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#### Abstract

Simulation program was developed to predict hot zone temperature and its extension rate for a crude oil fire in a large tank. The calculated results are summarized in this report. Authors believe that these calculated results are reliable enough for an actual size tank fire, since the calculated results can well explain why around $1[\mathrm{~m} / \mathrm{h}]$ is the maximum hot zone extension rate in an actual tank fire as reported by LASTFIRE. Possibility of boilover and required time to cool down the hot oil after extinguishment of a crude oil tank fire were also studied by using another simulation program developed separately. In case of a large tank fire, it was found that possibility of boilover occurrence after extinguishment seems too little and so long days are required to cool the hot oil.


## 1 Introduction

1.1 In related to boilover occurrence in crude oil fire, so many literatures had been issued and the results are summarized as follows.
(1) Hot zone temperature is to be increased with duration of burning
(2) Extension rate of the hot zone is approximately $1 \mathrm{~m} / \mathrm{h}$ as a maximum
(3) Boilover will occur when temperature of the water layer at the tank bottom is above 120 [degC].
(4) Extension rate of the hot zone become faster, when its temperature is lower.
(5) Hasegawa concluded and reported[1];
(a) Within the hot zone, density and composition of the oil are homogeneous as well as its temperature.
(b) Extension rate of the hot zone depends on an amount of distillation residue of the crude oil at the burning temperature.
1.2 It is common sense that mechanism of the hot zone formation is a process of distillation of the crude oil. This mechanism cannot be simulated only by a calculation of heat transfer by thermal conduction.
Bernd Broeckmann and Hans-Georg Schecker [2] presented the valuable idea on how to estimate the hot zone temperature and its extension rate. That is, the hot zone temperature was assumed to be the vaporization temperature and the vaporization process in the hot zone was thus calculated as a flash distillation with one theoretical plate.
Based on this idea, a simulation program was made to predict the temperature
and extension rate of the hot zone.
Calculated results shows good matching with the observations described in the above section-1.1.
1.3 In case that a crude oil tank fire is extinguished before boilover occurrence, there will be 3 liquid layers in the tank, the first one is hot zone layer, the second is lower oil layer (previous hot zone or initial oil), in which oil temperature is homogeneous, and the third one is water layer.
After extinguishment, no heat input is available to the tank, but heat will be transferred from the hot zone layer to the lower oil layer and to the water layer by thermal conduction. So there may be a possibility of boilover, even when the fire had been extinguished. Based on the assumption that the heat transfer is only by thermal conduction, a simulation program was developed to simulate the change in temperature profile of oil and water in the tank.
The program can calculate effect of cooling of the tank shell plate by wind or water streams.

The calculated results show that possibility of boilover occurrence is extremely low and so long time is required to cool the oil in case of a large tank fire.

2 Hot zone calculation model
2.1 Basic scenario

Based on the calculation model by Bernd Broeckmann and Hans-Georg
Schecker[2], scenario of the hot zone formation is considered as;
(1) When a crude oil tank is on fire, a lump of oil is rising up from the lower layer and distillated with heat from the fire to separate volatile components and residue.
(2) The volatile component is burned on the surface of the oil.
(3) The residue stays in remaining oil and forms the hot zone.
(4) The ratio between the volatile components and the residue are calculated by both heat balance and the distillation curve of the crude oil.


### 2.2 Calculation model

The simulation program (EXCEL VBA) had been developed based on the theoretical model described in this section.


Fig. - 1 Theoretical model of the hot zone formation in case of a crude oil tank fire

A crude oil tank, with diameter $\mathrm{D}[\mathrm{m}]$, is on fire, and the oil surface receives the radiative heat flux $\mathrm{Q}_{\mathrm{R}}\left[\mathrm{kcal} / \mathrm{m}^{2} / \mathrm{h}\right]$.

During a time period $\Delta \mathrm{t}\left[\mathrm{s}\right.$ ], a lump of oil of $\mathrm{T}_{0}$ [degC] is rising up from the lower oil layer at a rate of $\left(n_{V}+n_{L}\right)\left[\mathrm{kg} / \mathrm{h} / \mathrm{m}^{2}\right]$, and is distillated at $\mathrm{T}_{\mathrm{hz}}$ [degC] by the heat flux $Q_{R}$ to separate into the volatile components $n_{V}\left[\mathrm{~kg} / \mathrm{h} / \mathrm{m}^{2}\right]$ and the residue $n_{L}\left[\mathrm{~kg} / \mathrm{h} / \mathrm{m}^{2}\right]$.
$n_{L}$ is growth rate of the hot zone and $n_{V}$ is equal to the burning rate.
(1) Heat balance

Heat balance between the radiative heat flux and heat input to the hot one is described as follows.
$\mathrm{Q}_{\mathrm{R}}=n_{V}\left(\Delta h_{V}+h\left(T_{b, V}\right)-h\left(T_{0}\right)\right)+n_{L}\left(h\left(T_{h z}\right)-h\left(T_{0}\right)\right)$
$\mathrm{Q}_{\mathrm{R}}$; heat radiation from the flame of fire $\left[\mathrm{kcal} / \mathrm{h} / \mathrm{m}^{2}\right]$
$n_{V}, ~ n_{L}$; mass loss rate of the volatile components or mass gain rate of the
residue per unit area while burning. $\left[\mathrm{kg} / \mathrm{h} / \mathrm{m}^{2}\right]$
$\Delta h_{V}$;heat of evaporation the volatile components [kcal/kg]
$h(\mathrm{~T})$; enthalpy of the oil at temperature $\mathrm{T}[\mathrm{kcal} / \mathrm{kg}]$
$T_{b, V}$; the boiling temperature of the oil or cut temperature of the distillation
[ $\operatorname{degC}$ ]
$T_{0}$; temperature of the lower oil layer [ degC]
$T_{h z}$; hot zone temperature [ degC]

Cp is average specific heat of the oil [ $\mathrm{kcal} / \mathrm{kg} / \mathrm{degC}]$, then heat required to increase temperature of the oil of $n_{V}$ from $T_{0}$ to $T_{b, V}$ is;
$n_{V}\left(h\left(T_{b, V}\right)-h\left(T_{0}\right)\right)=n_{V}\left(\operatorname{Cp}\left(T_{b, V}-T_{0}\right)\right)$
For residue $n_{L}$,
$n_{L}\left(h\left(T_{h z}\right)-h\left(T_{0}\right)\right)=n_{L} * \operatorname{Cp}\left(T_{h z}-T_{0}\right)$

The hot zone temperature is equal to the boiling temperature of the oil, then;
$T_{b, V}=T_{h z}$
By substituting Eqs. (2), (3), (4), for Eq. (1), it can be simplified as;
$\mathrm{Q}_{\mathrm{R}}=n_{V} * \Delta h_{V}+\mathrm{C}_{\mathrm{p}} *\left(n_{V}+n_{L}\right) *\left(T_{h z}-T_{0}\right)$
This can be expressed as
$T_{h z}=\frac{\mathrm{Q}_{\mathrm{R}}-n_{V^{2}} * \Delta h_{V}}{\mathrm{C}_{\mathrm{p}} *\left(n_{V}+n_{L}\right)}+T_{0}$
or
$\mathrm{n}_{L}=\frac{\mathrm{Q}_{\mathrm{R}}-n_{V^{*}} \Delta h_{V}}{\mathrm{C}_{\mathrm{p}}^{*}\left(T_{h_{z}}-T_{0}\right)}-n_{V}$

The radiative heat flux $Q_{R}$ can be estimated by assuming flame temperature as $1100[\mathrm{~K}]=827[\operatorname{deg} \mathrm{C}]$.
$\mathrm{Q}_{\mathrm{R}}=\sigma \mathrm{T}_{\mathrm{f}}^{4}(1-0.08)\left[1-\left(1-\epsilon_{\mathrm{soot}}\right)\left(1-\epsilon_{\mathrm{w}}\right)\left(1-\epsilon_{\mathrm{CO} 2}\right)\right] * 0.85984523$
$\mathrm{T}_{\mathrm{F}}$; Flame temperature $1100[\mathrm{~K}]$
$\sigma$; Stefan-Boltzmann constant $5.67^{*} 10^{-8}\left[\mathrm{w} / \mathrm{m}^{2} / \mathrm{K}^{4}\right]$
$\epsilon_{\text {soot }}$; Spectrally average emissivity of soot
0.08 ; surface reflectivity of the oil
$\epsilon_{\mathrm{w}}$; Emissivity of $\mathrm{H}_{2} \mathrm{O}$
$\epsilon_{\mathrm{CO} 2}$; Emissivity of $\mathrm{CO}_{2}$
(2) Mass burning rate

The mass burning rate $\left[\mathrm{kg} / \mathrm{m}^{2} / \mathrm{h}\right]$ is equal to the fraction of the distillation $\left(n_{V}\right)$, which is processed within the hot zone.
For the calculation, experimental data are used for mass burning rate. In this study, $162\left[\mathrm{~kg} / \mathrm{m}^{2} / \mathrm{h}\right]$ is applied for all types of the crude oil.
(3) Cumulative mass fraction of the distillation (evaporated fraction) $\varnothing$
$\emptyset_{C}$ can be defined as;
$\emptyset_{C}=\frac{n_{V}}{n_{V}+n_{\mathrm{L}}}$
Hot zone temperature $T_{h z}$ is assumed at first, and then $n_{L}$ and $\emptyset_{C}$ is calculated from the Eqs. (7) and (9). And with the distillation curve of the crude oil, $\emptyset_{D}$ at cut temperature of $T_{h z}$ is obtained.
If $\emptyset_{D}$ is nearly equal to $\emptyset_{C}$, then $T_{h z}$ and $\mathrm{n}_{L}$ should be suitable values and the calculation is over, but if they are different values, $T_{h z}$ must be assumed again to continue the calculation.
(4) Oil surface regression

In a time period $\Delta \mathrm{t}$ [s], amount of burnt oil is $n_{V} * \Delta \mathrm{t}\left[\mathrm{kg} / \mathrm{m}^{2}\right]$, so regression of the surface height $\Delta \mathrm{H}[\mathrm{m}]$ is
$\Delta \mathrm{H}=n_{V} * \Delta \mathrm{t} / \rho_{\text {oil }}$
$\rho_{\text {oil }}$; density of oil $\left[\mathrm{kg} / \mathrm{m}^{3}\right]$
(5) Hot zone extension

In $\Delta \mathrm{t}$ [s], $n_{\mathrm{L}} * \Delta \mathrm{t}$ will be added to the hot zone and then $\Delta h_{z}$ [ m$]$ will be increased in the depth of the hot zone.
$\Delta h_{z}=n_{\mathrm{L}} * \Delta \mathrm{t} / \rho_{\text {oil }}$
(6) Distillation cycle

The distillation cycle is defined as number of unit distillation.
Hot zone temperature and its extension rate can be calculated as described above. If hot zone temperature is less than 120 [degC], boilover may not occur even if bottom of the hot zone reaches to the water layer. In other case, the next distillation will start after the first hot zone formation with new $T_{0}$,
which is the first $T_{h z}$ at the previous cycle．Such a distillation cycle will be repeated till $T_{h z}$ becomes 120 ［degC］or higher．
（7）Distillation curve
Most of distillation data of crude oils show there are volatile components with the boiling temperature between minus 89［degC］（ethane）and minus 5 ［degC］ （butane），and components from $36.1[\mathrm{degC}]$（pentane）in a stepwise fashion． There is lack of the component data between minus $0.5[\mathrm{degC}]$ and $36.1[\mathrm{degC}]$ ． Due to long term storage，most of ethane and butane may have been released from a crude oil in a tank，while components between minus $0.5[\mathrm{degC}]$ and $36.1[\mathrm{degC}]$ may be remained in the crude oil．These considerations have been reflected to the distillation curve used in this study．

2．3 Calculation by the simulation program
（1）Calculation conditions
（a）Crude oil
The crude oils used for the hot zone calculation are as follows：

| Crude oil No．－1 Oil Name | Big Hill，Sour |  |  |
| :---: | :---: | :---: | :---: |
| Density | $0.8723 \mathrm{~g} / \mathrm{cm} 3 @ 15^{\circ} \mathrm{C}$ |  |  |
| API | 30.7 （ $60^{\circ} \mathrm{F}$ ） |  |  |
| Sulfur | 1.46 \％ |  |  |
| Kinematic Viscosity | 8.368 cSt ＠ $30^{\circ} \mathrm{C}$ |  |  |
| Fraction and Cut Temperature |  |  |  |
| Temperature |  | wt |  |
| From（ $\mathrm{Tf}^{\circ} \mathrm{C}$ ） | $\mathrm{To}\left(\mathrm{Te}{ }^{\circ} \mathrm{C}\right)$ | （\％） | cum（\％） |
| －89 | －0．5 | 1.4 | 1.4 |
| 36.1 | 79.4 | 4.1 | 5.5 |
| 79.4 | 121.1 | 5.4 | 10.9 |
| 121.1 | 190.6 | 10.8 | 21.7 |
| 190.6 | 276.7 | 14.6 | 36.2 |
| 276.7 | 343.3 | 12.2 | 48.4 |
| 343.3 | 454.4 | 16.4 | 64.8 |
| 454.4 | 565.6 | 16.1 | 80.8 |
|  |  |  |  |
|  | Total | 80.8 | － |


| Crude oil No．－3 |  |
| :--- | :---: |
| Oil Name | アッパーザクムCrude Oil |
| Density | $0.8557 \mathrm{~g} / \mathrm{cm} 3 @ 15^{\circ} \mathrm{C}$ |
| API | $33.8\left(60^{\circ}\right.$ F） |
| Sulfur | $1.58 \%$ |
| Kinematic Viscosity | $7.08 \mathrm{cSt} @ 30^{\circ} \mathrm{C}$ |

Fraction and Cut Temperature

| Temperature |  | wt |  |
| ---: | ---: | ---: | ---: |
| From $\left(\mathrm{Tf}^{\circ} \mathrm{C}\right)$ | $\mathrm{To}\left(\mathrm{Te}^{\circ} \mathrm{C}\right)$ | $(\%)$ | cum（\％） |
| -89 | -0.5 | 2.4 | 2.4 |
| 36.1 | 70 | 5.4 | 7.8 |
| 70 | 100 | 2.3 | 10.1 |
| 100 | 150 | 6.8 | 16.9 |
| 150 | 190 | 6.6 | 23.5 |
| 190 | 235 | 7.2 | 30.7 |
| 235 | 280 | 7.7 | 38.4 |
| 280 | 343.3 | 10.9 | 49.3 |
| 343.3 | 565 | 33.0 | 82.3 |
| 565 |  | 17.7 | 100.0 |


| Crude oil No．－2 |  |
| :--- | :---: |
| Oil Name | Unknown（Crude Oil） |
| Density | $0.8558 \mathrm{~g} / \mathrm{cm} 3 @ 15^{\circ} \mathrm{C}$ |
| API | $33.8\left(60^{\circ} \mathrm{F}\right)$ |
| Sulfur | $1.8 \%$ |
| Kinematic Viscosity | $6.721 \mathrm{cSt} @ 30^{\circ} \mathrm{C}$ |

Fraction and Cut Temperature
Fraction and Cut Temperature

| Temperature |  | wt |  |
| ---: | ---: | ---: | ---: |
| From $\left(\mathrm{Tf}^{\circ} \mathrm{C}\right)$ | $\mathrm{To}\left(\mathrm{Te}{ }^{\circ} \mathrm{C}\right)$ | $(\%)$ | $\mathrm{cum}(\%)$ |
| -89 | -0.5 | 2.3 | 2.3 |
| 36.1 | 70 | 6.9 | 9.2 |
| 70 | 100 | 3.4 | 12.6 |
| 100 | 150 | 8.6 | 21.2 |
| 150 | 190 | 7.2 | 28.4 |
| 190 | 235 | 7.8 | 36.2 |
| 235 | 280 | 7.7 | 43.9 |
| 280 | 343.3 | 11.0 | 54.9 |
| 343.3 | 565 | 28.2 | 83.1 |
| 565 |  | 16.9 | 100.0 |


| Crude oil No．-4 |  |
| :--- | :---: |
| Oil Name | Unknown（Crude Oil） |
| Density | $0.884 \mathrm{~g} / \mathrm{cm} 3 @ 15^{\circ} \mathrm{C}$ |
| API | $28.5\left(60^{\circ} \mathrm{F}\right)$ |
| Sulfur | $2.48 \%$ |
| Kinematic Viscosity | $18.21 \mathrm{cSt} @ 30^{\circ} \mathrm{C}$ |

Fraction and Cut Temperature
Fraction and Cut Temperature

| Temperature |  | wt |  |
| ---: | ---: | ---: | ---: |
| From $\left(\mathrm{Tf}^{\circ} \mathrm{C}\right)$ | To $\left(\mathrm{Te}^{\circ} \mathrm{C}\right)$ | $(\%)$ | cum $(\%)$ |
| -89 | -0.5 | 0.7 | 0.7 |
| 36.1 | 70 | 2.7 | 3.4 |
| 70 | 100 | 3.1 | 6.5 |
| 100 | 150 | 6.7 | 13.2 |
| 150 | 190 | 6.6 | 19.8 |
| 190 | 235 | 6.6 | 26.4 |
| 235 | 280 | 6.6 | 33.0 |
| 280 | 343.3 | 9.4 | 42.4 |
| 343.3 | 565 | 31.1 | 73.5 |
| 565 |  | 26.5 | 100.0 |


| Crude oil No. -5 |  |
| :--- | :---: |
| Oil Name | Unknown (Crude Oil) |
| Density | $0.8442 \mathrm{~g} / \mathrm{cm} 3 @ 15^{\circ} \mathrm{C}$ |
| API | $35.9\left(60^{\circ} \mathrm{F}\right)$ |
| Sulfur | $1.4 \%$ |
| Kinematic Viscosity | $4.916 \mathrm{cSt} @ 30^{\circ} \mathrm{C}$ |

Fraction and Cut Temperature

| Temperature |  | wt |  |
| ---: | ---: | ---: | ---: |
| From $\left(\mathrm{Tf}^{\circ} \mathrm{C}\right)$ | $\mathrm{To}\left(\mathrm{Te}{ }^{\circ} \mathrm{C}\right)$ | $(\%)$ | cum $(\%)$ |
| -89 | -0.5 | 0.6 | 0.6 |
| 36.1 | 70 | 4.3 | 4.9 |
| 70 | 100 | 4.9 | 9.8 |
| 100 | 150 | 9.4 | 19.2 |
| 150 | 190 | 7.6 | 26.8 |
| 190 | 235 | 8.4 | 35.2 |
| 235 | 280 | 8.5 | 43.7 |
| 280 | 343.3 | 11.7 | 55.4 |
| 343.3 | 565 | 29.0 | 84.4 |
| 565 |  | 15.6 | 100.0 |


| Crude oil No. -7 |  |
| :--- | :---: |
| Oil Name | Bayou Choctaw Sour |
| Density | $0.8631 \mathrm{~g} / \mathrm{cm} 3 @ 15^{\circ} \mathrm{C}$ |
| API | $32.4\left(60^{\circ} \mathrm{F}\right)$ |
| Sulfur | $1.46 \%$ |
| Kinematic Viscosity | $6.356 \mathrm{cSt} @ 30^{\circ} \mathrm{C}$ |

Fraction and Cut Temperature

| Temperature |  | wt |  |
| ---: | ---: | ---: | ---: |
| From $\left(\mathrm{Tf}^{\circ} \mathrm{C}\right)$ | $\mathrm{To}\left(\mathrm{Te}{ }^{\circ} \mathrm{C}\right)$ | $(\%)$ | cum $(\%)$ |
| -89 | -0.5 | 1.6 | 1.6 |
| 36.1 | 79.4 | 4.2 | 5.8 |
| 79.4 | 121.1 | 6.1 | 11.9 |
| 121.1 | 190.6 | 11.9 | 23.8 |
| 190.6 | 276.7 | 15.5 | 39.3 |
| 276.7 | 343.3 | 11.9 | 51.2 |
| 343.3 | 454.4 | 15.6 | 66.8 |
| 454.4 | 565.6 | 15.2 | 82.0 |
|  | Total | 82.0 | - |


Fraction and Cut Temperature

| Temperature |  | wt |  |
| ---: | ---: | ---: | ---: |
| From $\left(\mathrm{Tf}^{\circ} \mathrm{C}\right)$ | $\mathrm{To}\left(\mathrm{Te}{ }^{\circ} \mathrm{C}\right)$ | $(\%)$ | cum $(\%)$ |
| -89 | -0.5 | 2.6 | 2.6 |
| 36.1 | 79.4 | 5.2 | 7.8 |
| 79.4 | 121.1 | 7.5 | 15.3 |
| 121.1 | 190.6 | 11.9 | 27.2 |
| 190.6 | 276.7 | 16.9 | 44.1 |
| 276.7 | 343.3 | 11.4 | 55.5 |
| 343.3 | 454.4 | 16.7 | 72.2 |
| 454.4 | 565.6 | 14.5 | 86.7 |
|  | Total | 86.7 | - |


| Crude oil No. -8 |  |
| :--- | :---: |
| Oil Name | Bryan Mound, Sour |
| Density | $0.8584 \mathrm{~g} / \mathrm{cm} 3 @ 15^{\circ} \mathrm{C}$ |
| API | $33.3\left(60^{\circ} \mathrm{F}\right)$ |
| Sulfur | $1.43 \%$ |
| Kinematic Viscosity | $5.846 \mathrm{cSt} @ 30^{\circ} \mathrm{C}$ |

Fraction and Cut Temperature

| Temperature |  | wt |  |
| ---: | ---: | ---: | ---: |
| From $\left(\mathrm{Tf}{ }^{\circ} \mathrm{C}\right)$ | $\mathrm{To}\left(\mathrm{Te}{ }^{\circ} \mathrm{C}\right)$ | $(\%)$ | cum $(\%)$ |
| -89 | -0.5 | 1.7 | 1.7 |
| 36.1 | 79.4 | 4.5 | 6.2 |
| 79.4 | 121.1 | 6.5 | 12.7 |
| 121.1 | 190.6 | 12.6 | 25.3 |
| 190.6 | 276.7 | 15.7 | 40.9 |
| 276.7 | 343.3 | 11.5 | 52.4 |
| 343.3 | 454.4 | 16.0 | 68.4 |
| 454.4 | 565.6 | 14.2 | 82.6 |
|  | Total | 82.6 | - |

(b) Tank on fire
-Diameter ; 80 [m]
-Height ; 22 [m]
-Height of the initial oil level from the bottom ; 20 [m]
-Water layer level from the bottom ; 1 [m]
(c) Temperature conditions
-Initial oil temperature ; 30 [degC]
-Water temperature ; 30 [degC]
-Ambient temperature ; 35 [degC]
-Minimum hot zone temperature required for boilover ; 120 [degC]
(d) Burning rate of $162\left[\mathrm{~kg} / \mathrm{m}^{2} / \mathrm{h}\right]$ is applied for every crude oil.
2.4 Calculated results
(1) Overall results

The results are shown in the graph as Fig. 2 for crude oil No. 2 and 3, and summarized in the Table - 1 for all crude oils.
Other than the distillation data, the same calculation conditions were applied for every crude oil fire. So variations in the hot zone temperature with time, extension rate, lapse time from initiation of fire to occurrence of boilover are
just depending on the distillation data. No linear correlation was found between those variations and physical properties, such as density, viscosity etc. It may come from the fact that chemical compositions are different for each crude oil, so there may not be linear correlations between density, viscosity etc. and its distillation data.
Crude oil No.-8 shows the lowest hot zone temperature, 283 [degC] and the highest hot zone extension rate, $0.2[\mathrm{~m} / \mathrm{h}]$. Crude oil No -5 shows the highest hot zone temperature, 399.1 [degC], and the lowest hot zone extension rate, 0.08 [ $\mathrm{m} / \mathrm{h}]$, which seems an extremely low speed.

The simulation model used in this study may not match all experimental results on the hot zone formation due to the assumptions, such as;

- Density of oil is constant against the change in temperature
- Burning rate is constant through whole period of fire

However, it should be noted that most of boilover experiments were performed with small tanks and extremely thin oil layers, which is quite different from an actual tank fire. It should also be noted that it is not practical to obtain density and burning rate data, having been assumed as described above. Authors believe that these calculated results are reliable enough for an actual size tank fire, since, as explained below, the calculated results can well explain why around $1[\mathrm{~m} / \mathrm{h}]$ is the maximum hot zone extension rate in an actual tank fire as reported by LASTFIRE

Table -1. Calculated results of the tank fires of sample crude oils

| Crude Oil | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Initial oil surface height [m] | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Hot zone Temp. [degC] | 373.4 | 300.4 | 314.4 | 359.9 | 399.1 | 290.3 | 306.7 | 283.0 |
| Last oil surface height [m] | 7.4 | 10.7 | 9.5 | 7.8 | 6.4 | 10.4 | 9.8 | 10.7 |
| Lapse time at boilover [h] | 68.1 | 49.4 | 55.3 | 66.3 | 70.8 | 49.9 | 54.3 | 49.4 |
| Hot zone extension rate [m/h] | 0.09 | 0.20 | 0.15 | 0.1 | 0.08 | 0.19 | 0.16 | 0.20 |
| Distillation cycle number | 1 | 3 | 1 | 1 | 1 | 1 | 1 | 1 |

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Hot zones are yielded repeatedly,
and hot zone temp. became
higher than $120^{\circ}$ Cat the $3^{\text {rd }}$ cycle.


Fig. -2 The hot zone calculated results for the crude oil No. -2 and 3
(2) Extension rate of the hot zone

The calculated temperature and extension rate of the hot zones are shown in Table -2.

Table -2. Calculated temperature and extension rate of the hot zone

| Crude Oil 1 | Duration of fire <br> [h] | Hot zone temp. <br> [deg.C] | Hot zone extension rate <br> $[\mathrm{m} / \mathrm{h}]]$ |
| :---: | :---: | :---: | :---: |
| Cycle1 | 68.1 | 373.4 | 0.09 |


| Cycle2 | None | - | - |
| :--- | :--- | :--- | :--- |


| Crude Oil 2 | Duration of fire <br> [h] | Hot zone temp. <br> [deg.C] | Hot zone extension rate <br> [m/h]] |
| :---: | :---: | :---: | :---: |
| Cycle1 | 2.1 | 40.7 | 8.97 |
| Cycle 2 | 3.64 | 66.2 | 3.64 |
| Cycle3 | 49.4 | 300.4 | 0.23 |


| Crude Oil 3 | Duration of fire <br> [h] | Hot zone temp. <br> [deg.C] | Hot zone extension rate <br> $[\mathrm{m} / \mathrm{h}]]$ |
| :---: | :---: | :---: | :---: |
| Cycle 1 | 55.3 | 314.4 | 0.15 |
| Cycle 2 | None | - | - |


| Crude Oil 4 | Duration of fire <br> $[\mathrm{h}]$ | Hot zone temp. <br> [deg.C] | Hot zone extension rate <br> $[\mathrm{m} / \mathrm{h}]]$ |
| :---: | :---: | :---: | :---: |
| Cycle 1 | 66.3 | 359.9 | 0.10 |
| Cycle 2 | None | - | - |


| Crude Oil 5 | Duration of fire <br> [h] | Hot zone temp. <br> [deg.C] | Hot zone extension rate <br> $[\mathrm{m} / \mathrm{h}]]$ |
| :---: | :---: | :---: | :---: |
| Cycle 1 | 70.8 | 399.1 | 0.08 |
| Cycle 2 | None | - | - |


| Crude Oil 6 | Duration of fire <br> [h] | Hot zone temp. <br> [deg.C] | Hot zone extension rate <br> $[\mathrm{m} / \mathrm{h}]]$ |
| :---: | :---: | :---: | :---: |
| Cycle1 | 49.9 | 290.3 | 0.19 |
| Cycle 2 | None | - | - |


| Crude Oil 7 | Duration of fire <br> $[\mathrm{h}]$ | Hot zone temp. <br> $[$ deg. C$]$ | Hot zone extension rate <br> $[\mathrm{m} / \mathrm{h}]]$ |
| :---: | :---: | :---: | :---: |


| Cycle1 | 54.3 | 306.7 | 0.16 |
| :---: | :---: | :---: | :---: |
| Cycle2 | None | - | - |


| Crude Oil 8 | Duration of fire <br> [h] | Hot zone temp. <br> [deg.C] | Hot zone extension rate <br> $[\mathrm{m} / \mathrm{h}]]$ |
| :---: | :---: | :---: | :---: |
| Cycle1 | 49.4 | 283.0 | 0.20 |
| Cycle2 | None | - | - |

Figure -3 is a graph of the temperature and the extension rate of Table -2 . Figure -3 well explains the observation in an experiment [extension rate of the hot zone become faster, when its temperature is lower].

The approximation formula for relation between the hot zone temperature $\mathrm{T}_{h z}\left[\mathrm{degC]}\right.$ and its extension rate $\mathrm{V}_{h z}[\mathrm{~m} / \mathrm{h}]$ is;
$\mathrm{V}_{h z}=18,000 * \mathrm{~T}_{h z}{ }^{-2.034}$

The lowest temperature at which boilover occurs is 120 [degC]. So the maximum extension rate may occur at $120[\mathrm{degC}]$ and is around $1[\mathrm{~m} / \mathrm{h}]$ as usually mentioned.

When $\mathrm{T}_{h z}=120[\mathrm{degC}]$ in Eq. 12, then $\mathrm{V}_{h z}=1.06[\mathrm{~m} / \mathrm{h}]$.
This means the calculated results well mach with the phenomena in an actual tank fire.


Fig.-3. Relation between hot zone temperature and hot zone extension rate

## (3) Distillation cycle

According to the many reports of boilover experiments, change in the hot zone temperature was observed along with burning time. It was also observed temperature within the hot zone is homogeneous. These observations mean the change in the hot zone temperature occurred step by step, but not continuously.
Crude oil No. -2 shows 3 times of the distillation cycle occur as shown in Fig.-2 and Table -2. Hot zone temperature becomes 40.7 [degC] at the first cycle, 66.2 [degC] at the second cycle, and, over 120 [degC] at the third.

The simulation program had been designed the calculation is stopped when the hot zone temperature becomes 120 [degC] or higher. This restriction was eliminated temporarily and tried to proceed the calculation furthermore.
As a result of this try, except crude oil No. -3, calculation could not be completed since distillation temperature at the next cycle may exceed the maximum temperature of the distillation curve. In case of crude oil No -3, when changing the boilover temperature from 120 to 250 [ degC ], the hot zone temperature stays in 314.4 [degC], but when changing to 350 [degC], the distillation cycle proceeds to the next cycle and the hot zone temperature is increased to 359.6 [degC] as shown in Fig. -4.

These results could explain the phenomena of the discontinuous change in the hot zone temperature and that the cycle number of unit distillation would be decided depending on a distillation curve.


Fig.- 4 Crude Oil No. - 3, Temperature at the boilover is assumed to be 350
[degC]. The distillation cycle proceeds and the hot zone temperature is increased to 359.6 [degC]. from 314.4 [degC].

3 Temperature profile in the tank after extinguishment
There are two purposes of this study, one is to predict boilover occurrence, and the other is to predict how long time is required to cool the oil.

### 3.1 Basic scenario

In case that a crude oil tank fire is extinguished before boilover occurrence, the oil surface is ones of the hot zone layer, and under which the lower oil layer exists at lower temperature than $120[\mathrm{degC}]$ and contacts with the water layer. At the beginning, the upper side oil is hotter and lighter than the lower oil and water. So convection does not occur likely and the heat transfer is mainly by thermal conduction. Heat loss from the oil surface may be considerable large, so the upper side of the hot zone will be cooled within a short time and its density becomes heavier than the oil just below the surface and also heavier than the lower oil layer, because components of the hot zone are obviously heavier than ones of the lower oil layer. This heavier oil surface zone will spread entirely like a lid of the pan and still remains at the upper position. That means convection may not occur likely and thermal conduction will be continued as a main heat transfer.

Heat transfer by thermal conduction is too slow in comparison with thermal convection. Therefore so long time is required to heat up the water layer.
3.2 Calculation model

The simulation program (EXCEL VBA) had been developed based on the theoretical model described in Fig. ${ }^{-5}$.


Fig. -5 Calculation model of the temperature profile after extinguishment of a crude oil tank fire.

## (1) Heat transfer

(a) In case that no heat loss from the tank shell plate is included in the heat balance, that is, $\mathrm{Qsc}=0$
This case is suitable for checking the possibility of boilover occurrence, because heat will be transferred much faster to heat up the water layer.

Thermal conduction is considered only for heat transfer, then;
In the oil layer;
$\rho_{\mathrm{f}} C_{p f} \frac{\partial T_{f}}{\partial t}=\lambda_{f} \frac{\partial^{2} T_{f}}{\partial z^{2}}$
In the water layer;
$\rho_{\mathrm{w}} C_{p \mathrm{w}} \frac{\partial T_{\mathrm{w}}}{\partial t}=\lambda_{\mathrm{w}} \frac{\partial^{2} T_{\mathrm{w}}}{\partial z^{2}}$
(b) In case that heat loss Qsc from the tank shell plate is included in the heat balance
If $\mathrm{Qsc}=0$, temperature of oil in the tank will be kept for so long time.
When predicting the time required for cooling of the oil in the tank, Qsc must be included in the heat balance.

In the oil layer;
$\rho_{\mathrm{f}} C_{p f} \frac{\partial T_{f}}{\partial t}=\lambda_{f} \frac{\partial^{2} T_{f}}{\partial z^{2}}+\frac{4 h}{D}\left(T_{a t m}-T_{f}\right)+\frac{4 \sigma}{D}\left[\left(\mathrm{~T}_{\mathrm{atm}}+273\right)^{4}-\left(\mathrm{T}_{\text {wall }}+273\right)^{4}\right]$
In the water layer;

$$
\rho_{\mathrm{w}} C_{p \mathrm{w}} \frac{\partial T_{\mathrm{w}}}{\partial t}=\lambda_{\mathrm{w}} \frac{\partial^{2} T_{\mathrm{w}}}{\partial z^{2}}+\frac{4 h}{D}\left(T_{a t m}-T_{\mathrm{w}}\right)+\frac{4 \sigma}{D}\left[\left(\mathrm{~T}_{\mathrm{atm}}+273\right)^{4}-\left(\mathrm{T}_{\mathrm{wall}}+273\right)^{4}\right]
$$

Where;
$\rho_{\mathrm{f}}$ or $\rho_{\mathrm{w}}$; density of oil or water $\left[\mathrm{kg} / \mathrm{m}^{3}\right]$
$C_{p f}$ or $C_{p \mathrm{w}}$; specific heat of oil or water [ $\left.\mathrm{kcal} / \mathrm{kg} / \mathrm{degC}\right]$
$\lambda_{f}$ or $\lambda_{\mathrm{w}}$; heat conductivity of oil or water $[\mathrm{kcal} / \mathrm{h} / \mathrm{m} / \mathrm{degC}]$
$D ;$ tank diameter [m]
$h$; convection heat transfer coefficient $\left[\mathrm{kcal} / \mathrm{h} / \mathrm{m}^{2} / \mathrm{degC}\right]$
$\sigma$; Stefan-Boltzmann constant
$T_{f}$ or $T_{\mathrm{w}}$; temperature of oil or water [degC]
$\mathrm{T}_{\mathrm{atm}}$; atmospheric temperature [degC]
$\mathrm{T}_{\text {wall }}$;temperature of tank shell plate [degC]
t ; time [h]
z ; height [m]
(2) Boundary condition
(a) Oil surface

Heat release to the atmosphere must be included in the heat balance at the oil surface, and then;
$\rho_{\mathrm{f}} C_{p f} \frac{\partial T_{f}}{\partial t}=\frac{1}{\Delta z}\left[\mathrm{~h}_{\text {air }}\left(T_{\text {atm }}-T_{f}\right)+\sigma\left[\left(\mathrm{T}_{\mathrm{atm}}+273\right)^{4}-\left(\mathrm{T}_{\mathrm{f}}+273\right)^{4}\right]\right]$
where;
$\mathrm{h}_{\text {air }}$; heat transfer coefficient at the oil surface $\left[\mathrm{kcal} / \mathrm{h} / \mathrm{m}^{2} / \mathrm{degC}\right]$
(b) Oil-Water interface

It is assumed that the variation of the temperature with time at the interface is an average of ones of oil and water. That is;
$\frac{\partial \mathrm{T}}{\partial t}=\frac{1}{2}\left(\frac{\partial T_{f}}{\partial t}+\frac{\partial T_{\mathrm{w}}}{\partial t}\right)$
(c) Tank bottom

The tank bottom is contacted with the foundation, which is like a heat insulation after a short time heating. So no heat loss is assumed in the calculation. That is;
$\lambda_{w} \frac{\partial T_{w}}{\partial z}=0$
3.3 Calculation by the simulation program
(1) Calculation conditions
(a) Hot zone depth, oil surface level and temperature profile of oil When the tank ( 80 m diameter) containing Crude Oil No. -2 is on fire, and extinguished after 8 hours or 40 hours burning, oil temperature and oil level in the tank was calculated by simulation program for hot zone temperature.
These calculated results are shown in Table 3, which are input to this simulation program for temperature variation calculation after extinguishment.

Table -3. Calculation conditions

|  | Case 1 | Case 2 | Case 3 | Case 4 |
| :--- | :---: | :---: | :---: | :---: |
| Initial oil surface height [m] | 20 | 20 | 5 | 5 |
| Lapse time of the fire [h] | 40 | 40 | 8 | 8 |
| Oil surface height at extinguishment [m] | 12.43 | 12.43 | 3.49 | 3.49 |
| Hot zone temp. at extinguishment [degC] | 300.4 | 300.4 | 300.4 | 300.4 |
| Hot zone bottom height [m] | 4.90 | 4.94 | 2.0 | 2.04 |
| Temp. of the lower oil layer [degC] | 66.2 | 66.2 | 66.2 | 66.2 |
| Water layer height [m] | 1.0 | 0.5 | 1.0 | 0.5 |
| Temp. of the water layer [degC] | 35 | 35 | 35 | 35 |

(b) Water temperature

It is assumed to be 35 [degC].
(c) Heat transfer coefficients

Assumed as;
Outside of the tank shell plate, by wind ; $10[\mathrm{kcal} / \mathrm{h} / \mathrm{m} 2 / \mathrm{degC}]$
Outside of the tank shell plate, by water stream ; $150[\mathrm{kcal} / \mathrm{h} / \mathrm{m} / \mathrm{degC}]$
Inside of the tank shell plate; $50\left[\mathrm{kcal} / \mathrm{h} / \mathrm{m}^{2} / \mathrm{degC}\right]$

### 3.4 Calculated results

The results are summarized in the Table $-4,5$ and 6 , and indicated in the graph for case 4 as Fig.-6, 7 and 8.
-Case A; Heat loss through tank wall is not included in the calculation.

Table -4. Temperature of oil after extinguishment in Case A

|  | Case 1 | Case 2 | Case 3 | Case 4 |
| :--- | :---: | :---: | :---: | :---: |
| Maximum Temperature around the interface <br> between water and oil layer [degC] | 66 | 66 | 73 | 66 |
| Maximum oil temperature 100 [h] after <br> extinguishment [degC] | 300 | 300 | 300 | 300 |
| Maximum oil temperature 300 [h] after <br> extinguishment [degC] | 300 | 300 | 282 | 280 |
| Maximum oil temperature 600 [h] after <br> extinguishment [degC] | 300 | 300 | 245 | 240 |




Fig. -6 Temperature profile of oil after extinguishment in case of no heat loss from the tank wall, case -4
-Case B; Heat loss through tank wall by wind only is included in the calculation.

Table -5. Temperature of oil after extinguishment in Case B

|  | Case 1 | Case 2 | Case 3 | Case 4 |
| :--- | :---: | :---: | :---: | :---: |
| Maximum Temperature around the interface <br> between water and oil layer [degC] | 66 | 66 | 66 | 66 |
| Maximum oil temperature 100 [h] after <br> extinguishment [degC] | 255 | 255 | 255 | 255 |
| Maximum oil temperature 300 [h] after <br> extinguishment [degC] | 190 | 190 | 182 | 180 |
| Maximum oil temperature 600 [h] after <br> extinguishment [degC] | 135 | 135 | 115 | 115 |



Fig. - 7 Temperature profile of oil after extinguishment in case of cooling the tank wall by wind, case - 4
-Case C; Heat loss through tank wall by water stream is included in the calculation.

Table 6 Temperature of oil after extinguishment in Case C

|  | Case 1 | Case 2 | Case 3 | Case 4 |
| :--- | :---: | :---: | :---: | :---: |
| Maximum Temperature around the interface <br> between water and oil layer [degC] | 66 | 66 | 66 | 66 |
| Maximum oil temperature 100 [h] after <br> extinguishment [degC] | 220 | 220 | 220 | 220 |
| Maximum oil temperature 300 [h] after <br> extinguishment [degC] | 120 | 120 | 118 | 115 |
| Maximum oil temperature 600 [h] after <br> extinguishment [degC] | 60 | 60 | 55 | 55 |




Fig. -8 Temperature profile of oil after extinguishment in case of cooling the tank wall by water stream, case -4

### 3.5 Possibility of boilover occurrence

On this aspect, calculated results in the attachment 5 should be evaluated. It is found that temperature near the interface between water and oil is lower than 70 [degC]. So it can be said that in such a large tank fire case, possibility of boilover occurrence after extinguishment seems too little.

For reference, it was tried to calculate in the case of 55gallons drum fire, and the calculated result showed the interface temperature becomes higher than 120 [degC] within a few hours after extinguishment to cause boilover.

Depending on the various calculated results by this simulation program, the following conclusions can be said.

- When the lower oil layer is thinner, then temperature of the interface rises up easily.
- When temperature of the lower oil layer is higher, then temperature of the interface rises up easily.
- Effect of thickness of the water layer seems not so big for the temperature rise of the interface.
- Possibility of boilover occurrence after extinguishment is almost none in a large crude oil tank fire

Apart from the calculated results, the scenario described in section 3.1 must be considered again.
The heavier oil surface zone like [a lid of the pan] will be continuing to remain at the upper position. But this position is very unstable and therefore the lid might be broken possibly with some shocks such as earthquake, direct impingement of large water discharge on the surface etc. If the lid is broken, there is a possibility of convection of the oil to cause boilover.
3.6 Variation of the oil temperature with time

When a large tank had been fired and extinguished, it is not easy to cool the oil and requires so long time for the cooling.
In case of cooling by wind only with its velocity of 6 to $8 \mathrm{~m} / \mathrm{s}$, oil temperature is ;

- 600 hours after extinguishment, oil level is $12.43 \mathrm{~m} ; 135$ [degC]
- 600 hours after extinguishment, oil level is 3.49 m ; 115 [degC]

In case of cooling by water streams, oil temperature is ;

- 300 hours after extinguishment, oil level is $12.43 \mathrm{~m} ; 120$ [degC]
- 600 hours after extinguishment, oil level is 3.49 m ; 115 [degC]

The calculation is on the assumption that whole circumference of the tank could be cooled equally at the same time, so actually, much longer time may be required to cool the oil in the tank.
Effect of water cooling is remarkable and cooling time is reduced to almost a half of ones by wind cooling.

## 4 Conclusion

Calculated results by using simulation programs indicate;

- the temperature and extension rate of the hot zone can be expressed in Equation
$\mathrm{V}_{h z}=18,000 * \mathrm{~T}_{h z}{ }^{-2.034}$ where, $\mathrm{T}_{h z}[\mathrm{degC}]$ and $\mathrm{V}_{h z}[\mathrm{~m} / \mathrm{h}]$
- hot zone formation is depending on only a distillation curve of a crude oil
- after extinguishment of a crude oil tank fire, possibility of boilover seems too little.
- after extinguishment of a crude oil tank fire, so long days are required to cool the hot oil.

The simulation programs seem practical enough for rough prediction of boilover occurrence and for estimation of a required period for cooling the hot oil after extinguishment,

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