A simple and reliable method for prediction of flash point of alcohols based on their elemental composition and structural parameters

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ARTICLE INFO

ABSTRACT

Flash point (FP) is an important parameter in hazard classification, safe handling, transportation, and storage of flammable liquids. On the basis of 929 experimental FPs of different alcohols, which were collected from different sources, a new correlation was developed for the estimation of FPs of alcohols. Different alcohols and phenols with various molecular structures were studied, that is, acyclic and cyclic alcohols as well as phenols and alcohols with composite aliphatic–aromatic structures. The new correlation is based on the elemental composition and some structural parameters, such as intermolecular hydrogen bonding, which can be found from the chemical structure of any type of alcohol. The root–mean–square deviation of the new model for external validation data set containing 164 compounds is 16.4 K. Absolute percent error of the new model is >10% in only 24 alcohols and <5% in 714 alcohols. As the measured FPs reported in the literature sometimes differ in tens of degrees, the new simple model was compared with one of the best available predictive methods associated with much more reliable results with maximum errors less than approximately 70 K.

1. Introduction

Flash point (FP) is the lowest temperature at which a liquid can form an ignitable mixture in air near its surface, where its measurement requires an ignition source. As FP of a volatile material is the lowest temperature at which vapors of a fluid will ignite, liquids with lower FP can be ignited easier. Moreover, the vapor may cease to burn when the ignition source is removed at the FP different from the fire point, that is, the temperature at which the vapor continues to burn after being ignited. Both the FP and fire point do not depend on the temperature of the ignition source. Because a certain concentration of vapor for each flammable liquid in air is necessary to sustain combustion, the FP of a flammable liquid is the lowest temperature at which sufficient flammable vapor exists to ignite when an ignition source of sufficient strength is applied.

The FP of a pure substance or mixture is a principal indicator of flammability, which is an important parameter in hazard classification of flammable liquids and for safe handling, transportation, and storage of many substances (Albahri, 2015; Katritzky et al., 1994; Mannan, 2012). Moreover, the knowledge of FPs helps firefighters to extinguish fires, because a fire pool caused by a high-FP liquid can be extinguished by cooling with water mist, whereas low-FP substances usually need to be blanketed by dry chemicals or foams (King, 1990; Mannan, 2012). For example, cooking oil has a high FP, and hence its temperature during burning is high (603–733 K). Its gasification heat is also high and additional thermal energy is required for fuel evaporation. The cooking oil fire can be extinguished by water mist mainly through cooling the fuel surface, as the rate of burning or supply of fuel vapor is reduced sufficiently not to support the flame (Liu et al., 2004). Water, because of its high heat capacity, absorbs large quantities of heat and reduces the temperature of fire, and hence it is a good choice for extinguishing fires of high-FP liquids. Foam, on the contrary, can be used for extinguishing high- or low-FP fires, because it can act as a blanket and not a heat absorber (Mannan, 2012). The FP is also used to determine the vapor explosion potential in industrial processes (Jones and Pujadó, 2006; Kong et al., 2003).

FP can be measured using two methods (King, 1990): (1) closed-cup method and (2) open-cup method. The former and latter methods are used for liquids with low and high FP, respectively. The open-cup tester approximates conditions that are met in open vessels and that would be encountered in spills (Lance et al., 1979). One disadvantage of the open-cup tester is that low-boiling components of mixture may be lost to the surrounding atmosphere before application of the flame, which results in higher values of FP (Lance et al., 1979). The closed-cup method provided relatively slightly lower values of FP, because the physical barrier prevents the escape of volatile particles and approximates an equilibrium between vapor and the air in the enclosed space (King, 1990; Lance et al., 1979). The closed-cup tester provides an insight into the flammability of materials within enclosed spaces such as sealed containers (Lance et al., 1979).

The procedures for various experimental determination of FP are described in various sources: (a) ASTM D56 (D56, 1993) (Tag closed-cup method) is used for materials with viscosity < 5.5 mm^2/s and FP $< 93\,^\circ$C; (b) ASTM D93 (D93, 2002; White and Montemayor, 2013) (Pensky–Martens closed-cup method) is used for materials with FP between 40 and 360 $^\circ$C, such as distillate fuels, lubricating oils, fuel oils, mixtures of petroleum liquids with solids, and biodiesel fuels; and (c) ASTM D92 (D92, 2005; White and Montemayor, 2013) (Cleveland open-cup method) is used for liquids with high viscosity and FP between 79 and 400 $^\circ$C, such as petroleum products, except fuel oils. The aforementioned standard methods can be selected based on the type of material and apparatus available. Methods for the determination of FP of unknown substances and the equality of the test methods have been reviewed elsewhere (Janes and Chaineaux, 2013; Rowley et al., 2010a).

The measured FPs are influenced by the following factors: (1) sample size as well as its viscosity and homogeneity (in mixtures); (2) the type, position, and dimension of the ignition source; (3) temperature rise rate; (4) stirring of liquid; (5) mixing of vapor phase above pool; (6) drafts; (7) ambient pressure; (8) operator bias; and (9) fuel container condition (open or closed) (Ding et al., 2013, 2014; Ishida and Iwama, 1986; Kong et al., 2003; Lance et al., 1979). Therefore, the measured FPs reported in the literature sometimes differ in tens

of degrees (Rowley et al., 2010a). It is important to develop suitable predictive methods for FP of those organic compounds. Moreover, the measurement of FP of toxic, explosive, or radioactive materials is very difficult and even impossible in some cases (Katritzky et al., 2001; Suzuki et al., 1991). All these considerations reveal that reliable prediction of FPs for different classes of organic compounds is desirable. At a given temperature, FP of a substance is directly proportional to its boiling point and inversely to its vapor pressure. As a general rule, flammable liquids with high vapor pressures at "normal" temperatures exhibit low boiling points and FPs (Lance et al., 1979).

Various theoretical methods have been developed for the calculation/prediction of FPs of pure compounds or mixtures of flammable liquids (Catoire et al., 2006; Liaw and Tsai, 2014; Liu and Liu, 2010; Phoon et al., 2014; Saldana et al., 2013; Valenzuela et al., 2011; Vidal et al., 2004). Catoire and Naudet (2004) presented a simple correlation for predicting the FPs of pure organic molecules based on their normal boiling point, standard enthalpy of vaporization, and the number of carbon atoms. Gharagheizi et al. (2012) presented a linear model for the estimation of FPs of pure compounds based on their normal boiling points and chemical structure-based parameters. For those methods that need experimental data of physical and thermodynamic properties of organic compounds for prediction of FPs, for example, the methods of Catoire and Naudet (2004) as well as Gharagheizi et al. (2012), they may provide large deviations for those compounds where the required physical and thermodynamic properties have not been reported in the literature. These methods can provide good predictions of FP for those classes of organic compounds where these models have been developed, if the experimental data of desired variables, such as normal boiling point, were available. Because the used experimental data for development of models are much more than variables, statistical analysis data have confirmed high reliability of these methods for those new compounds with similar molecular structures that have not been used in the development of methods.

Group contribution methods (Benson et al., 1969; Poling et al., 2001) have been used extensively for the prediction of different properties such as solid-phase heats of formation (Argoub et al., 2014), gas-phase heats of formation (Kamalvand et al., 2015), heats of fusion and fusion temperature (Jain et al., 2004; Yalkowsky, 2014), and heats of sublimation (Gharagheizi et al., 2013). Some group additivity methods have also been developed for the prediction of FP. Albahri (2003) introduced a group contribution method to predict FPs of hydrocarbons. This method cannot be used for some unsaturated hydrocarbons, because several group additivity values are not defined. Rowley et al. (2010b) introduced a more complete group contribution model for a wide range of organic compounds, including 62 group contribution values. The reliability of this model decreases as compounds with strong interactions between constitutive fragments are considered (Mathieu and Alaime, 2014), that is, polyfunctional molecules with complex molecular structures.

Quantitative structure property relationship (QSPR) methods, which are based on complex molecular descriptors and computer codes, have also been used for the prediction FPs of some classes of compounds. Tetteh et al. (1999) used 25 functional groups and their first-order molecular connectivity indices (Estrada, 2002) as inputs of a radial basis function neural network model to predict FPs and boiling points of 400 organic compounds. Later, Gharagheizi et al.