Assessment of the evaporation correlations performance

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1. Introduction

When performing a risk analysis on industrial facilities, various hazardous scenarios must be imagined. These scenarios may lead to the formation of a toxic or flammable gas cloud and it is therefore important to determine precisely the pool evaporation so as to estimate the size and the concentration of the cloud. Currently, different mass transfer evaporation correlations are used to quantify the evaporation rate. Some of them let easily calculate the evaporation rate only taking into account few parameters as the saturated vapour pressure, the liquid temperature, the substance molecular weight, the air wind velocity and the evaporation area. However, when these correlations are compared each other on a specified case, the evaporation rate results obtained are not necessary similar. A significant gap may be even noted between them. This point lets think that the use of these tools should be done with caution.

A survey, focusing on three correlations which appear regularly in the safety surveys, has been set up in order to well understand why such a difference may appear between results. Then, from this first work, the fair conditions of use, regarding the three different tools, have been identified. The three tools analyzed are adapted to the evaporation phenomena of pure evaporating liquids whom the saturated vapour pressure is weaker than the atmospheric pressure. Consequently, only the mass transfer evaporation phenomena may be assessed using these formulas.

2. The different correlations

The three correlations examined in this document are the followings:

- The UIC correlation: in the UIC « cahier de sécurité n°11 » [1], a mass transfer evaporation formula is proposed, based on the work of Clancey [2],
- The "Mackay and Matsugu's" correlation : based on their experimental work but also on Sutton's work [3] [4], Mackay and Matsugu [5] established a mass transfer correlation to calculate the pool evaporation rate,
- The "TNO" correlation: in the 3rd edition of the TNO « Yellow book » [6], an analytical correlation is proposed to assess the pool evaporation rate by mass transfer.

3. Correlations analysis

The table below compares the expressions of each correlation :

Table 1 : The expression of the three different correlations:

Name	Commonly expression used [g/s]
UIC	$D = 0.78 \cdot 10^{-3} \cdot v^{0.78} \cdot r^{1.89} \cdot M \cdot P / T$
Mackay and Matsugu	$D = 3.14 \cdot 4.786 \cdot 10^{-3} \cdot v^{0.78} \cdot 2^{-0.11} \cdot r^{1.89} \cdot Sc^{-0.67} \cdot M \cdot P / (R \cdot T)$
TNO	$D = 3.14 \cdot 5.15 \cdot 10^{-3} \cdot v^{0.78} \cdot r^{1.89} \cdot M \cdot P / (R \cdot T)$

After modifications of writing, the correlations are the followings :

$$\text{UIC} : D = 0.78 \cdot 10^{-3} \cdot r^{1.89} \cdot v^{0.78} \cdot M \cdot P / T \tag{1.1}$$

$$\text{Mackay and Matsugu} : D = 1.67 \cdot Sc^{-0.67} \cdot 10^{-3} \cdot r^{1.89} \cdot v^{0.78} \cdot M \cdot P / T \tag{1.2}$$

$$\text{TNO} : D = 1.95 \cdot 10^{-3} \cdot r^{1.89} \cdot v^{0.78} \cdot M \cdot P / T \tag{1.3}$$

The main comment arising from this comparison is the strong similarity between the three different expressions. Five parameters appear in these formulas associated with the same

exponent value: the wind velocity v, the pool radius r, the saturated vapour pressure P, the pool temperature T and the molecular weight M. The three correlations are based on Sutton's work [3] [4] regarding the pool evaporation phenomena. This work is based on the advection-diffusion equation. From this equation, Sutton proposed the following simplified expression to estimate the evaporation rate:

$$D \cong 0.38 * \lambda^{0.22} * k^{1.33} * z_1^{-0.11} * \underline{r^{1.89} * v^{0.78} * M * P / T} \qquad (1.4)$$

Pasquill [7] proposed to replace λ appearing into equation (4) by the diffusion coefficient.

$$D \cong 0.38 * Di^{0.22} * k^{1.33} * z_1^{-0.11} * \underline{r^{1.89} * v^{0.78} * M * P / T} \qquad (1.5)$$

The parameters v, r, P, T and M, appearing in the three first correlations associated with the same exponents values, may be clearly identified in this expression.

Just the opposite, the parameters Di, k, z_1 do not appear explicitly in the three correlations. The accurate assessment of these last ones seems to be really more difficult to carry out than the one of the parameters v, r, P, T and M. Di is the coefficient diffusion, k is the Von Karman's constant whose value is estimated to 0.4 by Pasquill [7] and the parameter z_1, minimal height from which the maximal wind velocity is reached.

So, it appears possible that the three correlations don't use this kind of parameters due to the difficulty to determine it. To replace it, some fitting parameters or coefficients seem to be present in the correlations expressions.

It implies that the experimental conditions (device, substances, environmental conditions...) from which the correlations are based on, may have a great influence on the determination of the coefficients. And, consequently, the correlations should be applied in similar conditions to be efficient. All of this leads to clearly analyse the testing conditions.

The following examples let lighten the importance that may have some fitting parameters or coefficients on the final evaporation results:

- The diffusion coefficient: the Mackay and Matsugu correlation takes directly into account the laminar diffusion coefficient Di through the laminar Schmidt number Sc. The expressions of the two other correlations don't let clearly take into account the laminar diffusion. However, after analyse, the fitting coefficients supposes a value regarding this point. So, the UIC correlation takes into account a diffusion coefficient about $7.5.10^{-6}$ m^2/s and the TNO correlation uses a diffusion coefficient of $1.9.10^{-5}$ m^2/s. Supposing a large part of chemicals is characterised by a laminar Schmidt number between 0.5 and 3, the evaporation rate, from the use of the Mackay and Matsugu correlation, is three times higher in the first case than in the second one.
- The height of reference z_1 : Pasquill [7] considers the assessment of the appropriate values of z_1 difficult. However, he explains that an error of 500 % regarding z_1 has only an influence of 20 % on the final results. In any case, this parameter is one of the toughest to assess and can vary significantly depending on the experiments conditions.

Finally, to increase the importance of this matter, it seems relevant to notice that all the exponents values which appear in the correlations are partly based on experimental results. So, even if these last parameters don't appear clearly in the different correlations, some fitting coefficients in the correlations determined experimentaly may indirectly take into account the parameters λ, k and z_1.

4. Experimental conditions

4.1 UIC Correlation (Pasquill experiments)

The experiments were carried out with four substances: water, aniline, methyl salicylate and bromobenzene. The saturated vapour pressure of the substances was always below 2000 Pa. The evaporation surface was about 200 and 450 cm^2. The application of equation (1.4) on bromobenzene was quite interesting: the maximal difference between the calculations and the experimental results was about 10 %. However, the use of the equation

(1.4) to estimate evaporation rate of other substances, whom the characteristics were different from the bromobenzene ones, was not so efficient. Pasquill [7] proposed to replace the kinematic viscosity k (m^2/s) in equation (1.4) by the diffusion coefficient Di (m^2/s) of the vapour in the air. The results were improved. In this case, taking into account the diffusion of the evaporating substance seems to be relevant.

4.2 Mackay and Matsugu, TNO correlations (Mackay and Matsugu experiments)

Cumene (450 Pa at 290 K), water (2300 Pa) and gasoline (between 50 - 100 kPa) have been tested. Tests were achieved with evaporation surfaces between 700 cm^2 and 3.14 m^2. From this work, Mackay and Matsugu set up a transfer coefficient to determine an evaporation correlation. Satisfying results were obtained for water and cumene, not for gasoline. Mackay and Matsugu suggested there might be a "liquid phase resistance" to evaporation in the gasoline due to the fact it is made up of different chemicals with different volatilities. The most volatile chemicals could create a fall of the liquid surface temperature hence reducing the saturated vapour pressure and in turn the evaporation rate. That could be an explanation of the overestimation of the Mackay and Matsugu's calculations regarding the gasoline evaporation.

4.3 Mackay and Matsugu, TNO correlations (Woodward [8] experiments)

The author developed an evaporation model in which Mackay and Matsugu's [5] mass transfer coefficient is used. However, the author modified their original works regarding the mass transfer coefficient in order to get a better fit between experimental results and calculations. According to Woodward [8], the observed discrepancy is due to the difference between the substances nature tested in this case and the chemicals used by Mackay and Matsugu. So, using the original Mackay and Matsugu's [5] correlation, the evaporation rate tended to be overestimated for the volatile ones and underestimated for the less volatile ones. This example distinctly lightens the influence of the experimental results on the final assessment of the evaporation rate.

5. Correlations field of use

For each of the reviewed correlation, the table below lists the conditions which are more likely to ensure a good prediction of the evaporation rate :

Table 2: summarize of the correlations fields of use

Correlation name	Saturated vapour pressure (Pa)	Wind or air flow velocity (m/s)	Pool area	Diffusion of the substance in the air
UIC	1 - 50000	> 1 m/s	Hundreds of centimers squares	Di = $7.5.10^{-6}$ m^2/s
Mackay Matsugu	500 – 2500	> 1 m/s	Few meters squares	Taken into account with Sc
TNO	500 – 2500	> 1 m/s	Few meters squares	Di = $1.9.10^{-5}$ m^2/s

The TNO and Mackay and Matsugu's correlations can be applied for the same evaporating substances in similar conditions. The same theory and the same experimental results have been used to develop the correlations. However, a major importance regarding the choice of the diffusivity value may have a significant influence on the final evaporation result. The Mackay and Matsugu's one takes into account the evaporating substance diffusivity through the Schmidt number whereas a fixed value of 0.8 is set for this parameter in the TNO equation. The range of application of the UIC correlation is significantly different from the two other ones especially in terms of evaporating substance volatility and diffusivity. The evaporation conditions are also quite different especially concerning the environmental conditions and the evaporating area.

6. Conclusion

The "Mackay and Matsugu", the 'TNO", and the "UIC" correlations derive, partly, from the same fundamental works of Sutton [3] [4] based on the diffusion-advection equation solving. After several simplifications of these works, several evaporation correlations have been set up as the three ones discussed here. A part of the simplifications realised is based on the use of experimental results from different experimental works.

The comparison between the results from the correlations and the experimental results lightened some fitting parameters which have been required to improve the equations performance. These fitting parameters are, however, strongly dependent on the substances tested and the experimental conditions. Consequently, it clearly appears that the three correlations, focused on here, are a mixing of a theoretical and experimental works. The use of these last ones narrow the field of use of the different correlations.

So, these observations tend to warn concerning the appropriate use of the various mass transfer evaporation tools. These latters should be used having in mind the theory used but also the experimental conditions which let the equation determination. These two determining parts have been identified in this article in order to let a performant use of the three correlations studied. This watching also reveals that more experiental tests would let better distinguish the field of use of these correlations and would let improve it. So, information regarding the assessment of the evaporation of large pools whom surface is about 100 m^2 or more, the evaporation of high volatile liquids (>> 50 kPa) or the evaporation with a low wind velocity below 1 m/s seems to miss.

7. References

[1] : Union des Industries Chimiques (UIC), « Cahier de sécurité n°11 », 1987,

[2] : Clancey V.J., « The evaporation and dispersion of flammable liquid spillages », Chemical Process Hazards Conference, Manchester 1974,

[3] : Sutton O.G., « Wind structure and Evaporation in a Turbulent Atmsophere », Proc.Roy.Soc, 1934,

[4] : Sutton O.G., « Micrometerology », McGraw-Hill, 1953,

[5] : Mackay D. and Matsugu R.S.,« Evaporation Rates of Liquid Hydrocarbon Spills on Land and Water », Canadian Journal of Chemical Engineering vol.51, August 1973,

[6] : Committee for the Prevention of Distasters, Methods for the calculation of physical effects, Chapter 3 "pool evaporation", third edition, 1997,

[7] : Pasquill, F., « Evaporation from a plane, free-liquid surface into a turbulent air stream », 1943,

[8] : Woodward J.L., « An integrated model for discharge rate, pool spread, and dispersion from punctured process vessels », Journal Loss Prevention Industry, vol3, January 1990.

8. List of symbols

D = Evaporation rate (g/s)
r = Pool radius (m)
v = Wind velocity (m/s)
M = Molecular weight (g/mol)
P = Saturated vapour pressure (Pa)
Sc = Schmidt number (-)
T = Pool temperature (°K)
R = Constant (J/mol.K)
Di = Diffusion coefficient (m^2/s)
λ = Kinematic viscosity (m^2/s)
k = Von Karman constant (-)
z_1 = Height of reference, minimal height from which the maximal wind velocity is reached (m)