

THE DILUTION OF FLAMMABLE POLAR SOLVENTS BY WATER FOR SAFE DISPOSAL*

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Summary

The theory predicting the 'Closed-up' flashpoint of polar solvents diluted with water is used to estimate the quantities of water required to render safe spillages of these solvents.

Introduction

Flammable water-miscible (polar) solvents form an important group of feedstocks for the chemical industry and are commonly transported by road in tankers and drums. Amongst the most frequently transported materials [1] are:

ethyl alcohol
methyl alcohol
acetone

The labelling of road tankers conveying hazardous substances has been the subject of a voluntary scheme since mid-1975 [16,17]. However such labelling is due to become the subject of legislation during 1978 [18]. Included with the Regulations will be a schedule of those materials to which the Regulations will apply, together with their 'Hazchem' code indicating the action to be taken in an emergency.

Spillages of flammable solvents in general both on roadways and the plant are dangerous incidents. Those involving polar solvents are more so in certain important respects.

The management of a flammable solvent spillage depends on the circumstances surrounding it. Two main types of spillage can be identified. The first is when the spillage has ignited and the second when ignition has not yet taken place.

The control and extinction of ignited spillages is often attempted by the use of foam. The range of normal foams, protein, fluoroprotein, 'AFFF' and

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medium and high expansion foams can be applied to non-polar solvents, but polar solvents can break down all these foams thus necessitating much higher rates of application than might be available and extinction may well not be achieved. Special 'alcohol resistant' or 'all purpose' foams are available for use on polar solvents; even these require high application rates for extinction.

If a spillage which has not yet been ignited is contained then its ignition and the spread of flammable vapours can be prevented by a covering of suitable foam. The considerations described above for the ignited spillage also apply in this case. If the unignited spillage is flowing into, say, a sewer or drain then an especially hazardous situation arises. Non-polar solvents can spread extensively in the drainage system especially if it contains water on which the solvent can float. Solvent vapour can percolate even further. The injection of foam into the sewer can alleviate the situation but the drainings from the foam can have the opposite effect. Foams containing little water such as high expansion foam have been used successfully in this type of situation.

In the case of polar solvents, the 'alcohol resistant' foams in addition to forming a layer of foam on the solvent surface have the advantage that the drainings will dilute the solvent and raise its flash point, and also lower its temperature should the solvent be hot.

In all the situations mentioned above water can be usefully applied to and mixed with polar solvents. However, although water is usually plentiful, the amounts required to achieve extinction or prevent ignition can be large and may cause a contained spillage to overflow. Provided that an adequate ratio of water to solvent is maintained, the flow of diluted solvent can be rendered non-flammable. Whereas non-polar solvents often require removal by pumping away, polar solvents, can be safely flushed into drainage systems, if the dilution is adequate.

This paper gives a theory describing how the flashpoint of mixtures of polar solvents with water increases with the amount of added water, and shows that the theory is supported by measurements. The amounts of water required to render safe spillages of flammable polar solvents are then calculated for two different conditions.

Theory of flashpoint of diluted solvents

In previous papers [2,3] a general theory was developed relating the flash points of mixtures of flammable and non-flammable liquids to their composition.

It was shown, as the general case, that:

$$\alpha_f \sim x_f = \frac{p_a^0 + kLP_T}{p_a^0 + k p_f^0} \quad (1)$$

For water (vapour) fuel systems k is relatively large (see Table 1) i.e. water has a low flame suppressing effect in the vapour phase compared with say

TABLE 1

Some values of k for water/fuel systems

| Fuel | k |
|----------|-----|
| Methanol | 70 |
| Ethanol | 40 |
| Methane* | 28 |

*Mixtures with water vapour.

halons. For the systems under consideration water is less volatile than the fuels,

$$\therefore RLP_T \gg p_a^0 \text{ and } kp_f^0 \gg p_a^0$$

and eqn. 1 reduces to

$$\alpha_f = \frac{L P_T}{p_f^0} \quad (2)$$

An alternative, explicit, equation to eqn. 2 can be derived by taking logs of eqn. 2 and differentiating with respect to T . Using the Clausius—Clapeyron equation,

$$\frac{d \ln p_f^0}{dT} = \frac{\Delta H_f}{RT^2}$$

and integrating, with rearrangement, gives:

$$1/T_m = 2.303 R/\Delta H_f \log \alpha_f + 1/T_f \quad (3)$$

A similar equation has been derived by Uehara [4]. Using eqns. 2 and 3 with the value of the various constants given in Table 2, theoretical correlations for methanol, ethanol and acetone solutions in water are shown in Figs. 1, 2 and 3 respectively together with experimental values of flash point measured by 'closed cup' methods [2, 4–6].

TABLE 2

Values of constants used in eqns. 2 and 3

| Fuel | T_f (°C) | L (% v/v) | ΔH_f (J mol ⁻¹) |
|----------|------------|-------------|-------------------------------------|
| Methanol | 11 | 7.5 | 3.82×10^4 |
| Ethanol | 13 | 4.0 | 4.23×10^4 |
| Acetone | -18 | 3.0 | 3.28×10^4 |

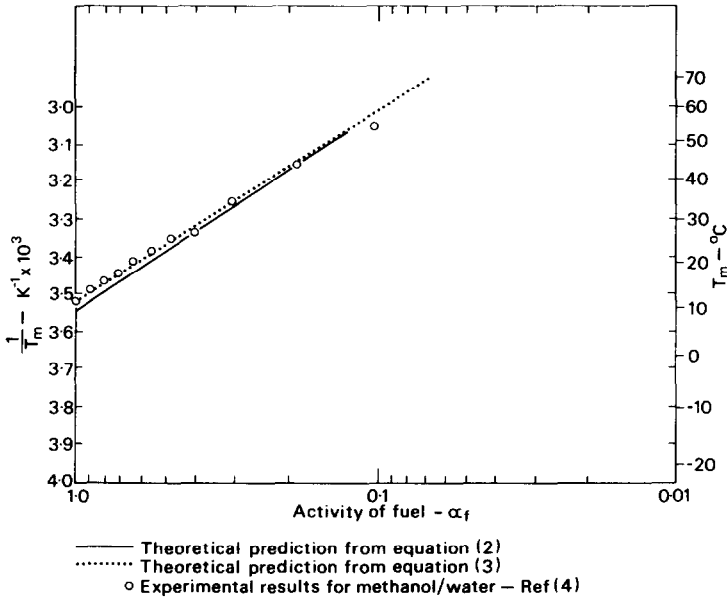


Fig. 1. Flash point—composition correlation for methanol—water mixture.

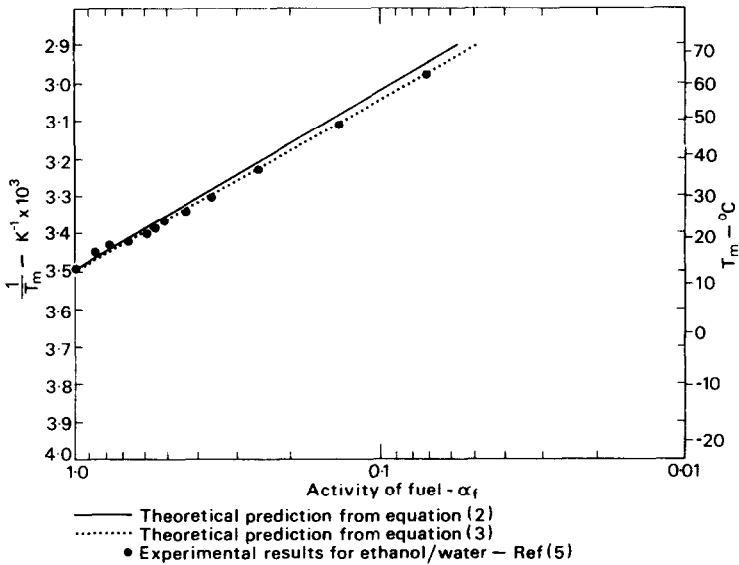


Fig. 2. Flash point—composition correlation for ethanol—water mixture.

Practical application

Figures 1, 2 and 3 have been replotted in Figs. 4, 5 and 6 to show the practical implications of the results. The number of volumes of water added per unit volume of solvent is plotted against the flash point of the diluted fuel.

Mixtures above the flash point curve present an ignition hazard; mixtures below it are safe. From these charts it is possible to read off the amount of dilution necessary to render a spillage non-flammable or to extinguish a contained fire.

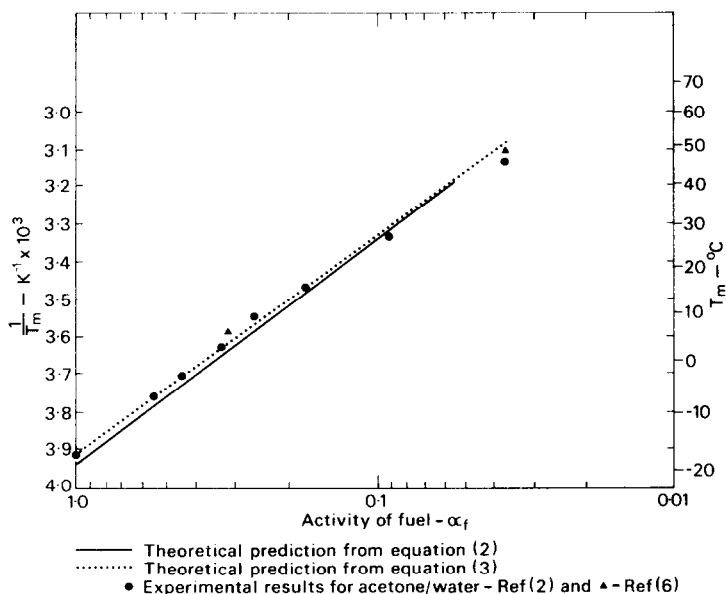


Fig. 3. Flash point—composition correlation for acetone—water mixture.

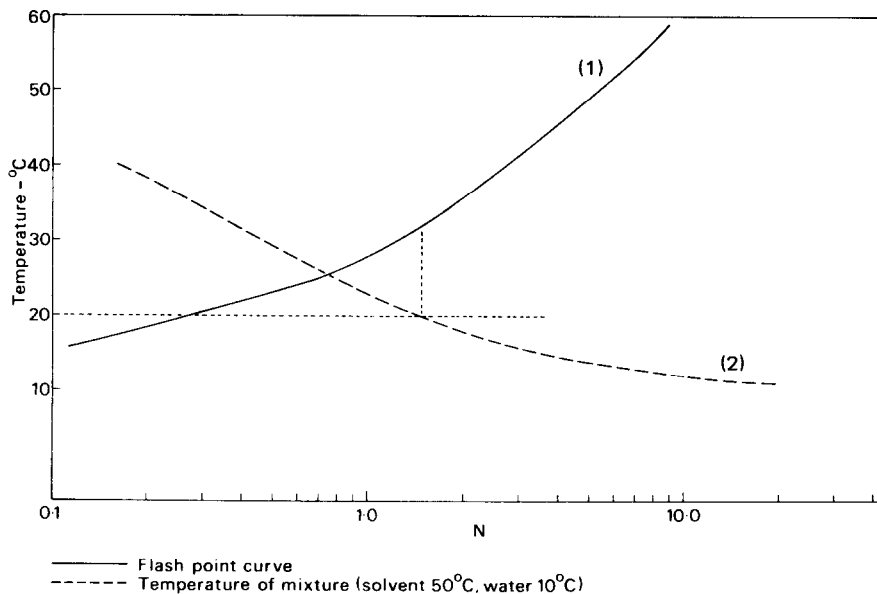


Fig. 4. Dilution of methanol by water.

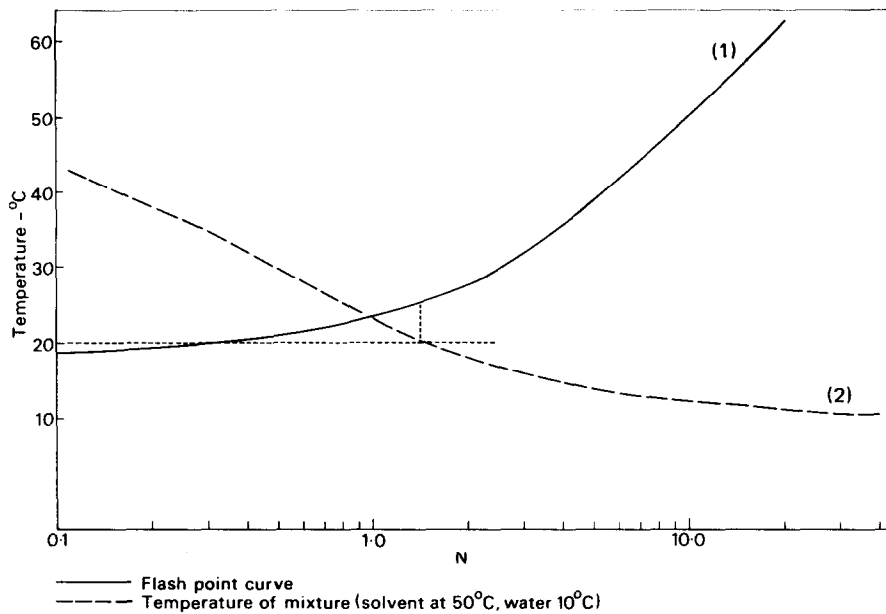


Fig. 5. Dilution of ethanol by water.

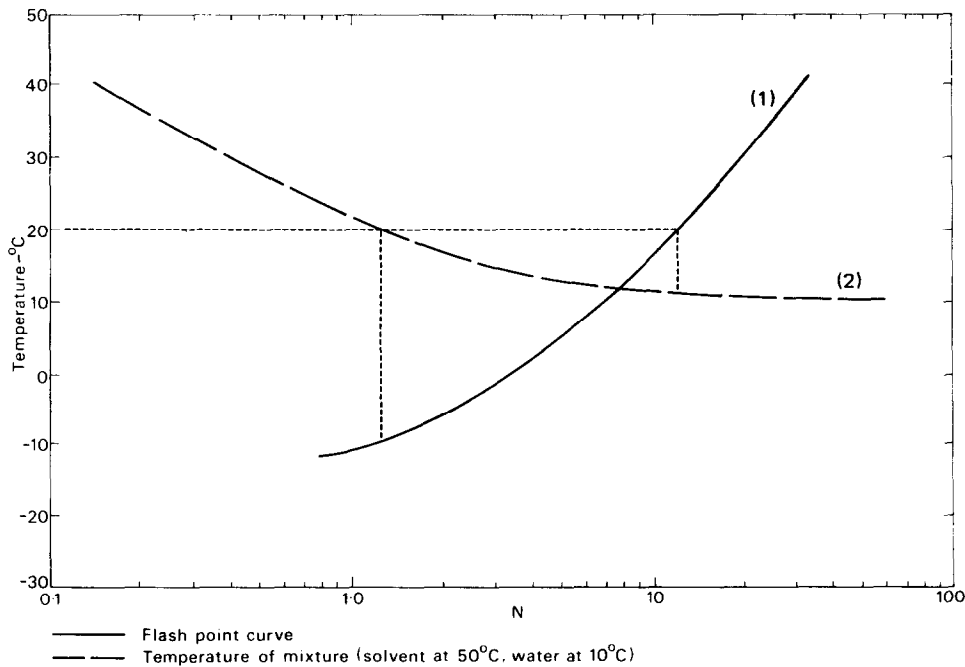


Fig. 6. Dilution of acetone by water.

In these figures two situations have been plotted. The first is the straightforward case where both the solvent and the water are at the same temperature, say 20°C. From the curves the amounts of water required have been read and are shown in Table 3.

TABLE 3

Amount of water N , (at 20°C) required to dilute solvent (at 20°C) to a mixture flash point of 20°C

| Solvent | N |
|----------|------|
| Methanol | 0.28 |
| Ethanol | 0.30 |
| Acetone | 12 |

Many chemical processes are carried out with heated reactants and the second case considered is where the solvent is at an arbitrary temperature of 50°C and the water is at a mains temperature of 10°C. The following values of specific heats were used [7]: methanol, 0.61 cal g⁻¹ °C⁻¹; ethanol, 0.6 cal g⁻¹ °C⁻¹, acetone, 0.535 cal g⁻¹ °C⁻¹. These being the values at the mean of the temperature range considered. It has been assumed that there is no heat of dilution.

On the graphs curve 2 represents the temperature of the diluted solvents. Points on curve 2 which lie below curve 1 correspond to mixtures which are cooler than the flash point and are unignitable. Similarly points on curve 2 which lie above curve 1 correspond to mixtures whose temperature is above the flash point and are therefore ignitable.

In order to provide a comparison with the first case the amounts of water required to dilute the solvents to 20°C have been read off and are shown in Table 4. The flash points of these diluted mixtures is also shown in the Table 4.

In the cases of methanol and ethanol the diluted mixtures have flash points

TABLE 4

Dilution of solvent (at 50°C) by water at 10°C

| Solvent | N_1 for mixture temp. = T_m | T_m at N_1 (°C) | N_2 for mixture temp. = 20°C | T_m at N_2 (°C) |
|-----------|---------------------------------|---------------------|--------------------------------|---------------------|
| Methanol | 0.74 | 25.5 | 1.4 | 32 |
| Ethanol | 1.0 | 23.5 | 1.45 | 25.5 |
| Acetone * | 7.8 | 12 | 1.2 | -9 |

*In order to dilute acetone to a flash point of 20°C, $N = 12$. The resulting mixture temperature is 11°C, c.f. Table 3.

greater than 20°C and are therefore unignitable. Acetone is a special case, the diluted mixture at 20°C is still ignitable, having a flash point of -11°C. In order to render the mixture unignitable more water must be added until curves 1 and 2 cross at a mixture temperature of 12°C. This is still not a safe condition if ambient conditions are such as to allow the mixture to warm up to the arbitrary reference temperature of 20°C. Even more water must be added until the mixture has a flashpoint of 20°C (as in the first case); the temperature of the diluted mixture then being 11°C.

There are practically no data available in the literature on fire points of diluted fuels. However, Burgoyne et al. [13] have reported that the concentrations of acetone in an aqueous solution should not exceed 10 per cent w/w (12.3 per cent v/v) if ignition of bulk liquid was to be avoided. This concentration of acetone corresponds to a dilution expressed as *N*, of 7.1. The flashpoint of this mixture is 10.5°C (from Fig. 6), compared with the reported fire point of 15°C.

Discussion

Although the water requirements described in this paper have been calculated on the bases of dilution to below the closed-up flashpoint of the diluted fuel; strictly speaking it is the 'fire point' of the diluted fuel which should be used as a basis for calculating extinguishing quantities of water.

Although fire point has long been recognised as a property of a liquid fuel [10] and a method for its measurement described* very few measurements even of pure liquid fuels have appeared in the literature, specified accurately enough to be of direct use. Fire point is generally thought to be 'a few degrees above the flashpoint'. The significance of 'open cup' flashpoint has been discussed [11] and as a result the following order of the three quantities might be expected:

Closed Cup Flash Point < Open Cup Flash Point < Fire Point

Reported measurements [8] of fire point of single component fuels have been compared with literature values of open-cup flash point [9] and closed-cup flash point [9] and are summarised in Table 5. The expected order is confirmed, and in all cases there is a substantial difference between the fire point and the closed cup flash point.

Roberts and Quince [8] observed anomalous behaviour with three hydrocarbons in that two distinct fire points, one of them transient, were observed. This behaviour was not repeated with three monohydric alcohols. The authors reported the ratio of the vapour pressure of the fuel at the fire point, the transient one in the case of the hydrocarbons, to that corresponding to the stoichiometric mixture. For the monohydric alcohols the mean of the ratio was 1.41, + 3.5 per cent, - 5.5 per cent. The ratio of the other fuels was in the range 1.39 to 1.92.

*Flash point (open) and fire point by means of the Pensky—Martens Apparatus [12a]; flash and fire points by Cleveland Open Cup [12b].

If the assumption is made that the ratio for $p_{\text{fire}}^0/p_{\text{stoich}}^0$ of 1.41 can be applied to the fuels of present interest then from known vapour pressure data their fire points can be calculated. This has been done and the results compared with 'closed' [2] and 'open' [9] flash points in Table 6.

Common experience suggests that these estimated fire points may be high. At present therefore, in view of the lack of sufficient experimental data on fire points not only for undiluted liquid fuels but also for liquid fuels containing additives, safe conditions should be achieved if the fuel is diluted to the closed-cup flash point. Graphs such as are shown in Figs. 4, 5 and 6, enable the necessary quantities of water to be estimated for a range of conditions.

In the absence of experimental data, N can be calculated using eqn. 3, which is the better of the correlating equations. The following parameters need to be known.

- (1) The temperature of the spilt liquid.
- (2) The temperature of the diluting water (assumed to be about 10°C if it is taken from the fire main).
- (3) The specific heat of the spilt liquid (that for water is known).
- (4) The closed-cup flash point of the spilt liquid (T_f) values for many of the water miscible liquids listed [18] can be found in the FPA Booklet 24 [14] and also in the NFPA guide on hazardous materials [5] and the FMRC Handbook [9].

TABLE 5

Comparison of Flash Points with Fire Points

| Fuel | 'Closed' Flash Point (°C) (ref. 9) | 'Open' Flash Point (°C) (ref. 9) | Fire Point (°C) (ref. 8) |
|-------------------|--|--|--------------------------------|
| Decane | 43.8 | | 66 |
| Dodecane | 73.9 | | 103 |
| <i>m</i> -Xylene | 25 | | 44 |
| <i>n</i> -Butanol | 35 | 43.3 | 50 |
| iso-Pentanol | 43 | 46.1 | 57 |
| Benzyl Alcohol | 100.5 | 104 | 110 |
| Glycerol | 160 | 176.7 | 207 |

TABLE 6

Values of 'Closed' and 'Open' Flash Points and estimated Fire Points of undiluted fuels

| Fuel | Closed Cup Flash Point (°C) (ref. 2) | Open Cup Flash Point (°C) (ref. 9) | Estimated Fire Point (°C)* |
|----------|---|---------------------------------------|-------------------------------|
| Methanol | 11 | 16 | 26 |
| Ethanol | 13 | 22 | 30 |
| Acetone | -18 | -9 | -5 |

*Estimated from data in ref. 8.

- (5) The density of the spilt liquid (see FMRC Handbook [9], FPA Booklet 24 [14] and Chemical Engineers' Handbook [15]). (The density of water is known.)
- (6) The latent heat of evaporation of the spilt liquid (ΔH_f) (values can be found in source books of chemical data, e.g. Chemical Engineers' Handbook [7]. In the absence of data methods are available for estimating this quantity e.g. Trouton's rule.)
- (7) The activities (α) of the fuel and water in diluted mixtures. This requires data on activity coefficients; such data are less numerous but estimates can often be made by analogy or the mixtures can be assumed to be 'ideal'.
- Equation 2 is a less good correlation of the experimental data but its parameters are less numerous. The important quantities required are the lower limit of flammability of the flammable liquid vapour in air (L) and its vapour pressure at different temperatures. It should be noted that the lower limit (L) can be used to estimate the closed-cup flash point (T_f); the concentration of fuel vapour in equilibrium with the liquid fuel at its flash point (T_f) is equivalent to its lower limit (L).

Conclusions

A method has been described, in principle, for estimating the quantities of water required to dilute spillages of flammable water-miscible liquids in order to render them unignitable. Three commonly transported materials have been taken as examples. With both the liquid and water at 20°C the following quantities of water are required to dilute 100 litres of spilt liquid so that the risk of ignition is avoided:

| | |
|----------------|-------------|
| methyl alcohol | 28 litres |
| ethyl alcohol | 35 litres |
| acetone | 1200 litres |

Less water would be required to extinguish a burning spillage, by dilution, but the above quantities should be applied in order to prevent reignition. However if the bulk liquid temperature has increased during the fire, then additional water would be required.

The 'Hazchem' markings specified for the above liquids allow the two alcohols to be flushed to drain. In practice, considerably more water might be required than those quantities indicated in this paper, in order to satisfy Water Authority requirements. The 'Hazchem' marking for acetone requires a spillage to be contained. The amount of water required to render a large spillage unignitable may present practical problems in this respect.

List of symbols

C_{st} Stoichiometric mixture of fuel vapour in air expressed as mole (volume) fraction.

| | |
|-----------------------|--|
| k | Slope of the lower limit limb of a flammability diagram $k = y_a/(y_f - L)$. |
| L | Lower limit of flammability of the fuel vapour in air expressed as mole (volume) fraction. |
| N | Volume of water added to unit volume of liquid fuel. |
| p_{fire}^0 | Equilibrium vapour pressure of liquid fuel at its fire point. |
| p_{stoich}^0 | Partial pressure of fuel vapour in its stoichiometric mixture with air |
| p_f, p_a | Partial vapour pressures of fuel and additive (mm Hg) |
| p_f^0, p_a^0 | Saturated vapour pressures of pure liquid fuel and pure liquid additive (mm Hg) |
| P_T | Total pressure (atmospheric) (mm Hg) |
| R | Gas constant $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ |
| T_f | Closed-cup flash point temperature of pure liquid fuel. |
| T_m | Closed-cup flash point temperature of liquid mixture. |
| U | Upper limit of flammability of the fuel vapour in air expressed as a mole (volume) fraction. |
| x_f, x_a | Mole fractions of fuel and additive in the liquid mixtures. |
| y_f, y_a | Mole fractions of fuel and additive in the vapour phase. |
| α_f, α_a | Activities of fuel and additive in the liquid mixture. |
| ΔH_f | Latent heat of vaporisation of liquid fuel (J mol^{-1}). |

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