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BOILOVER AND SLOPOVER PHENOMENA DURING A FIRE OF STORAGE TANKS CONTAINING CRUDE OIL

The paper presents the backgrounds of knowledge regarding fires of crude oil in tanks. Model of overheating, heat wave creation in liquid mechanism, boilover and slopover phenomena are presented. The paper is based on real experimental boilover data.

Słowa kluczowe: pożar ropy naftowej, warstwa przegrzana, wyrzut, transport ciepła **Key words:** crude oil fire, overheated layer, boilover, heat transport

Introduction

Boilover and slopover investigations are very important issues from the point of view of fire brigades. They have great cognitive meaning and practical aspects for fire extinguishing. The oil fire occurred in many petrochemical plants and refineries. In the period 1951–2003 480 tank fires with various fuels took place. In several cases boilover and slopover were observed (e.g. Czechowice-Dziedzice, Poland, Louisiana, USA). The outcomes of these accidents produce many man, environment and property losses [1]. The chemical and physical properties of crude oil play the main role in the fire hazard. The most important there are formation of heat wave and possible boilover and slopover. These are the characteristic phenomena of crude oil tanks fire and real threats for firemen, facilities and people.

Boilover and slopover phenomena

Slopover regards the high-viscosity liquids containing emulsified, insoluble, low boiling point substances. Usually it is water contained in the crude oil. Percentage of water in oil, in depending on its origin, oscillates from 0,3% to 4,5% [2]. During storage time and first stage of a tank fire, water is evenly distributed in the liquid.

During burning process top layer of oil reduces its viscosity due to heat transfer from flame to burning surface. Water drops deeper into liquid and stops at the depth where viscosity of liquid is comparatively high. Simultaneously water drops become heated and evaporated when adequate temperature is reached. Vapour formed creates emulsion with frothing liquid. The liquid enlarges its volume, lifts up and flows over the tank rim.

Crude oil and mazout are oil products with relativety high viscosity. Scientific literature states [2, 3, 4] that lower viscosity limit exists below which boilover is impossible. According to the literature this limit is 0,3%. Osuchow [4] observed, that if water content is over 20% the oil-water emulsion doesn't burn.

If the tank fires creates heat waves boilover phenomena occur quite often. Boilover requires water layer on bottom of the tank. If the hot layer of fuel contacts with water, the water overheating occurs followed by violent evaporation and finally ejection of burning oil products.









Fig. 1. Stages of boilover [5]

Boilover is a phenomenon during burning of certain oils in an open-top tank when, after a long period of quiescent burning, there is a sudden increase in fire intensity associated with expulsion of burning oil from the tank. Boilover occurs when the residues from surface burning become denser than the unburned oil and sink below the surface to form a hot layer, which progresses downward much faster than the regression of the liquid surface. When this hot layer, called a "heat wave", reaches water or water-in-oil emulsion in the bottom of the tank, the water is first superheated and then boils almost explosively, overflowing the tank. Oils subject to boilover consists of components having a wide range of boiling points, including both light ends and viscous residues. These characteristics are present in most crude oils and can be produced in synthetic mixtures [6].

Boilover occures when three condidions exist simultaneously [6]:

- open tank fire,
- water layer at the bottom of a tank,
- overheating heat waves in a fuel.

Slopover can occur when water is applied to the burning surface of the fuel and sink into the hot oil. The vaporisation of the water causes the ignited fuel to overflow [6].

Overheating model

Fig. 2 shows heat transport to liquid by thermal radiation from flame, conduction heat through wall and convection current in storage liquid. At the beginning increase of amount of vaporized liquid is very slow. The mixture with air is created over the tank. Hot combustion gases float up. The reason is reduction of local pressure and inflow of surrounding air into tank. It is mixing with vapour fuel below the uphill edge of the opened container. As a result of burning the level of liquid in the tank is systematically decreasing.

The heat transported to liquid is precipitating evaporation to its layer and causes a rise temperature of liquid staying in the tank. There are liquid fuels, in which overheated layer is formed and other without the generation of this layer during burning. As can be seen on Fig. 3a the overheated layer is very thin in the case of burning the first type of liquid. This layer retains the permanent thickness irrespective of the time of burning. All heat transported to liquid is used to evaporate the fuel.

Flamable liquids of second type create heated zone under surface (Fig. 3b). The transition from this heated zone (b) to the fuel unaffected by the fire (d) takes place in a relatively thin transitional zone (c). Thinkness of the heated zone steadily increases during the fire and may encompass, after considerable duration of the fire, all of the stored liquid.

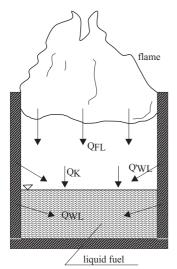


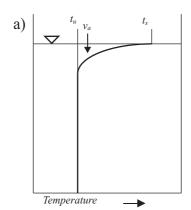
Fig. 2. Division of the heat backflow from the flame into the liquid [7]

 Q_{FL} – radiation from the flame to the liquid

 Q_{WL} – radiation from the tank wall to the liquid

 Q_K – heat transfer through convection

 Q'_{WL} – heat transfer from the tank wall to the liquid in the area immediately below the surface of the liquid



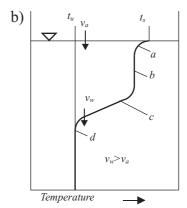


Fig. 3. Temperature distribution in liquid fuels without a) and with a heated zone formation b) [7]

a – temperature gradient on the surface of the liquid,

b – heated zone with constant temperature,

c – transitional area between the heated zone and the fuel unaffected by fire,

d – fuel unaffected by fire,

 t_s – boiling temperature,

 t_{y} – temperature of the fuel unaffected by the fire,

 v_a – burning rate,

 v_w – transitional velocity of the heated zone toward the fuel unaffected by the fire.

The transitional velocity depends on the type of fuel and has to be determined experimentally. The simple heat balance that occurs in liquid fuels without heated zone does not occur here [7, 8].

Burning of crude oil during a tank fire is a function of many variables: composition, density, viscosity, water and salt content, and admixtures of sulfur

compounds. All of variables and contaminations determine time of fire, height of flame, radiation from flame and type of the secondary phenomena created during the fire (eg. boilover).

During the crude oil fire, temperature of liquid surface equals boiling temperature. Under the surface of crude oil a change in the way of heating the deeper layers of the liquid occurs. As a result of the heat effects and oil distillation under the surface, two layers are formed: the upper, located just below the surface, and the bottom. During the fire, the temperature of the upper layer exceeds the boiling temperature of the crude oil. The thickness of this layer increases during the fire. However, in the bottom layer, the temperature distribution from the border of two layers rapidly decreases to the initial temperature. Hence, in the response activities the importance of fire safety is related to the effects of the formation of upper layer – superheated layer. Such is the nature of combustion caused by strong convection current forming into a crude, especially when it is stored in tanks of large diameter (>50 m). Convection heat flows are closely linked to heating the tank walls under fire conditions. The temperature of the steel wall with crude oil tanks during the fires is much higher than the temperature of the wall parts being in contact with oil.

This creates convection currents in liquid, which is a consequence of overheating the oil inside. The crude oil always includes a certain percentage of salt and water – the so-called brine. At temperatures above 100°C, brine (mainly water), changing into a volatile state, increases its volume 1700 times. As

a result, bubbles of steam floating up, covered with oil, create new turbulence, increasing the speed of overheating the oil inside. Overheating temperature and speed of overheating depend on the type of crude oil and water content. In Fig. 4 spreading out a layer of superheated during the fires in oil tanks is shown.

Flames and decomposition products
1300°-2000° F

Light fractions rising Heat wave 450°-500° F

Fuel oil unchanged In composition

80° F

Water & bottom settings

Fig. 4. Spreading a layer of super-heated (heat wave) during the tank fire containing heavy petroleum products [6]

The boilover and slopover

Table 1 shows the temperature and overheating speed of crude oil during fire in tanks with a diameter greater than 50 meters with a wind speed 1 m/s.

The moisture content Temperature overheating, The speed of oil overheating, in crude, % °C mm/min 190 5,83 3,8 0,7 210 4,91 240 4,7 0,45 0,27 260 4,58 290 0,1 3,12

Table 1. Temperature and speed overheating of crude oil while fires [9]

Table 2 shows the temperature and overheating speed of crude oil during the oil fires in tanks with a diameter of 50 meters (wind speed 10 m/s).

•	1	
The moisture content in crude, %	Temperature overheating, °C	The speed of oil overheating, mm/min
3,8	190	17,01
0,7	210	13,15
0,45	240	10,01
0,27	260	9,83
0,1	290	5,85

Table 2. Temperature and speed overheating of crude oil while fires [9]

The data contained in the tables indicate that crude oil has the ability to overheat in greater depth, the thickness of superheated layer increases as the duration of the fire – this layer is moving more and more towards the bottom of the tank at the same time expanding. This property of oil during fires and firefighting activities can cause a serious hazard to people and property due to the possibility of boilover and slopover phenomena.

The decrease of the viscosity of crude oil in the process of combustion leads to the fact that the vapor surrounded by oil takes it and throws from the tank. After the first throw, heated to very high temperatures, the oil layer in contact with water again, causes another, more powerful explosion (boilover). Typically, boilover takes several minutes and is characterized by many splashes – boilovers

of oil. Extent of the boilover depends on the mass of oil and size of the surface layer of water, which contacts the overheated oil. It can be assumed that during the boilover 25% to 65% of the original volume of oil contained in the tank is thrown away. The height of boilover can be several meters and the diameter of the affected area by the burning oil can go up to 300 meters. For example, during a fire in the Czechowice-Dziedzice refinery the oil was thrown at ranges from 90 m to 250 m. Ejected from the tank, the oil did not complete combustion with the exception of light fractions, which evaporated and burned, but falling down on the roads, rooftops, equipment and facilities, burned continuously [10].

In the tanks of large diameter, greater than 50 meters, boilover ocurrs faster than in the small tanks. The thicknes of water layer does not have a decisive impact on the extent of the boilover. The most important is the size of surface of the contact between the water layers and the overheated layer. As reported by Bradley [11], a sudden transformation of a layer of 15 kg water on a small area produces 25 500 liters of steam in the air and makes a shock wave, which energy is equal to the shock wave caused by detonation of 5 kg of TNT. Of course, such a comparison is a major simplification, resulting from the elide of a medium in which an explosion is created and the mass of oil thrown out but formed during the boilover. Nevertheles, the pressure generated has a considerable destructive power.

REFERENCES

- [1] Peterson H.,. Lonnermark A.: Tank Fires. Review of fire incidents 1951–2003, Brandforsk Project 513-021, SP Swedish National Testing and Research Institute, Boras, 2004.
- [2] Arthur E.: Cote (ed.), Fire Protection Handbook, NFPA, 1991.
- [3] Blinov V.I., Khudyakov G.N.: Diffusion burning of liquids, T-1490ASTIA AD, 1961, p. 754–762.
- [4] Molchanov V.P., Suchkov W.P.: Varianty rozvitiya pozhara w hranilishchah nefteproduktov, Pozharnoe Delo, Moskva, 1994 (in Russian).
- [5] Jarosz W.: Environmental hazards caused by the slopover and boilover phenomena during fires of tanks containing hydrocarbon liquids, PhD thesis, Warsaw University of Technology, 2006 (in Polish).
- [6] NFPA 30 "Flammable and Combustible Liquids Code Handbook", 2000
- [7] Seeger P.G.: On the combustion and heat transfer in fires of liquid in tanks, Heat Transfer in Fires, P. Blackshear, New York, 1974.
- [8] Pofit-Szczepańska M.: Physical chemistry of combustion and explosion, SGSP, Warsaw, 1997 (in Polish).

[9] Pofit-Szczepańska M., Jarosz W.: Analysis of creation of boilover and slopover during a fire of crude oil tanks, part I, Study of a time to boilover, *Archiwum Spalania* 2002, No. 2, p. 5–21 (in Polish).

- [10] Czechowice-Dziedzice refinery fire, on-duty issue, KGSP, Warszawa, 1971 (in Polish).
- [11] Bradley J.W.: Shock waves in chemistry and physics, J. Widley and Son Inc., New York, 1962.

SUMMARY

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BOILOVER AND SLOPOVER PHENOMENA DURING A FIRE OF STORAGE TANKS CONTAINING CRUDE OIL

The most interesting research regarding burning fuel tankers has been the work of Blinov and Khudiakov [3], who first described the formation of overheated layer in the liquid during the fire and the way of its moving into the fuel.

This work of Blinov and Khudiakov has begun the research process on overheated layer and its impact on the speed of slopover and boilover. Currently, the most interesting works are carried in research centers of Japan, USA and Germany and they concentrate on:

- a fuel burning rate,
- a way of heat transfer from the flame to the surface of a burned liquid,
- a flame height,
- an overheating model,
- slopover and boilover models,
- distribution of temperature in liquid during tank fire.