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Assessing the Flammability of Liquid Mixtures by Predictive Approach as a Complement to Experimental Measurements

Guillaume Fayet*, Patricia Rotureau, Benoit Tribouilloy

INERIS, Parc Technologique Alata, BP2, 60550 Verneuil-en-Halatte, France
guillaume.fayet@ineris.fr

The flammability of organic mixtures can be dramatically changed upon concentrations and can reveal, in some cases, more flammable than its components taken as pure liquids. For this reason, estimating the flammability of mixtures represents a great challenge with high importance in industrial safety.

In that context, efforts were engaged in the development and use of predictive methods to estimate the flash point of liquid mixtures for practical industrial applications as a complement to the classical experimental approach. Different predictive approaches are proposed according to the level of information available on the investigated mixture (in terms of properties of pure compounds) based on mixing rules and/or QSPR (Quantitative Structure-Property Relationship) models.

Different case studies are proposed to illustrate how they can complement experimental tests. These case studies highlight the precautions to be considered for their accurate use (e.g. choice of the model), their limits notably for specific types of flammable mixtures (like halogenated substances) and their complementarity with the information provided by experimental measurements to improve industrial safety issues.

1. Introduction

Flash point (FP) characterizes flammability hazards of liquids and is a key safety issue in the risk assessment of industrial processes. It is defined as the temperature above a liquid generates flammable vapors which can be ignited in air by a pilot flame under the condition of the specified condition of test. In the case of organic mixtures, flash point can be dramatically changed upon concentrations in flammable compounds and, in many cases, following non-linear trends. In the most extreme cases, mixtures can reveal more flammable than their constituents taken as pure. For this reason, predictive methods are of great interest to avoid any underestimation of fire and explosion hazards without systematic experimental testing.

This contribution aims to illustrate how predictive methods can be used as a complement to the classical experimental approach to evaluate the flammability of liquid mixtures for classification purpose and process safety issues. In addition to mixing rules allowing estimation of the flash point of mixtures based on the knowledge of single constituent ones, new predictive approaches were developed and used by INERIS using the QSPR approach to access predictions based on the only knowledge of the composition of the mixture and of the molecular structures of its constituents. These methods are now part of tools available at INERIS in its expertise on physical hazards. After a brief presentation of these predictive approaches, different case studies are presented to illustrate how to use these predictive methods and the predictions themselves in the contexts of classification and risk assessment of industrial processes. They will also evidence their limit for specific liquid mixtures like those containing halogenated compounds.

2. Predictive methods

Depending on the level of knowledge on the mixture and its components and depending on the context of use, various approaches are available to complement experimental campaigns.

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At first, predictive mixing rules can be used to estimate the flash point of mixtures based on the knowledge of those of its constituents. Notably, Gmehling and Rasmussen (1982) combined a vapor-liquid equilibrium (VLE) model with the Le Chatelier rule, to account for the flammability of vapor mixtures. Such approaches were then adapted and successfully used, in particular with the approach of Liaw (2002), to various types of mixtures including ternary (Liaw et al., 2004), partially miscible (Liaw et al., 2008) and aqueous mixtures (Liaw et al., 2003).

Unfortunately, the flammability of the different constituents of the mixture is sometimes unknown. To fill this gap, Quantitative Structure-Property Relationships (QSPR) can be used to predict the flash point of pure compounds. This kind of models is increasingly used to access the properties of pure compounds and accurate models already exist for the flash point. Besides, the combination of the QSPR models like the one of Carroll (2011) with the mixing rule of Liaw provided reliable estimation of flash point of binary (Gaudin et al., 2014) and ternary mixtures (Fayet et al., 2016) (including partially-miscible mixtures).

At last, the QSPR methodology, initially limited to the prediction of pure compound properties, has been adapted to develop new models for the flash point of mixtures based on mixture descriptors (Gaudin et al., 2015). These mixture descriptors are defined combining the molecular descriptors of the different constituents of the mixture and their respective molar fraction in the mixture. If the obtained model presented in Eq. 1 offers lower performances (with a mean absolute error (MAE) of 10.3°C evaluated on an external validation set of 151 binary mixtures) than the combination of QSPR and mixing rules (MAE = 2.9°C obtained on 284 binary mixtures), this approach could be useful for other properties for which no mixing rule already exist or for screening of mixtures even in absence of liquid-vapor equilibrium model.

where x is the molar fraction, $^3\chi$ is the Randic index (order 3), *HDCA* is the HDCA H-donors charged surface area (order 2), $\Delta\alpha$ is the anisotropic polarizability and $V_{min,H}$ is the minimum valency of a H atom.

3. Case studies

3.1 Classification of flammable liquids

The use of predictive models to access the properties of mixture is allowed for regulatory purpose even if it requires some precautions, as stated by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (section 2.6.4.2) (UN, 2017). The use of mixing rule (the method of Gmehling and Rasmussen (1982)) is particularly addressed to estimate the flash points of flammable mixtures.

For instance, alcoholic beverages, depending on their concentration in ethanol can be classified as flammable liquids. If FP < 23°C, a liquid is classified of category 1 or 2 depending on its boiling point (if lower or higher than 35°C). If 23°C < FP < 60°C, it is classified of category 3, or not classified if FP > 35°C and negative results are obtained in the sustained combustibility test L.2 of the UN Manual of Tests and Criteria of TDG recommendations (section 32.5.2) (UN, 2015).

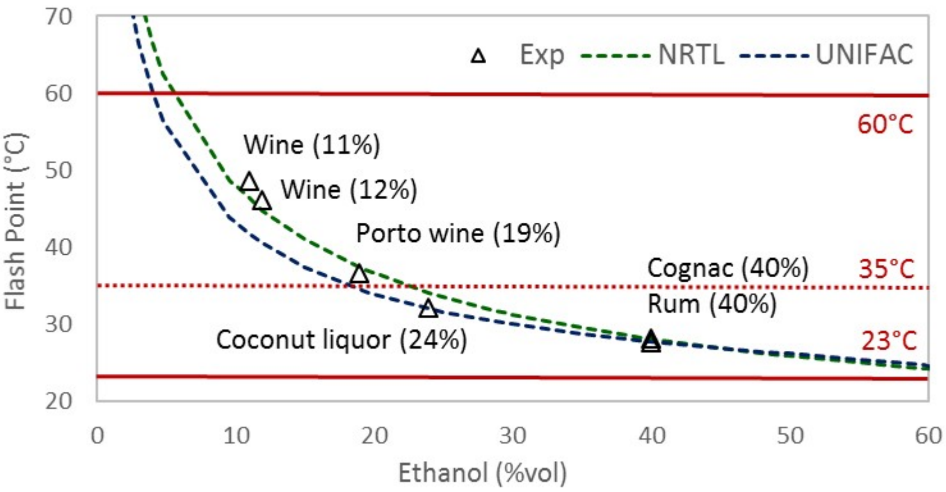

Figure 1: Flash point of alcoholic beverages compared to predictive ethanol-water profiles

In Figure 1, the experimental flash points obtained at INERIS for different commercial beverages (Cwilinski, 1994) are compared to the regulatory thresholds and to predicted ethanol-water profiles obtained with the Liaw mixing rule using NRTL and UNIFAC models for the VLE.

The application of the mixing rule requires knowledge of the flash point of the pure compounds. The flash point of ethanol was measured at 13°C in closed cup apparatus (Liaw et al., 2003). To model the VLE, the NRTL and UNIFAC models were used with the parameters available in Simulis Thermodynamics (ProSim, 2014). NRTL parameters are unique for each pairs of interacting constituents in the mixtures. So, they are not always available for a particular mixture. In such situation, UNIFAC model, based on a group contribution approach, can often be used. In the case of ethanol-water, predictions proposed using both VLE models were found good, as shown in Figure 1.

Based on the predictive mixing rule, classifications of Cognac and Rum are classified as flammable liquids of category 3. Indeed, when considered as water-ethanol solutions at 40%vol, their flash points are predicted at 28°C (with the NRTL model), i.e. between 23°C and 35°C, in agreement with experimental values (27.5°C and 28°C, respectively).

For the 11% and 12% wines, predicted values for 11%vol and 12%vol ethanol-water solutions are 46°C and 45°C respectively (vs. 48.5°C and 46°C, experimentally), i.e. clearly between 35°C and 60°C. Both are classified as flammable liquids of category 3 or even not classified as flammable liquid if negative results are obtained in the UN sustained combustibility test L.2.

For the Porto wine and the coconut liquor, the prediction of flash point for aqueous solutions between 19% and 24% in ethanol are between 37°C and 34°C, i.e. close to the 35°C threshold. In a conservative approach, both liquids may be considered as flammable liquids of category 3 (since the prediction for 19% ethanol-water solution is lower than 5°C above the 35°C threshold). In such case, an experimental characterization is recommended. The classification of coconut liquor is confirmed with an experimental flash point of 32°C. For the Porto wine, the experimental flash point of Porto wine is 36.5°C, confirming the flash point slightly above 35°C. So, it could be considered as not flammable if negative results were obtained in the L.2 sustained combustibility test.

3.2 Estimation of the dilution level to reduce the flammability of a liquid mixture

Predictive mixing rule can also help to define the level of dilution needed to lower the flammability of a solution. For instance, INERIS was asked by a chemical industry to evaluate the possibility to lower the flammability of a 40%vol dimethylamine (DMA) aqueous solution by increasing the dilution in water. To answer this question, both predictive and experimental tools were used.

The safety datasheet of the industrial 40%vol DMA solution indicated a flash point of -18.5°C with a boiling point between 51°C and 100°C. Considering these data, the solution was classified as flammable liquid of category 2. At such low temperature, the flash point measurement is not easy and larger error can be expected than at room temperature due to release of flammable compounds (here DMA) from the liquid solution before the implementation of the test, during the sample preparation, even if dedicated protocols are applied in such cases.

To predict the DMA-water flash point profile, we used the mixing rule of Liaw. Unfortunately, contradictory values of flash point were found in literature. For this reason, new experimental flash point were measured on the original solution (40%vol) and on dilutions at 20%vol, 10%vol and 5%vol. These measurements confirmed the complexity to access reliable flash point for the 40%vol solution with a dispersion of measured flash points between different tests performed on this solution (between -7.5°C and -11°C). On the contrary, the ones performed on the 5%vol solution are well repeatable (all at 31.5°C).

Then, the mixing rule has been applied by adjusting the flash point of pure DMA in such a way that the profile is adjusted on new experimental data (see Figure 2), the most confident profile being the one adjusted on the flash points measured on the 5%vol solution which presented the best repeatability.

From this theoretical profile, it was possible to identify the level of dilution in water required to avoid or reduce the flammability of DMA solutions. Under 9.5%vol, the FP is higher than 23°C and the solution is classified as flammable liquid of category 3 but very low concentration (< 0.7%vol) are required to access a flash point over 60°C and to be not classified as flammable liquid. Even for reaching 35°C in FP (from which liquids may be not classified in negative results are observed in the L2 test), lower than 3.8%vol is required. In these conditions, the 5% solution was selected by the industrial customer for its practical application even if still classified as flammable.

This case study not only demonstrates the possibility to help the selection of safer formulations for industrial applications but also illustrates how it can be used as a complement to experiments when measurements are difficult.

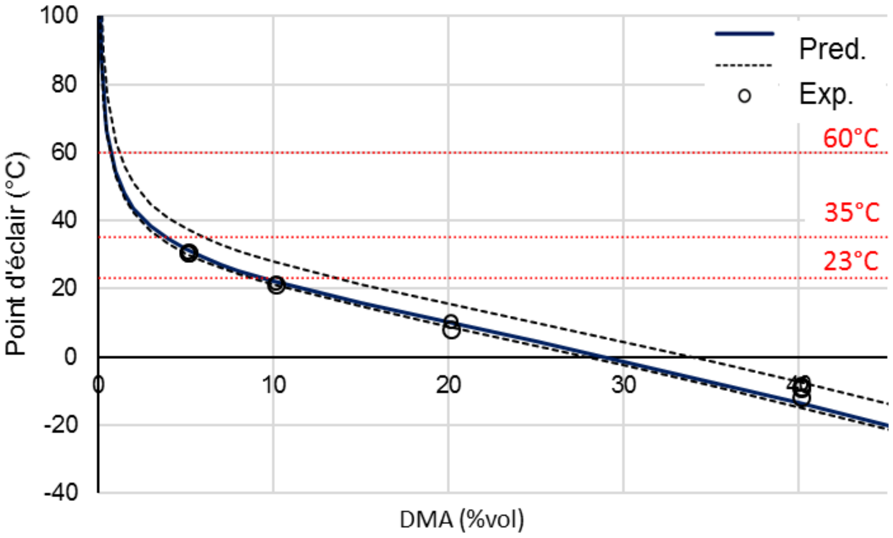

Figure 2: Flash point profile of DMA / water mixtures

3.3 Minimum/Maximum Flash point behavior and process safety

In the risk assessment of industrial processes, flash point is used to assess the possibility of ignition of the vapor above a flammable liquid by external sources (in particular flames), that could lead, in some conditions, to a fire or an explosion. When considering a mixture of flammable liquids and in absence of measured flash point, a common practice consists in taking the flash point of the most flammable constituent in the mixture. This assumption is often considered as a conservative approach.

Unfortunately, this assumption can be not conservative in some cases. Indeed, some mixtures present minimum flash point behavior, i.e. presenting a minimum in the flash point profile such a way that, at some concentrations, the mixture is more flammable than the most flammable constituent taken as pure. This is notably the case for the n-octane/i-propanol mixture presented in Figure 3.

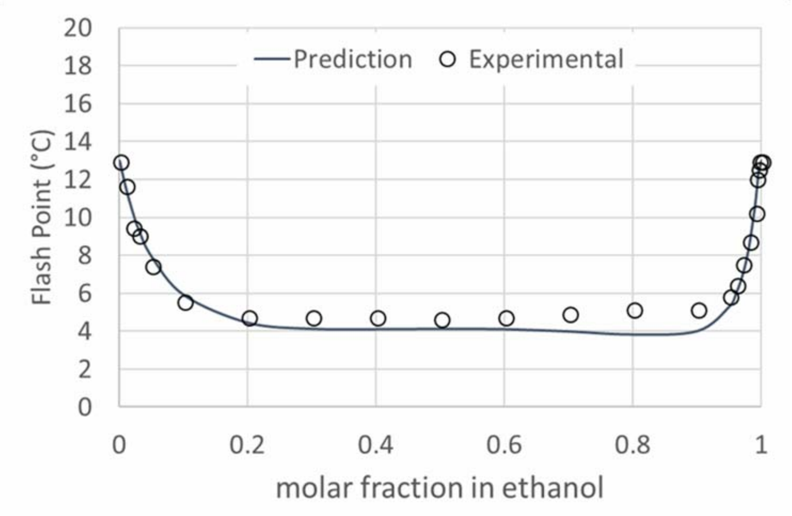

Figure 3: Flash point profile of n-octane/ethanol binary mixtures

Both ethanol and octane present flash points of 13°C (Liaw et al., 2011). In mixture, the repulsive interaction between the ethanol and octane molecules exceeds the ones between ethanol molecules and between octane molecules. As a consequence, molecules more likely release from the liquid to the vapor phase than in an ideal mixture, concentration in flammable vapor above the liquid is increased, so the flash point is lower, as evidenced experimentally (Liaw et al., 2011). As shown in Figure 3, this behavior is perfectly predicted by the mixing rule of Liaw using the UNIFAC model.

In this case, taking into consideration the flash point of the pure compounds (13°C) for the mixture is erroneous since ignition is observed at nearly 5°C for most part of the concentration profile, i.e. 8°C lower. So, the predictive approach represents a powerful tool to identify if the mixture of two compounds could reveal more flammable, to provide an estimation of the flash point for the mixture and, upon cases, recommend the compositions for which the flash points may be confirmed by new tests.

Maximum flash point behavior can also be found when the cohesion between molecules of the different components of the mixture is strongly better than between molecules of the single components, disfavoring the release in the vapor phase. For instance, Liaw et al. (2007) observed this behavior for the binary mixtures of phenol with cyclohexanol, cyclohexanone, acetophenone and p-picoline. This work also demonstrated the capability of the predictive mixing rule to predict these profiles. Prediction can be also useful for such profiles to check if modification of the composition could increase the flammability of the mixture, e.g. by evaporation of one of the components of the mixture by ageing in storages.

3.4 Mixtures containing halogenated compounds

If these predictive models are powerful tools, they present some limitations. In particular, the mixing rule are based on hypothesis that must be known and taken into consideration. For this reason, the GHS regulation indicates that this method is not yet validated for the mixtures containing halogenated compounds. To better evaluate and analyze the capability of the predictive method for such mixtures, the flash points of a series of toluene / 1,1,1-trichlorethylene were measured (Fayet et al., 2018).

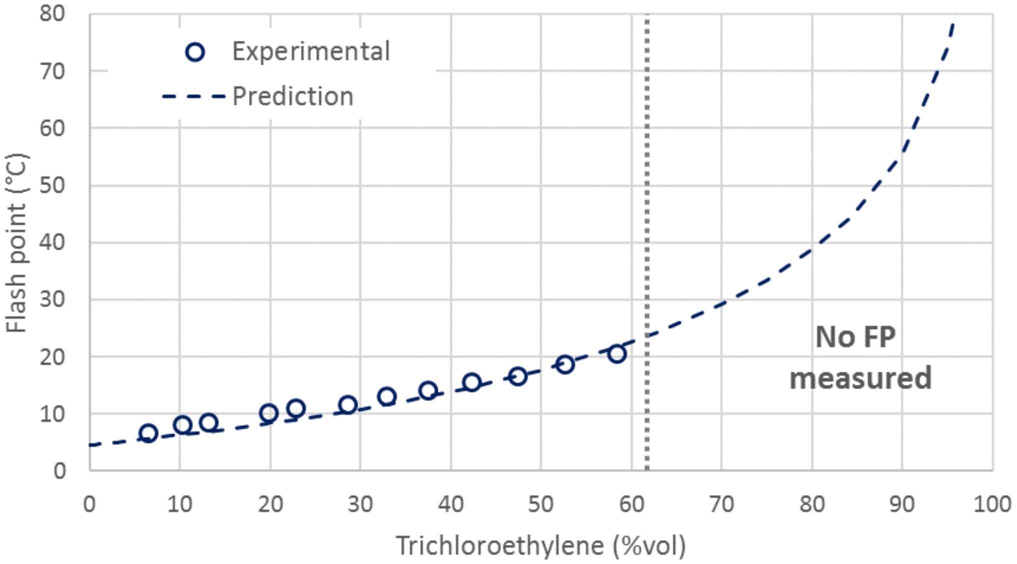

Figure 4: Flash point profile of toluene/1,1,1-trichloroethylene binary mixtures (Fayet et al., 2018)

As seen in Figure 4, the flash point slightly increases with the concentration in trichloroethylene until about 60%vol. For all compositions with concentration higher than this concentration, no proper flash in observed when the pilot flame is applied above the liquid surface, but a blue halo is observed in the cup during the time the flame is presented. So no flash point is determined. In fact, this phenomenon can be associated to the formation of halogenated radical, presenting flame retardant behaviors, by decomposition of 1,1,1-trichloroethylene (Won, 2009) in the vapor at the contact of the flame.

Predicted flash points were calculated using the mixing rule of Liaw using the UNIFAC model and considering 1,1,1-trichloroethylene as non-flammable and the measured value of 4.5°C for pure toluene. Predictions are very good for all measured FP but the model is not able to account for the particular phenomenon observed from about 60%vol. Indeed, the mixing rule is based on the principle that the change of flash point with concentration is only related to a change of VLE. But in this case, particular reactivity phenomenon become an issue. Nevertheless, predictions represent a conservative estimation in this case.

4. Conclusions

Prediction methods represent interesting complementary tools to experimental characterizations of liquid mixture flammability. They can help to classify substances and propose safer formulations in industrial applications. Nevertheless, their use requires particular attentions and does not avoid further experimental research. In this contribution, the case of halogenated mixtures well illustrates the limits of the prediction approach. It also highlights the need of further experimental investigation to better understand subjacent phenomenon that could be taken into account depending on possible process situation.

For this reason, some types of mixtures, for which such model may be inefficient or for which the flash point may be not relevant to assess fire risk, would also require further experimental investigations, like heterogeneous solutions, viscous liquids or mixture involving substances decomposing into the liquid phase (e.g. aqueous solutions of ammonium sulfate releasing H_2S). Beside, particular attention is required at experimental level too and specific experimental protocols may be recommended.

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