

SUPPLEMENTARY DOCUMENT

Title: Experimental procedure for laboratory studies of *in-situ* burning – flammability and burning efficiency of crude oil

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S.1. Crude Oil Flammability Apparatus (COFA) (Figs. 1, 4 and S1)

The COFA is a stainless steel water basin of 1.0 x 1.0 x 0.50 m³ featuring two opposite walls with glass windows of 0.86 x 0.37 m² for additional observation capabilities of the oil-water interface. It stands on four stainless steel feet with a height of 0.26 m. The top edges of the COFA are extended to a width of 5 cm, so that extensions can be placed on the COFA such as the holder for the surface temperature thermocouples (Fig. 4). An inlet connection for water is attached to one of the metal side walls near the bottom plate and a drain is attached to the bottom plate.

The exhaust hood directly above the COFA has an intake area of 1.5 x 1.5 m² and is placed on four legs of 0.07 x 0.07 x 2.05 m³. The exhaust area is located 2.3 m above the bottom of the COFA and has an area of 0.50 x 0.16 m². Air is extracted with a velocity of 6.8-8.4 m/s or 8.4-10.4 m/s (higher velocities are used for more sooty fires) and the combustion gases are discharged through a connected exhaust duct with a diameter of 0.21 m.

The infrared (IR) heaters that are used in the COFA for the surface temperature upon ignition are modified versions of the standard M110 modules provided by their manufacturer (see the Materials/Equipment table). These heaters consist of two short wave twin tube emitters (heating elements) with a total radiative power of 1.9 kW and a heated length of 0.20 m. The backside of these heating elements is coated with a thin gold layer to redirect radiation towards the front of the heater and as such amplify the effective output of the heaters. The temperature of this part of the heating element should not exceed 500 °C in order to preserve its gold layer. In the original design, the casing and heating elements are cooled by a fan that sucks in cold air from the back of the heater and blows it through the heater in the same direction as the heating direction. In order to avoid the air flow from the cooling fan from

reaching the oil surface, a custom-made water-cooled holder was designed for the two heating elements. This water-cooled holder functions as an alternative cooling method for the heating elements while blocking the air flow from the fan. A schematic overview of the modified heaters is shown in Fig. 3S.

Water is pumped through the IR heaters using an aquarium pump (with an adjustable flow) in a basin with at least 20 L of water. The pump and IR heaters are connected with plastic tubes with an internal diameter of 4-10 mm. At maximum power, the gold-coated backside of the heating elements should stabilize at a maximum temperature of about 450 °C and the water flow should be calibrated accordingly. To calibrate the cooling of the IR heaters, place the heaters in an initial position in the COFA (*i.e.* opposite of each other and approximately 5 cm from the Pyrex glass cylinder as in Step 8.1). Place a 1 mm thick K-Type thermocouple between the backside of each heating element and the water-cooled holder and connect the thermocouples to a data logger. Start the data logger, turn on the pump and turn on the IR heaters. Carefully increase the power output percentage while monitoring the temperature of the heating elements. If the measured temperatures reach above 450 °C, turn down the power output of the IR heaters, increase the water flow and start increasing the power output of the IR heaters again. Once the backsides of the heating elements reach a stable temperature of 450 °C for at least 15 minutes at maximum power, the corresponding water flow is the calibrated flow that should be used during all experiments. It should be noted that the front of the heating elements may be much hotter than its backside (> 600 °C). Ensure therefore that the glass type of the heating elements is resistant to high temperature gradients.

In the COFA setup, each IR heaters is, through its custom-made housing, attached to a stainless steel tube of 0.03 x 0.03 x 0.40 m³. The angle between the IR heater clamp and its connected tube is fully adjustable so that the IR heater can be placed to face the Pyrex glass cylinder from any angle between 0-90 °. Each stainless steel tubes slides into another stainless steel tube of 0.04 x 0.04 x 0.20 m³ that is attached to a metal foot, which is placed freely in the COFA. The height of the tube attached to the heater clamp inside the other tube is freely adjustable, so that the distance between the metal foot and IR heater can be varied between 0.40-0.60 m. This highly flexible setup for the IR heaters relative to the Pyrex glass cylinder is an important feature of the COFA because it is used to ensure an incident heat flux to the oil surface that will result in ignition.

S.2. Cone heater with gas analyzer (Figs. 2, 3 and S2).

The cone heater that is used in Steps 5-7 is a standard mass loss calorimeter, as described in ISO 17554¹, apart from the custom-made circular sample holder (Fig. 3). The full cone setup (Fig. 2) is placed on a 0.90 m high table under the exhaust hood. The exhaust hood used in connection with the cone setup has an intake area of 2.6 x 2.6 m² and is placed on four legs of 0.10 x 0.10 x 2.0 m³. The exhaust area is located at a height of 3.4 m from the floor in the center of the hood and is connected to an exhaust duct with a diameter of 0.315 m. Air is extracted with a velocity of approximately 6 m/s. The exhaust duct is equipped with a duct insert that includes the sampling probes, pressure transducer, thermocouples and a laser (which are part of the gas analyzer) at a distance of 3.26 m from the duct inlet. In addition to measuring the O₂, CO₂ and

CO concentrations in the exhaust gases, the duct insert is used to measure the temperature of the exhaust gases and the pressure difference created by the suction of the hood. An additional, separate thermocouple was suspended in the air in the laboratory to measure the ambient temperature. These six measurements are used to calculate the heat release rate as described below. More details on the gas analyzer can be found in ISO/TR 9705-2².

S.3. Calculation method for the heat release rate based on O₂, CO₂ and O₂ concentrations.

The calculation method for the heat release rate as described by Janssens³ was used to obtain the shown heat release rate results in Fig. 8. This method has also been included in ISO/TR 9705-2². Here, a concise overview of the assumptions and equations from Janssens³ is given that can be used to calculate the heat release rate based on the acquired data from the gas analyzer. For a more detailed discussion of this method, see Janssens³.

The following equations are used, in order, to calculate the heat release rate. A description of all the terms and symbols in these equations, including relevant assumptions and the acquisition methods, is provided below.

$$\dot{m}_e = \frac{A \cdot k_c}{f(RE)} \sqrt{\frac{\Delta p}{T_e}} \quad (S1)$$

$$\ln(p_s) = 23.2 - 3816/(-46 + T_a) \quad (S2)$$

$$X_{H_2O}^\circ = \frac{RH \cdot p_s}{100 p_a} \quad (S3)$$

$$M_a = M_{dry}(1 - X_{H_2O}^\circ) + M_{H_2O} \cdot X_{H_2O}^\circ \quad (S4)$$

$$\phi = \frac{X_{O_2}^{A^\circ}(1 - X_{CO_2}^A - X_{CO}^A) - X_{O_2}^A(1 - X_{CO_2}^{A^\circ})}{(1 - X_{O_2}^A - X_{CO_2}^A - X_{CO}^A)X_{O_2}^{A^\circ}} \quad (S5)$$

$$\dot{q} = \left[E\phi - (E_{CO} - E) \frac{1 - \phi}{2} \frac{X_{CO}^A}{X_{O_2}^A} \right] \frac{\dot{m}_e}{1 + \phi(\alpha - 1)} \frac{M_{O_2}}{M_a} (1 - X_{H_2O}^\circ) X_{O_2}^{A^\circ} \quad (S6)$$

In Eq. (S1), the area of the duct (A) is 0.078 m², the velocity profile shape factor (k_c) was assumed to be 0.9 (*i.e.* close to unity) and the Reynolds number correction ($f(RE)$) is taken as 1.08. The pressure difference (Δp) is measured in volt by the pressure transducer in the duct insert and converted to pascal by using the calibration points that are provided by the manufacturer. Finally, the temperature of the exhaust gases (T_e) is directly measured by a thermocouple in the duct insert.

The saturation pressure (p_s) in Eq. (S2) is calculated based on a set of constants and the measured ambient temperature (T_a). This number is then used in Eq. (S3) to calculate the mole fraction of water in the ambient air ($X_{H_2O}^\circ$), in combination with the relative humidity (RH) and

the ambient pressure (p_a), which is taken as 101,325 Pa (1 atm). The relative humidity (in %) is typically obtained through a weather forecast and was taken as 60% for the data shown in Fig. 8. It should be noted that the Eq. (S6) is very insensitive towards the relative humidity and that the accuracy of the weather forecast is thus insignificant with respect to the final calculated heat release rate. The molar mass of the ambient air (M_a) in Eq. (S4) can then be calculated by taking the molar masses for dry air (M_{dry}) and water (M_{H_2O}) as 29 and 18 kg/kmol, respectively.

The calculation method for the oxygen depletion factor (ϕ) depends on which gas concentrations in the exhaust gases are measured by the gas analyzer. For gas analyzers that measure O_2 , CO_2 and CO , the oxygen depletion factor is calculated with Eq. (S5). In this equation, $X_{O_2}^{A^\circ}$ and $X_{CO_2}^{A^\circ}$ are the measured molar fraction of oxygen and carbon dioxide, respectively, in the ambient air. This measurement is typically obtained at the start of an experiment between the period that the data logger is started and the crude oil sample is actually subjected to incident heat flux from the cone heater. The remaining terms in this equation consist of the measured concentrations of O_2 , CO_2 and CO in the exhaust gases during the experiment ($X_{O_2}^A$, $X_{CO_2}^A$ and X_{CO}^A , respectively).

The heat release rate (\dot{q}) can then be calculated with Eq. (S6), based on the calculated terms in the previous equations and a set of constants. The used calculation method assumes a constant value for the net heat release rate per unit mass of oxygen consumed (E) and for the net heat release rate per unit mass of oxygen consumed for the combustion of CO to CO_2 (E_{CO}). These values are taken as 13,100 and 17,600 kJ/kg of O_2 , respectively. The combustion expansion factor (α) is taken as 1.105. By calculating the heat release rate for all measurements taken during the experiment, the heat release rate is as such calculated as a function of time, as shown in Fig. 8.

FIGURE AND TABLE LEGENDS:

Figure S1. Photos of the COFA setup (top left), a close-up view of the Pyrex glass cylinder with the water surface approximately 1 cm below the cylinder edge (top right), the COFA setup including two unmodified IR heaters, the spark igniter and the thermocouples to measure the surface temperature of the oil (bottom left) and a close-up of the spark igniter and thermocouples above the Pyrex glass cylinder (bottom right). These photos are intended to give a visual impression of the experimental setups and cannot be used as a replacement of the setup schematics (Figs. 1 and 4)

Figure S2. Photos of the plastic container including the O-ring for the evaporative weathering of crude oil (top left, Step 2), an overview of the cone setup featuring the control unit, cone heater, sample holder, water cooling reservoir and peristaltic pump (top right), close-up of the cone heater with the sample holder (bottom left) and a close-up of the sample holder (bottom right). These photos are intended to give a visual impression of the experimental setups and cannot be used as a replacement of the setup schematics (Figs. 2 and 3).

Figure S3. Schematics of the modified IR heater showing a top view (top left), front view (bottom left) and the respective cross-section side views (right).

REFERENCES

- 1 ISO 17554:2014(E) Reaction to fire tests – Mass loss measurement. 28 (International Organization for Standardization, Geneva, 2014).
- 2 ISO/TR 9705-2:2001(E) Reaction-to-fire tests – Full-scale room tests for surface products – Part 2: Technical background and guidance. 39 (International Organization for Standardization, Geneva, 2001).
- 3 Janssens, M. L. Measuring Rate of Heat Release by Oxygen Consumption. *Fire Technol.* **27** (3), 234-249, doi:<http://dx.doi.org/10.1007/bf01038449>, (1991).