Contribution to boilover and frothover quantification

P. Michaelis, Guy Mavrothalassitis, Jean-Philippe Pineau

P. MICHAELIS

TOTAL RAFFINAGE EUROPE

Département Environnement Sécurité

PARIS (France)

G. MAVROTHALASSITIS, J.P. PINEAU

INERIS

VERNEUIL EN HALATTE (France)

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INTRODUCTION

Frothing phenomena are related to the presence of water and liquid hydrocarbons in a tank heated by a fire or heaters.
One may quote accidents occurred in Signal Hill (USA), Milford Haven (UK), Pernis (NL), Thessaloniki (GR), Port Edouard Herriot (F), Tacoa (VA), Yokkaichi (JN) ... each of them with important damage.
One first has to distinguish between boilover and frothover, the main difference being in the piston-effect created.
To have a boilover three conditions are necessary : 1) generation of a heat wave that enters into contact with water below the hydrocarbon, 2) presence of water to be converted to steam, 3) a viscous hydrocarbon which steam cannot readily pass from below.
To have a frothover similarly : 1) a tank heated at a temperature exceeding the boiling point of the accidental fluid, 2) either water or light hydrocarbon being pumped into the tank by mistake, or a layer

of water in the tank bottom being disturbed, or an emulsion water to hydrocarbon being dissociated, 3) a viscous hydrocarbon contained in the tank.

Piston Effect

Creation of steam generates a volume resulting from an adiabatic expansion and acting like a piston. The positive displacement of that piston is equal to the ratio of the steam volume by the cross section area of the tank. The displacement velocity of the piston can be quantified by identifying the adiabatic expansion energy with the cinetic energy transmitted to the liquid hydrocarbon contained into the tank.

Volume of steam created can be simply calculated using the Avogadro and Ampere law, the ideal gas law or the Callendar and Mollier equation.

In case of boilover we can write,

$$VVAP = (.25.\pi.DEQU^2.\ EP.\ \rho_{H20}.\ TWAV.R)/PVAP \qquad (m^3) \qquad \text{(eq. 1)}$$

with DEQU, the diameter of the tank (m)

EP , the thickness of water bottom (m)

ρ_{H20}, the density of water (kg/m^3)

TWAV, the heat wave temperature (K) is defined hereunder

R , the specific ideal gas constant (J/kg.K)

PVAP, pressure at the interface hydrocarbon/water bottom (Pa)

TWAV is calculated :

$$TWAV = F(t).\exp((\ln DENSL - 3.094)/.594) \qquad \text{(eq. 2)}$$

$$F(t) = (2.693\ 10^{-6}\sqrt{TBUL})\ t^2 - (2.693\ 10^{-5}\sqrt{TBUL})\ t + .044\sqrt{TBUL}$$

(eq. 3)

$t = (DENSL.CSPE.DEQU.TWAV)/4\ \Phi$ (s) (eq. 4)

t is the time when heat wave is reaching tank bottom ;

DENSL, the gravity of liquid hydrocarbon (kg/m^3)

TBUL, the boiling point of the hydrocarbon (K)

CSPE, the specific heat of liquid hydrocarbon (J/kg .K)

Φ, the radiation intensity of the tank fire devoted to heat the hydrocarbon deeper and deeper (W/m^2), taken equal to 60 kW/m^2.

PVAP is calculated :

$PVAP = PATM + (HLIQo.DENSL\ .\ 9.81)$ (eq. 5)

with, PATM, the atmospheric pressure (Pa)

HLIQo, the liquid hydrocarbon height when boilover occurs, (m)

The piston velocity can be expressed as follows :

$VMAX = 142.33\ [a/b]^{0.5}$ (m/s) where

$a = (1 + (9.684\ 10^{-5}.HLIQo.DENSL))(VVAP-VO)$ and

$b = MLIQo\ (\gamma -1)$ (eq.6)

with : Vo, volume of accidental fluide before expansion (m^3)

MLIQO, mass of hydrocarbon expelled by the steam piston (kg).

Tank Roof Ejection

The cinetic energy of the expelled hydrocarbon is converted into energy for tearing section of the roof from the shell of the tank (case of frothover) and/or into energy of froth expulsion filling and overflowing of the diked area.

Tank roof ejection involves the problem of quantifying trajectory and impact conditions of plate-like fragment or missile.

Three main steps are developed :

1) <u>The definition of the roof fragment</u> : shape, mass, area.

We suggest to consider the missile corresponding to a circular break in the roof, the diameter of which is 75 % of that of the tank, and which is tangent to the tank shell.

2) <u>The calculation of the initial velocity and elevation angle</u>

The piston effect hereabove described, increases the tank pressure causing the roof to rupture.

The initial velocity of the missile is a function of the available energy at the time of bursting and can be written as,

$$VMIS = [(2.F.\Delta P.(VEQU-VLIQ))/(MEQU\ (1+\epsilon_{Fr})^{3\gamma-3}\ (\gamma-1))]^{0,5}\ (m/s) \quad (eq.7)$$

with : VEQU, the tank capacity (m^3)

VLIQ, volume of liquid hydrocarbon at time of frothing (m^3)

MEQU, mass of tank + liquid content, at time of frothover (m^3)

ΔP, pressure difference in tank at bursting (Pa)

F, yield factor for fragment energy

F = 0,2 with brittle fracture

F = 0,6 with ductile fracture

ϵ_{Fr}, fraction of strain of the tank material on fracture

γ, ratio of the specific heats in vapor phase.

The system is a cylinder under pressure generating vertical force field within a conical roof : direction of ejection will be quasi-vertical, and we consider accordingly an elevation angle of 80°.

3) <u>The calculation of the trajectory</u>

Once the roof fragment has acquired its initial velocity, ballistic calculations take account of gravitational forces and fluid dynamic forces, namely drag and lift components.

Drag coefficient is quantified using CLANCEY's velocity relation (mainly valid for bulky fragments). Lift coefficient is determined as a function of the angle of attack. The problem implies the movement of a solid body expelled with an 80° elevation angle into an uniform gravity field and subjected to resisting environment. Equations of motion are written for acceleration in the vertical and horizontal directions. Solving of the differential equations is performed using RUNGE-KUTTA or EULER-CAUCHY methods.

Conservative solution may be easily expressed neglecting the lift coefficient ; the maximum impact distance of the roof fragment becomes,

$RMIS = (.102/CDG)\ln(1 + 1.703\ VMIS.\ t_f.CDG)$ (m) (eq. 8).

with :

CDG, the drag term divided by gravitational acceleration (s/m^2)

t_f, the total time of flight, (s).

Overflowing and spillage

The model proposed to assess overflowing phenomenon inside and outside diked area, assumes a concentric stream tubes configuration, and calculates for every tube the maximum horizontal impact distance, being the source of an elementary spillage.

Four steps are developed :

1) The definition of the stream tubes configuration upstream the passage through the tank roof : 1 central cylindrical stream tube and n-1 annular stream tubes with the condition that every stream tube contains the same mass of hydrocarbon (see fig. 1).

2) The alteration of the stream tubes configuration when passing trough the roof hole, due to constriction and asymmetry phenomena :

1 annular external stream tube tangent to the tank shell, 1 central cylindrical stream tube, and n-2 lens shaped stream tubes between, all of them tangent to the cylindrical stream tube (see fig. 1).

3) The velocity and angle of elevation distribution.

Initial velocities are assumed to be distributed according a parabolic law. For tube i, the velocity is given by :

$$V_i = (VMAX'/\omega^2).(1 - 4(r_i^2/DEQU^2)) \quad 1 \leq i \leq n \qquad \text{(eq. 9)}$$

with,

ω, the constriction factor (ratio between area of the hole in the roof, and tank cross section)

r_i, the radius of the circle being the external perimeter of the stream tube i in the roof cross section.

VMAX' = VMAX in case of surface burning tank, the roof being yet destroyed

$$VMAX' = (2.(MLIQ.VMAX^2 - MMIS.VMIS^2)/MLIQ)^{0,5} \qquad \text{(eq. 10)},$$

otherwise.

The angle of elevation α_i (degrees) of the stream lines leaving the tank varies from 10° when the stream line is in contact with the shell, to 45° when the stream line is in coincidence with the tank axis, according to the law :

$$\alpha_i = K_1.(V_i/PERI_i) + K_2 \quad 1 \leq i \leq n \qquad \text{(eq. 11)}.$$

with :

$$K_1 = 35.(PERI_1/V_1) / (1 - (Vn.PERI_1/V_1.PERI_n)) \qquad \text{(eq. 12)}$$

$$K_2 = 10 - (K_1.V_n/PERI_n) \qquad \text{(eq. 13)}$$

$PERI_i$, the external contour of the stream tube i cross section in the plan of the tank roof (m).

4) The calculation of the expelled hydrocarbon trajectories. The trajectories are identified with the movement of an unitary mass particle along the meridional stream line of every stream tube. Horizontal range of any trajectory can be written as :

$$R_i = V_i . \cos \alpha_i . (.2038\ V_i \sin \alpha_i + .2258 \sqrt{HEQU}) + .5\ (r_{i+1} + r_i) \quad \text{(eq. 14)}$$

with HEQU, the height of the tank above the ground level (m).

Those distances R_i allow to locate the source strength for the n elementary spillages generating the image of the complete overflowing phenomenon contour.

Model proposed determines geometry, contour and maximum spreading of the liquid pool developed inside and outside the diked basin, assuming the following approaches :

a) Quantification of hydrocarbon mass filling the diked basin and overflowing outside the dikes.

b) Definition of four elementary geometrical spillage modules (see fig. 2) :

- annular sector type spillage : normal use for outside diked area spill description ;
- ring type spillage : to describe the spillage induced by the annular stream tube tangent to the tank shell ;
- circular segment type spillage : applied to the first stream tube exceeding the diked area in a certain direction ; the chord of it is identified with the dike external slope ;
- circular area type spillage : it concerns the stream tube with maximum momentum and elevation angle, when radius inherent in the circular spillage, is neither secant nor tangent to the external perimeter of the preceding elementary spillage.

Accuracy of the spillage model is increasing with the number of elementary stream tubes. A minimum of four stream tubes is required. The procedure of quantification is to be iterated in every direction normal to each side of the dike.

Fire ball

Fire ball is a complex phenomenon and not easy to quantify.
At the start of a strong boilover a quickly ascending column of rich vapor burns at a high elevation when air mixes to support combustion. A mushroom shaped flame, accompanied by suddenly increased radiant heat, may be the spectacular part of the phenomenon.
Vapor mass available for burning into a fireball is calculated as follows :

1) Determination of the liquid mass remaining in the tank when boilover starts.

In the case of a tank fire, one may write :

$$MLBO = MLIQ - (.25.\pi.\ DENSL.\ v1.\ t.DEQU^2) \quad (kg) \quad (eq.\ 15)$$

With MLIQ, the mass of liquid hydrocarbon into the tank at the time the fire starts, (kg)

v1, the hydrocarbon burning rate (m/s)

2) Calculation of the fictive increase in temperature of the liquid mass MLBO when piston effect generates depressurization to atmospheric pressure : $\Delta T1$.

3) Calculation of temperature increase due to heat exchange by radiation and convection through the cylinder of flames of the burning reservoir : $\Delta T2$.

4) Quantification of the fraction of liquid mass MLBO flashing off :

$T = TWAV + \Delta T1 + \Delta T2$ (K) (eq. 16)

$EVAP1 = 1 - \exp [(CSPE (T)/CVAP (T)).(TBUL-T)]$ (eq. 17)

$EVAP2 = EVAP1. [(1/(.7 EVAP1 + .3))-1]$ (eq. 18)

$MVAP = (EVAP1 + EVAP 2).MLBO$ (kg) (eq. 19)

An order of magnitude for hydrocarbon mass participating to fireball phenomenon is about 1 percent of the mass contained into the tank before fire happens.

Fireball size and thermal radiant heat flux are quantified assuming a spherical model.

Fireball combustion is laminar and assumed to burn at the upper flammability limit. Intensity of the radiation at the source may be about 150 kW/m² in this case. Temperature of fireball is about 1440 K. This intensity of radiation is less than the value ordinarily considered for a bleve fireball (200 to 300 kW/m²). This is likely due to smoke environment of the fireball in the case of liquid hydrocarbons.

For estimating effect distances to receivers, one has to quantify the fireball duration, θ and the threshold values related to radiation effects on human being.

An other approach we propose, is to correlate value of heat flux received on target with prequantified consequence as a function of the time of exposure :

$\Phi_i = \exp (A_i . \ln \theta + B_i)$ (kW/m²) (eq. 20)

with lethality threshold, $A_1 = - .823$ $B_1 = 5.031$

pain is felt , $A_2 = - .776$ $B_2 = 4.2378$

Distances with damage to receivers can then be expressed as :

$R_i = [r_{max}^2 (150.\tau/\Phi_i)-h^2]^{.5}$ (eq. 21) with R_i, distance measured from the tank axis (m)

h, center height of the ball above ground (m)

r_{max}, maximum radius of fireball (m)

$$r_{max} = (.75.(MVAP/(UEL.DENSG)/\pi)^{.333} \qquad \text{(eq. 22)}$$

UEL, upper explosion limit of hydrocarbon (% vol)

DENSG, gravity of vapour hydrocarbon at fireball temperature (kg/m^3)

τ, attenuation factor.

Methods to prevent boilover or frothover

Boilover or frothover generation is nowadays uncompletely understood. Some ideas arise when studying the mechanisms.

A frothover can be detected by very high level measurement, increase of presure sensor and froth detector. Modern heated tanks are generally fitted with. The signals delivered by these sensors are usually actionning to close valves on the heating and feeding circuits of the tank. These devices reduce the energy available in the system and lessen the potential effects of the phenomenon. Reducing the increase of pressure in the tank may be obtained by weakening the link from roof to shell.

About boilover, few litterature is available, among which Hasegawa and Risinger. The methods mentioned are :

- draining of water in the bottom of the tank or eliminating it before the heat wave reaches it,
- cooling of tanks and/or extinguishment of the fire by base foam injection,
- use of agitation methods (mechanical or pneumatical).

These methods are to be tested. The devices and procedures they need may rise difficulties and make necessary a modelization of what may happen in the typical case studied.

CONCLUSION

A quantification of boilover and frothover has been proposed. These phenomena need further research, mainly related to fireball aspects. One of the main features of these phenomena is that they need a delay to occur.

Methods to prevent boilover and frothover are quoted. They have to be tested.

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FIG. 1

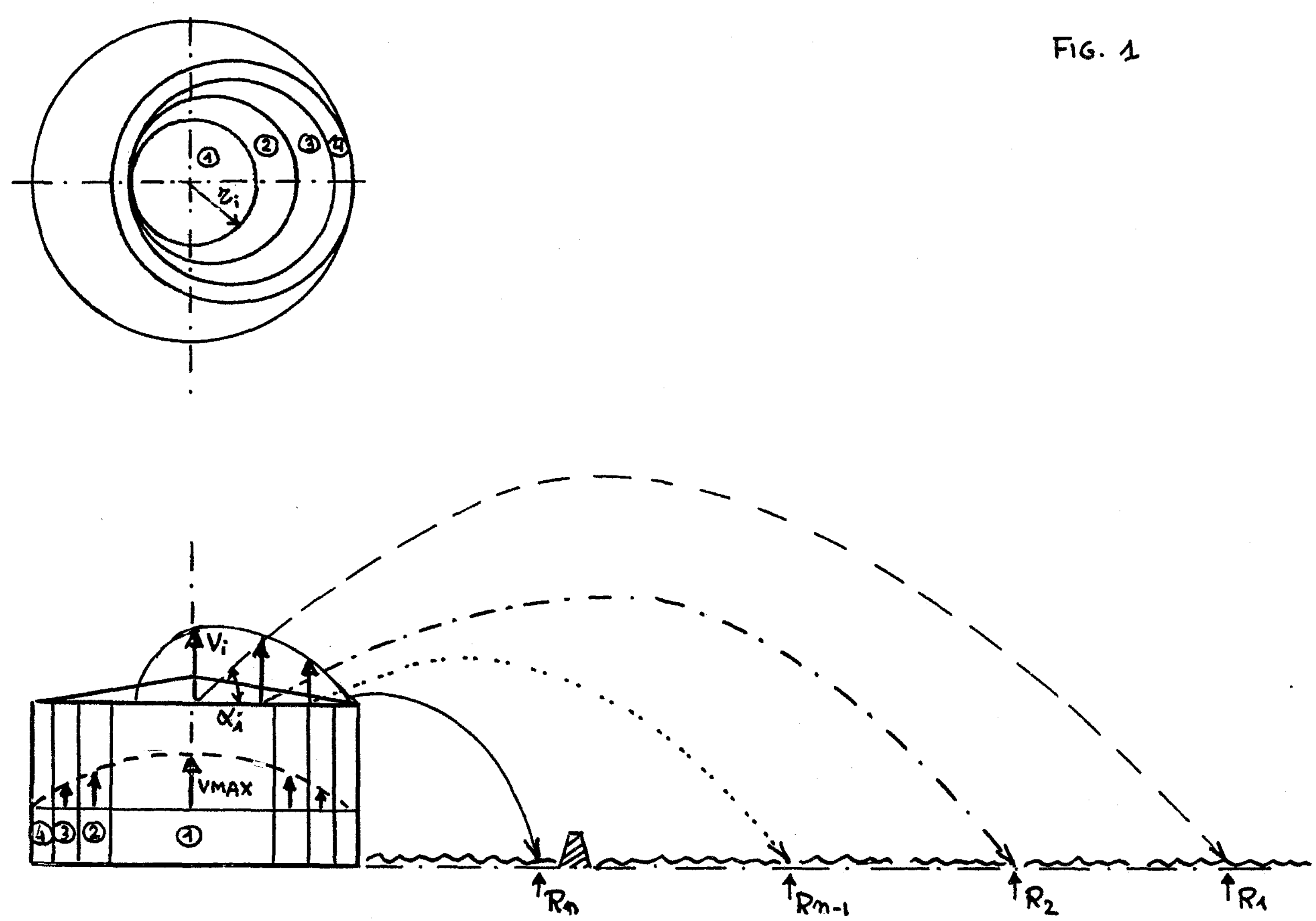
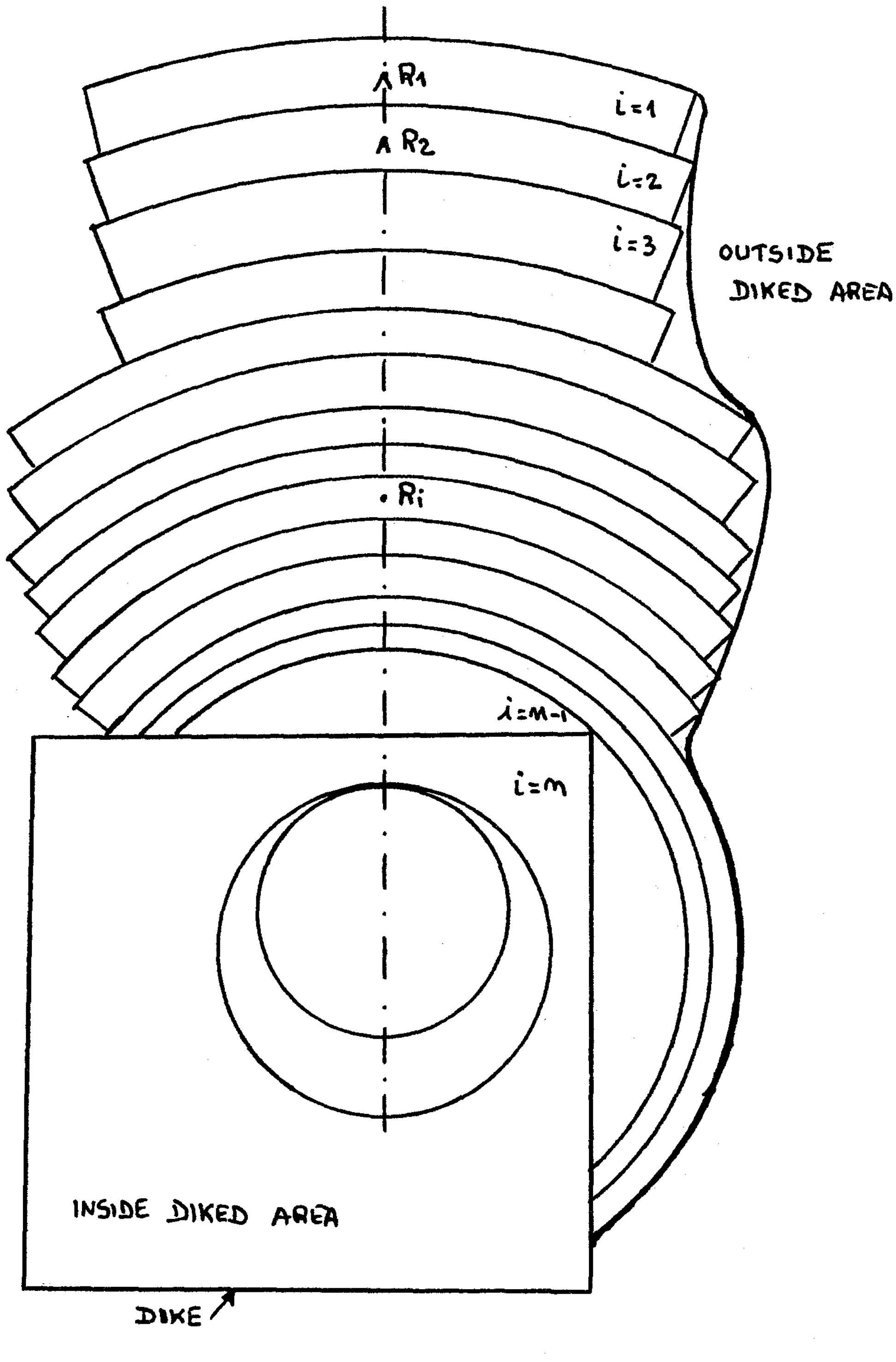


FIG. 2


R1
R2
i=1
i=2
i=3
OUTSIDE
DIKED AREA
Ri
i=m-1
i=m
INSIDE DIKED AREA
DIKE