CHEMICAL ENGINEERING TRANSACTIONS

VOL. 48, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eddy de Rademaeker, Peter Schmelzer

ISBN 978-88-95608-39-6; **ISSN** 2283-9216

DOI: 10.3303/CET1648017

Pool Evaporation at Higher Vapour Pressures

Abdelkarim Habib*, Bernd Schalau

Bundesanstalt für Materialforschung und –Prüfung (BAM), Unter den Eichen 87, 12205 Berlin
karim.habib@bam.de

Hazardous substances with a boiling point close to ambient temperatures will evaporate at higher vapour pressures, so that the evaporation takes places in the smooth transition between the evaporation at boiling point and below boiling point, representing the transition between two different physical phenomena. Whilst the evaporation at boiling point is driven by the available heat flux, the evaporation below boiling point is driven by the concentration gradient between the pool surface and the ambient air. Available evaporation models usually focused on the correct description of the mass transfer coefficient for temperatures below boiling point. A formulation of the correct equation for the mass flow is rarely documented. Whilst the mass transfer coefficient formulation is more or less equivalent in most models, the main difference occurs in the formulation of the mass flow equation. In Fact two types of models can be identified: the models with a linear pressure term and the models with a logarithmic pressure term. Whilst the logarithmic formulations result in an infinite mass flow near boiling point, which is not plausible, the linear formulations reach (different) finite values. Due to a lack of published experimental data it was not possible to determine whether the linear approach is conservative, under predicting or more or less accurate close to the boiling point.

To evaluate the accuracy of each type of formulation, test series on liquid pools have been carried out at BAM for substances like Water, Ethanol, Cyclohexane, and Acetone. The tests were done under ambient conditions with a heatable, 90 cm diameter pool, so that the vapour pressures investigated ranged from 0 to close to 1 bar. The experimental data showed that neither of the linear nor the logarithmic formulation of the evaporation models is able to predict correctly the mass flow close to the boiling point. The logarithmic approach heavily over predicts the mass flow, while the linear approach is not conservative anymore when the vapour pressure exceeds 0.7 bar.

1. Introduction

When assessing the hazards of the release of flammable and/or toxic liquids the evaporation has to be considered. Releasing liquids with a boiling point close to the ambient temperature or heated substances, will lead to an evaporation process at higher vapour pressures. Whilst the evaporation at temperatures far from the boiling point is mainly dominated by the concentration gradient in the gas phase, a transition towards a heat dominated process takes place when the liquid temperature approaches the boiling point. When releasing a pressure-liquefied gas, the liquid phase forms a pool at boiling temperature. This temperature is maintained as long as the heat flux from the surrounding, mainly the floor, is high enough to provide the heat needed for the evaporation. When the floor cools down, the pool will also cool down and a transition from the evaporation at a vapour pressure of 1 bar(a) towards the evaporation at lower vapour pressures will take place.

Empirical evaporation models (e.g. Mackay 1973, Clancey 1974) exist in different formulations. Not only the equations for the mass transfer coefficient differ significantly but the main difference results from the formulation of the pressure term in the mass flow equations. In the original publication of Mackay/Matsugu the mass flow is considered as linearly dependent on the vapour pressure. In the german Guideline KAS-18 (2010) a formulation of the Mackay/Matsugu model is used where the vapour pressure is taken into account by a logarithmic function. The latter results from the work of Deutsch (1995) who used Stefan's law to derive this logarithmic formulation and found it to be conservative compared to his own experimental data.

Close to the boiling point, the linear pressure gives a finite value whilst the logarithmic term gives an infinite value. As there is no experimental series known to the authors that can be used to evaluate both approaches,

Please cite this article as: Habib A., Schalau B., 2016, Pool evaporation at higher vapour pressures, Chemical Engineering Transactions, 48, 97-102 DOI:10.3303/CET1648017

own outdoor experiments of the evaporation under atmospheric conditions have been carried out at the Federal institute for Materials Research and Testing.

Another relevant question when considering the evaporation of liquids is the evaporation in absence of wind. This is mainly of interest when doing the hazard assessment for a hazardous substances warehouse. To calculate the exact flow regime inside a warehouse is very complex and not expedient. Nevertheless it can be assumed that the flow velocities inside a warehouse are very low. Most evaporation models are based on the boundary layer assumption / theory and are therefore strongly dependent on the wind speed. For the theoretical case of a "no wind" situation no mass flow can then be calculated. In order to investigate the lower application limit of the empirical models, own experiments in a storage room and a warehouse were carried out at BAM to assess the influence of natural venting as realistic as possible.

2. Experiments

In 2008 outdoor evaporation experiments were carried out with ethanol and cyclohexane in 3 basins of 0.5 m, 0.74 m and 1 m diameter (Habib 2011). The maximum liquid temperature reached during these trials was 50°C corresponding to a vapour pressure of 0.3 bar(a). As the interesting vapour pressure range is between 0.3 bar bas and 1 bar(a), which is not covered by these data, new experiments have been carried out in 2014 and 2015 with water and acetone in a basin of 0.88 m diameter heated by 7 heating plates of 2 kW power each. The maximum liquid temperatures reached were 92°C (0.8 bar(a)) for water and 54°C (0.94 bar(a)) for acetone.

The evaporation in a storage room or warehouse was also investigated. In 2008 measurements were done with ethanol and cyclohexane in a storage room, reaching maximum temperatures of 44°C and maximum vapour pressures of 0.25 bar(a). Comparable to the outdoor experiments of 2008 the range of high vapour pressures was not covered in these test series, so that in 2015 new experiments were done in a warehouse (L x W x H 22 m x 12 m x 6.75 m). As the risk for the formation of an ignitable gas cloud was very high due to the high temperatures aimed at and a number of sources of ignition were present (e.g. heating plates and other electrical equipment) only water was used. The maximum temperature reached was 89°C (0.7 bar(a)).

3. Evaporation models

Most empirical evaporation models are based on the assumption of convective material transport with a linear dependency of the vapour pressure of the released liquid (Brauer 1971):

$$\dot{m} = \frac{\beta A M}{R T_A} p^* \tag{1}$$

$$p^* = p_A - P_{A,\infty} \tag{2}$$

Derived from the Stefan-diffusion equation, some models use a logarithmic correlation with the vapour pressure.

$$p^* = p \, ln \left(\frac{p - p_{A,\infty}}{p - p_A} \right) \tag{3}$$

Close to the boiling point, the logarithmic correlation leads to unrealistic values of the mass flow.

The reference Temperature for calculating the physical properties of the gas phase is the average temperature in the boundary layer as stated by (Brauer 1971, Eckert 1959):

$$T_b = 0.58\, T_A + 0.42\, T_\infty \tag{4}$$

The mass transfer coefficient depends from the wind speed and the characteristic length in nearly all empirical evaporation models. Some of them also take into account the physical properties of the substances by implementing the diffusion coefficient and the kinematic viscosity through the Schmidt-Number. As shown in earlier investigations (Habib 2011) the empirical evaporation models cover a broad range of values even for low vapour pressures up to 0.3 bar(a). The model of Mackay/Matsugu with a logarithmic formulation of the pressure term has proven to be conservative. The model of Clancey (1974) gives lower mass flow rates which are closer to the experimental values (Habib et al. 2010). As the results of both models can be seen as the upper and lower limit of the mass flows calculated by evaporation models, they are chosen for further investigations.

Mackay / Matsugu

$$\beta = b\ \frac{u^{0,78}}{L^{0,11}Sc^{0,67}}\ ; b = 4.819 * 10^{-6} \tag{5}$$

Clancey for circular pools

$$\beta = 2.12 * 10^{-2}\ \frac{u^{0,78}\ d^{1.89}}{R} \tag{6}$$

4. Pressure term

To assess the influence of the pressure Term (linear or logarithmic) on the mass flow, the evaporation models are reformulated as to obtain a pressure Term p*:

$$p^* = \frac{\dot{m}RT_A}{\beta AM} \tag{7}$$

The pressure Term is calculated based on the experimentally determined mass flow, the fluid temperature and the wind speed, as well as the mass transfer coefficient from the empirical models. Therefore if the value of p* is below the curves of the linear or logarithmic pressure term, then the measured value is lower than the calculated one and the model is conservative. Figure 1 and 2 show respectively the calculated pressure term values with the model of Mackay/Matsugu and the model of Clancey.

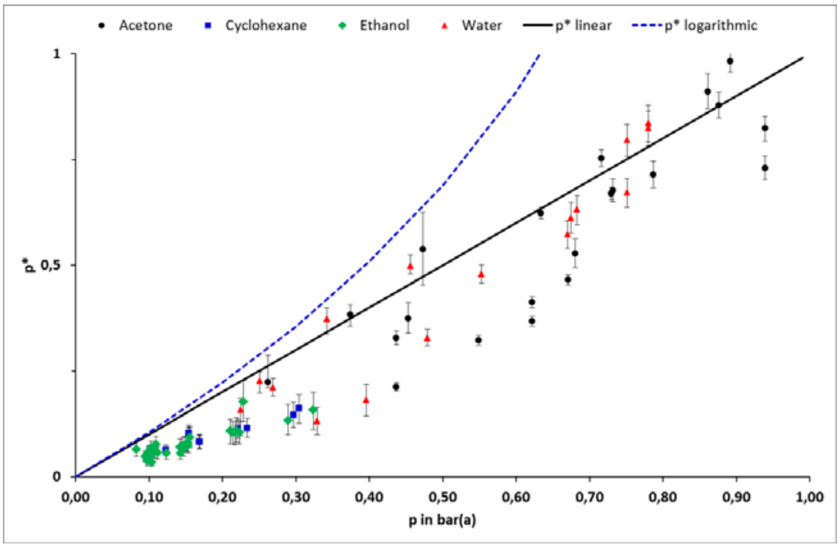

Figure 1: Pressure term values calculated with the model of Mackay/Matsugu; reference Temperature: average Temperature in the boundary layer

The temperature difference between the liquid and the surrounding air in the experiments reached a maximum of 70 K. With such a high temperature difference a significant impact on the physical properties of the substances and therefore on the Schmidt-Number and the calculated pressure Term is to be expected. In Figure 1 the reference temperature is chosen as described by Eq(4) for the model of Mackay/Matsugu. Up to a vapour pressure of 0.7 bar(a) the linear pressure term would give conservative results for most of the cases. At higher vapour pressures, the linear pressure term is not conservative anymore, whilst the logarithmic pressure term would always be conservative, but with unrealistic high values of the mass flow for vapour pressures above 0.5 bar(a). In Habib and Schalau (2015) it was shown that choosing the temperature of the ambient air as reference temperature would lead to a better agreement between the logarithmic assumption and the measured values up to a vapour pressure of 0.7 bar(a). When the temperature of the ambient air is chosen, the linear assumption is not conservative anymore. From that observation it can be concluded that using the average temperature in the boundary layer from Eq(4) is the best choice when dealing with high temperature gradients between the liquid phase and the surrounding atmosphere and will therefore be used in the following.

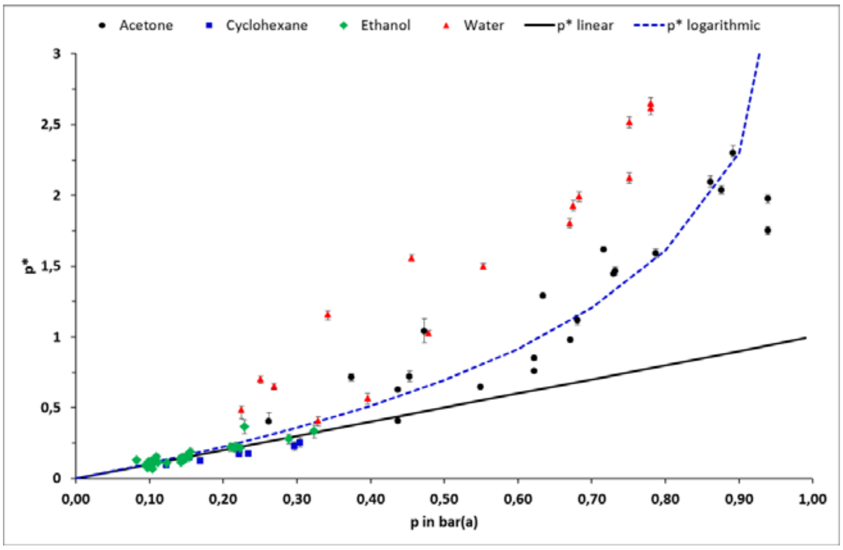

Figure 2: Pressure Term Values calculated with the model of Clance;, reference Temperature: average Temperature in the boundary layer

The mass transfer coefficient from the model of Clancey leads to higher deviations between the measured and the calculated values than for the model of Mackay/Matsugu. As can be seen in Figure 2, nearly all values lay above the linear curve and also above the logarithmic curve. Therefore the model of Clancey is not conservative for the presented cases. The scatter of the values for the model of Clancey is mainly due to the fact that no physical properties of the substances (apart from the molecular weight) are taken into account. Whilst this approach allows us to carry out calculations even for substances for which no sufficient physical properties are known, it leads to a considerably higher inaccuracy.

Based on the model of Mackay/Matsugu it was found by the authors, that increasing the factor b in Eq(5) from $4.89*10^{-6}$ to $5.6*10^{-6}$ leads to a conservative assessment of the evaporating mass flow by the linear pressure term approach for all considered vapour pressures (Figure 3). For low vapour pressures below 0.3 bar(a) the overestimation by the model of Mackay/Matsugu with the increased factor b increased. To get a better approximation for all vapour pressures the authors propose to take the linear pressure Term at an exponent of 1.2, leading to a decrease of the overestimation for low vapour pressures and still giving conservative results over the whole vapour pressure range except for a very few number of experiments as shown in Figure 3. In summary this newly derived model is defined as follows:

$$\dot{m} = 0.1 * \beta \, \frac{AM}{RT_A} \left(p_A - p_{A,\infty}\right)^{1.2} \tag{8}$$

$$\beta = 5.6 * 10^{-6} \, \frac{u^{0,78}}{L^{0,11} Sc^{0,67}} \tag{9}$$

5. Evaporation in a confined space

Due to the direct proportionality of the mass flow and the wind speed in all evaporation models, in absence of wind no mass transfer will be calculated, excepted for the model of Brötz who introduced a minimum Value for this case (LIS 1995). Measurements in a storage room (Habib et al. 2010) and in the actual measurements in a Warehouse showed that the wind speed in such confined spaces is very low and in the range of respectively 0.05 m/s and 0.1 m/s.

Based on Fick's Equation and Stefan's law the following formula can be derived for the (theoretical) case of no wind situation:

$$\beta = \frac{D}{a} \tag{10}$$

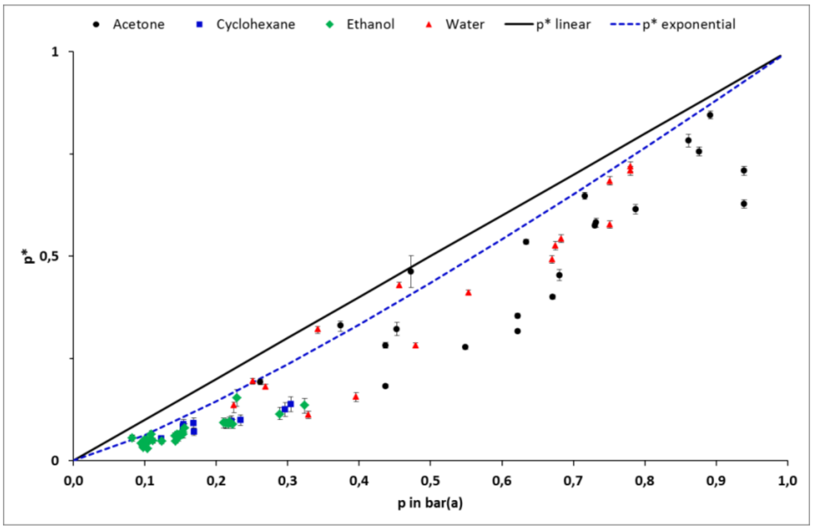

Figure 3: Pressure Term Values calculated with the Habib/Schalau model presented in this paper; reference Temperature: average Temperature in the boundary layer

Based on the results of the own indoor experiments, the factor a was fitted to the experimental values and found to be 2.5. Incorporating this equation into the model described by Eq(8) and Eq(9) leads to a new set of equations able to describe the evaporation for the whole range of wind speeds and vapour pressures.

$$\dot{m} = 0.1 * \beta \, \frac{AM}{RT_A} \, \left(p_A - p_{A,\infty}\right)^{1.2} \tag{8}$$

$$\beta = max\left(\frac{D}{2.5}\ ;\ 5.6 * 10^{-6}\ \frac{u^{0,78}}{L^{0,11}Sc^{0,67}}\right) \tag{11}$$

Figure 4 shows the comparison of the new model presented in this paper with the model of Mackay/Matsugu (with logarithmic pressure Term (pronuss 2015)) and the model of Clancey (with linear pressure Term) as well as experimental values for the case of a 0.74 cm diameter pool of Ethanol at 30°C (vapour pressure = 0.1 bar(a)) over the wind speed. The new model is not only conservative but also more accurate than the model of Mackay/Matsugu, whilst the model of Clancey is the closest to the experimental values but with a clear tendency to underestimation.

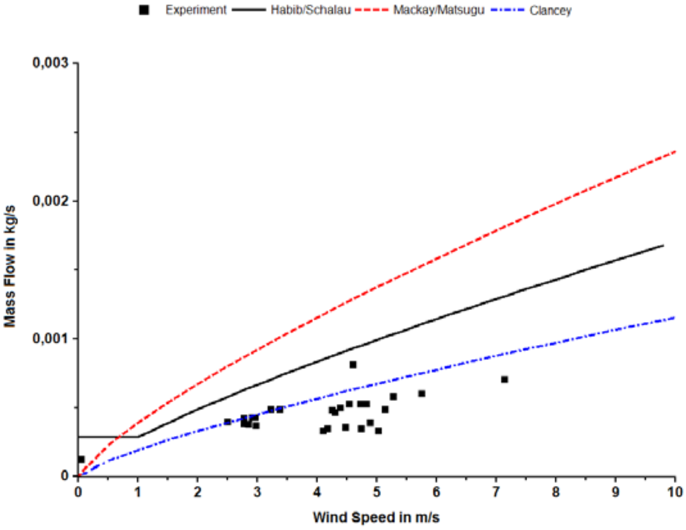

Figure 4: Experimental and calculated values from the three evaporation models investigated in this paper for a 0.74 cm diameter Ethanol pool at 30°C

6. Conclusions

Experimental investigations of the evaporating mass flow in outdoor experiments under atmospheric conditions as well as experiments in confined spaces were carried out at different vapour pressures ranging up to values close to the boiling point. From the comparison of these experimental values with empirical evaporation models it could be found, that the definition of the reference temperature has a significant impact on the calculation results and that the average Temperature in the boundary layer should be used. The experimental results also confirmed that the logarithmic formulation of the pressure term always leads to conservative but, at higher vapour pressures, unrealistic high values, whilst the linear formulation underestimates the mass flow for high vapour pressures. With a slightly increased mass transfer coefficient in comparison to that of Mackay/Matsugu and the introduction of an exponential formulation of the pressure term an equation was derived that results in a more accurate prediction of the experimental values. For the case of evaporation in a no wind situation, based on the experiments carried out, a formulation was found, enabling the authors to present a model able to cover all scenarios from no wind up to high vapour pressures.

Symbols

A in m²	Pool area	p^*	Pressure Term
D in m²/s	Diffusioncoefficient	R in J/(mol K)	Universal Gas constant
L in m	Characteristic Length	Sc	Schmidt Number
M in g/mol	Molar Mass	T_b in K	Reference Temperature
$\dot{m}$ in g/s	Mass flow	T_A in K	Liquid temperature
p in Pa	Ambient pressure	u in m/s	Wind speed in 10 m height
p_A in Pa	Vapour pressure of the substance	β in m/s	Mass transfer coefficient
$p_{A,\infty}$ in Pa	Vapour pressure of the substance in the ambient		

Reference

Brauer H., 1971, Stoffaustausch einschließlich chemischer Reaktionen. Verlag Sauerländer, Aarau und Frankfurt am Main, Germany

Brötz, W., 1979, Sicherheit von Chemieanlagen im Hinblick auf den Nachbarschaftsschutz , Gutachten im Auftrag des Ministers für Arbeit, Gesundheit und Soziales des Landes Nordrhein-Westfalen, Germany

Clancey V.J., 1974, The evaporation and dispersion of flammable liquid spillages, Chemical Process Hazards Conference, Manchester, UK

Deutsch S.; 1995, Evaporation from liquid pools under atmospheric conditions, PhD Thesis, University of Dortmund, Germany (in German)

Eckert E.R.G., 1959, Einführung in den Wärme- und Stoffaustausch. Springer, Berlin/Göttingen/Heidelberg, Germany

Habib, A., 2011, Transient calculation of the evaporation out of a liquid pool using a boundary layer method, PhD Thesis, Technical University of Berlin, Germany (in German).

Habib A., Schalau B., 2015, Lachenverdunstung bei höheren Dampfdrücken. Technische Sicherheit , Bd.5, Nr. 9, Germany

Habib, K.; Schalau, B.; Zeps, R.; Frank, S., 2010, Vergleich von Modellen zur Simulation einer Lachenverdunstung. TÜ Bd.51 Nr. l/2

KAS-18 Leitfaden, 2010, Empfehlungen für Abstände zwischen Betriebsbereichen nach der Störfall-Verordnung und schutzbedürftigen Gebieten im Rahmen der Bauleitplanung - Umsetzung § 50 BImSchG.

LIS Bericht Nr. 115, 1994, Ermittlung des Gefährdungspotentials ereignisbezogener Stofffreisetzungen unter dem Aspekt der Störfall-Verordnung. Landesanstalt für Immissionsschutz Nordrhein-Westfalen, Germany

Mackay D., Matsugu R. S.. 1973, Evaporation Rates of Liquid Hydrocarbon Spills On Land and Water. The Canadian Journal of Chemical Engineering, Vol. 51

Pronuss, 2015, www.pronuss.de, accessed 24.08.2015.