

# FLASH POINT DETERMINATION OF BINARY MIXTURES OF ALCOHOLS, KETONES AND WATER

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## Abstract

The flash point of pure organic compounds, their mixtures, and their mixtures with water is a datum of great interest toward the prevention of accidents when using chemicals as a consequence of fires and explosions that may be originated by the substance/mixture when get in contact with the oxygen in the presence of an ignition source, just as the fire triangle establishes.

The flash point of a substance or mixture of substances is a variable of necessary knowledge to determine the fire and explosion risks, providing an index for his classification (i.e., Code of Federal Regulations of the Department of Transport, or the NFPA 30, both of U.S.A.).

In this researching work, some alcohols and ketones of common use as solvents or similar were choosed. Then, the flash point of diverse mixtures alcohol-alcohol, alcohol-water, alcohol-ketone, ketone-ketone, and ketone-water were determined experimentally. Later on, the obtained experimental data were analyzed, to estimate the flash point theoretically with appropriate accuracy using diverse models and correlations to obtain the diverse necessary parameters. So for the vapor pressure of the pure compounds ( $P_i^{sat}$ ), the following equations were used: Antoine, Clausius-Clapeyron, and so on. To determine the activity coefficients of the different components in the liquid mixture ( $\gamma_i$ ) equations like Margules, Van Laar, and UNIFAC were used. For the determination of the lower flammability limit ( $LFL_i$ ) the equations of Hanley, Prugh, Le Chatelier, and Kanury were used.

Lastly, the different proposed procedures to estimate the flash point were compared, determining those that offer better results, when contrasting with the obtained experimental results.

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## 1. INTRODUCTION

The flash point of a chemical or a mixture of several chemicals is a variable of main interest when we evaluate the safety of a product or a process (Liaw and Chiu (2003)). The data of pure compounds are usually available, but there is only a little information about the empirical behaviour of mixtures. In a previous work (Martínez *et al.* (2002)), a first attempt in this way for some binary mixtures alcohol-water was published. Some authors have studied several aspects of this problem i.e. Suzuki *et al.* (1990), Gmehling and Rasmussen (1982), Hanley (1998) and Lenoir (1975), but there is not very much information about a general method or equation to determine flash point based on experimental data.

## 2. CHEMICALS AND EQUIPMENT

### 2.1. Chemicals

In this work, we have selected some common industrial alcohols and ketones widely used in the industry as solvents or reagents towards obtain mixtures of practical importance. The main criterion to select the chemicals has been the importance given to them in Papa and Sherman (1981), Parrish (1983), Falbe *et al.* (2003), Siegel and

Eggersdorfer (2003), Stoye (2003) and Werle and Morawietz (2003). Specifically, the solvents selected, with their physical properties, the presented in table 1:

TABLE 1: The studied compounds and their physical properties.

COMPOUND	MW (g/mol)	BP (°C)	D <sub>20</sub> °C (g/cm <sup>3</sup> )	FP (°C)	LFL (%)	ΔH <sub>v</sub> (kJ/mol)
Acetone	58.08	56.0	0.790	-18	2.6	29.1
Acetophenone	120.15	202.0	1.028	82	1.4	38.8
Diacetone alcohol	116.16	167.9	0.939	58	1.8	41.48
Diisobutyl ketone	142.24	169.4	0.806	49	0.8	39.9
Ethanol	46.07	78.2	0.789	13	3.3	38.6
Ethylene glycol	62.07	197.3	1.115	111	3.2	50.5
Isobutanol	74.12	107.8	0.802	25	1.6	41.8
Methanol	32.04	64.6	0.792	15	6.0	35.2
Methyl ethyl ketone	72.11	79.5	0.805	-3	1.4	31.3
Methyl isobutyl ketone	100.16	116.5	0.798	18	1.2	34.5
1-propanol	60.10	97.0	0.804	25	2.1	41.4
2-propanol	60.10	82.3	0.786	12	2.3	39.9
Water	18.02	100.0	0.998	N.F.	N.F.	40.5

With these chemicals, we prepared samples of binary mixtures with a known composition.

## 2.2. Equipment

An Automatic Flash Point Tester Abel IP 170 Herzog MC 306, coupled to a cooler model LAUDA RK 8 CS was used. This equipment is adequate to measure flash points between - 40 and 100 °C with an ethylene glycol-water cooling mixture. In addition, a Flash Point analyzer Herzog HFP 360 - Pensky Martens was used. With this one, flash points between 10 and 370 °C can be measured.

## 3. EXPERIMENTAL

Once the composition of the desired sample is selected, it is prepared in a volume of 78.5 ml as it is established in the IP 170 standard. The selected sample is then introduced in the sample vessel of the apparatus. The expected flash point is programmed in the frontal board, and the test is run. The results of all tests are repeated twice more, and the mean is calculated. The experimental data measured for some representative binary mixtures selected between the prepared, are resumed in the following tables, 2 to 11, where  $x$  is the molar fraction, and  $FP$  is the flash point:

Table 2: Flash point of mixtures acetone-water

x	0.0095	0.0200	0.0302	0.1003	0.4079	0.4951	0.6060	0.6881	0.7862	0.9053	1.0000
FP(°C)	31.0	20.0	14.5	-4.0	-14.0	-15.0	-15.0	-15.5	-16.0	-17.5	-19.5

Table 3: Flash point of mixtures methanol-water

x	0.0399	0.0718	0.1310	0.1915	0.2974	0.3978	0.4947	0.6313	0.7511	0.8747	1.0000
FP (°C)	63.0	50.0	37.5	31.5	27.0	24.5	20.5	16.5	16.5	12.0	9.5

Table 4: Flash point of mixtures ethanol-water

x	0.0101	0.0203	0.0305	0.0600	0.0911	0.1986	0.3541	0.4987	0.6478	0.7991	1.0000
FP (°C)	84.5	64.0	51.5	39.5	32.0	25.8	32.0	19.8	19.0	15.8	12.5

Table 5: Flash point of mixtures 1-propanol-water

x	0.0098	0.0453	0.0695	0.1193	0.2011	0.3501	0.4936	0.6523	0.8214	1.0000
FP (°C)	73.0	50.0	33.0	26.0	20.0	16.0	16.0	15.5	15.0	15.0

Table 6: Flash point of mixtures 2-propanol-water

x	0.0092	0.0215	0.0312	0.0496	0.1001	0.1813	0.2516	0.3967	0.5049	0.7488	1.0000
FP (°C)	56.5	43.0	38.0	31.3	26.0	24.0	21.0	20.0	18.5	16.3	12.0

Table 7: Flash point of mixtures isobutanol-water

x	0.0210	0.1111	0.2113	0.3499	0.5013	0.6225	0.7501	0.8802	1.0000
FP (°C)	77.0	42.0	37.5	35.5	33.0	33.0	32.5	32.0	32.0

Table 8: Flash point of mixtures 1-propanol-ethylene glycol

x	0.0000	0.0098	0.0695	0.1193	0.2011	0.3501	0.6523	1.0000
FP (°C)	117.0	73.0	33.0	26.0	20.0	16.0	15.5	15.0

Table 9: Flash point of mixtures 2-propanol-ethylene glycol

x	0.0000	0.0093	0.0270	0.0615	0.1140	0.1500	0.2496	0.4023	0.5987	0.8458	1.0000
FP (°C)	117.0	85.0	63.5	47.0	36.0	31.0	26.5	22.5	22.0	14.3	12.0

Table 10: Flash point of mixtures isobutanol-ethylene glycol

x	0.0000	0.0307	0.0710	0.1487	0.2498	0.3995	0.5151	0.7512	0.8517	1.0000
FP (°C)	117.0	64.0	51.5	45.0	40.0	37.0	35.0	33.0	32.5	32.0

Table 11: Flash point of mixtures 2-propanol-isobutanol

x	0.0000	0.1997	0.3496	0.5200	0.7990	1.0000
FP (°C)	32.0	24.5	21.5	18.5	14.5	12.0

#### 4. RESULTS AND DISCUSSION

The flash point of a pure substance is achieved when its partial pressure is equal to the lower flammability limit. In a general way, the flash point of a flammable compound  $i$  in a mixture, may be mathematically expressed as equation [1]:

$$LFL_i \cdot P = \gamma_i \cdot x_i \cdot P_{i,FP}^{sat} \quad [1]$$

Where  $LFL_i$  is the Lower Flammability Limit of  $i$ ,  $P$  is the total pressure of the system,  $\gamma_i$  is the activity coefficient of  $i$ ,  $x_i$  is the molar fraction of the liquid and  $P_{i,FP}^{sat}$  is the saturation pressure of  $i$  at flash point temperature.

Equation [1] is valid if there is only one flammable compound in the mixture (i.e. binary aqueous mixtures). In other cases, we must improve the equation, because it gives one flash point condition for each flammable compound, and the mixture has only one flash point.

The main problem is to give a lower flammability limit representative of the whole mixture. In this way Le Chatelier (1891), Prugh (1973) Hanley (1998) and Kanury (1983) have developed some methods and equations whose accuracy have been tested in this work.

The second problem is to estimate the saturation pressure. It is obvious that if we use better correlations when estimating the needed parameters, we will obtain better results. The equations of Antoine and Clausius-Clapeyron have been selected to estimate the saturation pressure. The parameters  $A$ ,  $B$  and  $C$  for Antoine's equation and  $\Delta H_v$  for Clausius-Clapeyron one, were obtained from Poling *et al.* (2001), and Lide (1995).

The third and last problem, and the worst, is the activity coefficient. If experimental data are available, fitting of them is always possible, but we usually don't have them. The best equations, if we have experimental data, are that of Margules and that of Van Laar, and UNIFAC if we don't have them.

As an example, we will develop the equation obtained applying the equations of Antoine and Margules, and Le Chatelier's rule (1891):

If temperature is under the flash point:

$$y_i < LFL_i \quad \therefore \quad \frac{y_i}{LFL_i} < 1 \quad [2]$$

Then, using the Le Chatelier's rule, at the flash point:

$$\sum_i \frac{y_i}{LFL_i} = 1 \quad [3]$$

From Dalton's and Raoult's laws:

$$y_i = \frac{\gamma_i x_i P_i^{sat}}{P} \quad [4]$$

Substituting the value of  $\gamma_i$  from Margules and  $P_i^{sat}$  from Antoine:

$$y_i = \frac{\exp\left(x_j^2(A_{ij} + 2(A_{ji} - A_{ij})x_i)\right) x_i 10^{\frac{A_i - B_i}{T + C_i}}}{P} \quad [5]$$

Where  $i, j = 1, 2$  ( $i \neq j$ );  $A_i$ ,  $B_i$ ,  $C_i$  are the Antoine's coefficients for  $i$ , and  $A_{ij}$ ,  $A_{ji}$  are the Margules coefficients for the binary mixture considered.

Then, with [3] and [5], making  $T = FP$ :

$$\sum_i \frac{\exp\left(x_j^2(A_{ij} + 2(A_{ji} - A_{ij})x_i)\right) x_i 10^{\frac{A_i - B_i}{FP + C_i}}}{P LFL_i} = 1 \quad [6]$$

Solving [6], we obtain the flash point expected for the mixture. If we don't have the value of  $LFL_i$ , it may be calculated from  $FP_i$  and Antoine's equation:

$$LFL_i = \frac{10^{\frac{A_i - B_i}{FP_i + C_i}}}{P}; \quad \frac{\exp(x_j^2(A_{ij} + 2(A_{ji} - A_{ij})x_i))x_i}{10^{\frac{A_i - B_i}{FP_i + C_i}}} = 1 \quad [6.a]$$

Where  $FP_i$  is the flash point of the pure compound  $i$ .

Similar equations have been tested to determine which combination gives the best results.

From our work, we have reached the conclusion that a modification of the equation proposed by Prugh (1973), gives better results:

$$LFL_i = a C_{st} \quad [7]$$

Where  $a$  is a constant (Prugh gave  $a = 0.55$ ) and  $C_{st}$  is the theoretical stoichiometric concentration of oxygen needed in the combustion of the molecule. After fitting with more than 400 compounds, we have obtained a better correlation with  $a = 0.515$ . And the stoichiometric concentration is calculated as:

$$C_{st} = \frac{83.8}{4(C) + 4(S) + (H) - (X) - 2(O) + 0.84} \quad [8]$$

Where  $C$ ,  $S$ ,  $H$ ,  $X$  and  $O$  are the numbers of the respective element in the molecular formula of the compound ( $X$  means halogen). Better results are obtained if the stoichiometric concentration of oxygen is calculated through [9]:

$$C_{st} = \frac{0.21}{(C) + (S) + 0.25(H) - 0.625(X) - 0.5(N) - 0.5(O)} \quad [9]$$

In table 12 a sample of our results for the mixture 1-propanol-water is shown.

Table 12: Correlations for 1-propanol-water

x	FP <sub>E</sub>	MARGULES				VAN LAAR				UNIFAC			
		FP(1)	FP(2)	FP(3)	FP(4)	FP(1)	FP(2)	FP(3)	FP(4)	FP(1)	FP(2)	FP(3)	FP(4)
0.0098	73.0	87.5	72.4	86.8	82.7	87.8	72.7	87.1	83.0	57.4	45.7	52.9	51.3
0.0453	50.0	67.2	53.9	66.6	60.9	68.0	54.7	67.4	61.8	46.3	35.5	42.2	39.3
0.0695	33.0	46.8	35.4	46.3	39.0	48.2	36.6	47.7	40.5	35.1	25.3	31.4	27.2
0.1193	26.0	38.0	27.2	37.4	29.4	39.8	28.9	39.3	31.4	34.0	24.2	30.3	26.0
0.2011	20.0	30.8	20.6	30.3	21.6	33.1	22.7	32.6	24.1	34.1	24.3	30.3	26.1
0.3501	16.0	25.9	16.1	25.4	16.3	27.9	17.9	27.4	18.4	33.5	23.8	29.8	25.4
0.4936	16.0	25.7	15.9	25.2	16.2	26.9	17.0	26.4	17.3	31.4	21.9	27.8	23.1
0.6523	15.5	25.5	15.7	25.0	16.0	25.8	16.0	25.3	16.3	29.2	19.9	25.7	20.8
0.8214	15.0	24.7	15.4	23.1	15.5	24.9	15.5	23.3	15.6	26.6	17.5	23.5	17.9
1.0000	15.0	24.0	15.0	21.2	15.0	24.0	15.0	21.2	15.0	24.0	15.0	21.2	15.0

(1): Hanley equation + Antoine equation

(2): Antoine equation

(3): Antoine equation + modified Prugh

(4): Clausius-Clapeyron

The accuracy of the correlations may be seen in figures 1, 2 and 3.

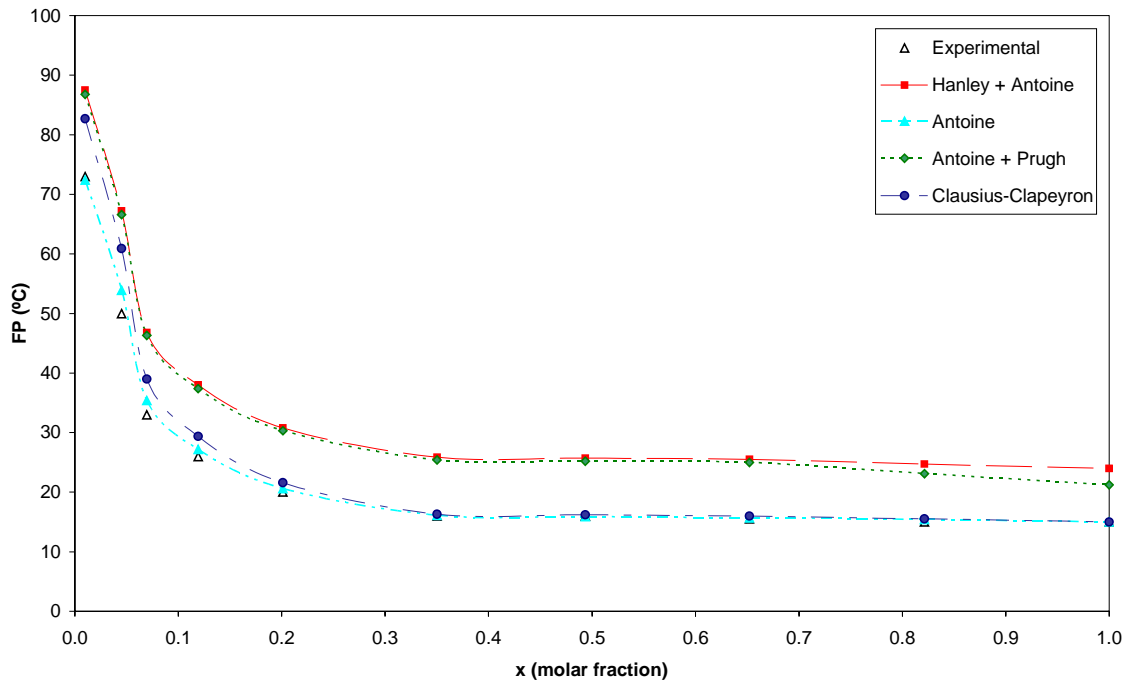


Figure 1: Flash point of 1-propanol-water mixtures.  
(Margules equation for activity coefficients).

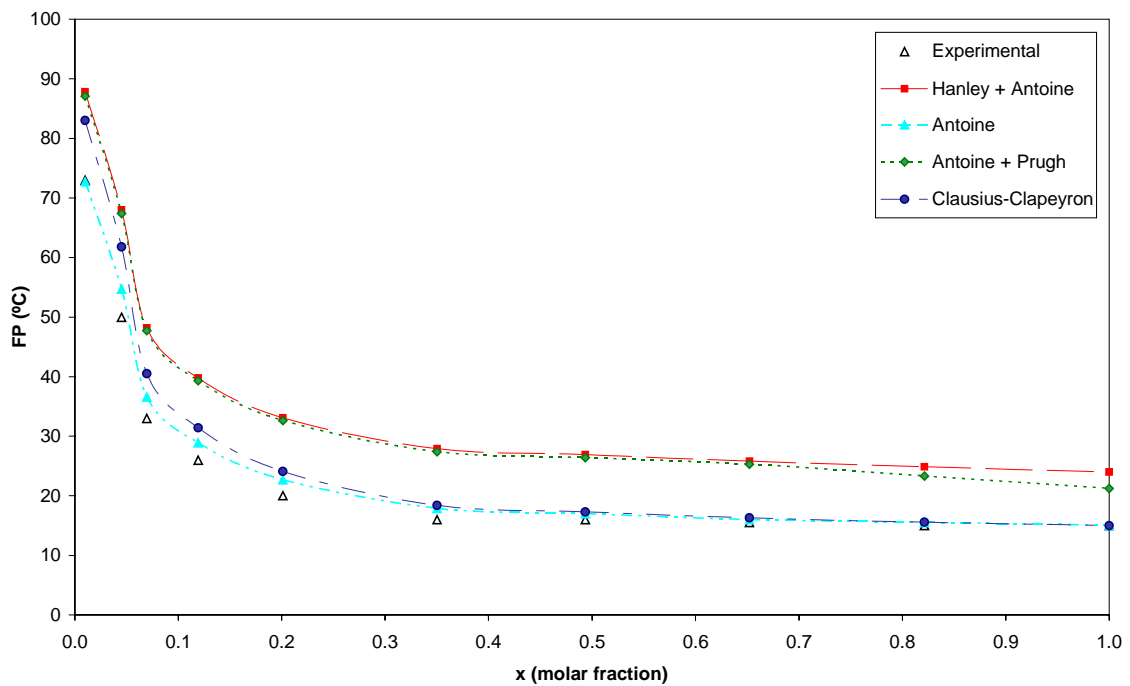


Figure 2: Flash point of 1-propanol-water mixtures.  
(Van Laar equation for activity coefficients).

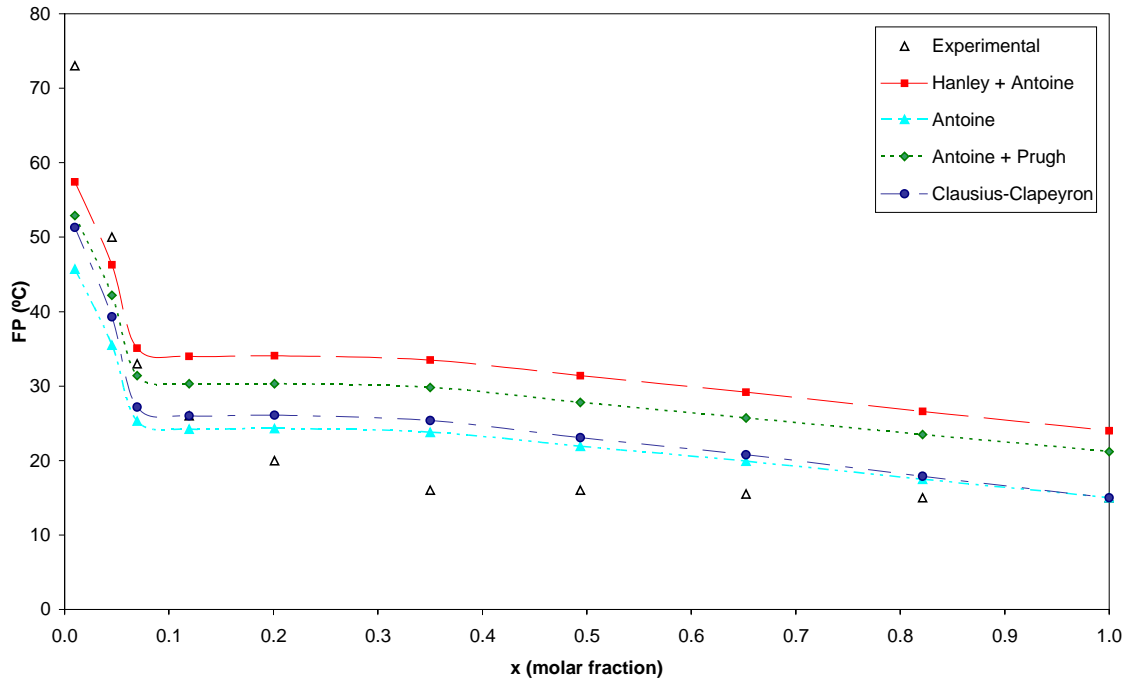


Figure 3: Flash point of 1-propanol-water mixtures. (UNIFAC for activity coefficients).

## 5. CONCLUSIONS

Once all the data have been analysed, the following conclusions have been achieved:

1. All the hypothesis give equations to estimate the flash point of pure compounds and binary mixtures accurately. The greater deviations are consequence of worse correlations to estimate the activity coefficients. Specifically:

- a) The saturation pressure is better estimated trough Antoine's equation. Clausius-Clapeyron gives too high values for the flash point.
- b) Margules and van Laar equations give approximately the same accuracy. UNIFAC gives greater deviations.

2. Hanley's equation and a modification of Prough's equation provide a similar fitting to experimental data.

3. The best proposed method is that one which use Antoine's equation for determination of the saturation pressures and Margules or van Laar's equations for determination the activity coefficients. The worst equation is that which use Clausius-Clapeyron's equation for determination of the saturation pressures and UNIFAC for determination of the activity coefficients.

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