Development of a Burning Bench Dedicated to In Situ Burning Study: Assessment of Oil Nature and Weathering Effect

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Abstract

Since the Deepwater Horizon spill (2010), the controlled In Situ Burning (ISB) of oil has been demonstrated to be a "primary" response option and not only an "alternative" solution to treat offshore oil spills (Allen, 2011). However, like the other techniques usually deployed (mechanical recovery, dispersion), the efficiency of the response option depends on various parameters (the pollutant itself and environmental conditions). Considering ISB, the efficiency is related to the oil nature, slick thickness, weathering degree, water content. In order to assess the influence of these parameters on the ignitability and burning efficiency, an experimental device was developed at Cedre. The Burning Bench comprises a burning cell which was designed to avoid any boilover phenomenon and to ensure water temperature homogenization during the burning. Glass barriers, a specific hood and plume exhaust system complete the device to ensure safety conditions. Burning tests are conducted on a maximum of 300 mL of oil sample. During the combustion, water and flame temperature are recorded at different heights by using 4 temperature probes. A gravimetric impactor is mounted in the hood to continuously collect the particles produced during the burning and afterwards, to quantify the PM 2.5, PM 10 and PAH content in the soot. At the end of a burning test, residues are collected and quantified after solvent extraction. Different analyses are then performed on the residues: density, viscosity, simulated distillation, chemical family separation (saturates, aromatics, resins, asphaltens), PAH and alkane distribution and content, ... Potential PAH transfer from the oil to the water column is assessed by PAH extraction and quantification.

During the burning bench development, many tests were performed on different products (light refined products, fresh or weathered crude oil, heavy fuel oil, ...). The preliminary results highlighted a very good reproducibility of the tests. For the refined product, more than 70% of the product burnt. For most of the fresh crude oils tested, the burning efficiency was measured between 50 and 60%. While testing heavy fuel or weathered products, the burning efficiency never exceeded 40%.

1 Introduction

When oil is spilled at sea, one response option consists in containing the spill with boom and recovering it with skimmers. However, in some cases, it is not possible to recover the oil due to the oil properties, weather conditions or logistical problems. Other response techniques such as dispersant application or burning of oil slicks can be proposed to the authority in charge of the decision-making process.

One of the first attempts at burning oil slicks during a real oil spill was made in 1967 during the *Torrey Canyon* spill (United Kingdom, 1967). Even if the operation was not successful in this case (ITOPF, 2013), many scientific studies have been performed in order to better understand the science of oil burning on water and to develop appropriate materials for this technique. This includes many field trials and laboratory experiments which point to the benefit of the technique due to the removal of high amounts of oil from the sea surface in a very short period of time (Buist et al., 1994). However, the burning of oil generates a plume of soot and gases which are disseminated in the high layer of the atmosphere.

The efficiency of the technique is dependent on various parameters which have to be studied to ensure a successful ISB operation. For example, the oil nature is an important parameter as crude oils are ignited easily and have a higher burning efficiency while heavy fuel oils are more difficult to burn. This is due to the higher abundance of light hydrocarbons in crude oil than in heavy fuel oil. Oil thickness is also a major parameter: a minimum thickness of 2 – 3 mm is usually required to ignite oil slick (Fingas, 2000; ASTM, 2008). In weathered oil in which a significant part of the lightest hydrocarbons may have evaporated naturally, ignition of the slick can be difficult or not possible without primer. In the same way, the emulsification rate of the oil has an influence on the ignitability of the slick and reduces the burning efficiency of ISB due to the incorporation of water droplets into the oil (Buist, 1999).

In order to assess the influence of these parameters on the ignitability and burning efficiency, an experimental device was developed at *Cedre*. Combined with an oil weathering study, the burning bench can be used to define the windows of opportunity for using ISB for a defined oil. In addition, the composition and physical properties of the burn residues are measured in the laboratory, as is the potential water contamination with PAHs during burning.

2 Material and Methods

2.1 Design of the Burning Bench

The burning bench (Figure 1) is composed of:

- a galvanized steel frame (1),
- a smoke hood (2) including a programmable cyclonic vacuum (soot recovery),
- a smoke exhaust (3),
- a gravimetric impactor (not visible) used for soot characterization (PM10, PM2.5) and sampling,
- a magnetic stirrer (4),
- a glazed enclosure to protect personnel in case of oil/water projection (5),
- a burning cell (6) composed of:
 - a 5L beaker (h = 30 cm, \emptyset = 20 cm) (7)
 - a confinement ring (h = 3 cm, ϕ = 10 cm) into which the oil is poured before ignition (8)
 - temperature probes (3 in air, 1 in water) (9) connected to a temperature logger.

The equipment ensured consistent burning conditions for all the successive tests. This ensured that each burning test was conducted in exactly the same way, and comparative tests could be performed.

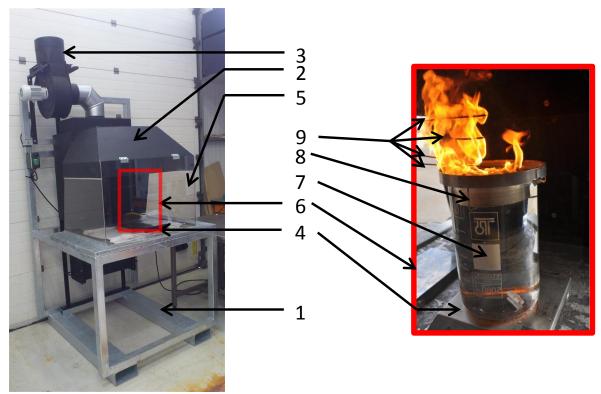


Figure 1. The Burning Bench.

2.2 Burning Protocol

2.2.1 Preparation of the Test

Burning tests are conducted on approximately 100 mL of oil poured into the confinement ring. This volume gives an oil slick with a minimum thickness of 1 cm. The exact quantity of oil is measured for each test. The temperature logger (Testo 176T4, Testo SARL, France) is turned on before the oil ignition. The magnetic stirrer is turned on and set at the lowest speed in order to prevent any surface turbulence but sufficient to allow water column movement which ensures temperature homogenisation during the test. Moreover, this "cooling" system recreates a movement of water beneath the oil slick as is observed, in the field, while the slick is towed with fire boom. If the magnetic stirrer is not used, an intensification of the fire is systematically observed at the end of the burning. This phenomenon, also called the "vigorous burning phase", is caused by significant heat transfer from the oil slick back to the water surface while the oil slick thickness decreases. During this vigorous phase, burn rate, flame temperature and radiative output increase significantly (Buist et al., 1994). This has never been observed during operations at sea due to the continuous movement of the slick (Fingas, 1994; Fritt-Rasmussen, 2010).

2.2.2 Burning Test

A propane torch is used to ignite the oil for 10 seconds (Figure 2). In case of failure, the ignition was repeated twice before the oil is classified as "not ignitable". (Brandvik et al., 2010). At the end of burning, the residue is collected after 15 minutes of cooling. Most of the residue is collected using a spoon and transferred into a glass beaker. The residue remaining on the confinement ring is extracted with methylene chloride and the solvent/oil mixture is transferred into the same beaker.

In addition, water is sampled before and at the end of each test and PAH concentrations are measured by the SBSE (Stir Bar Sorptive Extraction) technique (Balcon et

al., 2011). The objective is to assess whether burning promotes a transfer of PAHs from the oil to the water column during burning. The PAH concentrations in the water sample are compared to the concentrations obtained in a water sample exposed to the same amount of oil for the same duration but without any burning.



Figure 2. Oil ignition using a propane torch.

3 Results and Discussions

3.1 Evolution of Flame and Water Temperature

For each oil tested, the ignition was immediate and there was no need to repeat the ignition protocol. Figure 3 presents an example of temperature measurements in the water beneath the oil slick and in the flame at different heights (+4, +8 and + 12 cm). There were no significant differences in temperature profiles during the different tests. The highest temperatures reached 600°C at 4 cm height during the first minutes of burning. The temperature then decreased progressively to 300°C at the end of burning. The burning test conducted on 100 mL of oil lasted around 15 ± 0.81 minutes. The water temperature remained in the range of 21 to 24°C. This confirms that there was no boilover (or vigorous phase) whereby the highest flame temperature would have been recorded at the end of the burning test.

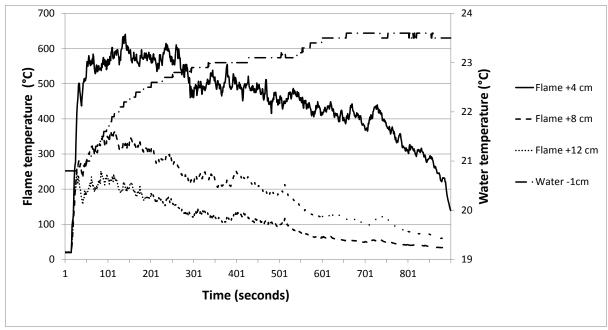


Figure 3. Flame and water temperature evolution during a burning test.

The influence of air addition into the fire was also studied by using a compressed air system for 6 minutes after ignition. Figure 4 presents the flame and water temperatures recorded during this test. The flame temperature at +4 cm reached 1000°C and remained constant while compressed air was used. Once the compressed air system was turned off, the flame temperature decreased immediately to 600°C until the end of the burn. The two increases of temperature after 500 seconds corresponded to 2 tests of ignition of the burn residue using the propane torch.

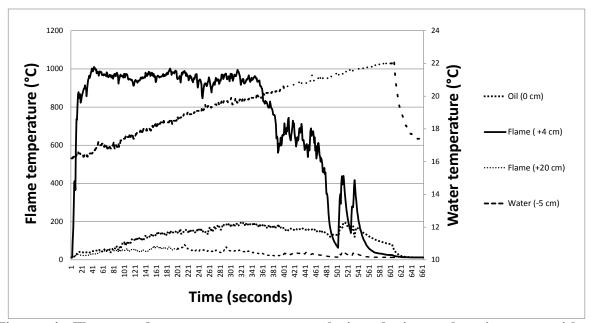


Figure 4. Flame and water temperature evolution during a burning test with a compressed air system.

3.2 Burning Measurement

3.2.1 Burning Rate

The burning rate (or regression rate) was calculated using equation (3) (SL Ross, 1999). It is usually expressed in millimeters of oil slick burnt per minute of burning (mm/min). It is well known that for small fires, the burning rate is dependent on the fire diameter (Blinov and Khudiakov, 1961). Burning rates are high (≈ 5 mm/min) for very small pools (1 cm diameter) and decrease significantly (0.5 mm/min) for pools of 10 cm in diameter (laminar flow regime). For pools between 10 cm and 100 cm diameter, burning rates increase on a straight-line basis (transition regime) and reach a constant value (around 3 to 4 mm/min) for pools larger than 100 cm diameter (turbulent flow regime).

Burning rate =
$$\frac{m_{oil initial} - m_{residue}}{d_{oil} * A * t}$$
 (3)

with m_{oil} initial, the initial mass of oil (g)

m_{residue}, the mass of the residue (g)

d_{oil}, the density of the oil at the time of ignition (g/mm³)

A, the surface area of the ring (mm²)

t, the burn duration (min)

Table 1 presents the results obtained with 3 different African crude oils. The values obtained are in agreement with the data published by Blinov and Khudiakov (1961), SL Ross

(1999) and more recently by Rangwala et al. (2013) (0.4 - 0.6 mm/min) while studying burning of oil in ice cavities of 10 cm diameter.

The last rows present the results obtained with different thicknesses of oil. It is interesting to note that these results indicate that there was no increase in burn rates with thickness from 10 mm to 30 mm. These results are consistent with those published by SL Ross and Energetex (1986), Garo (1996) and Buist (1997). Below a thickness of 10 mm, burning rates are reported to decrease progressively as the thickness decreases.

Table 1. Results of burning rates of different oils using the burning bench.

Oil reference	Volume of oil (mL)	Slick thickness (mm)	Burn duration (min)	Burning rate (mm/min)
Crude A	97	12.4	14.5	0.53
	95	12.2	14.3	0.55
Crude B	96	12,3	12.0	0.34
	95	12,0	13.6	0.32
Crude C	37	4.8	5.70	0.47
	96	12.2	13.73	0.54
	153	19.5	22.80	0.52
	225	28.6	33.75	0.52

3.2.2 Burning Efficiency and Density Results

The density was measured according to the ASTM standard (1997).

To quantify the burn residue, liquid-liquid extraction was conducted with methylene chloride and the amount of residue was measured gravimetrically after complete solvent evaporation. The burning efficiency (BE%) was calculated using the following equation (1) (SL Ross, 1999, Brandvik et al., 2010):

BE (%)=
$$100 \times \left(1 - \left(\frac{mass\ of\ residue\ (g)}{mass\ of\ initial\ oil\ (g)}\right)\right)$$
 (1)

While emulsified oil was tested, water content was taken into account in the calculation of the initial mass of oil.

Table 2 presents the results of burning efficiency and densities of burn residues for 4 types of crude oils, one light refined product and one heavy fuel oil (IFO 380). For the crude oils, the efficiencies appeared low (from 35% to 64%) in comparison with the results from literature which usually exceed 80% for fresh crude oils (SL Ross, 1999). This was due to the scale of this device: large scale burns generate more heat and higher temperatures which probably increase the burning efficiency. However, most of the results obtained are in the same range as the results published by Fritt-Rasmussen et al. (2013) using the SINTEF burning cell.

For each type of oil, the densities of the residues obtained at the end of the burning test were still below the sea water density (1.025 @ 25°C), suggesting that the residue will float on seawater in calm conditions. In case of waves or in the presence of suspended matter, residue drifting in midwater or near the surface could probably be observed.

Table 2. Burning efficiency and density measurements of different oils before and after burning at lab-scale.

Oil		Efficiency (%)	Density (@ 20 °C)	
			Initial	Residue
Diesel		89	0.812	0.826
Crude	Asphaltenic	43	0.869	0.976
	Waxy	35	0.849	0.958
	Paraffinic	64	0.804	0.931
	Naphtenic	61	0.873	1.001
IFO 380		26	0.928	1.013

3.2.3 Chemical Analyses of Burn Residue

Simulated Distillation

The analyses were performed by high temperature gas chromatography coupled to a flame ionisation detector (HTGC-FID). The GC is an HP 7890A (Hewlett-Packard, Palo Alto, CA, USA) equipped with a cool on column injector (flow 15 mL/min). The injector temperature is maintained at 400 °C. The column is ZB-5HT Inferno: Phenomenex (30 m x 250 μ m x 0.25 μ m). The GC temperature gradient is from 50°C (1 min) to 400°C (20 min) at 30°C/min. The carrier gas is Hydrogen at a constant flow of 2.5 ml/min. This method provides a general view of the oil, from the lightest compounds (around 10 carbons) to the heaviest ones (around 90 carbons).

Figure 5 presents a chromatogram of a Russian crude oil and its residue after burning. The oil was analysed prior to burning and the relative response of the two samples compared. Assuming that the fraction up to 540°C is preserved during burning (Buist et al., 1997), GC data and calculation of burning rate are expressed relatively to this fraction. Compounds in the boiling range up to 250°C were almost completely removed (97%) while the compounds with a boiling range between 250°C and 540°C (*n*-C₄₃) appeared to be partially removed (40%) and the heaviest compounds were still present in the burn residue. From these results, a global burning rate of 48% was calculated which is in the same range as the results obtained using classical gravimetric quantification of the burn residue collected at the end of the burning test (44%).

After burning, the residue was composed of 76% of compounds with a boiling range between 250 and 540°C, and 23% of compounds with a boiling range of up 540°C.

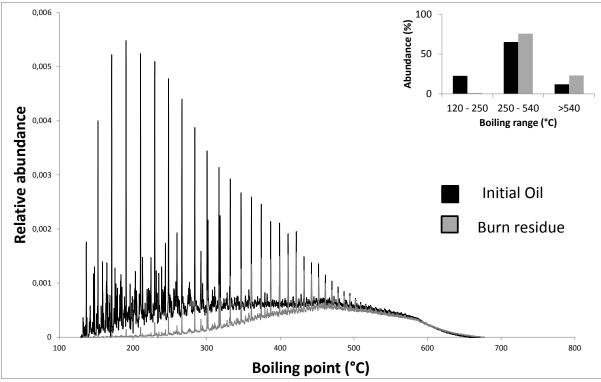


Figure 5. HTGC-FID chromatogram of Russian crude oil and its residue after burning.

- *n*-alkanes and PAH analyses

Prior to GCMS analysis, samples of oil were purified and saturate and aromatic fractions were isolated simultaneously through an SPE column packed with silica/cyanopropyl (SiO2/C3-CN) (1.0/0.5g, 6ml) (Interchim, Montluçon, France) (Alzaga et al., 2004). The GC was an HP 7890N (Hewlett-Packard, Palo Alto, CA, USA) equipped with a split/splitless injector (Splitless time: 1 min, flow 50 mL/min). The injector temperature was maintained at 300 °C. The interface temperature was 300°C. The GC temperature gradient was from 50°C (1 min) to 300°C (20 min) at 5°C/min. The carrier gas was Helium at a constant flow of 1 ml/min. The capillary column used was a HP-5 MS (HP, Palo Alto, USA): 30 m x 0.25 mm ID x 0.25 μm film thickness. The GC was coupled to an HP 5975 Mass Selective Detector (MSD) (Electronic Impact: 70 eV, voltage: 1200V). *n*-alkanes and PAHs semi-quantifications were performed using Single Ion Monitoring mode with the most representative fragment (saturates) or the molecular ion (PAH) of each compound at a minimum of 1.4 cycles/s. 17α(H),21β(H)-hopane (m/z=191) was used as a conserved internal biomarker during analysis (Prince et al., 1994, Venosa et al., 1997).

Figure 6 and Figure 7 present an example of the distributions of *n*-alkanes and PAHs obtained with a crude oil before and after burning.

These two figures demonstrate the removal of a significant part of *n*-alkanes and PAHs during the burning process (BT: Benzothiophenes, N: Naphthalenes, F: Fluorenes, P/A: Phenanthrenes / Anthracenes, D: Dibenzothiophenes, Fl/Py: Fluoranthenes / Pyrenes, BA: Benzo[a]anthracene, BBF: Benzo[b]fluoranthene, BKF: Benzo[k]fluoranthene, BEP: Benzo[e]pyrene, BAP: Benzo[a]pyrene, PE; Perylene, IN: Indeno(1,2,3-cd)pyrene, DBA: Dibenz(a,h)anthracene and BPE: Benzo(g,h,i)perylene). As previously described, compounds in the boiling range of up to 250°C (*n*-C₁₄) were highly removed while the compounds with a

boiling range between 250°C and 470°C (n-C31) appeared to be partially removed and the heaviest compounds were still present in the burn residue.

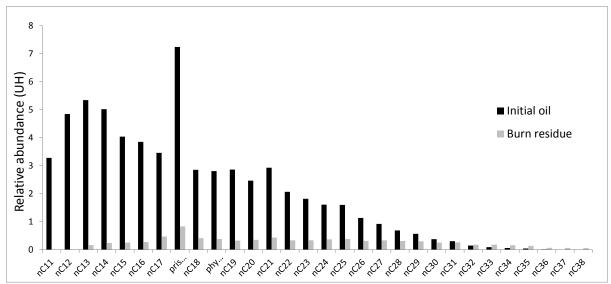


Figure 6. *n*-alkanes distribution (Hopane Unit) for a crude oil before and after burning.

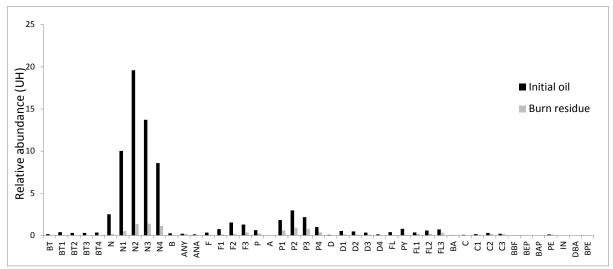


Figure 7. PAH distribution (Hopane Unit) for a crude oil before and after burning.

3.3 Influence of Weathering on Burning Efficiency

To assess the influence of oil weathering on the burning efficiency, samples of oil were collected during a weathering experiment conducted at pilot scale using the *polludrome* (*Cedre*'s flume tank) (Guyomarch et al., 2012). Samples (100 mL) of oil were collected after 8, 24, 48 and 72 hours of weathering and transferred immediately into the burning cell. An example of results is presented in Figure 8. Due to the evaporation of light compounds and the emulsification process, the burning efficiency decreased significantly with time. After 2 days of weathering, the efficiency was lower than 10%. After 3 days, it was not possible to ignite the oil even if light refined oil was used as an igniter.

The densities of all the residues obtained following the burning process (from 0.995 to 1.005) were still below the sea water density (1.025).

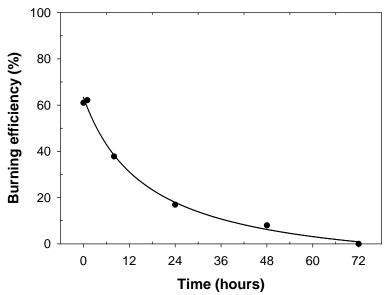


Figure 8. Example of the evolution of the burning efficiency of a crude oil assessed during a weathering experiment at the pilot scale.

4. Conclusion

The burning bench was developed in order to assess the ignitability of oil in case of in-situ burning deployment. The aim is to better understand the technique and additionally to characterize the residues (composition, behavior, potential impact). The preliminary results obtained during the burning bench development appear to be in agreement with data published in the scientific literature with similar device (Brandvick et al., 2010). The results highlight low efficiencies of burning using the lab-scale burning bench compared to results coming from larger scale experiment. This scale effect will be investigated specifically during the next step of the project which is dedicated to larger burns tests. This new device will be further used to assess the windows of opportunity for ISB according to the weathering degree of crude oil.

The next step of the Burning Bench development will focus on soot characterization by using the gravimetric impactor (PM10 and PM 2.5 distribution).

5. Acknowledgments

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6. References

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