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Flashpoint As An Operational- And Safety Factor In Oil Spill Recovery

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Abstract
In oil spill recovery, the flashpoint of the oil is a very important safety factor. In the Netherlands, only so-called first-line recovery vessels like the m.v. Arca are allowed to deal with liquids with a flashpoint below 60 °C. The flashpoint depends on the composition of the oil. After a spill, the light components quickly evaporate and the flashpoint increases. Model calculations and experiments have shown that the thickness of an oil layer is the prime factor determining the speed of the flashpoint increase.
Two conclusions were made:
- When measuring a flashpoint higher than 60 °C, one can assume that this is the case for the entire layer.
- The time it takes for an oil slick to reach a flashpoint of 60 °C primarily depends on the layer thickness. As a rule of thumb, it takes 2 to 6 times the layer thickness (in mm) in hours for an oil slick to reach the safe flashpoint.
In practice, this means that all oil spills with the appearances sheen, rainbow, metallic and discontinuous true oil colour can be safely combated using any kind of recovery vessel. However, first-line recovery vessels remain necessary. Due to floating booms or natural barriers, the layer thickness may rapidly increase, with a corresponding decrease in evaporation as a result. In particular when fresh oil is concentrated close to the point of release.

1 Introduction

In the Netherlands the flashpoint of an oil spill plays an important role in oil spill recovery. Flashpoint is defined as the lowest temperature, corrected to one atmosphere (101.3 kPa) at which a vapour above a liquid can be ignited in air when exposed to a flame under specified test conditions. Liquids with a flashpoint higher than 60 °C are not considered flammable and not dangerous in transport of liquids.

In mechanical oil recovery, the first (and still only) response method in the Netherlands, oil is removed from the water surface and pumped into a tank on board of the recovery vessel after which it is transported to a harbour. This transport and storage on board must be in compliance with tanker regulations when the flashpoint is below 60 °C. Vessels like the Dutch Arca are specially designed for handling these kind of spills. When dealing oil with a flashpoint higher than 60 °C these regulations are less strict and so-called second-line recovery vessels can be used.

Because oil is a mixture of various components like alkanes, the flashpoint depends on the composition of the oil and the difference in evaporation rate between the various components in the oil mixture once the oil has been spilled into the water.

A study was carried out to determine the factors influencing the flashpoint. For this purpose a literature was reviewed and laboratory experiments were done. This data was used for verification and comparison of three oil behaviour models.

2 Factors Determining Flashpoint

As mentioned before, oil is a mixture of various components which have different characteristics. The components of crude oil all have a different boiling point. Extensive literature can be found on composition of crude oils in relation to oil spill recovery. In a real spill situation the oil is influenced by so-called weathering processes, like dissolving, dispersion, spreading and evaporation. Flashpoint depends on the initial boiling points of the components of the oil. Light components, with a low boiling point, have a higher evaporation rate than components with a high boiling point. Therefore these heavier components will remain longer in the oil. This influences the flashpoint directly.

Length	Name	Boiling point °C	Density (kg/m^3)	Pour point °C	Flash point °C	LEL[1] %	UEL[2] %	Vapour pressure Pascal (20°C)
C1	Methane	-162	466	-186	Gas	5	15	80704633.95
C2	Ethane	-89	572	-186	Gas	2.7	12.45	3850000
C3	Propane	-42	585	-191	Gas	1.7	9.5	900000
C4	Butane	-0.5	601	-141	Gas	1.3	8.41	210000
C5	Pentane	36	626	-133	-40	1.4	7.8	57300
C6	Hexane	69	660	-98	-22	1.1	6.9	16000
C7	Heptane	98	684	-94	-4	1	7	4800
C8	Octane	126	703	-60	12	0.84	3.2	1400
C9	Nonane	151	718	-57	31	0.74	2.9	429
C10	Decane	174	730	-33	47	0.69	2.6	246.04
C11	Undecane	196	740	-29	65			107.12
C12	Dodecane	216	749	-13	74			50.30

[1] LEL = Lower Explosion Level
[2] UEL = Upper Explosion Level

So, flashpoint is mainly influenced by the lighter components. Evaporation itself is determined on a number of factors in operational response. Most important factor influencing the evaporation rate is the layer thickness of the spilled oil. This is because oil slicks show great variation in layer thickness (microns – centimetres or sometimes meters). Also temperature of the oil cannot be neglected, but because of the little variation in water temperature in the marine environment, it is of less importance. Other factors are the vapour pressure, the type of oil, wind speed and air pressure.

3. Flashpoint in relation to layer thickness

The flashpoint of oil can be determined by measuring it with e.g. a closed cup tester. In the Netherlands the recovery vessels the Setaflash tester is used for this purpose. This test is always performed before mechanical recovery operations are started. Unfortunately no data of flashpoints in relation the layer thickness of an oil slick has been found in logs or literature.

To determine the influence of the layer thickness of the oil on its flashpoint three mathematical models were compared and laboratory studies were performed.

3.1 Mathematical Models

Most methods use the relative volume of evaporated oil. However, the flashpoint can also be determined using the change in oil composition.

From literature it became clear that in oil behaviour models several methods are used to determine the flashpoint. For this study three methods were examined:

- Mol fractions * MK (used by North Sea Directorate in OILSPILL)
- Sum of partial vapour pressures
- Relative volume evaporated oil and boiling point of the residue (used by ASCC in DDO)

3.1.1 Mol fractions times MK

For oils with flashpoints >60 °C the following equation has been found:

$$\sum molfracties * MK \leq 1{,}03$$

The shorter the carbon chain of a component, the more influence this component has on the flashpoint of the oil. For example, Pentane (MK =112) has 487 times more influence on the flashpoint than tridecane (MK = 0,23) in an oil mixture.
In this method the composition is determined again in every time step and the sum of the mol fractions times the MK-product as a function of time is presented in a graphic. At the crossing point of the MK product 1,03 the time needed to reach a flashpoint >60 °C can be read from this graphic (Figure 1). In this case (oil density 840 kg/m3, 10 °C, layer thickness 0,2 mm), the flashpoint exceeds 60 °C after 0,6 hours.

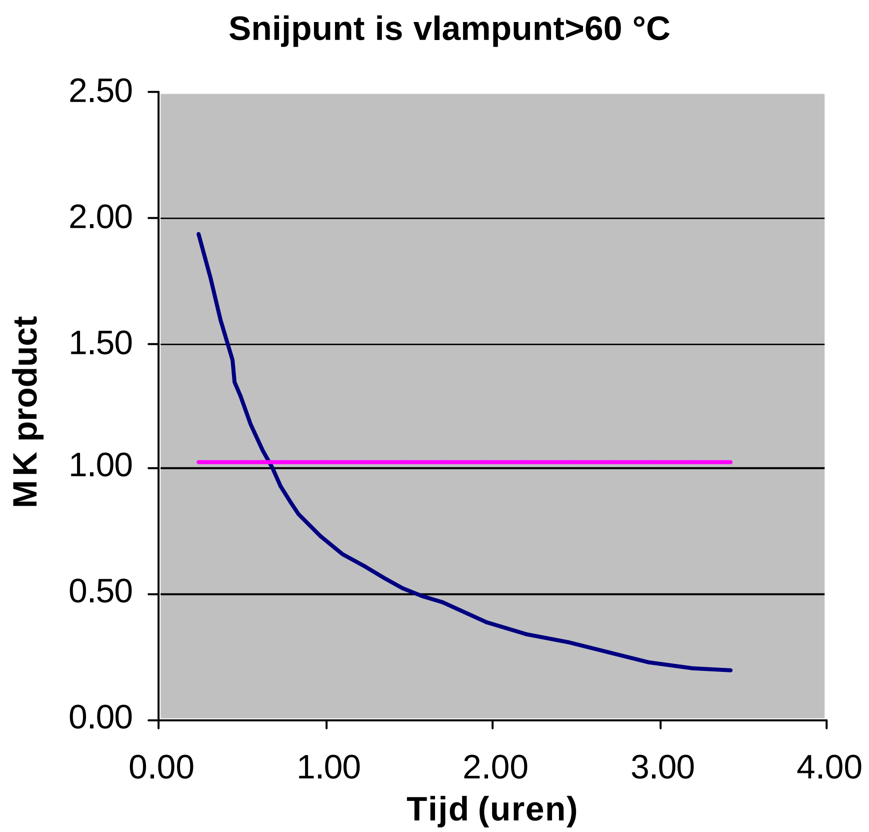


Figure 1 Grafische weergave 'Som MK product x molfractie' methode

3.1.2 Sum of partial vapour pressures

In this method, the changing partial vapour pressures of residual component due to the difference in evaporation rates of the single components, the evaporation of the components C_1 tot C_{20} en $C_{20}+$ is calculated again after every time step. After every time step the amount of evaporation and the amount left behind of a certain component is determined.

At a constant temperature a relation between the vapour pressure of a component and its flashpoint can be found:

$Vp = -16{,}591 * LN(P) + 137{,}75$ (at 20 °C)

in which:

Vp = Flashpoint (°C)

P = Vapour pressure (Pascal)

A second method calculates the flashpoint indirectly using the direct relationship between the vapour pressure and the boiling point on one hand

$Kp = -26{,}112 LN(P) + 318{,}41$

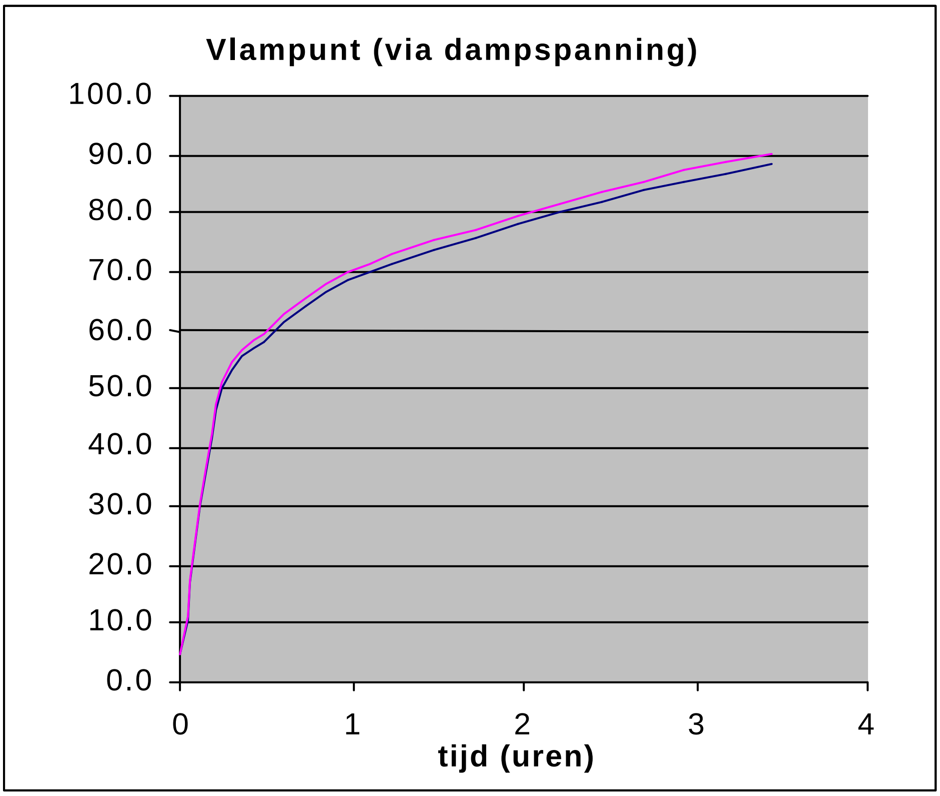
and the boiling point and the flashpoint on the other hand

$Vp = 0{,}6498 * Kp - 66{,}157$

in which:

Kp = Boiling point (°C)

Results of calculations using both methods are presented in Fig. 3.



Figuur 2 Vlampunt als gevolg van partiële dampspanning van overige componenten

As can be seen from Fig. 3, both methods give almost the same results. The flashpoint of an oil with density of 840 kg/m3, at 10 °C and a layer thickness of 0,2 mm exceeds 60 °C after 0,5 hours.

3.1.3 Relative volume evaporated oil and boiling point of the residue

In the oil behaviour model DDO (developed by ASCC) the flashpoint is calculated by determining the evaporation of oil as a function of the density of the oil, determining the initial boiling point of the residual fraction of oil and through a relation with the initial boiling point.

The relationship between the flashpoint and the initial boiling point in the DDO method is:

$Vp = 0{,}72 * Kp - 72{,}6$.

In which:

Vp = Flashpoint (°C)

Kp = Initial boiling point (°C)

Using the straight part of a distillation curve and when relative volumes at two temperatures are known, temperature at every other relative volume distilled can be calculated using the following equation:

$$Kp = T_1 + \frac{T_2 - T_1}{F_2 - F_1} * (F - F_1)$$

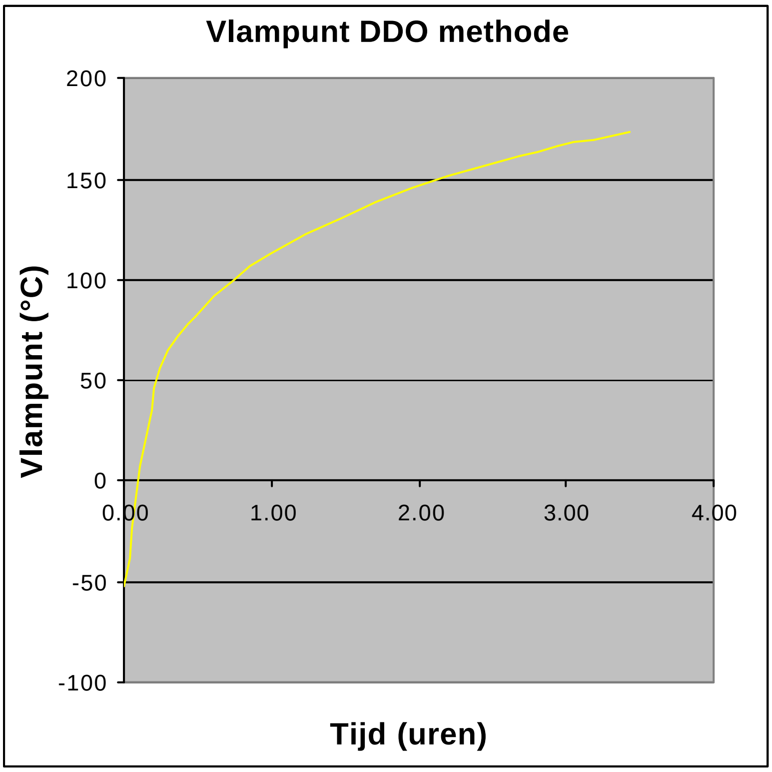
By doing this for various types of oil a relationship between the flashpoint and the fraction evaporated (F) can be determined. For this study two temperatures were chosen (T_1 = 93,3 °C, T_2 = 260 °C), because they normally represent evaporation within 4 hours

(T_1) and 8 to 12 hours (T_2) and because much data is known (Koops, 1988). When applied to the above mentioned equation this equation results in:

$$Kp = 93{,}3 + \frac{166{,}7}{F_2 - F_1} * (F - F_1)$$

in which:
F = fraction evaporated
Kp = boiling point (vapour)

In Fig 4 flashpoint as a function of time is represented (oil density 840 kg/m3), layer thickness 0,2 mm, temperature 10 °C).



Figuur 3 Vlampunt als functie van de tijd (DDO berekeningsmethode)

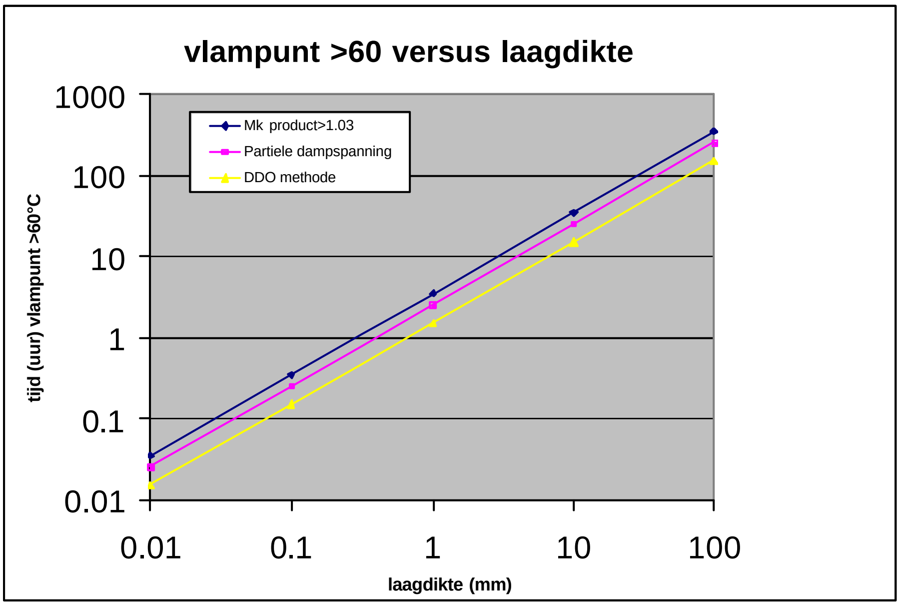
As the figure shows, a flashpoint of 60 °C is found after approx. 0,25 hours.

3.1.4 Calculations

The three calculation methods were used to study a number of scenario's. The most relevant parameters (layer thickness, temperature, oil type) are described.

3.1.4.1 Layer thickness

When dealing with an oil type with density 840 kg/m^3 at a constant temperature (10 °C) and with variation in layer thickness, time was determined to reach the flashpoint of 60 °C.

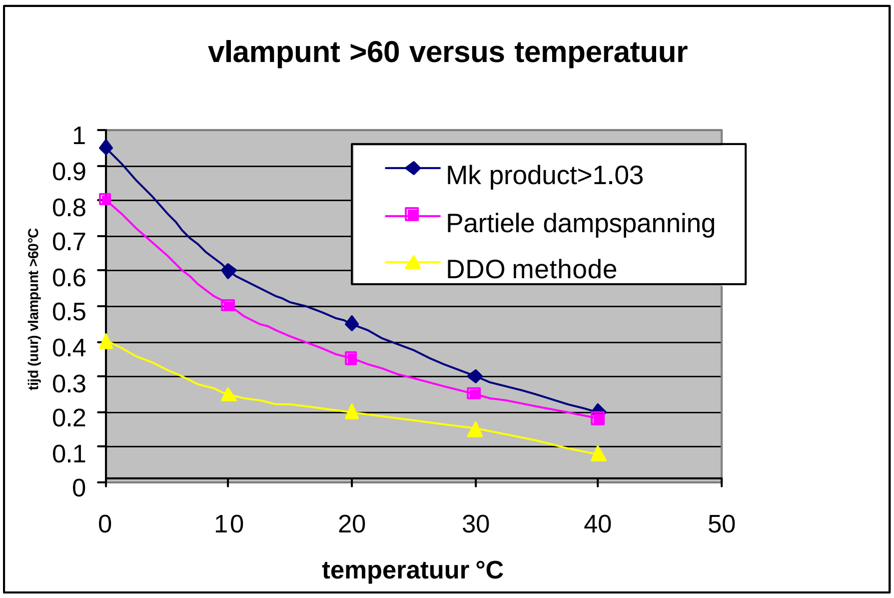


Figuur 4 Verloop vlampunt in de tijd in relatie met de laagdikte

The figure shows that all three methods show a clear relationship with the layer thickness, but that with the DDO-method the flashpoint criterion is met faster then with the other methods. For oil spill recovery the area between layer thickness of 0,1 to 1 mm is most important. At a layer thickness of 0,1 mm flashpoint will exceed 60 °C within the hour, whereas it will take several hours when dealing with a layer of 1 mm thick.

3.1.4.2 Temperature

With the same oil type time was calculated for the oil to reach a flashpoint of 60 °C. Layer thickness was constant (0,2 mm) (Figuur 5).



Figuur 5 Verloop vlampunt in de tijd in relatie tot de temperatuur

The figure shows that temperature has least influence in the DDO-method.

3.1.4.3 Oil type

The type of oil was the third variable to test the three calculation models. Results of calculations are presented in

Table 1.

Table 1 Time needed (hours) for the oil to exceed flashpoint of >60 °C as a function of the oils density.

Density (kg/m^3)	MK<1,03 method	Vapour pressure method	DDO method
802	1,1	0,9	0,2
825	0,7	0,5	0,35
850	0,5	0,4	0,5
876	0,4	0,25	0,9
904	0,35	0,25	2,2
934	>60	>60	2
966	>60	>60	4

No clear relationship between the MK-method and time and vapour pressure and time was found. In the DD-method time to reach the safety criterion increases with increasing density.

All three methods used the composition of the oil by using the density or distillation curves.
The structure of the oil behaviour model in order to calculate the flashpoint determines which method should be used. The DDO method needs only the relative amount of evaporated oil and the density of the crude, whereas for the other methods the composition of the oil is needed to calculate the flashpoint. All calculation methods give the relationship with layer thickness, type of oil and temperature.

Because we deal with safety a certain safety factor must be used. Conservatively, the time it takes (in hours) for the flashpoint to increase above 60 °C is to 2 to 6 times the average layer thickness (in millimetres).

3.2 Laboratory Tests
In beakers tests were done to determine the influence of the mass transport in an oil layer due to evaporation on the flashpoint. There are two types of mass transport:
- mass transport from the inner part of the layer to the surface;
- mass transport from the surface to the atmosphere.

To determine the vertical mass transport in an oil layer, so-called 'worst-case scenario' tests were done by creating a 8 cm thick layer. If tests show an equal development of the flashpoint within the entire layer, it can be concluded that in normal situations (average layer thickness of approx. 0,2 mm) this will also be the case. The results were also used to validate the calculation methods with the mathematical models.

A PE bucket (Ø 22 cm, height 17 cm) containing 3 litres of natural seawater 3 litres of Arabian heavy crude (D15 = 889,1 kg/m3, flashpoint < 20 °C) was carefully added to reach a layer thickness of approx. 8,4 cm. Total volume reached just underneath the top of the bucket. To prevent saturation with oil vapours, air was continually blown over the bucket at wind speed of 2 m/s). Room temperature during the experiment was 21 °C.

At different time steps (0, 10, 30, 60, 120, 180, 240, 300, 360, 480, 1440, 2880 en 4320 minutes after dosage) oil samples were taken with a syringe at 1,0; 2,5 en 5,0 cm depth respectively. Samples were contained in 8 ml glass cups for analysis on oil composition and flashpoint and stored at 4 °C. Decrease in volume at every time step (approx.. 45 ml) was compensated by carefully adding seawater underneath the oil layer to make sure that total volume in the bucket was constant.

In a second test the development of the flashpoint in time was studied using layer thickness of respectively 1, 5, 10 and 100 mm. This experiment was done in 1 litre glass beakers (diameter 10 cm) to which 8, 40, 78 and 780 ml crude oil was added in natural seawater. With the Setaflash tester set at 60 °C the time it took for the oil to reach this temperature was determined.

From samples on three different time steps (directly after start evaporation, after 1440 minutes and after 4320 minutes) of two extreme depths (1 cm depth and 5 cm depth) oil composition was determined.

Table 2 Composition of the oil in g/kg (alkanes)

	1 cm 0 min	**1 cm 10 min**	**5 cm 10 min**	**1 cm 1440 min**	**5 cm 1440 min**	**1 cm 4320 min**	**5 cm 4320 min**
< C8	7	8	9	< 5	< 5	< 5	< 5
C8 - C9	16	16	18	10	11	6	7
C9 - C10	17	16	19	13	14	9	10
C10-C11	16	16	17	15	15	11	12
C11-C12	16	16	17	16	16	14	15
C12-13	15	15	16	16	16	16	17
C13-14	15	15	16	16	16	17	17
C14-15	14	14	15	16	16	16	16
C15-16	14	14	15	15	15	16	16
C16-17	13	13	13	14	14	14	15
C17-18	13	13	13	14	14	15	15
C18-19	13	13	13	14	14	14	14
C19-C20	12	12	13	13	13	14	14
> C20	150	150	160	170	160	170	170

Results show that the light components evaporate the fastest. It also shows that from C_{12} vapourization becomes less, thereby increasing the relative amount of these components in the oil.

Analysis of oil samples shows that hardly any change in composition took place in vertical direction.

After 24, 48 and 72 hours some additional flashpoint measurements were done. This results indicated that at 5 cm flashpoint was still < 26 °C, while at 1 cm flashpoint had increased > 40 °C. At the other two time steps the flashpoint hardly showed any difference at the two depths, 50-55 °C en 60 °C respectively. Results of the second experiment are listed in Table 3.

Table 3 Results of second experiment: flashpoint in relation to time and layer thickness

Time (hours)	1 mm	5 mm	10 mm	100 mm
0,5	<	<	<	<
1	<	<	<	<
2	>	<	n.a.	n.a.
4	>	<	<	n.a.
24	n.a.	>	<	<
28	n.a.	n.a.	<	<
72	n.a.	n.a.	>	<
134	n.a.	n.a.	n.a.	<

<: flashpoint below 60 °C
>: flashpoint above 60 °C
n.a.: not analysed

It is clear that with thin layers (1 mm), the flashpoint increases above 60 °C within 2 hours. With thick layers (100 mm) the flashpoint is still below 60 °C after 134 hours.

Test results proved that in a ‘worst-case scenario’ for an operational spill (layer thickness 8,4 cm) diffusion was fast at given temperature and wind speed. This could explain visual observation of foam and bubbles in the first period after the test was started.
One day after starting the test, additional measurements of the flashpoint showed some difference at 0-1 mm (> 40 °C) and 1 cm (< 26 °C). For spill recovery operations this means that when dealing with a layer thickness above 1 cm, the flashpoint should be determined from samples from the lower part of the slick. From the second test it can be concluded that in the most observed oil slicks (a couple of millimeters) flashpoint reaches the safety criterion of 60 °C within only a couple of hours. Also, the composition of the oil in the vertical direction of the oil layer was stable. As the flashpoint came near 60 °C, the variation of the flashpoint in vertical direction became less till zero. This means that when a flashpoint of 60 °C is measured, one can assume that this is true for the entire layer.

4. Conclusions & recommendations

4.1 Conclusions
The time it takes for an oil slick to reach a flashpoint of 60 °C primarily depends on the average layer thickness.
Conservatively, the time (hours) it takes for an oil spill to reach the safety criterion of 60 °C is 2 to 6 times the layer thickness (in mm).
Because most common oil spills have a maximum layer thickness of 0,2 mm, these spills will meet the safety criterion for mechanical recovery already at 0,4 to 1,2 hours.
In bigger spills and in situations where spreading of oil is limited, thicker oil layers can be observed (mm tot cm’s). When using booms, in harbours and when oil is concentrated by wind, oil layers can reach up to centimetres thick. In this situations it can take more than 24 hours before the flashpoint of the oil meets the safety criterion of 60 °C.

Determination of flashpoint with the aid of oil behavior models must be done carefully, because at bigger spills the variation of the layer thickness within a slick can be significantly and because these calculations are based on calculations of spreading and evaporation with their uncertainties.

4.2 Recommendations

Small to medium oil spills which easily spread will not be a problem what the flashpoint is concerned for mechanical recovery. In this case the so-called second-line recovery vessels can recover these kind of oil spill almost immediately because sailing time will be longer than the time for the oil to reach 60 °C.

If an oil spill is concentrated after it has spread, it is important to know how old the spill is before concentration started.

In case of a thin oil slick (0,1 – 0,2 mm) it can sometimes be recommended to wait some time before using oil booms to concentrate the slick to let the flashpoint exceed 60 °C.

The need for first-line recovery vessels is clear in order to be able to recover oil near the source (leaking tanker).

Second-line recovery vessels can be used when dealing with thin oil layers (<0,2 mm) (most common in Dutch situation) or when the oil has been on the water surface for a while. In practice this means that all oil spills with appearance of sheen, rainbow, metallic and discontinuous true oil colours can be recovered with second-line recovery vessels without any risk for safety.

When the volume of spilled oil is known, the average layer thickness can be estimated using the surface area. If this is not the case, also mathematical models cannot be used without any uncertainties. Then, actual measurements of flashpoint are needed to make sure the safety criterion is met.

Sampling for flashpoint measurements should be taken in the thicker part of the spills.

5. Literature

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