



Table 2. NFPA fire hazard classification of fluids [2,8]

Fluid classification	Sub-category	Hazard rating	Criteria, °C
Flammable (Class I) $T_f < 37.8$ °C	IA	4	$T_b < 37.8$ ; $T_f < 22.8$
	IB	3	$T_b \geq 37.8$ ; $T_f < 22.8$
	IC	3	$22.8 \leq T_f < 37.8$
Combustible $T_f \geq 37.8$ °C	II	2	$37.8 \leq T_f < 60$
	IIIA	2	$60 \leq T_f < 93.4$
	IIIB	1	$T_f \geq 93.4$

When the flammability characteristics cannot be determined experimentally, empirical equations for their determination are available [1].

The flash point increases almost linearly with the normal boiling point of the molecule. This linear relation is observed for all the different classes of hydrocarbons including paraffins, olefins, naphthenes and aromatics. Based on that observation a rough estimation of the flash point of hydrocarbons can be obtained using the following linear equation (Bodhurtha, cited in [1]):

$$T_f = 0.683 \cdot T_b - 71.7 \quad (1)$$

where both the flash point,  $T_f$ , and the boiling point,  $T_b$ , are in °C.

Other correlations that relate the FPT of various organic compounds with the boiling point have been developed for estimation of the flash point. Riazi and Daubert (cited in [1]) proposed the following equation for pure hydrocarbons and petroleum fractions:

$$1/T_f = -0.014568 + 2.84947/T_b + 1.903 \cdot 10^{-3} \ln T_b \quad (2)$$

where both the flash point,  $T_f$ , and the boiling point,  $T_b$ , are in °R.

The Patil's correlation (cited in [1]) which is reported to predict the flash point of organic compounds with a correlation coefficient of 0.9 has the following form:

$$1/T_f = -4.656 + 0.844 \cdot T_b - 0.234 \cdot 10^{-3} T_b^2 \quad (3)$$

where both the flash point,  $T_f$ , and the boiling point,  $T_b$ , are in Kelvin.

Satyanarayana and Kakati (cited in [1]) improved the above correlations by introducing the specific gravity as an additional correlating parameter as follows where  $T_f$  and  $T_b$  are in °C:

$$T_f = -83.3362 + 0.5811 \cdot T_b + 0.1118 \cdot 10^{-3} / T_b + 38.734 \cdot \gamma \quad (4)$$

A rough estimation of the lower flammability limit (LFL) in air, Figure 1, may be obtained using the following rule of thumb relation developed by Spakowski (Bodhurtha and Crowl & Louvar, cited in [1]):

$$LFL = -4354 / \Delta H_{comb} \quad (5)$$

where  $\Delta H_{comb}$  is the standard upper heat of combustion in kJ/mol and LFL is in volume percent.

Another rule of thumb relations for the flammability limits in air are those of Jones (Bodhurtha and Crowl & Louvar, cited in [1]):

$$LFL = 0.55 \cdot C_{est} \quad (6)$$

$$UFL = 3.5 \cdot C_{est} \quad (7)$$

where  $C_{est}$  is the stoichiometric concentration of the flammable product for complete combustion in air, and UFL is the upper flammability limit (UFL), Figure 1. This rule of thumb relationship between UFL and LFL with the stoichiometric ratio shows a greater reliability in the lower limit estimation while significant errors are observed in the values of the upper limits (Santamaria-Ramiro & Braña-Aisa, cited in [1]). Furthermore, the above relations are only approximate and fail with low molecular weight compounds (Sheldon, cited in [1]) which demonstrates the need for more accurate prediction methods.

## 2. Flash point measurement

Flash point is used in transportation and safety regulations to define flammable and combustible liquids [6]. Usually, flash point is mea-

sured in air. Typically, flash points are measured using standardized testing methods in either open cup (ASTM D92) [5] or closed cup (ASTM D93) [2,5] testers. To measure the flash points of some flammable liquids in air and oxygen an "equilibrium closed bomb" (ECB) apparatus was developed [6].

The ECB test apparatus (Fig. 2) is a cylindrical stainless steel vessel with an internal diameter of 67 mm and a depth of 122 mm. The internal volume of the apparatus is approximately 430 ml. The apparatus is placed in the liquid bath of a chiller/heater with an automatic temperature control. Three K-type thermocouples are used to measure the temperature of the liquid bath, the headspace of the bomb, and the liquid sample, respectively. A continuous electrical arc produced by a 10 kV, 2.5mA dc power source is used as the ignition source.

When conducting a flash point test, the temperature of the liquid bath is stabilized at a desired temperature. The bomb is purged thoroughly with the oxidant gas (dry air or oxygen) and the internal pressure is adjusted to slightly below one atmosphere. Then, a certain amount of sample is injected into the bomb to form a pool of sample at the bottom of the bomb. A sufficient period of time is allowed for the liquid-vapor system to reach equilibrium. As the sample temperature is stabilized, the pressure in the apparatus can be slightly higher than one atmosphere. Therefore, an exhaust valve is opened slightly as needed to adjust the pressure downward. A slight positive pressure is maintained in order to prevent air from entering the apparatus. Then, the ignition source is activated. If no ignition is observed, a second ignition is tried. Typically, the interval between the two trials is 30–40 s. If no ignition is observed in the second trial, the temperature is increased typically by 1–2°C and the ignition trials are repeated at the new temperature. If an ignition occurs, the temperature of the liquid is taken as the measured flash point. The pressure of the test atmosphere affects the measured flash point and the higher the pressure the higher the flash point. The effect of pressure on the measured flash point is

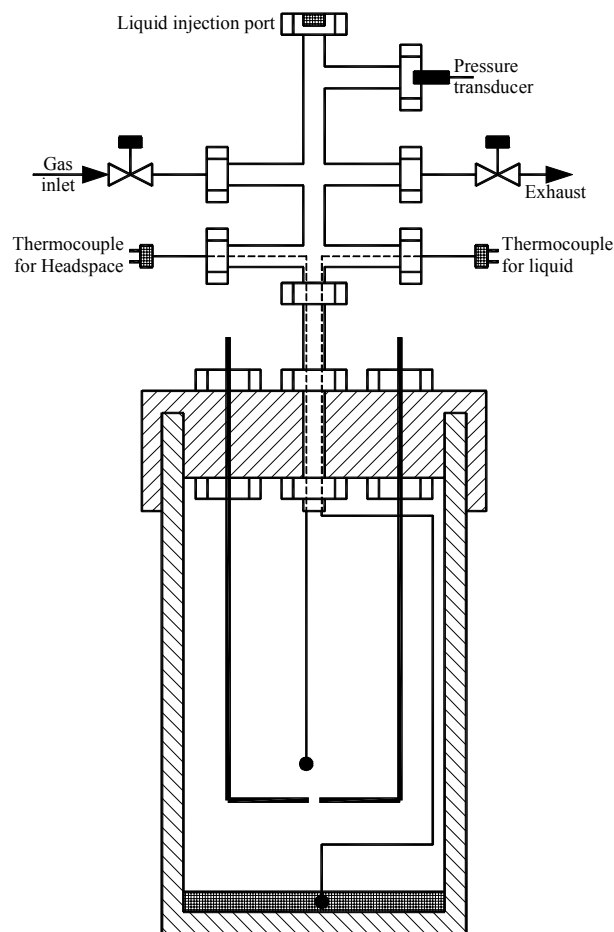


Figure 2. Equilibrium closed bomb apparatus [6].

corrected to atmospheric conditions (760 mmHg) using the following equation:

$$T_{f \text{ corrected}} = T_{f \text{ measured}} - 0.033 \times (p - 760) \quad (8)$$

where  $T_{f \text{ measured}}$  (°C) and  $T_{f \text{ corrected}}$  (°C) are the measured flash point at pressure  $p$  (mmHg) and the corrected flash point at 1 atm (760 mmHg), respectively.

### 3. Oxygen index method

To fully assess the fire hazards of hydraulic fluids requires a very wide ranging test programme [4]. Flame propagation on a fluid-soaked wick (ISO 14935) is a test based on the ignition of a fluid on an absorbent medium [3,4]. A pilot flame is then applied to the wick and removed. The propagation of the flame along the wick and the time required for self-extinguishment are reported as test results [3]. It has been of interest to establish the feasibility of evaluating the hydraulic fluid combustibility on the basis of the oxygen index, which has come into use in recent years in evaluating the combustibility of polymeric materials intended for various purposes [7]. The essence of this method is the determination of the minimum oxygen concentration that will support stable combustion of the material.

In [7], the oxygen index was determined in a unit that is shown schematically in Figure 3. The working chamber 2 is a length of 100 mm diameter heat-resistant glass. A calcined asbestos cord 3, 5-6 mm in length and 5 mm in diameter, is impregnated with the test fluid and fixed in the holder 1. By means of the reducing valves 7 and flowmeters 6, a mixture of nitrogen and oxygen of known composition is fed to the working chamber through the cap 5, which is designed to give complete mixing of the gases and uniformity of flow. The gas flow velocity in the working chamber was 3 cm/sec. This velocity was chosen experimentally, to remove the gaseous combustion products from the combustion zone on a continuous basis during the time of the test, but should not be so strong as to put out the flame when combustion is weak. Ignition of the fluid-soaked asbestos cord was accomplished by means of an electric coil 4 from the upper end of the cord, in such a manner that the flame could spread into the incoming gas stream.

The oxygen index (OI) was defined as the minimum concentration of oxygen (in %) that would give stable combustion of the liquid and propagation of the flame along the cord [7].

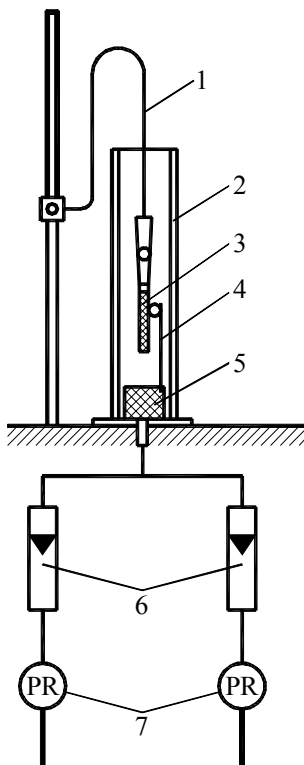


Figure 3. Unit for determination of oxygen index [7].

Fluids of various chemical compositions were tested. On the basis of the values obtained for the oxygen index [7], the tested fluids can be divided into three groups. Group I (OI = 16.8-17.4) consists of fluids based on mineral and synthetic hydrocarbons and esters of carboxylic acids (AMG-10, 7-50s-3, IPM-10). Group II (OI = 18.9-20) consists of polysiloxane fluids (KhS-2-1, FS-T-5, PMS-50, FM-1322). Group III (OI = 23.2-26) consists of phosphate-base fluids (NGZh-4, TBP, TCP).

Since air at atmospheric pressure contains about 21% oxygen, the fluids with OI = 21 do not support combustion under normal atmospheric conditions and do not propagate a flame when they are spilled. Such fluids are classed in Group III. The data indicate that the oxygen index can be used to establish the dependence of combustibility on the chemical nature and molecular structure of the fluid. It can be stated that the use of the method for determining the OI, when used to supplement the present methods for determining the flammability of fluids, permits a more thorough and objective evaluation of the fire hazard of these fluids by means of laboratory tests [7].

### 4. Manifold ignition test

The International Standard ISO 20823:2003(E) specifies a test method to determine the relative flammability of fluids when contacted with a hot metal surface at a fixed temperature, but it is also possible to gauge fluid ignition temperatures by adjustment of the manifold temperature [9]. In principle, a 10 ml test portion of fluid is dropped from a predetermined height and at a specified rate, onto a tube heated to 700°C, or another temperature in a series. The resulting spray is examined for flash or burn, both on the tube and after dripping from the tube.

Basically, the Standard ISO 20823:2003(E) is to determine the flammability characteristics of fluids as petroleum and related products [9]. Since the test temperature is 700°C, the test can be extended to engine compartment fluids (motor oils, transmission oils, break fluids, windshield washers) [2], as the exhaust valves are operating under arduous conditions with temperatures rising above 800°C [10]. In this way, the manifold ignition test can be used to assess the passenger survivability in vehicle crash fires.

The manifold test rig consists of a heated simulated manifold supported in a box frame, as is illustrated in Figure 4. The box frame is a sheet metal box of dimensions 300 mm x 300 mm x 450 mm, open at the top and front. The simulated manifold is constructed from corrosion-resistant steel tubing of 75 mm nominal outside diameter, 1 mm wall thickness and 500 mm in length. The exterior of the tube is sandblasted. A corrosion-resistant steel rod, 3 mm in diameter and 250 mm in length, is tack welded to the exterior surface of the tube such that the major axes are parallel, and the mid-point of the long axis of the rod corresponds to that of the tube. Holes of 78 mm nominal diameter are cut in the sides of the box frame in such a position that the simulated manifold is positioned and supported so that its major axis is held at an angle of 7° to the horizontal, and the centre-point of the manifold is 270 mm above the surface of the drip tray or bottom of the support. The bottom of the box contain a separate drip tray for all drips of liquid falling from the manifold.

A heating element is mounted centrally within the manifold tube by means of suitable washers constructed from thermal insulation material. The element is capable of heating and maintaining a temperature of 700°C ± 5°C on the exterior surface of the manifold tube over the central portion of approximately 305 mm of the tube, whilst the enclosure ventilation is switched on.

Temperature sensors are mounted in contact with the manifold tube surface in order to monitor the temperature close to the expected point of impact of the fluid. Each sensor is connected to a temperature indicator.

A fluid dispenser device, mounted vertically at 300 mm above the centre-line of the manifold [11], can measure 10 ml ± 0.5 ml of fluid and dispense it at a controlled and constant rate over 50 s ± 10 s. The dispenser is mounted on a positioning device that allows measured movements horizontally along the axis of the tube and parallel to it.

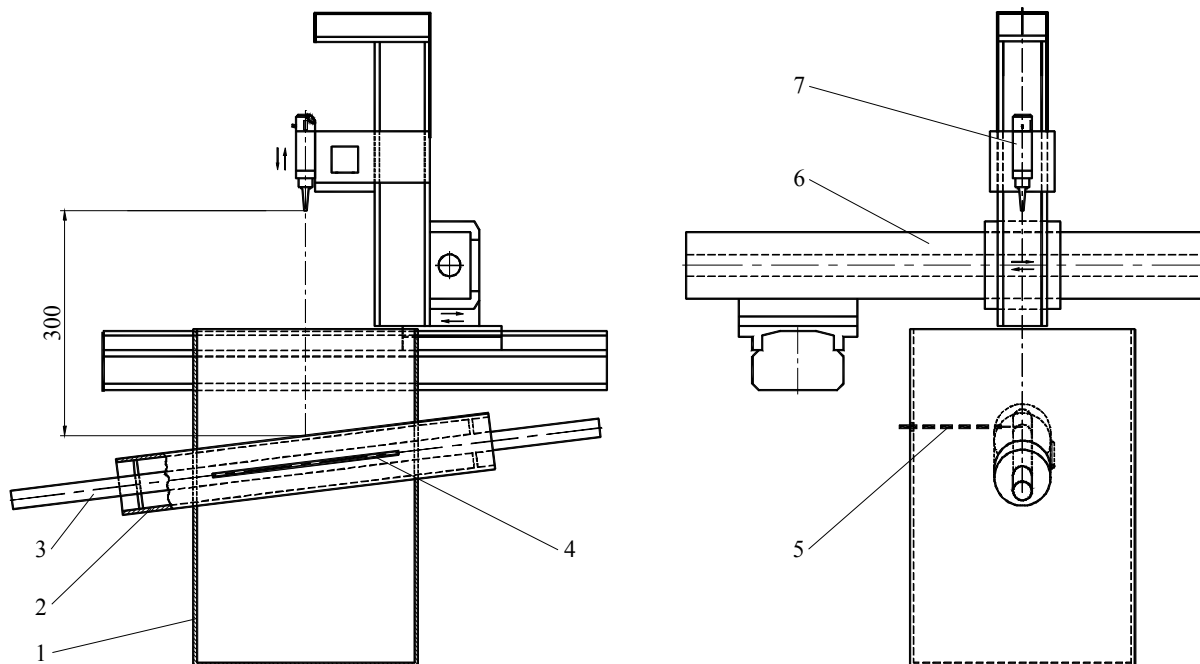


Figure 4. Manifold test rig: 1- sheet metal box; 2-simulated manifold tube; 3- heating element; 4-rod; 5-thermocouple; 6-3D positioning device; 7-dispenser [11].

The simulated manifold test procedure starts with the manifold tube equilibrated at 700°C. Then, the tested fluid at 20°C to 25°C is dispensed onto the tube at a constant rate so that the 10 ml test portion is expelled in 40 s to 60 s.

Since three repeat tests are to be carried out on a single cleaned tube portion, the procedure starts at the lowest position on the tube and move upwards. Then, the test is repeated twice more at the same temperature at new positions on the tube, each at least 50 mm higher up the tube from the previous contact area.

The behaviour of the fluid both on the surface of the tube and as it drips from the rod into the tray below is observed, and any flashes or burning on the tube or when collected in the tray below are recorded. The test is repeated twice more at the same temperature by following the procedure at new positions on the tube, each at least 50 mm higher up the tube from the previous contact area.

The results are reported in one of the following categories:

- a) "I(T)" when the fluid flashes or burns on the tube, but does not continue to burn when collected in the tray below;
- b) "I(D)" when the fluid flashes or burns on the tube, and continues to do so when collected in the tray below;
- c) "N" when the fluid does not flash or burn at any time. Category "N" may also be described as "pass".

#### 4. Conclusions

The flash point and combustibility of some flammable liquids in certain conditions can be determined by using two unstandardised testers and methods.

The equilibrium closed bomb apparatus provides reliable and accurate flash point data for various oxidant atmospheres for those materials whose flash points may not be able to be measured using other closed cup methods due to the quenching effects of the small vessel diameter on flame.

The method for determining the oxygen index, when it is used to supplement the present methods for determining the flammability of fluids, permits a more thorough and objective evaluation of the fire hazard of these fluids by means of laboratory tests.

The designed manifold test rig (according to ISO 20823:2003) is to determine the relative flammability of fluids when contacted with a hot metal surface at a fixed temperature, but it is also possible to gauge fluid ignition temperatures by adjustment of the manifold temperature.

#### 5. Acknowledgements

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