

FLAMMABILITY PREDICTIONS FOR WATER-BASED HYDRAULIC FLUIDS

P. Chatterjee, M.M. Khan and J.L. de Ris

FM Global, 1151 Boston-Providence Turnpike, PO Box 9102, Norwood, MA 02062, USA

ABSTRACT

A methodology is developed to predict the flammability of water-based hydraulic fluids. The methodology is based on the heat release rate of an atomized spray and the calculated adiabatic flame temperature of the fluid for cases where the fire point (ASTM D-92) cannot be measured, because of the presence of water. NASA equilibrium code yields the adiabatic flame temperature from the knowledge of elemental composition of the fluid as well as its gross heat of complete combustion (oxygen bomb calorimetry). A criterion has been developed to identify less flammable water-based hydraulic fluids. It is that for a fluid showing no fire point, have a chemical heat release rate less than or equal to 130 kW in FM Global's standardized spray fire test and its adiabatic stoichiometric flame temperature is less than or equal to 2100 K. For fluids having fire points one would use the traditional spray flammability parameter (SFP) FM Approval Standard².

KEYWORDS: Hydraulic fluid, Adiabatic flame temperature, Chemical heat release rate, Equilibrium

INTRODUCTION

Petroleum based or synthetic fluids generally form the base for hydraulic fluids used in industry. Petroleum based hydraulic fluids are not preferred where sources of ignition may be present. Potential sources of ignition include molten metal, sparks, flames and hot surfaces. The risk of ignition and fire is reduced by using suppression equipment and/or fire resistant hydraulic fluids. Fire resistant hydraulic fluids are not necessarily fireproof. However, these fluids resist ignition and are able to resist fire spread when a source of ignition is present¹. Fire resistant hydraulic fluids are less flammable than mineral/petroleum oil based fluids and are approved by FM Global².

The worst-case fire hazard scenario involving hydraulic fluids is a high-pressure release of an atomized spray near an ignition source, resulting in a long torch-like flame having a high heat release rate. Fire resistance of hydraulic fluids is generally enhanced by changing their chemical structure as well as by adding chemical inhibitors. Addition of water is also used for providing fire resistance to the fluids; examples are water-in-oil emulsions and glycols and/or polyglycols in water³. The flammability of hydraulic fluids is categorized by the spray flammability parameter (SFP), based on both the chemical heat release rate of an atomized spray fire and the fluid volatility expressed by the fire point temperature². SFP works well with fluids whose fire points (FP) can be measured in an open cup burner (ASTM D-92). This method, however, cannot be applied for water-based hydraulic fluids whose FP cannot be readily measured. Water, being relatively volatile, interferes with the FP measurement. This occurs for water-glycol and water-emulsion fluids. Absence of a FP indicates that it is hard to ignite the above mentioned fluids. However, it is necessary to confirm that any unexpected combustion phenomenon involving these fluids does not occur. To establish the reduced flammability of the fluid, one needs to evaluate another important flammability parameter, such as the adiabatic stoichiometric flame temperature in addition to the chemical heat release rate of the spray fire.

The chemical heat release rate of the atomized spray fire, \dot{Q}_{ch} (kW), is measured here under a 200 kW calorimeter using a nozzle 0.33 mm diameter at a pressure of 6.9 MPa. To achieve ignition and maintain the spray fire, the nozzle is surrounded by a propane ring burner (≈ 14 kW). The effect of drop size on combustion is eliminated by using such a high pressure nozzle issuing fine drops so that the fluid can be assessed only on the basis of its fire resistance⁴.

The use of the adiabatic flame temperature for predicting flammability of hydrocarbons is prevalent in the process industry. Britton⁵ summarizes flammability prediction rules for single and mixed organic fuels in air under atmospheric conditions. The author showed that the maximum flame temperature can be approximately computed as a function of the net heat of complete combustion, ΔH_c , and the stoichiometric ratio of oxygen to fuel, S . Recently, Melhem⁶ proposed a general method for estimation of flammability envelopes for chemical mixtures based on chemical equilibrium calculations. The author developed an algorithm based on the Gibbs free energy minimization concept to determine the adiabatic flame temperature. Mashuga and Crowl⁷ used a commercial code applying Gibbs free energy minimization to compute the adiabatic flame temperature of mixtures of fuel, oxygen and nitrogen. The techniques for computing the adiabatic flame temperature in the studies mentioned above involved simple sets of known hydrocarbons as the reactants and were restricted by the limited choice of products species.

In this study, a methodology based on Gibbs free energy minimization is developed to evaluate an adiabatic stoichiometric flame temperature, T_{ad} (K) for a diffusion flame. The input parameters required for this methodology are: a) the elemental composition of the fluid, i.e., %mass of carbon, hydrogen, oxygen, nitrogen, etc. and b) the gross heat of complete combustion per unit mass of fluid consumed, as measured in the oxygen bomb calorimeter. The objective of this study is to come up with a criterion to identify less flammable water-based hydraulic fluids based on the adiabatic stoichiometric flame temperature and chemical heat release rate. The method is not limited to hydrocarbons.

DEVELOPED METHODOLOGY

A critical condition for sustained combustion of a hydraulic fluid is determined here on the basis of whether its adiabatic stoichiometric flame temperature (ASFT) is above or below a critical prescribed temperature. Water-based hydraulic fluids that are submitted to FM Approvals for flammability classification² are composed of unknown chemicals – often glycols or synthetic esters. Therefore, a computational tool has been developed for calculating the ASFT for chemical mixtures of unknown chemical composition. The code uses the NASA CEA (Combustion Equilibrium and Applications) code⁸ as the solver to compute ASFT. There have been many studies reported in the literature suggesting the existence of a critical flame temperature for sustained combustion. A critical temperature is often used by engineers to estimate the flammability of chemical mixtures⁹. Based on a review of literature⁹, de Ris¹⁰ recommended a value of 1710 K for determining the concentration of various gaseous diluents needed to suppress a fire. In the absence of chemical inhibitors, the critical temperature is insensitive to the nature of the fuel and/or oxidant for the burning of diffusion flames characteristic of fires. The value of 1710 K was also used by de Ris¹¹ for successfully estimating the amount of water dilution needed to prevent the sustained combustion of propylene glycol/water mixtures. In other words, if the adiabatic stoichiometric flame temperature of the chemical mixture is less than the critical temperature, the flame is not sustained. Calculating the adiabatic stoichiometric flame temperature is possible provided the elemental composition of the chemical mixture and its heat of combustion is known. The heat of combustion can be obtained by using the oxygen bomb calorimeter. The elemental composition of the fluid is obtained by standard analytical chemical techniques. The following steps illustrate the technique developed for computing the ASFT:

1. The hydraulic fluid sample is sent to a laboratory to determine its elemental composition, i.e. mass% of carbon, hydrogen, oxygen, nitrogen, metals, etc. The elemental composition results will include the presence of water in the samples (measured by the Karl Fischer method per ASTM D4014). Because of interference in elemental composition measurement due to the presence of water in the samples some of the Karl Fischer water content is included in the mass percent of oxygen (O atom). To correct for this overlap the following methodology is developed:

- a. Suppose, Y_i is the reported mass fraction of element i , where i can be K, P, Ca, O, Br, Cl, F, S, Karl Fischer water, C, H, N, etc.
- b. The sum of all the elements including Karl Fischer water (Y_W) is:

$$\sum_i = Y_K + Y_P + Y_{Ca} + \dots + Y_W \quad [1]$$

- c. The error in the sum is $E_{error} = \sum_i - 1$. Note that $E_{error} < Y_W$. This is because much of the reported oxygen and hydrogen is also included in the Karl Fischer water mass fraction.
- d. With the observation that some of the Karl Fischer water comprises of hydrogen and oxygen of the original undiluted fluid, the actual mass fractions for oxygen and hydrogen in the absence of any water are calculated as follows:

$$Y_{O,a} = \frac{Y_O - \frac{16}{18} E_{error}}{1 - Y_W}; \text{ and } Y_{H,a} = \frac{Y_H - \frac{2}{18} E_{error}}{1 - Y_W} \quad [2]$$

- e. The corrected actual mass fractions of each element in the absence of any water are calculated as:

$$Y_{K,a} = \frac{Y_K}{1 - Y_W}$$

$$Y_{P,a} = \frac{Y_P}{1 - Y_W} \quad [3]$$

$$Y_{Ca,a} = \frac{Y_{Ca}}{1 - Y_W}$$

and so on.....

- f. The gross heat of complete combustion per unit mass of fluid consumed (ΔH_c in kJ/kg) is also measured in the oxygen bomb calorimeter at the laboratory. The corrected heat of complete combustion, $\Delta H_{c,a}$ is calculated as:

$$\Delta H_{c,a} = \frac{\Delta H_c}{1 - Y_W} \quad [4]$$

The accuracy of the above calculation methodology can be demonstrated by comparing a water-glycol fluid with its concentrate sample. The correction procedure to evaluate the actual mass fractions of elements is followed for the two fluids. The water-glycol mixture originally had 43.75 % Karl Fischer water (%mass) and its concentrate contained 16.72% Karl Fischer water. After applying the correction, data of both samples match quite well (as shown in Table 1).

However, it is strongly recommended that the undiluted (i.e., concentrate) fluid samples should be used for determining elemental composition and gross heat of complete combustion data. The developed code allows adding water (%mass) to a fuel concentrate as an input to determine the ASFT. The gross heat of complete combustion of the fuel water mixture is automatically adjusted by the code to exclude the effect of water content in the sample and the elemental composition is adjusted to include the water content in the mixture. It is important that as an

input to the NASA code, the total elemental composition must sum up to exactly 100%. For example, % mass of C, H, O, N, F, S etc. must add up to 100%. In most cases, the elemental compositions measured for the samples sum up to slightly over or below 100%, which is due to typical variations in measurements. The data then needs to be normalized to ensure that the sum total of the mass fractions is exactly 100%.

TABLE 1. Comparison of water-glycol mixture with its concentrate

Mass Fraction	Water-glycol	Concentrate
$Y_{K,a}$	4.683×10^{-5}	4.758×10^{-5}
$Y_{P,a}$	6.0×10^{-6}	8.91×10^{-6}
$Y_{Ca,a}$	6.0×10^{-6}	8.91×10^{-6}
$Y_{O,a}$	4.016×10^{-1}	3.939×10^{-1}
$Y_{Br,a}$	3.602×10^{-5}	3.564×10^{-5}
$Y_{Cl,a}$	2.402×10^{-5}	2.851×10^{-5}
$Y_{F,a}$	1.201×10^{-5}	1.782×10^{-5}
$Y_{S,a}$	6.0×10^{-4}	8.91×10^{-4}
$Y_{W,a}$	0	0
$Y_{C,a}$	4.904×10^{-1}	4.931×10^{-1}
$Y_{H,a}$	1.013×10^{-1}	1.031×10^{-1}
$Y_{N,a}$	6.0×10^{-3}	8.91×10^{-3}
$\Delta H_{c,a}$ (kJ/kg)	24220	24700

- The atomic elements from the elemental composition are converted to their zero enthalpy of formation state, i.e. C(graphite), H₂, O₂, N₂, Br₂, etc. The NASA-CEA code minimizes the Gibbs free energy for a mixture of elements. For a mixture of N elements, the Gibbs energy per kilogram of mixture g is given by:

$$g = \sum_{j=1}^N \mu_j n_j \quad [5]$$

where n_j is the number of kilogram-moles of species j per kilogram of mixture and the chemical potential per kilogram-mole of species j is defined as:

$$\mu_j = \left. \frac{\partial g}{\partial n_j} \right|_{T,P,n_{i \neq j}} \quad [6]$$

Chemical equilibrium corresponds to the minimization of the Gibbs free energy. This minimization is subject to certain constraints⁸, like the mass-balance constraint. By adhering to these constraints, determination of equilibrium compositions for thermodynamic states specified by an assigned temperature, $T_0 = 298.15 \text{ K}$, and pressure, $P_0 = 1 \text{ bar} = 10^5 \text{ Pa}$, is possible. A constant temperature and pressure process calculation is performed with the NASA-CEA code with the zero enthalpy formation state elements/molecules as the reactants. The calculation

provides the enthalpy of products, h_{prod} , formed at 298.15 K. The calculation also provides the number of moles of air required for stoichiometric combustion of the reactants.

- The enthalpy of products, h_{prod} , computed in the last step is shown in the enthalpy diagram (see Fig. 1). This enthalpy corresponds to the state where products of reaction at constant temperature and pressure exist. If the hydraulic fluid (fuel) in its molecular form reacts with air at stoichiometric proportions, the same product species will be produced and the enthalpy of products will be equal to h_{prod} . We can compute the enthalpy of the reactant (in our case the unknown molecular form of the hydraulic fluid (the fuel) from h_{prod} and $\Delta H_{c,a}$ obtained from the measured gross heat of complete combustion, ΔH_c , in an oxygen bomb calorimeter:

$$h_{reac@298.15K} = h_{prod@298.15K} + \Delta H_{c,a} \quad [7]$$

Here, $\Delta H_{c,a}$ has a positive value and h_{prod} has a negative value. Fig. 1 shows the various enthalpy levels – C(graphite), H₂, O₂, N₂, Br₂, etc. sit at the zero enthalpy level whereas the actual fuel mixture is at a negative enthalpy level. To account for the lower enthalpy level of the fuel, the equilibrium calculation is performed to determine the enthalpy of products at 298.15 K. The difference between the enthalpy of products at 298.15 K and heat of combustion yields the enthalpy of reactants that must be used for the adiabatic flame temperature calculation.

- A second calculation is performed with the NASA-CEA code with the enthalpy of reactants, h_{reac} , assigned to C(graphite), H₂, O₂, N₂, Br₂, etc. The amount of air needed for stoichiometric reaction is obtained from the previous NASA-CEA calculation and a constant enthalpy and constant pressure process calculation is performed. The adiabatic stoichiometric flame temperature (ASFT) is obtained from this calculation.

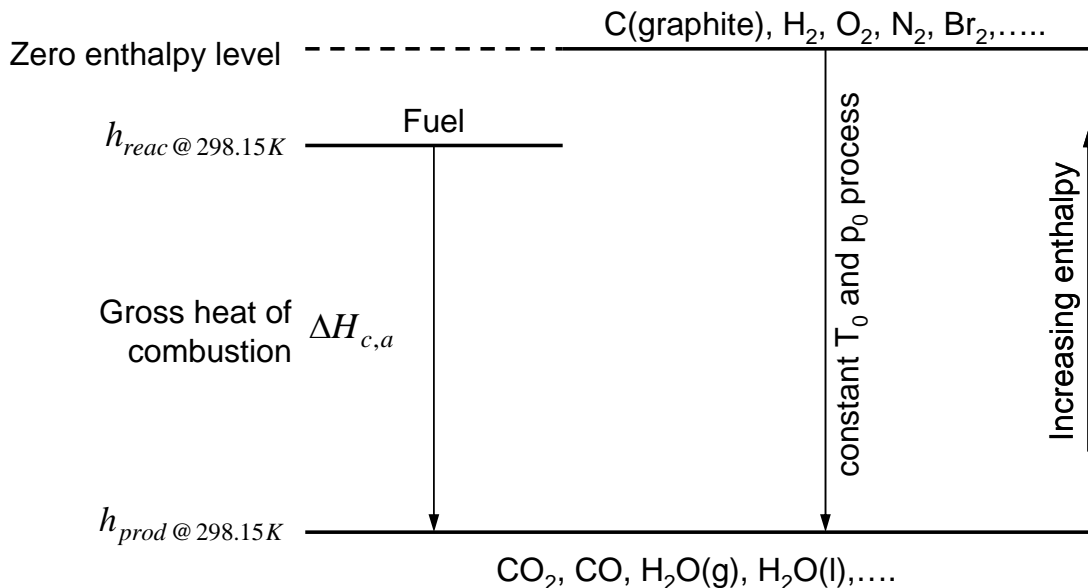


FIGURE 1. Enthalpy diagram showing the three enthalpy levels – the zero enthalpy level: elemental composition; h_{reac} level: fuel at 298.15 K; and h_{prod} level: equilibrium products at 298.15 K. $\Delta H_{c,a}$ is the total heat of combustion obtained from the oxygen bomb calorimeter.

Manufacturers sending samples for approval² do not divulge the molecular composition of the samples (fuel). Therefore, the enthalpy of the reactant (fuel, h_{react}) is unknown. As discussed above, the constant temperature and constant pressure reaction using the elemental composition of the fuel is performed to obtain the enthalpy of the products, h_{prod} , formed at equilibrium. The h_{react} value is then computed with the knowledge of the total heat of combustion of the fuel and the enthalpy of equilibrium products. The adiabatic stoichiometric flame temperature, T_{ad} , can then be computed for the sample.

VALIDATION OF THE METHODOLOGY

The code has been validated against available reference values of adiabatic flame temperatures of common hydrocarbons¹². A further validation study has been performed by comparing flame temperatures predicted for water-propylene glycol mixtures with calculations performed earlier¹¹. It was predicted in the previous study that a 56.7% by weight content of water in water-propylene glycol mixture corresponds to the critical temperature of 1710 K (1437 °C). The present code accurately predicts the weight percentage of water in the mixture corresponding to the critical temperature (54.5% water). Fig. 2 shows the comparison of these present calculations along with those of a previous study. As discussed later, spray fire tests were conducted with water-propylene-glycol mixtures and it was found that the mixture with around 53% water was non-flammable (see Fig. 3).

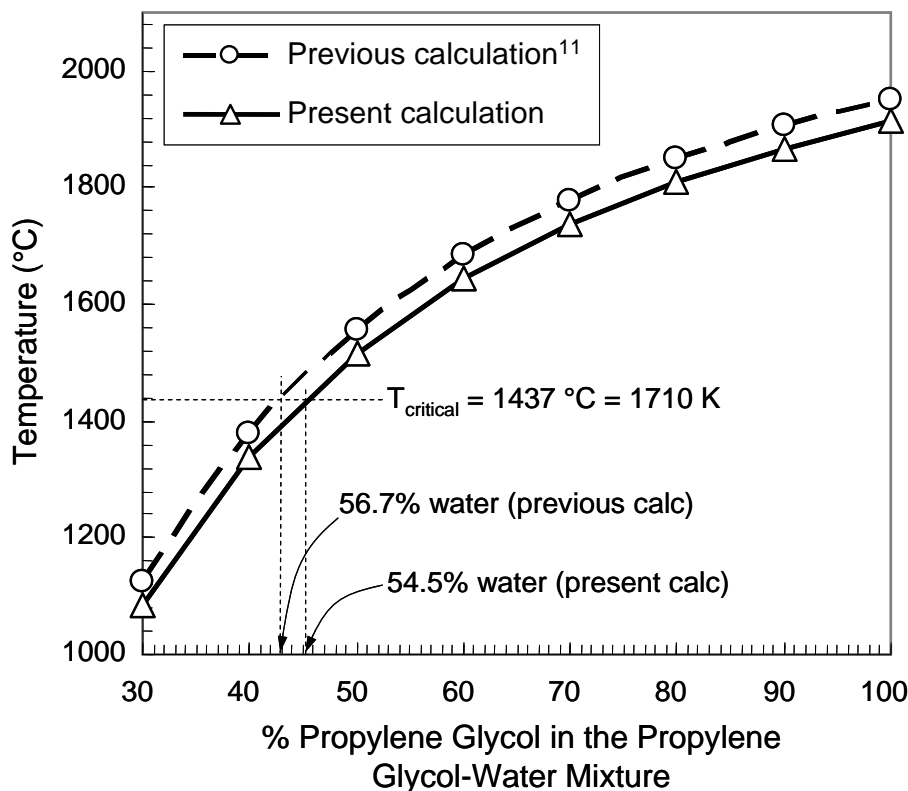


FIGURE 2. Adiabatic stoichiometric flame temperature of water-propylene glycol mixtures calculated using the developed methodology

PRACTICAL APPLICATION OF THE DEVELOPED METHODOLOGY

Using elemental compositions and gross heats of complete combustion data, adiabatic stoichiometric flame temperatures were estimated using the NASA-CEA code for several fluids. The reproducibility

in elemental composition, gross heat of combustion and Karl Fischer water measurements were within 2%. A two percent variation in O and H produces one percent change in adiabatic flame temperature. Similarly a two percent variation in gross heat of combustion measurement produces in one percent change in adiabatic flame temperature.

Table 2 shows the measured chemical heat release rates and fire points (FP) from tests conducted at FM Global. Excellent repeatability in the measurements of chemical heat release rate, \dot{Q}_{ch} , mass flow rate and FP for propylene glycol were observed. The maximum variation between data is within 1%. The addition of 10% water in propylene glycol does not have any effect on \dot{Q}_{ch} compared to propylene glycol with no water. It should be noted that FP could not be obtained for propylene glycol with 20% water content (Table 2). About 16% and 5% reduction in \dot{Q}_{ch} and T_{ad} , respectively, are observed for propylene glycol with 20% water.

TABLE 2. Propylene glycol spray fires and fire point temperatures

Water (%mass)	Chemical Heat Release Rate in Spray (kW)	Mass Flow Rate (g/s)	Fire Point* Temperature (K)
0	87.04	3.84	383
0	89.37	3.87	387
0	89.23	3.82	384
10	89.58	4.14	396
10	88.45	4.15	395
10	88.78	4.17	397
10	88.56	4.18	
10	87.62	4.17	
20	75.27	4.0	No Fire Point
20	75.57	4.0	No Fire Point
20	74.79	4.0	No Fire Point
20	75.40	4.03	No Fire Point
20	74.41	4.03	No Fire Point

*ASTM D-92 Cleveland Open Cup method.

The computed adiabatic stoichiometric flame temperatures are plotted against the measured chemical heat release rates from spray fires in Fig. 3 for several hydraulic fluids including propylene glycol. From Table 2 one observes that one can not obtain the fire point for propylene glycol with a water dilution greater than 10%. The adiabatic stoichiometric flame temperature for 10% water diluted propylene glycol is approximately 2100 K. On the basis of engineering judgment, a criterion was developed to approve commercial water-based hydraulic fluids:

- Fire point test (ASTM D-92 Open Cup method) should not yield a fire point;
- Spray fire test (FM Approval Standard²) gives a chemical heat release rate less than 130 kW ;
- Adiabatic stoichiometric flame temperature is less than or equal to 2100 K.

Absence of a fire point would indicate that in case of a hydraulic fluid spill, the possibility of ignition is low. A chemical heat release rate less than 130 kW from the spray fire test would mean that a fire caused by a spray leak can be contained by installed sprinkler protection. [A mineral oil spray fire would produce a corresponding spray fire heat release rate of 260 kW]⁴. The 130 kW value is chosen by FM Global engineers based on loss history and experience with installed protection capacity to control spray fires. A water-based hydraulic fluid is approved² when all the three criteria mentioned above are met. It is not always possible to alter the composition of commercial water-based hydraulic fluids by adding more water and reducing their adiabatic stoichiometric flame temperatures. Water

dilution causes changes in other properties of the hydraulic fluid – for example, higher water content hydraulic fluids may cause higher corrosion rates. Therefore, the theoretical critical temperature of 1710 K is not selected as an upper limit for approval. However, the critical temperature is needed for defining a lower limit for approval of hydraulic fluids with high water content. In the approval process, the following steps are taken when a sample is tested for susceptibility to ignition:

- The elemental composition and the bomb calorimeter total heat of combustion are determined;
- The NASA-CEA code is used to compute an adiabatic stoichiometric flame temperature;
- The fire point test is conducted (ASTM D-92);
- The spray fire test is conducted (FM Approval Standard²).

In case the adiabatic stoichiometric flame temperature is computed to be less than or equal to 1710 K , and a fire point is not obtained, the sample is approved without the need for a spray test. This way the approval process for hydraulic fluids with high water contents is quicker compared to the approval process for fluids with lower water content. For propylene glycols with greater than 60% water content, the adiabatic stoichiometric flame temperatures are less than 1710 K (see Fig. 3) and fire points are not obtained. These fluids are approved without the need for a spray fire test. Spray fire tests conducted on propylene glycols with water contents between 0% and 50% show that their chemical heat release rates are less than 130 kW . However, propylene glycols with less than 10% water content show a fire point and are therefore not approved. Propylene glycols with water content between 20% and 50% are approved because they do not show a fire point and their chemical heat release rates are lower than 130 kW . Commercial water-glycols (shown in Fig. 3) all show chemical heat release rates lower than 130 kW and do not show a fire point. These fluids are also approved. Commercial water emulsions show an adiabatic flame temperature slightly higher than 2100 K but with chemical heat release rates equal or lower than 130 kW . These fluids would be approved if the manufacturer were to add a little quantity of water so that their adiabatic flame temperatures were less than 2100 K .

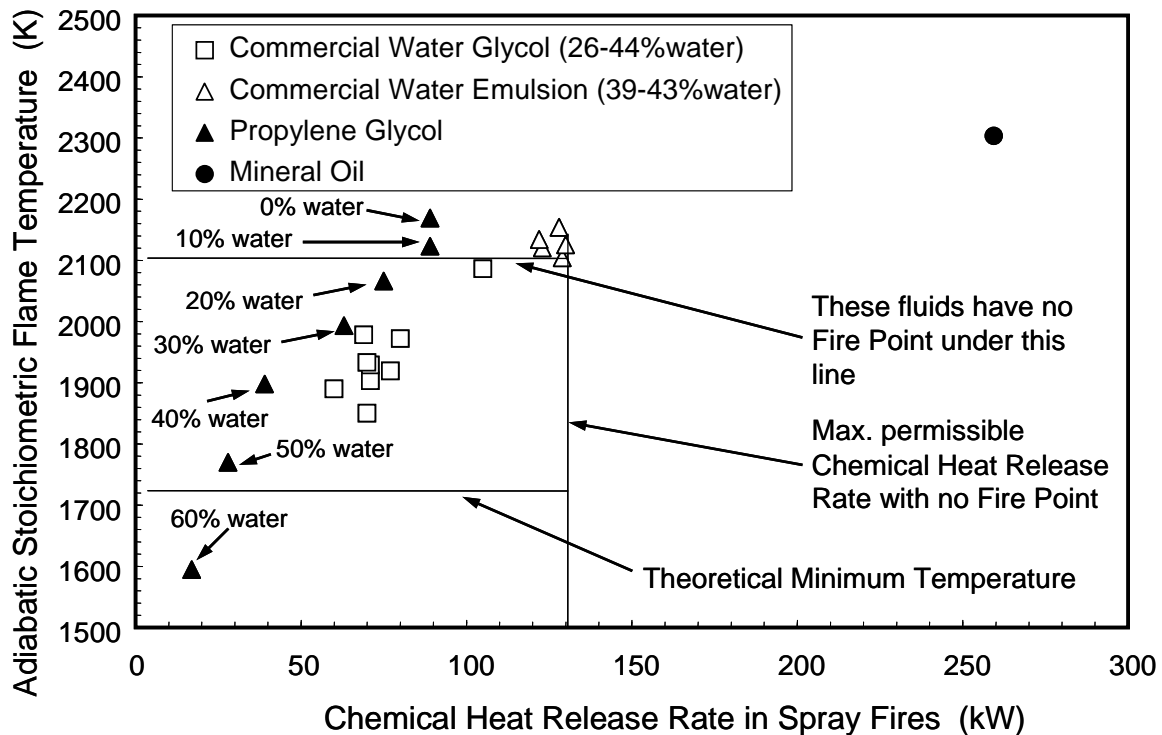


FIGURE 3. Computed adiabatic stoichiometric flame temperatures plotted against chemical heat release rates for several hydraulic fluids.

SUMMARY AND CONCLUSIONS

A methodology has been developed to compute the adiabatic stoichiometric flame temperatures for hydraulic fluids with unknown chemical composition. The NASA-CEA code has been utilized to compute the adiabatic stoichiometric flame temperature with the knowledge of the elemental composition of the fluid and its oxygen bomb calorimeter total heat of combustion. The computed adiabatic stoichiometric flame temperature is used to augment the approval process currently followed by FM Approvals for water-based hydraulic fluids. Approval is given to fluids that show no fire point, have a chemical heat release rate less than or equal to 130 kW in a spray fire test and their adiabatic stoichiometric flame temperature is less than or equal to 2100 K. This approval criterion has been developed by FM Global engineers on the basis of engineering judgment and previous experience in controlling hydraulic fluid spill fires and spray fires. A critical temperature (1710 K) is also used to approve hydraulic fluids with high water content if they do not show a fire point. The spray fire test for these fluids are not conducted if their adiabatic stoichiometric flame temperature comes out to be less than or equal to 1710 K. The use of adiabatic stoichiometric flame temperature in approval process is not restricted to hydraulic fluids. Criteria for approving other fluids based on their adiabatic stoichiometric flame temperatures are currently being developed at FM Global Research.

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