#### ABSTRACT

Since the Deepwater Horizon spill (2010), the controlled In Situ Burning (ISB) of oil has demonstrated to be a possible solution to treat offshore oil spill. As other techniques usually deployed (mechanical recovery, dispersion), ISB efficiency depends on various parameters such as the oil nature, its evaporation 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 created to avoid any boilover phenomenon. Glass barriers, specific hood and plume exhaust system complete the device to ensure safety conditions. Burning tests are conducted on a 100 mL volume of oil sample. During the combustion, the flame is characterized by using various temperature probes set at different heights. In addition, temperature of seawater is also recorded during each test. A gravimetric impactor is mounted in the hood to collect continuously 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 alkanes distribution and content, ... Potential PAH transfer from the oil to the water column is measured after SBSE (Stir Bar Sorptive Extraction) of water samples and quantification by GC-MS.

During the burning bench development, many tests were performed on different products (light refined products, fresh crude oil, weathered crude oil, heavy fuel oil,  $\ldots$ ). 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 between 50 and 60%. While testing heavy fuel or weathered product, the burning efficiency never exceeded 40%. In addition, different burning techniques were investigated such as igniter efficiency, compressed air influence, thermo resistant sorbent efficiency, ...

### **OBJECTIVES OF THE BURNING BENCH**

According to oil nature (crude oil, heavy fuel oil, light refined product) and its weathering degree, burning tests are conducted to assess....

#### Interest of ISB?

Ignitability of the oil?

Efficiency of ISB? (residue quantification)

#### Potential Impact?

Assess the behavior and composition of residue (viscosity, density, PAHs, SARA, toxicity)

Assess a potential water contamination after ISB (PAHs transfer to water column)

Characterization of plume (PM10, PM 2.5, PAHs)

#### REFERENCES

Balcon, A.-L., Kanan, R., Van Ganse, S. and Guyomarch, J. 2011. "Analysis of Dissolved BTEX and PAHs in Seawater Following an Oil Spill: Development of Sensitive, Operational Methods for Rapid Diagnosis". IN Proceedings of the International Oil Spill Conference Proceedings 2011. March 2011, vol. 2011, n°. 1, pp. 164. ASTM International. 2003. "F 2230-02 Standard Guide for In-situ Burning of Oil Spills on Water: Ice Conditions". IN Volume 11.04. Waste Management. American Society for Testing and Materials, 6 p. Fritt-Rasmussen, J., Ascanius, B. E., Brandvik, P. J., Villumsen, A. and Stenby, E. H. 2012. "Composition of weathering conditions". Marine Pollution Bulletin vol. 67, n°1 – 2, pp. 75–81.



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





# Assessment of oil burning efficiency development of a Burning Bench



#### THE BURNING BENCH

Smoke Exhaust system Smoke hood including a programmable cyclonic vacuum for soot recovery

Gravimetric impactor (soot characterization) Glazed enclosure to protect personnel in case of oil/water projection



ment ring (h = 3 cm, ø = ) into which the oil is poubefore ignition

emperature probes

#### PROTOCOL OF A BURNING TEST

Approximately 100 mL of oil are poured into the confinement ring (slick thickness  $\approx$  1 cm) A The magnetic stirrer is turned on at the lowest speed in order to avoid any surface turbulence but sufficient to allow water column movement which ensure the temperature homogenisation during the test. This recreates the movement of water beneath the oil slick as it is observed, in the field, while the slick is towed with fire boom.

A propane torch is used to ignite the oil for 10 seconds. In case of failure, the ignition is repeated twice before the oil is classified as "not ignitable".

At the end of burning, the residue is collected after 15 minutes of cooling. Liquid – liquid extraction is conducted and the amount of residue is measured after complete solvent evaporation.

Water can be sampled at the end of each test and PAHs transfer to the water column is measured by the SBSE technique (Stir Bar Sorptive Extraction) (Balcon *et al.*, 2011).

After solvent extraction, the following physico-chemical properties are measured on each sample to characterise the burn residue: density, SARA fractionation, n-alkanes and PAH concentrations







on the burning efficiency. The tests were conducted in triplicates to assess the reproducibility of the test. The low Standard Deviation suggest a good reproducibility of the burning test. To ignite the oil slick, the thickness needs to be higher than 3 mm to allow the oil ignition. This result is in good agreement with the scientific literature published on ISB (ASTM, 2003). The residue density is measured at the end of each experiment. For the oil tested, the density never exceeds 1,025 (average seawater density) suggesting that in calm condition, no sinking of oil will be observed. In case of waves or presence of suspended matter, a drifting in midwater or close to the surface could probably be observed.



## EXAMPLE OF RESULTS

#### EVOLUTION OF TEMPERATURE DURING A TEST OF BURNING

Temperature is continuously recorded, simultaneously in the flame and in the water. The following figure presents an example of data obtained during the burning test of a light crude oil. This test lasted around 15 minutes. The maximum temperature is recorded at +4cm. It reaches around 600°C after less than 2 minutes and then it decreases progressively.





The following figure gives an example of results obtained while studying the influence of oil thickness



#### CONCLUSIONS

The Burning Bench was developed in order to collect experimental data on In Situ burning. The aim is to better understand the technique, its efficiency and 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 scientific literature. The results show a low SD which suggest a high reproducibility of the tests with the Burning Bench.

The next step of the Burning Bench development will be focus on the soot characterization by using the gravimetric impactor (PM10 and PM 2,5 distribution). In addition, the new tests will be conducted on samples of oil collected during weathering experiment in order to assess the "window of opportunity" of ISB according to oil nature.

In 2014, additional tests will be conducted at a larger scale in order to validate / correlate the results obtained at lab scale using the Burning Bench.

The following figure presents a mass balance calculation for a waxy crude oil before and after a burning test. The samples are analyzed by GCMS (abundance of saturates + aromatics fraction) and HPLC (SARA fractionation: Saturates Aromatics Resins Asphaltens). The results are expressed in Hopane Unit (used as internal conservative biomarker) in order to calculate the level of degradation of the oil.



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#### **ANALYSES OF BURN RESIDUE:** Mass balance calculation

After 15 minutes of burning, the results of chemical analyses show a degradation rate of 36% relatively to the initial oil. This rate is in the same range than the results (35%) obtained <sup>s</sup> by gravimetric analyses of the burn residue.

The burn efficiency appears low for a crude oil however this result is in good aggreement with published data of burning test conducted on a waxy crude oil (Fritt-Rasmussen, 2012). The SARA fractionation do not changed significantly between the two samples. Only a very slight increase of the polar fraction (asphaltens + resins) is observed for this type of oil.

#### **ANALYSES OF BURN RESIDUE:** *n*-alkanes / PAHs analyses

Samples of residue are analysed by GCMS (gas chromatography and mass spectrometry detection ) in SIM mode (Single Ion Monitoring) in order to characterize the n-alkanes and PAHs distribution. Analyses are also conducted in Scan mode in order to assess the whole degradation of the oil (see chromatograms). The following figures illustrate the degradation of the oil while subjected to burning for 15 minutes. Most of the lightest compounds are removed especially the naphtalenes family which is abundant in the fresh oil tested. More than 85% of the n-alkanes and PAHs compounds are removed during the burning.





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