However, the extent of its effects (a fireball of several hundred meters) is such that it is necessary to take it into account notably within the scope of urban environments.

The existing models described in this chapter allow us to obtain a conservative estimation of these effects.

5. CONCLUSIONS AND PERSPECTIVES

In the case of a tank fire in the presence of a water deposit, 3 situations may be observed at the end of combustion:

- the liquid is not sufficiently viscous and no projection is observed. This is the case of petrol for example. No particular effect besides the tank fire is to be feared and no additional modeling is to be carried out;
- a so-called « thin layer » boil-over with the occurrence of a heat gradient over only a few centimeters of hydrocarbon which are susceptible to being suspended. This is what has been observed, for the time being, only with gasoil, domestic fuel oil and JET-A1. The estimation of the consequences may be carried out by means of the model described in chapter 3;
- a so-called « standard » boil-over is observed when the product is sufficiently viscous and when it is capable of forming a heat wave following its distillation into light ends and heavy ends. This is what may be observed with light crude oil for example. The estimation of the radiative consequences may be carried out by means of the model described in chapter 4.

In order to know the propensity of another flammable liquid to produce standard boil-over, thin layer boil-over or to have no effect, it is necessary to do a specific study. This study may, for example, be limited to doing tests similar to those done by INERIS: small scale tests in order to see whether there is projection of inflamed liquid and measurement of the heat gradient in order to find if there is a heat wave.

This combination allows, on the one hand, to make sure that the fuel is sufficiently viscous that it may be projected by the vaporization of the water present at the bottom of the tank and to verify, on the other hand, in the case of liquid projections whether or not the latter occur in the presence of a heat wave.

6. REFERENCES

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3. MUDAN, CROCE
   Fire hazards calculations for large open hydrocarbon fires; SFPE Handbook of fire protection engineering, 1986

INERIS studies were used to draw up the texts of the July 23rd 2007 circular mentioned hereafter.

4. Circular DPPR/SEI2/AL-07-0257 as of July 23rd 2007 relating to the evaluation of risks and of effect distances around terminals of flammable liquids and flammable liquefied gas terminals (address: http://aida.ineris.fr/textes/circulaires/text4593.htm)

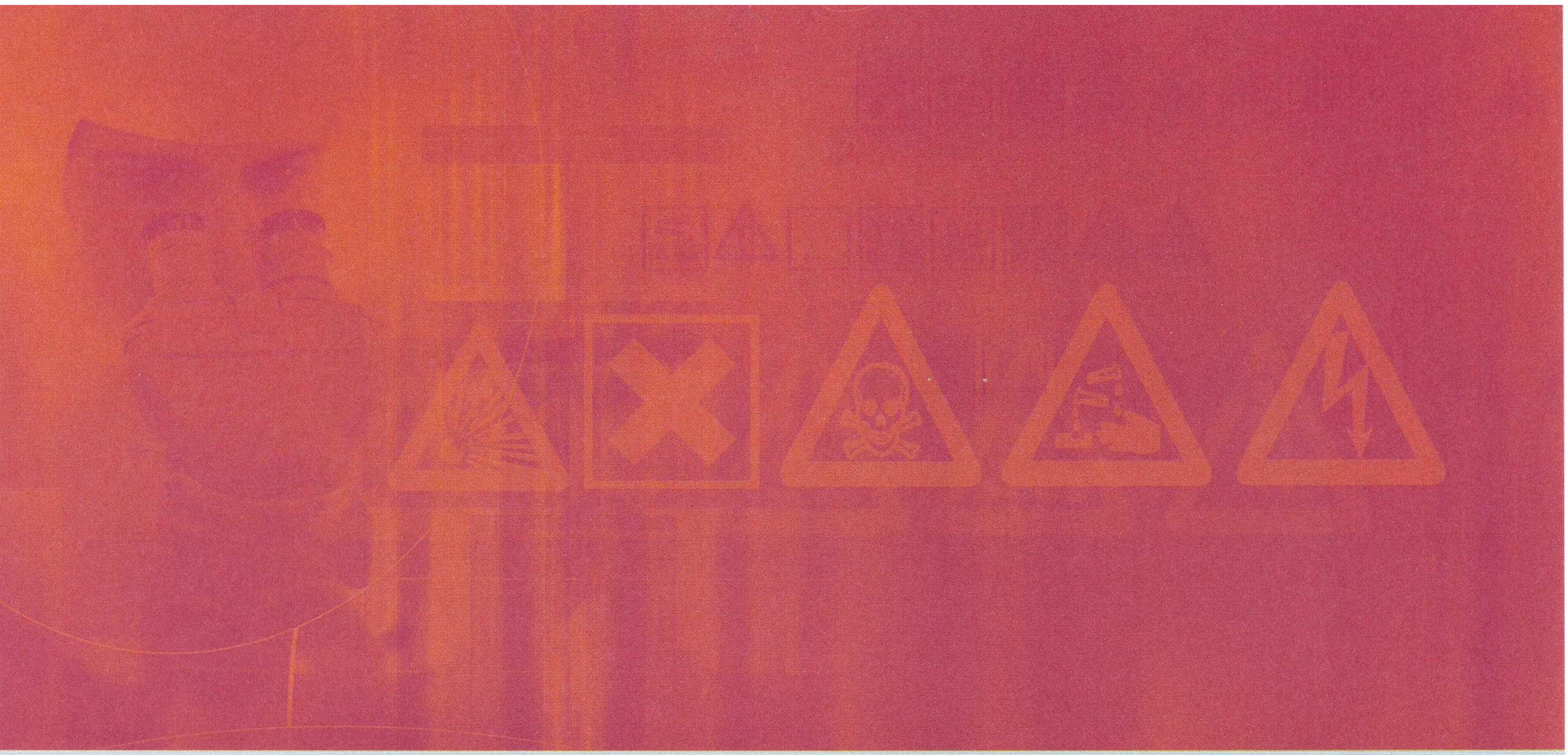
5. Boil-overs and other phenomena generating fireballs concerning the tanks of flammable liquid terminals (address: http://aida.ineris.fr/textes/circulaires/images/text4593_01.pdf)

6. UVCE in a terminal of flammable liquids: non-technical memo

7. UVCE in a terminal of flammable liquids: technical note

8. Boil-overs and other phenomena generating fireballs relating to tanks of flammable liquid terminals: non-technical memo

9. Annex V – Calculation spreadsheet: thin layer boil-over
   (Downloadable tool at the following address: http://aida.ineris.fr/textes/circulaires/images/text4593_05.xls)



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